METAL COMPLEXES OF BLACK WATTLE TANNINS AND RELATED MODEL POLYPHENOLS

by

NEVILLE PATRICK SLABBERT, M.Sc. (CAPE TOWN)

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FOREWORD

This thesis is submitted in accordance with the regulations for the Degree of Doctor of Philosophy of Rhodes University. The work was carried out at the Leather Industries' Research Institute, Grahamstown, and is wholly original except where due reference is made in the text. It has not been submitted in whole, or in part, for any degree at any other University.

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C O N T E N T S

INTRODUCTION

Apart from their general usage as tanning agents for hides and skins, the natural tannins have been used since earliest times for various other purposes. The blue-black iron tannate complex was used by ancient Egyptians as a hairdye and for many centuries this complex was the main source of writing inks.

Wattle tannin is known to form complexes with many metal ions.[1] The chief use of tannin complexes has been in gravimetric analyses,[1] since aqueous solutions of tannins readily precipitate metal ions under certain experimental conditions. At the present time the nature of the precipitated complexes has not been investigated however, because in the gravimetric method the complexes are ignited and the metal determined as its oxide; hence no knowledge of the complexes themselves was required.

The present investigation was carried out to determine the physicochemical properties of metal-tannin complexes. This study was undertaken so that it would form the fundamental basis for applied uses of metal-tannin complexes, eg. in the transfer of trace elements to plants in high pH soils,[2] as complexing agents in foliar sprays,[3] depressants in the froth flotation of various mineral ores,[4] as corrosion inhibitors for metals,[5] and as fishnet preservatives,[6] etc. The metal ions, iron(III), germanium(IV), aluminium(III), boron(III), cobalt(II), nickel(II), copper(II), zinc(II), magnesium(II), calcium(II), lead(II), vanadium(IV), titanium(IV) and molybdenum(VI) were chosen for investigation because of the possible applied usage of their wattle tannin complexes.

Wattle tannin has been shown to be made up of polymeric polyphenolic flavanoid molecules, linked by direct nucleus to nucleus bonds.[7] The average number of flavaoid units per polymer chain has been established to be approximately equal to four.[8] Because of the complicated structure of wattle tannin, the complex formation of the individual phenolic monomers was investigated initially.

Pyrocatechol, pyrogallol, resorcinol and phloroglucinol nuclei have been shown to constitute the major aromatic portion of the tannin molecules.[7] The first two phenols were found to be the most important ligands due to the presence of an o-dihydroxo group capable of forming chelates with metal ions. For this reason the complex formation of a series of twenty-three o-dihydroxybenzene and 1,2,3-trihydroxybenzene derivatives has been investigated. These include the wattle tannin monomers, catechin, robinetinidol, leucofisetinidin, fustin, dihydrorobinetin and the closely related flavaoids brazilin and dihydroquercetin. The results obtained for these complexes were subsequently related to those of wattle tannin.

A large number of solid pyrocatechol complexes have been isolated and analysed[9] and structures have been proposed on the basis of the analytical data. This type of investigation is not suitable for complexes of wattle tannins because of the polymeric nature of the tannins. Hence, the present investigation deals only with complex formation in aqueous media and no attempt has been made to isolate pure complexes.

Because the formation of phenolic complexes involves the liberation

of the hydroxylic protons by the metal ion, it was possible to follow the reaction by potentiometric methods. In certain cases where complex formation occurred at low pH values the equilibria were studied by ultraviolet spectrophotometric methods. Changes in the ultraviolet absorption spectra of the phenolic ligands on complex formation form the basis of this method. Visible spectrophotometric methods were used to determine the complex component ratios of the highly coloured complexes. Electrophoretic methods were used to determine the overall charges of the complexes.

From the results of the potentiometric methods, the complex stability constants were calculated. The stability constants of the simple model phenolic complexes and the wattle tannin monomers were then related to those of wattle tannin to determine whether the latter conforms to the normal complexation behaviour of phenolic compounds. The complex stability constants were related to the phenolic dissociation constants. The relationships which were obtained proved useful for comparing the bonding of the protonated species with those of the metal complexes. Wider correlations were also obtained by comparing the stability constants for different pairs of metals.

The absorption spectra of the coloured metal phenolic complexes were recorded and the spectral data used in various correlations. The visible absorption bands of the highly coloured complexes were established to be due to charge transfer processes and were interpreted on electrostat-

ic[10,11] and molecular orbital[12,13] models.

In the present work the phenolic compounds with an ortho-dihydroxyl group are generally referred to as o-diphenols and are represented as H_2L. However, because different results were obtained for some of the metal complexes with o-dihydroxybenzene and 1,2,3-trihydroxybenzene derivatives, the latter are symbolised as H_3R.

For the determination of the stability constants for metal complexes of o-diphenols, a knowledge of the ligand dissociation constants is necessary. The latter constants were determined by potentiometric and spectrophotometric methods. Because of the overlapping nature of the polyphenolic dissociations, special techniques were employed to obtain accurate values. A method for determining the dissociation constants of the flavanoid compounds was derived. This method utilises the germanium(IV) complex which simplified the interpretation of the results. The dissociation constants for eight of the twenty-three phenols investigated have previously been determined under the same experimental conditions of ionic strength and temperature as used in the present investigation.[14]

Interest in the iron(III) complexes of phenolic compounds lies in the fact that the highly coloured wattle tannin complex forms the basis of a colorimetric method of tannin analysis.[15] The intensely coloured Fe(III) complexes of o-dihydroxybenzene derivatives have been used for the analytical determination of iron.[16] The empirical formulae of the Fe(III)-Tiron (4,5-dihydroxybenzene-1,3-disulfonate) complex species have been

determined by spectrophotometric methods.[17] The complex species formed were found to be dependent on the pH of the solution. The successive complexes formed with increasing pH were found to have component ratios of metal to ligand equal to 1 : 1, 1 : 2 and 1 : 3. Stability constants for this system have been determined by potentiometric and spectrophotometric methods.[18] Of the other iron(III) complexes of o-diphenols studied in the present investigation, the stability constants of the 3,4-dihydroxybenzenesulfonate[19] and 2,3-dihydroxynaphthalene-6-sulfonate[20] complexes have also been determined.

The bis- and the tris(pyrocatecholato)iron(III) anions have been isolated.[21,22] The molecular formulae of these complexes were found to be $Na\left[Fe(C_6H_4O_2)_2\right].H_2O$ and $K_3\left[Fe(C_6H_4O_2)_3\right]$. The infrared spectrum of the tris(pyrocatecholato)iron(III) trianion has been recorded.[23] No O-H stretching vibrations were observed, as would be expected if all the hydroxylic protons are liberated on complexation.

The value of the magnetic moment for tris(tetrachlorocatecholato)ferrate(III) has been found[24] to be equal to 5.93 B.M., indicating that the iron(III) complexes of o-diphenols are high-spin.

The visible absorption spectra of a number of iron(III) complexes of o-dihydroxybenzene derivatives have been recorded in an investigation into suitable analytical reagents for the determination of iron.[25] The strong visible absorption bands have been assigned to a charge transfer process.[26]

The possible use of wattle tannin solutions for the extraction of

germanium has been investigated.[27] Tannin solutions have also been used for the detection of small quantities of germanium in solution.[28] Similarly, the pyrocatechol complex has been used for the extraction[29] and the determination[30] of germanium. Germanium exists in aqueous solutions as an uncharged hydrated oxide, GeO_2.[31] Polyphenols with an o-dihydroxyl group have been found to react with GeO_2 in solution to give the tris-chelate.[32] Paper electrophoresis established that such complexes are anionic.[33] This was confirmed[32] by the isolation of the pyrocatechol complex as the pyridine salt, $(C_5H_6N)_2\left[Ge(C_6H_4O_2)_3\right]$. Stability constants of a number of germanium(IV) complexes of o-diphenols have been determined and have been related to the dissociation constants of the ligand.[34] Linear relationships were obtained in accordance with the usual general relationship between complex stability and ligand basicity.[34] The bis(pyrocatecholato)-germanium(IV) complex was found to form only in solutions of very high acidity.[34] This complex has been isolated as the bis-pyridine adduct from non-aqueous solvents.[35] Therefore it was suggested[34] that the bis(pyrocatecholato)germanium(IV) complex formed in aqueous solutions was 6-co-ordinate, with water molecules occupying the unco-ordinated positions. This was confirmed[36] by the isolation of the complex, $\left[Ge(C_6H_4O_2)_2(H_2O)_2\right]$.

Trivalent aluminium chloride is commonly used as a diagnostic reagent for the elucidation of the hydroxylation pattern of flavanoids.[37] Combinations of aluminium salts and tannin solutions are also used in the tannage of hides.[38] Aluminium(III) ions have been found to form successive o-dihydroxybenzene complexes with molar ratios of metal to ligand equal to

1 : 1, 1 : 2 and 1 : 3.[39-41] The last two pyrocatechol species have been isolated[42] viz. $Na\left[Al(C_6H_4O_2)_2\right].4H_2O$ and $Na_3\left[Al(C_6H_4O_2)_3\right].7H_2O$. Conflicting reports have been made concerning the values of the stability constants for the aluminium(III) complexes of pyrocatechol and Tiron.[39,40] Also no relationship was observed between the complex stability constant and the ligand dissociation.[40] However as only three related phenolic complexes had been correlated it was hoped that the much larger range studied in the present investigation would clarify the position.

The effect of ionic strength on the stability constants of the aluminium(III)-Tiron system has been found to be large because of the high ionic character of this complex.[41] The influence of ionic strength has been found to be much smaller for those phenolic complexes without ionic substituents.[34]

An attempt has been made to resolve the tris(pyrocatecholato)aluminium(III) trianion into optical isomers.[43] It was found that due to rapid exchange of the ligand the complex was too labile to be resolved by classical chemical methods.

The reaction of boric acid with certain organic compounds having adjacent hydroxyl groups is well known.[44] The boric acid complex is also one of the basic reagents used to determine the hydroxylation pattern of flavanoids.[37] The reaction of natural tannins with boric acid has been investigated.[45] However, the potentiometric method employed was the reverse of that normally used to investigate metal phenolic complexes viz. the boric acid was titrated against a neutralised solution of the tannin.

The results obtained were inconclusive and did not shed light on the nature of the complex formation. A number of boric acid complexes of o-diphenols have been studied potentiometrically.[46,47] These complexes were found to have the general formula, $B(OH)_2L^-$. A direct relationship has been found to exist between the acidity of the phenolic ligands and the complex equilibrium constants.[46] The complex where two pyrocatechol ligands are co-ordinated to the central atom has been isolated,[48] viz. $\left[B(C_6H_4O_2)_2\right]K$. However, the existence of this species in aqueous solution, with excess of ligand, could not be detected by potentiometric[46] or calorimetric[49] methods.

The o-dihydroxybenzene complexes of the divalent first transition metals, cobalt(II), nickel(II), copper(II) and zinc(II) have been investigated extensively.[50-54] The mono- and bis-complexes were generally found to form in aqueous solutions, although protonated species (MHL^+) have also been detected in solutions of low ionic strength.[55] The complex stability order with a single phenolic ligand has been established to be, $Co < Ni < Cu > Zn$ with $Zn > Ni$.[51-54] The former of the two orders is in agreement with that of Irvine and Williams[56] whereas the latter is in disagreement with that of Mellor and Maley.[57] However the stability order $Zn > Ni$ has been occasionally observed with oxygen-type ligands.[58,59] Conflicting reports have however been made concerning the relationship between the complex stability constants and the ligand association constants. Reverse,[51] direct,[54] and lack of correlation[60] have been reported to exist.

Both mono- and bis-pyrocatecholato complexes of the divalent first

transition metals have been isolated.[61] From the results of an infrared spectroscopic investigation of the bis(pyrocatecholato)copper(II) dianion, it has been proposed that the two pyrocatechol ions are co-ordinated to the copper ion as unidentate ligands, linked with two hydroxo groups through H-bonding.[23] This is in disagreement with the generally found bidentate nature of the pyrocatechol ligand.[52-54,63]

The electronic absorption spectra of the copper(II), nickel(II) and cobalt(II) complexes of pyrocatechol and Tiron have been recorded.[23,64] Because the absorption spectra of the Co(II) and Cu(II) complexes differ in solid and solution forms it has been proposed[23] that the structures of the complexes in these two states are also different. The nickel(II) complexes with the above two ligands have been established to have octahedral symmetry with water molecules making up the octahedral co-ordination in the bis-chelate.[23]

Because of the similarity that has been established to exist[63] between the vanadyl(IV) complexes of o-diphenols and those of the divalent first transition metals, the former complexes have been included in the discussion section dealing with the cobalt(II), nickel(II), copper(II) and zinc(II) complexes. Potentiometric methods have been used to determine the equilibrium constants of a number of vanadyl(IV) complexes of o-diphenols.[65]

The complex formation between the alkaline-earth metal ions, magnesium-(II), calcium(II), and strontium(II) and o-dihydroxybenzene derivatives has been studied by potentiometric methods.[51,54] The stability order, $Sr < Ca < Mg$ has been found to hold for the pyrocatechol complexes.[51] This order is in agreement with the theoretical[56] relationship

between ionic radii and complex stability.

One of the methods of purifying wattle tannin is by the precipitation of the lead(II) complex.[66] Potentiometric methods have been used to investigate the soluble Tiron complex.[55] This investigation revealed that the complex species, $PbHL^+$ and PbL are formed in solution.

The oxidisable nature of the phenolic ligands results in the formation of highly coloured charge transfer complexes with reducible metal ions.[25] Charge transfer complexes involve a redistribution of electron densities within a molecule made up of an electron donor and an electron acceptor.[10,11] The first charge transfer bands to be characterised were those of the halide ions,[67] where the excited state was found to consist of a halide atom and an electron which has been transferred to a cavity bounded by solvent molecules. The spectra of the alkali metal halides have been interpreted in a similar manner,[68] but here the electron has been transferred to an orbital of the alkali metal ion.

The charge transfer spectra of molecular addition compounds in organic chemistry have been widely investigated.[69-71] In inorganic compounds, colour is generally associated with d-d transitions, but there are d^0 and d^{10} compounds which are intensely coloured eg. HgI_4^{2-} is brick-red and has been assigned to charge transfer from the readily oxidisable iodide ion to low energy empty orbitals on the metal.[72] Charge transfer processes are not confined to d^0 and d^{10} metal compounds, but occur frequently in transition metal complexes.[73]

In general there are two types of charge transfer processes in

complexes. When an electron is transferred from an orbital lying principally on the ligand to an orbital lying principally on the metal, it is termed a ligand to metal and, in the reverse process, metal to ligand charge transfer. Both types of transitions have been interpreted on a molecular orbital model.[12,13,74] Certain complexes eg. metal cyanides, are capable of exhibiting both ligand to metal and metal to ligand transitions.[75,76]

The metal ions, iron(III), titanium(IV) molybdenum(VI) and tungsten(VI) have been found to form highly coloured charge transfer complexes with phenolic ligands.[25,77] These complexes have been shown to exhibit ligand to metal transitions.[25]

Molybdenum(VI) and tungsten(VI) complexes have been used in electropheretic investigations of flavanoid compounds.[78] These complexes are strongly coloured, red for molybdenum(VI) and yellow for tungsten(VI). The visible absorption spectra of a number of Mo(VI) complexes of o-diphenols have been recorded.[79] The colour of these complexes is due to the presence of strong absorption bands in the region of 400 nm. Spectrophotometric methods established that the tungsten(VI) complex of pyrocatechol[80] and the molybdenum(VI) complex of 4-chlorocatechol[81] have 1 : 2 component ratios of metal to ligand. This has been confirmed[82,83] by the isolation of the complexes, $NH_4H\left[WO_2(C_6H_4O_2)_2\right]H_2O$ and $(C_5H_6N)_2\left[MoO_2(C_6H_4O_2)_2\right]$. The latter complex has been shown to be dimeric on the basis of its crystal structure.[84] In addition the infrared spectrum of this complex was found to exhibit no free O-H stretching vibrations,[85] which is in agreement with the above formula.

A detailed spectrophotometric and electrophoretic investigation has been carried out[86] on the titanium(IV) complexes of pyrocatechol, protocatechuic acid and Tiron. Complicated equilibria, dependent on the pH and especially the concentration of the ligand, were shown to occur in aqueous solution. The final yellow species has been established to have a 1 : 3 ratio of metal to ligand.[25,86] This stoichiometric ratio has been confirmed by the isolation of the pyrocatechol complex, $K_2\left[Ti(C_6H_4O_2)_3\right]H_2O$.[87]

In general it was found from the literature survey that extensive investigations have been made on the metal complexes of o-dihydroxybenzene derivatives and especially those of pyrocatechol and Tiron. Few reports concerning the 1,2,3-trihydroxybenzene complexes were, however, found. In many of the previous investigations only a few representative o-diphenol complexes were studied. The large range of o-diphenol derivatives used in the present investigation on metal complexes proved useful in comparing the results obtained with those for the monomeric flavanoid and wattle tannin complexes.

LIST OF PHENOLIC LIGANDS

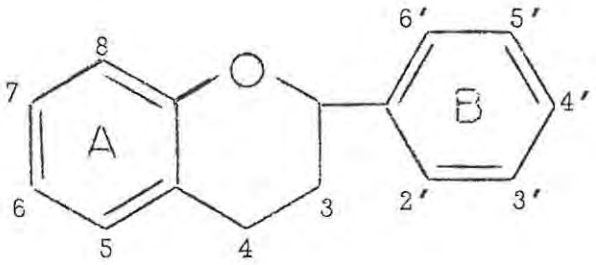
(a) Simple phenolic ligands.

Trivial Name	I.U.P.A.C. Nomenclature
pyrocatechol	1,2-dihydroxybenzene
4-methylcatechol	4-methyl-1,2-dihydroxybenzene
4-tert.-butylcatechol	4-tert.-butyl-1,2-dihydroxybenzene
4-hydroxycatechol	1,2,4-trihydroxybenzene
3-methylcatechol	3-methoxy-1,2-dihydroxybenzene
protocatechuic acid	3,4-dihydroxybenzoic acid.
-	2,3-dihydroxynaphthalene
-	3,4-dihydroxybenzenesulfonate
-	2,3-dihydroxynaphthalene-6-sulfonate*
Tiron	4,5-dihydroxybenzene-1,3-disulfonate
4-chloroacetylcatechol	α-chloro-3,4-dihydroxyacetophenone
protocatechuic aldehyde	3,4-dihydroxybenzaldehyde
4-nitrocatechol	4-nitro-1,2-dihydroxybenzene
pyrogallol	1,2,3-trihydroxybenzene
gallic acid	3,4,5-trihydroxybenzoic acid
propyl gallate	n-propyl 3,4,5-trihydroxybenzoate

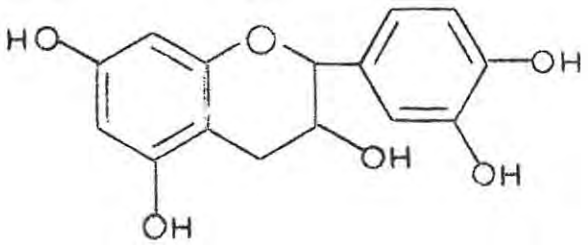
*abbreviated DHNS.

(b) Flavanoid compounds.

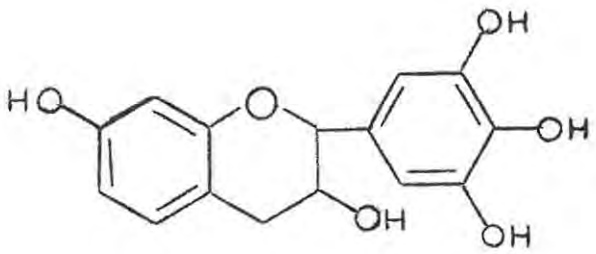
Parent structure :



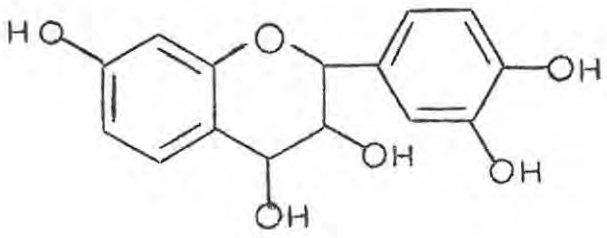
Trivial name	I.U.P.A.C. Nomenclature
catechin	3',4',5,7-tetrahydroflavan-3-ol



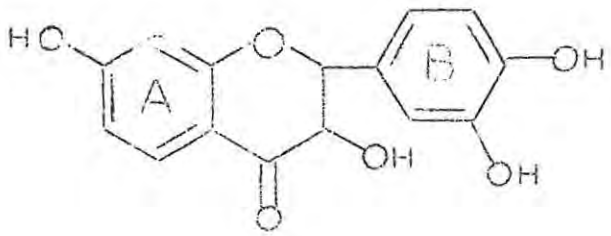
robinetinidin	3',4',5',7-tetrahydroxyflavan-3-ol



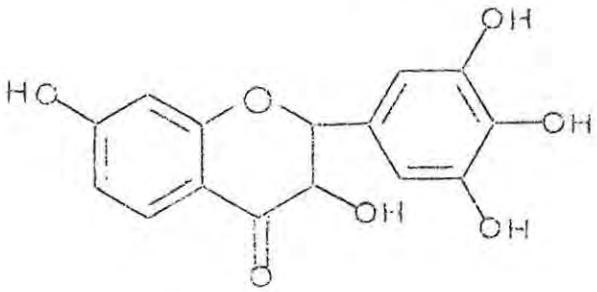
leucofisetinidin	3',4',7-trihydroxyflavan-3,4-diol



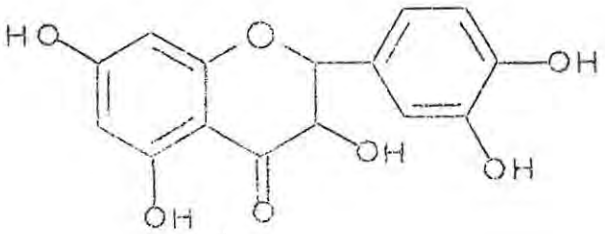
fustin 3,3',4',7-tetrahydroxyflavan-4-one



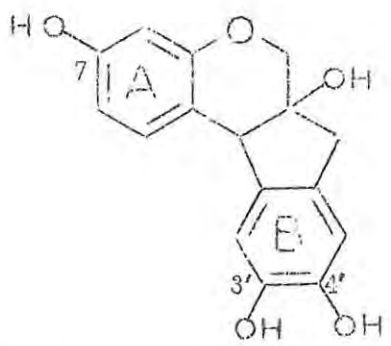
dihydrorobinetin 3,3',4',5',7-pentahydroxyflavan-4-one



dihydroquercetin 3,3',4',5,7-pentahydroxyflavan-4-one



brazilin



Note : For brevity, trivial names are used throughout this thesis.

DEFINITIONS OF EQUILIBRIUM CONSTANTS

For the dissociation of an acid, HL,

$$HL \rightleftharpoons L^- + H^+$$

the dissociation constant, Ka, is defined :

$$Ka = \frac{[L^-][H^+]}{[HL]}$$

For the formation of the metal complex, ML,

$$M^+ + HL \rightleftharpoons ML + H^+$$

the equilibrium constant, k_1 , is defined :

$$k_1 = \frac{[ML][H^+]}{[M^+][HL]}$$

For the formation of the metal complex, ML,

$$M^+ + L^- \rightleftharpoons ML$$

the stability constant, K_1 , is defined :

$$K_1 = \frac{[ML]}{[M^+][L^-]}$$

The product of the successive stability constants is the overall stability constant, β . The constants for any other types of equilibria have been defined in the text. For the sake of simplicity, the charges of ionic species in general equations have been omitted in the text.

Because the potentiometer, which was used to measure the pH of the

solutions, was calibrated with standard buffers, the hydrogen ion activity and not the hydrogen ion concentration should be used more correctly in the above equations. Equilibrium constants are then termed mixed constants because the equations contain both activity and concentration terms. Since mixed or Bronsted equilibrium constants are only valid for a particular ionic medium,[188] all experiments were conducted under the same conditions of ionic strength (KCl) and temperature. The method of Irvine and Rossotti[89] enabled the use of potentiometric data in acid and alkaline media. Thermodynamic equilibrium constants were not determined since the present investigation was on a comparative basis and only results determined herein were compared.

EXPERIMENTAL

Reagents.

Pyrocatechol (Merck)-purified by sublimation, m.p.105° (lit.[128] 105°).

Pyrogallol (Merck) - purified by sublimation, m.p.132° (lit.[128] 133°).

4-Methylcatechol (K and K Lab.) - purified by sublimation, m.p. 65° (lit.[128] 65°).

4-tert.-Butylcatechol (Koch-Light) - purified by sublimation, m.p. 54° (lit.[128] 54-55°).

3-Methoxycatechol (Koch-Light) - purified by sublimation and stored in a refrigerator, m.p. 38 - 42° (lit.[128] 38-41°).

Protocatechuic acid (BDH) - recrystallised from water, with one molecule of water of crystallisation, m.p. 199° (lit.[128] 199°).

Gallic acid (Merck - extra pure) - unpurified, contains one water of crystallisation, m.p. 253° (lit.[128] 253°).

2,3-Dihydroxymaphthalene (Koch-Light) - recrystallised from water, m.p. 159° (lit.[128] 160-161°).

2,3-Dihydroxynaphthalene-6-sulfonic acid sodium salt (Koch-Light) - recrystallised from water, with 0.5 waters of crystallisation.[34]

Tiron (4,5-dihydroxybenzene-1,3-disulfonic acid disodium salt) (Merck) - unpurified, contains one water of crystallisation.

Propyl gallate (Koch-Light) - recrystallised from water, m.p. 152° (lit.[128] 153°).

4-Chloroacetylcatechol (Fluka) - unpurified, m.p. 173° (lit.[128] 173°).

4-Nitrocatechol (Fluka) - recrysallised from benzene, m.p. 175° (lit.[128] 176°).

Protocatechuic aldehyde - recrystallised from benzene, m.p. 153° (lit.[128] 154°).

3,4-dihydroxybenzenesulfonic acid potassium salt - this derivative was prepared by the sulfonation of pyrocatechol[221] thus : 10 g. pyrocatechol and 6 ml. concentrated sulfuric acid together with a trace of iodine were heated at 55° for 2 hours. The product was poured into 100 ml. water. The free sulfuric acid was removed with barium hydroxide and the acid liberated from the filtrate by neutralising with dilute sulfuric acid. The solution of the free acid was concentrated and was poured into a saturated solution of potassium chloride from which the potassium salt of 3,4-dihydroxybenzene-sulfonate separated as white platelets. (Yield, 70%). The product was recrystallised from water. Potentiometric titrations with potassium hydroxide after addition of an excess of germanium dioxide[34] gave assays of 99.8%.

4-hydroxycatechol was prepared by the hydrolysis of 1,2,4-triacetoxybenzene[222] (Koch-Light). 50 g. 1,2,4-Triacetoxybenzene was dissolved in 100 ml. methanol. 10 ml. Concentrated hydrochloric acid was added and the solution was refluxed for 1 hour. The product was concentrated by distillation under reduced pressure below 30° until the dark green liquid acquired a brown colour. On cooling, 4-hydroxycatechol separated as small grey crystals. (Yield, 75%). 4-Hydroxycatechol was purified by recrystallisation from ether. m.p. 140° (lit.[128] 141°). The infrared spectrum of the purified compound showed no evidence of a carbonyl absorption band. This indicated that complete hydrolysis of the starting material had been achieved.

(±)-Fustin was extracted from the heartwood of Rhus glabra.[223] Drillings from the heartwood of Rhus glabra (2 kg.) were extracted with 500 ml. cold water. Concentration of the extract in a rotary evaporator yielded a bright yellow powder consisting of fustin and fisetin. 5 g. Quantities of this impure product were dissolved in 200 ml. water and the fustin was

separated by means of column chromotography using cellulose powder. The fustin fraction was concentrated to dryness under reduced pressure. The product was dissolved in ethyl alcohol and treated with charcoal. On concentration of the filtrate, white crystals of (±)-fustin were obtained. These were recrystallised from water. m.p. 223° (lit.[224] 225°). The infrared spectrum was found to be identical with that of (±)-fustin.[224]

Wattle tannin was extracted from the bark of the black-wattle tree (Acacia mollissima). Bark was collected from mature trees, cut into slivers with a stainless-steel knife and immersed in methanol within 1 - 2 hours of being stripped from the tree. After 24 hours the methanol extract was concentrated to a dry powder (pale buff) in a rotary evaporator. The percentage tannin was determined by photometric methods,[15] and was found to contain 75 percent wattle tannin. The remaining constituents of the extract are aqueous insoluble material, solvent molecules and a small percent simple sugars. The insolubles were removed from the aqueous wattle tannin solutions by filtration. Although the aqueous solutions were still impure the nature of the impurities did not affect the potentiometric of the spectrophotometric results. The lead tannate method[66] of purifying wattle tannin was not used because it was found that it was impossible to remove all the lead from the extract. In addition during the isolation of such a purified extract, a fair amount of colour-darkening, due to oxidation, was found to be unavoidable.

The sulfited derivative[225] of wattle tannin was prepared by heating a concentrated solution of tannin and 10 percent sodium bisulfite under increased pressure for 2 hours. The solution was concentrated to a dry powder in a rotary evaporator. The nature of the sulfited derivative of wattle tannin is not fully known. A chromatographic investigation[158] suggested that

sulfonic acid-type addition compounds are formed, probably on the heterocyclic ring of the flavanoid molecules.

Brazilin (Fluka), m.p. 128° (lit.[128] 130°).

(±)-Dihydroquercetin (Fluka), m.p. 232° (lit.[128] 234-6°).

The following phenolic compounds were kindly supplied by Dr. H.M. Saayman.

(+)-Catechin - contains 4 waters of crystallisation.[128] m.p. 95° (lit.[128] 96°).

(-)-Robinetinidol - contains 1.5 waters of crystallisation.[226] m.p. 206° (lit.[226] 207°).

(+)-Leucofisetinidin - contains 2 waters of crystallisation.[227] m.p. 105° (lit.[227] 105-106°).

(+)-Dihydrorobinetin, m.p. 225° (lit.[228] 225-226°).

All the chemicals including the metal salts used were of analytical reagent grade. Hydrated metal nitrates or chlorides were used except for germanium dioxide, boric acid, sodium molybdate and sodium tungstate. The above reagents were chosen on the basis of the highest reported purity and were used without recrystallisation.

Preparation of standard solutions

Boiled de-ionised water was used for all the preparations. Aqueous, standard solutions (0.05 - 0.005M) of the phenolic compounds were prepared by direct weighing. Only freshly prepared stock solutions were used, because it was found that even if precautions were taken, the oxidisable phenolic compounds still showed signs of decomposition (solutions became discoloured) after a period of one day. Aqueous, standard solutions (0.02 - 0.002M) of the metal ions were prepared in a similar manner. The

titanium stock solution was prepared by adding the liquid $TiCl_4$ dropwise to a concentrated hydrochloric acid solution and only then diluted. The presence of the acid was necessary to prevent hydrolysis of the Ti(IV) ions. The titanium(IV) stock solution contained a 50 : 1 molar ratio of acid to metal ion and was standardised spectrophotometrically.[25] The germanium stock solution was standardised by potentiometric titration with potassium hydroxide after addition of mannitol.[34] The stock solutions of iron(III), aluminium(III), copper (II), vanadyl(II) and lead(II) were standardised by potentiometric titrations of the stable Tiron complexes with standard potassium hydroxide. The nickel(II), cobalt(II), zinc(II), magnesium(II) and calcium(II) stock solutions were standardised by the usual complexometric methods.[229] Standard solutions of potassium chloride, sodium acetate, boric acid, sodium tungstate and sodium molybdate were prepared by accurate weighing of the AnalaR grade (BDH) compounds. Standard solutions of potassium hydroxide and hydrochloric acid were made up to volume from standard ampules (Merck).

Potentiometric measurements.

Potentiometric titration curves were obtained on a Metrohm automatic potentiometer, Model E436 with a combination glass and calomel electrode (Metrohm EA121 UX). Instrument driven plunger type burettes of 10 and 20 ml. capacity were used. All the potentiometric measurements were made at 20 $\pm$ 0.5°C. The ionic strength of the aqueous solutions was made 0.1 N by suitable addition of potassium chloride. In potentiometric titrations with 0.1 N KOH as the titrant, the decrease in ionic strength, resulting from the increase in volume as the titration proceeds, is compensated for by the ionic strength of the titrant. However, with 0.01 N KOH, the ionic

of the titrant had to be increased to 0.1 N with KCl.

The potentiometer was calibrated with aqueous buffer solutions prepared from standard ampules (Merck).

Potentiometric procedure : The required volumes of metal ion and ligand stock solutions were pipetted into the reaction vessel. A suitable volume of standard KCl was added so that the final ion strength, I, was 0.1. A total volume of 50 - 60 ml. was used, depending on the solubility of the ligand. Before the reaction vessel was placed in position, the pen was zeroed on the chart paper in order to eliminate any error due to backlash of the gears. The reaction vessel was then attached to the covering lid, which contained the combination glass and calomel electrode, thermometer and alkali and nitrogen inlet tubes. Pure, presaturated nitrogen was bubbled through the solution for ten minutes prior to commencement of the titration. During the titration a magnetic stirrer was used to agitate the solution. The speed of the titration was determined by the rate of equilibrium. This was checked periodically during the titration by stopping the addition of alkali and observing if any drift in the pH reading occurred. The instrument which was used, is also equipped with an automatic speed control which slows down the titration speed in the region of the end points, where rapid increases in the pH occur with small additions of alkali. After each titration was run the caustic residues that adhere to the electrode were neutralised with dilute acid and thoroughly rinsed with water.

Spectrophotometric measurements.

Ultraviolet and visible spectral data were obtained on Beckman DK-2, Beckman DU (converted to mains supply) and Zeiss PMQ-11 spectrophotometers, at 20 $\pm$ 0.5°C, using 1 cm. quartz cells.

Spectrophotometric procedure : The required volumes of metal ion and ligand stock solutions were pipetted into a volumetric flask. Buffer and KCl solutions were added so that the final ionic strength was 0.1. An acetate + KOH buffer system was used. The pH of the solution was obtained on the same instrument which was used for the potentiometric titrations. The solution was allowed to equilibrate in the cell before recording the spectral data.

In the spectrophotometric method for determining the dissociation constants of the phenolic ligands, it was found that although precautions were taken (only boiled out de-ionised water, saturated with nitrogen, was used), optical interference as a result of oxidation of the phenol was still observed. This was especially noticable at the very high pH values required for the determination of the dissociation constants of the less acidic phenolic groups. For this reason a small amount of antioxidant was added to eliminate this interference. It has been found[105] that hydrazine hydrate is a convenient antioxidant for spectrophotometric investigations of phenolic compounds at high pH, because this antioxidant only absorbs light at wavelengths less than 220 nm. It was found that the presence of 0.01 M hydrazine hydrate had no effect on the value of the phenolic dissociation constants, by determining the dissociation constants of a stable phenol eg. Tiron in the presence and absence of the antioxidant.

The absorption spectra of the divalent first transition metal phenolic complexes were obtained from solutions containing stoichiometric concentrations of metal, ligand and alkali.

Electrophoretic measurements.

Electrophoretic measurements were obtained using L.K.B. Paper Electrophoresis Equipment. Suitable buffers were prepared from sodium acetate,

acetic acid and sodium hydroxide. A final ionic strength of 0.1 N was used. Both tanks were filled with a buffer solution and the levels were equalised with a syphoning tube. The paper strips were soaked in the buffer and then positioned on the perspex connecting bridge. Solutions of the metal complexes were made up with the buffer of the required pH and spotted on the paper. A constant direct current was applied and in general the ionic complexes were observed to migrate within 30 minutes. This technique was only used to determine the electronic sign of the complex species and no attempt was made to interpret the mobilities of the various complexes. An internal non-migrating standard was however used to compensate for electroendosmosis.[231]

Infrared absorption spectra were determined on Nujol mulls between potassium bromide plates on a Beckman IR-10 spectrophotometer.

Melting points were determined on a Kofler hot stage.

All calculations were made on a Hewlett-Packard 9100B calculator fitted with an extended memory, Hewlett-Packard 9101A.

RESULTS AND DISCUSSION

A. POLYPHENOLIC DISSOCIATION CONSTANTS.

For the determination of stability constants for the metal-polyphenolic complexes, a knowledge of ligand acidity constants is essential. These values have been determined for twenty-three related polyphenols.

Phenols are weak acids and owe their acidity to the dissociation :

$$PhOH \rightleftharpoons PhO^- + H^+ \qquad (1)$$

For the general equilibrium,

$$H_cL \rightleftharpoons H_{c-x}L^{-x} + xH^+ \qquad (2)$$

the dissociation constant, Ka, is given by :

$$Ka = \frac{\left[H_{c-x}L^{-x}\right]\left[H^+\right]^x}{\left[H_cL\right]} \qquad (3)$$

Two methods were used to obtain values for Ka, viz. potentiometry and spectrophotometry.

1. Potentiometric determination of the phenolic dissociation constants.

All the potentiometric titrations were determined at 20°C in aqueous solutions with an ionic strength of 0.1 (KCl). The presence of a high concentration of an extraneous salt ensures that the ionic strength of the solution remains constant during the titration. Dissociation constants determined under identical conditions of ionic strength and temperature can therefore be related. This also applies to the stability constants of metal complexes.

This practice is quite general for such an investigation.[88]

(a) o-Dihydroxybenzene derivatives.

The dibasic nature of these derivatives results in a two step dissociation :

$$H_2L \rightleftharpoons HL^- + H^+ \qquad Ka_1 = \left[HL^-\right]\left[H^+\right]\Big/\left[H_2L\right] \tag{4}$$

$$HL^- \rightleftharpoons L^{2-} + H^+ \qquad Ka_2 = \left[L^{2-}\right]\left[H^+\right]\Big/\left[HL^-\right] \tag{5}$$

where Ka_1 and Ka_2 are the first and second dissociation constants respectively. Examples of the type of titration curve obtained are shown in Fig. 1. The distinct inflection, after addition of one equivalent of alkali which is observed in the titration curve of the more acid derivative, 4-nitrocatechol, indicates that these derivatives dissociate separately, according to equations (4) and (5). Thus no special calculations were required to obtain accurate values of the dissociation constants. The very low acidity of the second phenolic dissociation for some of these derivatives prohibited the determination of the constant, Ka_2, by this method.

The dissociation constants were obtained by first calculating the value of $\bar{n}_a$, the mean number of dissociable protons bound per phenol - in whatever form, at various pH values by the electroneutrality equation[89] :

$$\bar{n}_a = c - \frac{(v'' - v')(N + E^o)}{(V^o + v')T_L^o} \tag{6}$$

where v'' and v' are the respective volumes of alkali required to reach the same pH in titrations of the phenolic derivative plus free acid, and the free acid alone; T_L^o, the initial concentration of the phenol; V^o the

initial total volume of the solution; E^{o}, the initial concentration of the free acid; N, the normality of the alkali and c, the total number of dissociable protons of the phenol.

If no free acid is added then the equation becomes :

$$\bar{n}_a = c - \frac{(v'' - v')N}{V^{o}T^{o}_{L}} \qquad (7)$$

where v'' and v' are the respective volumes of alkali required to reach the same pH in titrations of the phenolic derivative and solvent alone. The constants were then calculated from the $\bar{n}_a$ values according to the following equations :

$$pKa_1 = pH - \log \frac{2 - \bar{n}_a}{\bar{n}_a - 1} \qquad (8)$$

$$pKa_2 = pH - \log \frac{1 - \bar{n}_a}{\bar{n}_a} \qquad (9)$$

For protocatechuic acid, the value of the carboxylic dissociation constant was calculated from the equation :

$$pKa = pH - \log \frac{3 - \bar{n}_a}{\bar{n}_a - 2} \qquad (10)$$

The experimental data used to calculate a few representative constants and the results are given in Tables 13 and 14. The values of all dissociation constants calculated according to this method are listed in Table 1.

TABLE 1.

Dissociation constants, Ka, determined potentiometrically and spectrophotometrically for the o-dihydroxybenzene derivatives.

Phenol	pKa_1		pKa_2	
	a_p	b_S	a_p	b_S
4-methylcatechol	9.54	9.56	-	14.05
4-tert.-butylcatechol	9.55	9.54	-	14.05
pyrocatechol	9.35	9.37	-	13.65
3-methoxycatechol	9.31	9.30	-	13.60
protocatechuic acid	8.82 4.38[c]	8.82	-	13.20
2,3-dihydroxynaphthalene	8.55	8.55	12.36	12.43
3,4dihydroxybenzenesulfonate	8.38	8.40	12.35	12.45
DHNS	8.18	8.19	12.14	12.19
Tiron	7.65	7.66	-	12.58
4-chloroacetylcatechol	7.40	7.40	12.02	11.98
protocatechuic aldehyde	7.19	7.21	11.79	11.80
4-nitrocatechol	6.76	6.75	10.91	10.90

a and b, P and S represent the potentiometrically and the spectrophotometrically determined values, respectively.
c, dissociation constant for carboxylic substituent.

(b) Trihydroxybenzene derivatives.

The general type of titration curve obtained for these derivatives is shown in Fig. 1. Their trihydric nature results in three possible dissociation steps. However, from the titration curves it was obvious that up to pH = 11, only two phenolic groups dissociate. The absence of a distinct inflection at the end point of the first dissociated proton, points to an overlap of the successive titration curves. Equations (6) - (9) would therefore yield inaccurate results especially in the region of $\bar{n}_a = 2$, because it has been shown[91] that a separate determination of Ka_1 and Ka_2 is only valid if $Ka_1/Ka_2 > 10^3$. Accurate results were, however, obtained by application of the following methods :

(1) Least squares treatment[90] : The values of $\bar{n}_a$, which were calculated from equation (6), were used to determine the constants by means of a least squares treatment of the following equation for a straight line :

$$\frac{1 - \bar{n}_a}{(\bar{n}_a - 2)[H]} = \frac{(3 - \bar{n}_a)[H]}{(\bar{n}_a - 2)Ka_1Ka_2} - \frac{1}{Ka_2} \qquad (11)$$

for c = 3 i.e. for trihydroxybenzene derivatives.

(2) Overlapping ionisation treatment[91] : The following equations were also used to calculate the constants :

$$Ka_1 = \frac{Y_1Z_2 - Y_2Z_1}{X_1Y_2 - X_2Y_1} \qquad (12)$$

$$Ka_2 = \frac{X_1Z_2 - X_2Z_1}{Y_1Z_2 - Y_2Z_1} \qquad (13)$$

where : $X = [H^+](B - C + [H^+])$ (14)

$$Y = 2C - (B + [H^+]) \qquad (15)$$

$$Z = [H^+]^2(B + [H^+]) \qquad (16)$$

where C is the total concentration of the phenol and B the concentration of the alkali added. Pairs of readings have to be selected from either side of the mid-point, when X_1, Y_1 and Z_1 will be the readings obtained with less than one equivalent, while X_2, Y_2 and Z_2 refer to readings given by more than one equivalent of titrant. The values of B and C were obtained from the titration data :

$$B = \frac{N(v'' - v')}{(V^o + v'')} \qquad (17)$$

$$C = \frac{T_L^o \times V^o}{(V^o + v'')} \qquad (18)$$

(3) Correction term treatment[90] : This method is based on the theoretical symmetric nature of the potentiometric titration curve about the mid-point, $\bar{n}_a = 2$ for $c = 3$. The following equations apply for $c = 3$:

$$z = \log \frac{1 - d}{d} + \log \left[1 - \frac{(1 + d)\left[H^+\right]_{2-d}}{(1 - d)\left[H^+\right]_{2+d}} \right] \qquad (19)$$

where z is the correction term; $d = 0$ at mid-point ($\bar{n}_a = 2$) and $d = 0.5$ at $\bar{n}_a = 2.5$ and $\bar{n}_a = 1.5$; $\left[H^+\right]_{2+d}$ and $\left[H^+\right]_{2-d}$ are obtained from the pH at $\bar{n}_a$ mid-point + d and $\bar{n}_a$ mid-point - d, respectively.

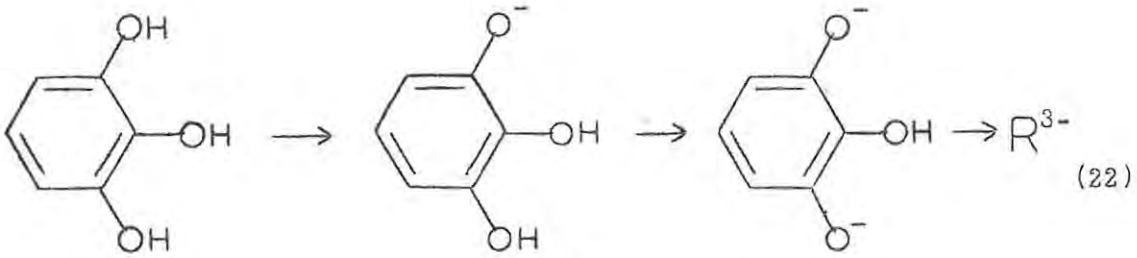
Then :

$$\log Ka_1 = pH_{2+d} - z \qquad (20)$$

$$\log Ka_2 = pH_{2-d} + z \qquad (21)$$

The values of $\bar{n}_a$ calculated from equation (6) were used to plot a curve of $\bar{n}_a$ vs. pH. From this curve the required readings were obtained.

The experimental data and results, according to methods (2) and (3), for pyrogallol are shown in Tables 15 and 16 and Fig. 4. The dissociation constants for other derivatives of this class are listed in Table 2. From this Table it may be seen that all three methods give consistent results. The values of Ka_1 and Ka_2 for pyrogallol compare favourably with published values, cf. Table 5. The dissociation order for pyrogallol has been established[103] and is illustrated as follows :



(22)

The similarity between the dissociation constants of resorcinol and pyrogallol (Table 2) supports the above order.

TABLE 2.

Dissociation constants, Ka, for the trihydroxybenzene derivatives and resorcinol determined potentiometrically and spectrophotometrically.

Phenol	Method[a]	pKa_1	pKa_2	pKa*
pyrogallol	1	9.05	11.23	
	2	9.04	11.22	
	3	9.05	11.23	
	5	9.05	11.25	
4-hydroxycatechol	1	9.10	11.56	
	2	9.09	11.53	
	3	9.11	11.55	
gallic acid	1	8.96	11.32	
	2	8.68	11.30	
	4			4.28
	5	8.70	11.39	
propyl gallate	4	7.88	11.02	
	5	7.90	11.05	
resorcinol	1	9.31	11.22	
	3	9.29	11.23	
	5	9.30	11.22	

a. Method : Potentiometric; (1) least squares, (2) overlapping ionisation, (3) correction term, (4) equations (6) - (10); (5) spectrophotometric.

*Dissociation constant of the carboxylic acid substituent.

(c) Polyphenolic compounds.

The wattle tannin monomers are polyphenolic flavanoids with up to four phenolic groups. Therefore a simple calculation of the dissociation constants from the potentiometric titration curves is not possible, because of the multiple overlapping dissociations. However, if some of the phenolic groups can be complexed with a metal ion then this will remove those groups involved in the complex from the titration curve of the unco-ordinated phenolics. Pre-requisites of the complex are (a) that it should be completely formed at sufficiently low pH values, in order not to interfere with the phenolic titration and (b) that the phenolic groups involved in the complex may be pin-pointed. These requirements are satisfied by the germanium(IV) complexes (to be discussed later, Section C) which were found to be completely formed in acidic solution. In addition germanium(IV) only forms complexes with an o-dihydroxobenzene function resulting in a five-membered chelate. Solutions of germanium dioxide (GeO_2) and o-diphenols react as follows :

$$GeO_2 + 3H_2L \rightleftharpoons GeL_3^{2-} + 2H^+ \qquad (23)$$

However the assumption has to be made that the presence of the metal ion does not affect the dissociation process of the uncomplexed phenolics. The flavanoid structure of wattle tannin monomers consists[92] of two benzene rings separated by a saturated heterocyclic ring as illustrated on page 14. The two aromatic portions are therefore unconjugated and any reaction involving the one benzene ring would not be expected to have any affect on the properties of the other.

(1) Catechin, robinetinidol and brazilin : The structures[93,94] of these compounds are illustrated on pages 14 and 15.

Examples of the potentiometric titration curves obtained for the free phenolics and the Ge(IV) complexes are given in Fig. 2. The continuous nature of the free phenolic curve indicates multiple overlapping dissociations. The distinct inflection observed at $\bar{z} = 2$ ($\bar{z}$, the number of moles of alkali added per mole of metal) in the Ge(IV) complex curve, with stoichiometric concentrations (i.e. 1 : 3 moles) of GeO_2 and ligand, is in accordance with the requirements of equation (22). This illustrates that the o-dihydroxo group on the B-ring is completely co-ordinated. Since the titration curves for the uncomplexed phenolics of catechin and robinetinidol did not show distinct inflections, methods (1) - (3) were required to obtain accurate values. The results of method (1) for catechin and method (2) for robinetinidol are given in Tables 17 and 18 respectively. These constants, calculated by the other methods, are given in Table 3. The dissociation constant for the single uncomplexed hydroxyl of brazilin required no special calculations. The value obtained using equations (6) and (9) is given in Table 3. The assignment of pKa values to a particular meta-hydroxyl group for catechin was not possible as the constants could equally apply to either group. The more acidic of the two pKa values for the uncomplexed hydroxyl groups of robinetinidol, viz. 9.65, was assigned to the hydroxyl group of the A-ring because of the similarity between its value and that of brazilin, viz. 9.69. The less acidic value of 11.21 may therefore be assigned to the third unco-ordinated group on the B-ring. The latter value is, however, specifically for the Ge(IV) complex and need not be the same in the uncomplexed phenol. However, an approximate value of 11.25 for the dissociation constant of this group in the uncomplexed form was determined from plots of $\bar{n}_a$ vs. pH, by interpolation at half $\bar{n}_a$ values. Complexation of the two ortho-hydroxyl groups adjacent to this group thus appears to have very little

TABLE 3.

Dissociation constants, Ka, for catechin, robinetinidol and brazilin determined potentiometrically.

Polyphenol	Method[a]	pKa_1	pKa_2	pKa_3
		[b] $C_{3' \text{ or } 4'}$	$C_{5 \text{ or } 7}$	$C_{7 \text{ or } 5}$
catechin	1		9.18	11.22
	2		9.18	11.20
	3		9.17	11.24
	4	9.01		
		[b] $C_{3' \text{ or } 4'}$	C_7	
brazilin	5		9.69	
	4	9.21		
		[b] $C_{3' \text{ or } 5'}$	C_7	$C_{5' \text{ or } 3'}$
robinetinidol	1		9.65	11.21
	2		9.64	11.19
	3		9.65	11.22
	4	8.80		

a. Methods : (1) least squares, (2) overlapping ionisation, (3) correction term, (4) difference technique, (5) equations (7) - (9).
b. Assignments of pKa values to a particular hydroxyl group attached to the flavanoid carbon atoms, C_x (where x = carbon numbering).

effect on its dissociation constant. The similarity of this value with that obtained for pyrogallol supports the above assignment.

In order to determine the dissociation constants of those hydroxyl groups involved in the Ge(IV) complex formation, a difference technique was used. The difference between the titration curves of the polyphenol with, and without, GeO_2 present will give the titration curve of the hydroxyl groups involved in the complex. Allowance has to be made for the protons liberated on complex formation. Stoichiometric concentrations (i.e. 1 : 3 mole ratio) of GeO_2 and polyphenol need not necessarily be used. The concentration, T_L^o

used in equation (7) is then determined by the concentration of GeO_2, provided excess ligand is present. Although free acid was used to compensate for the protons liberated on complex formation, equation (7) had to be used to calculate $\bar{n}_a$ values in this type of difference technique because now the v'' readings refer to the uncomplexed titration and v' to the Ge(IV) complex titration curve. An example of this application for robinetinidol is given in Table 19. The constants for the other polyphenols determined by this method are given in Table 3. The dissociation constant for the other o-hydroxyl group could not be determined potentiometrically because of its very high pK value.

For robinetinidol the pKa value of 8.8 for the most acidic B-ring phenolic group was assigned to one of the two meta-hydroxyl groups as in the case of pyrogallol. For catechin and brazilin the B-ring value could be assigned to either of the o-dihydroxyl groups.

(2) Fustin and dihydrorobinetin : These two wattle tannin monomers have structures[95] illustrated on page 15. The titration curves obtained for these phenols are illustrated in Fig. 3. The similarity between them is evident from the curves. A much more acidic phenolic group than found for the previous polyphenols results. The presence of this acidic group separates the titration curves sufficiently to allow calculation of the dissociation constants without recourse to the Ge(IV) complex method. A correction method was still necessary because of the overlapping nature of the curves. The application of method (3) to the titration data for fustin is shown in Fig. 4 and Table 20. The constants calculated by the other methods are listed in Table 4.

The dissociation constants of the hydroxyl groups involved in the Ge(IV)

TABLE 4.

Dissociation constants, Ka, for fustin and dihydrorobinetin determined potentiometrically.

Polyphenol	Method[a]	pKa_1	pKa_2	pKa_3
		[b] C_7	$C_{3'}$ or $4'$	
fustin	1	7.04	9.01	
	2	7.05	8.98	
	3	7.05	9.00	
	4		9.00	
		[b] C_7	$C_{3'}$ or $5'$	$C_{5'}$ or $3'$
dihydrorobinetin	1	7.05	8.81	11.19
	2	7.06	8.78	11.18
	3	7.05	8.80	11.20
	4		8.79	
wattle tannin	4		8.80	

a. Methods : as for Table 3.

b. Assignments.

complex were also determined by the difference method, for comparison. The values obtained are given in Table 4.

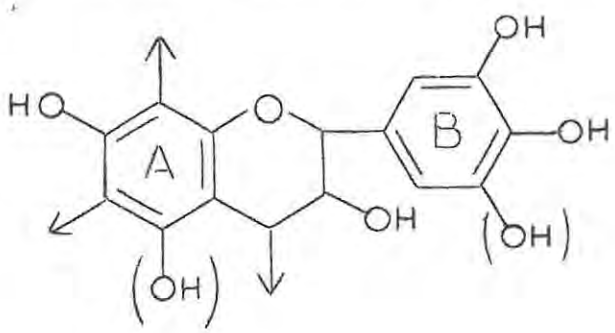
The most acidic value viz. 7.05 for both polyphenols was assigned to the hydroxyl group attached to the C_7 atom, because it was unaffected by Ge(IV) complex formation. The strongly electron-withdrawing character of the para-carbonyl group explains its more acidic nature. The other dissociation constants were assigned on the same basis as those for catechin and robinetinidol.

The similarity of the B-ring phenolic dissociation constants for fustin and dihydrorobinetin with those for catechin and robinetinidol, respectively, indicates that the dissociation process is unaffected by the carbonyl groups in the former two compounds. This also illustrates the unconjugated nature

of the flavanoid molecule.

The close agreement of the values, for the most acidic B-ring hydroxyl group, calculated by the Ge(IV) complex method and the free phenolic methods (Table 4), supports the assumption made previously - that the presence of the metal ion does not affect the dissociation of the uncomplexed phenolic groups.

(3) Wattle tannin : The structure of wattle tannins has been established[7] as being made up of polymeric polyphenolic flavanoid molecules :



(arrows indicate polymer bonds)

The average number of flavanoid units per polymer chain was found to be approximately equal to four.[96] The polymer linkage has been shown[97] to be either between carbon atoms C_4 - C_6 or C_4 - C_8. It has been established[7] that wattle tannins are made up of about 70 percent flavanoid analogues based on a resorcinal A and pyrogallol B nuclei, 25 percent resorcinol A and pyrocatechol B nuclei and 5 percent phloroglucinol A and pyrogallol and pyrocatechol B nuclei.

The potentiometric titration curve obtained for wattle tannin is given in Fig. 2. The continuous nature of the curve points to multiple overlap of the phenolic dissociations - as expected from its polyphenolic structure. The Ge(IV) complex method was therefore used to calculate the dissociation constants. A special experimental procedure was necessary because the

Ge(IV) complex of wattle tannin was found to precipitate from solutions of high ionic strength. When the potentiometric titration of the Ge(IV)-wattle tannin system was conducted in the absence of KCl no precipitate formed. If the KCl was only added after complete complexation, to give I = 0.1, then still no precipitate formed. The reason for this will be discussed later (Section C). The results of the difference technique applied to the titration readings with, and without, GeO_2 present using the above experimental procedure are given in Table 21.

Because of the polymeric nature of wattle tannin molecules a large excess of wattle tannin was found to be necessary in order to ensure complete formation. The average value of 8.8 from Table 21 was assigned to the most acidic B-ring hydroxyl group. It should be noted that this value is specifically for those hydroxyl groups involved in the Ge(IV) complex. Therefore, because of the similarity of this value with those for robinetinidol and dihydrorobinetin (Tables 3 and 4), it appears that only the pyrogallol B-ring analogues are complexed by Ge(IV).

The dissociation constants for the other phenolic groups could not be determined, because stoichiometric concentrations of GeO_2 and wattle tannin were found to give incomplete complex formation as will be shown in Section C.

2. Spectrophotometric determination of the phenolic dissociation constants.

The spectrophotometric method proved useful in determining the dissociation constants of the less soluble compounds and also of the compounds available in limited amount. The constants for the weakly acidic phenolic

groups could be determined by this method since at high pH values the spectrophotometric measurements are not complicated by the presence of hydroxide ions as in the potentiometric method.

Changes in the ultraviolet absorption spectra of the phenolic compounds with pH form the basis of this method. The absorption spectra were first recorded at various pH values to obtain an analytical wavelength most suitable for the determination. A desirable wavelength is one which shows the greatest difference in absorbance for the two species of the dissociation process being investigated. The general form of the absorption spectra and the extinction curves (absorbance vs. pH plots) obtained at fixed wavelengths are illustrated in Figs. 5 and 6.

The following equation[98] was used to calculate the dissociation constants of the more acidic phenolic groups :

$$pKa_x = pH + \log \frac{A^o_x - A}{A - A^o_{x-1}} \qquad (24)$$

where A is the absorbance at the corresponding pH and A^o_{x-1} and A^o_x are the absorbances of the undissociated and dissociated species respectively.

(a) o-Dihydroxybenzene derivatives.

It was found in the potentiometric investigation that the pKa_1 and pKa_2 values of this class of phenolics are sufficiently spaced so as not to interfere with each other. This is illustrated by the definite plateaus observed in their extinction curves (Fig. 6). Examples of the calculations are given in Table 22.

Because of the very weak acidic nature of the second dissociation for

most of the phenols, the "pure" absorption spectrum of the di-anion could not be determined, because the constant ionic strength of 0.1 used, restricted the upper pH limit. Since the values of A_2^o were unobtainable equation (24) could not be used. However, the above equation can be rearranged[91] :

$$A = A_2^o - \frac{\left[H^+\right](A - A_1^o)}{Ka_2} \qquad (25)$$

The method of least squares applied to the values of A and $\left[H\right](A - A_1^o)$ gave the required values of A_2^o and Ka_2. Using the calculated value of A_2^o, the dissociation constant, Ka_2, was determined for each pH value from equation (24). An example is given in Table 23.

The dissociation constants, Ka_1 and Ka_2, determined spectrophotometrically for all the o-dihydroxybenzene derivatives are listed in Table 1.

Owing to the large extrapolations required for the very high pKa_2 values, the constant for pyrocatechol was also determined for comparison at ionic strengths of 1.0. A value of 13.62 was obtained, which is very similar to the value obtained at an ionic strength of 0.1 (Table 1). The effect of ionic strength on the value of pKa_2 for 4-chlorocatechol has been investigated,[99] - little difference was found between the values at I = 0.1 and 1.0. However, for a highly ionic derivative such as Tiron the effect of I has been found to be quite substantial.[100]

The published pKa_2 values for pyrocatechol show considerable variation, ranging from 11.59 to 13.7.[14] However the lower values of pK_2 have been shown to be erroneous.[53] The dissociation constants, Ka_1 and Ka_2, obtained by Sommer and Bartusek[101-110] were found to compare favourably with those determined in the present investigation. The values of Ka_1 and Ka_2

obtained by the above authors are listed in Table 5.

TABLE 5.

Dissociation constants, Ka_1 and Ka_2, for phenolic compounds determined by the authors Sommer and Bartusek.

Phenol	pKa_1	pKa_2	references
pyrocatechol	9.37	13.7	101,102,103
resorcinol	9.30	11.06	102
phenol	9.62	-	102,104
pyrogallol	9.05	11.19	103
protocatechuic acid	8.82	13.0	10[illegible],106
3,4-dihydroxybenzenesulfonate	8.50	12.8	102,107
2,3-dihydroxynaphthalene	8.68	12.5	108
DHNS	8.19	12.16	109,110
4-nitrocatechol	6.84	11.1	108
Tiron	7.66	12.6	103,105

I = 0.1, temperature = 20°C.

(b) 1,2,3-Trihydroxybenzene derivatives.

Potentiometrically derived values of pKa_1 and pKa_2 for these derivatives were found to be within 3 units of each other; hence a separate treatment for each dissociation was not possible. The main difficulty was in determining the "pure" absorbance of the mono-anion, A_1^o. However, if an analytical wavelength is available where two of the species have the same absorbance values and the absorbance of only one of the ionic species changes with pH, then equation (24) may be used. Suitable wavelengths were found for all the derivatives of this class and the results of calculations for propyl gallate and pyrogallol are given in Table 24. The spectrophotometrically determined constants as shown in Table 2 compared favourably with the potentiometrically determined values. The dissociation constant for the third hydroxyl group could not be determined however, probably as a result

of its very high value.

(c) Polyphenolic compounds.

Due to the multiple overlapping dissociations observed in the potentiometric investigation of these compounds, determination of the dissociation constants from the spectrophotometric data could only be accomplished by employing the Ge(IV) complex to simplify the calculations.

(1) Catechin, robinetinidol, brazilin and leucofisetinidin : The structure of leucofisetinidin[111] is shown on page 14.

The type of extinction curves obtained for the Ge(IV) complexed and uncomplexed phenol at the analytical wavelength are shown in Fig. 6. Stoichiometric concentrations of GeO_2 and phenol were used so that all the o-dihydroxo groups on the B-ring were co-ordinated. The dissociation constants for the unco-ordinated phenolic groups in the Ge(IV) complex were calculated initially using equation (24). The results of this treatment for brazilin are given in Table 25. The absorbance values of the Ge(IV) complex spectra were subtracted from those of the free phenolic spectra to give ΔA values for the phenolic groups which are involved in the complex formation. The ΔA values were used subsequently to calculate (equation (24)) the corresponding dissociation constants as illustrated for leucofisetinidin in Table 26.

Due to the very low acidity of the second, B-ring o-dihydroxyl groups of catechin, brazilin and leucofisetinidin the dissociation constants were calculated directly from the free phenolic spectrophotometric data. Equation (25) was used in this calculation, as illustrated for leucofisetinidin in Table 27.

Table 6 lists the assignments and the pKa values obtained for these polyphenolic compounds.

TABLE 6.

Dissociation constants, Ka, for the polyphenolic compounds determined spectrophotometrically.

Phenol	- log dissociation constant					
	[a] $C_{3'}$ or 4'	$C_{3'}$ or 5'	C_5	C_7	$C_{5'}$ or 3'	$C_{4'}$ or 3'
catechin	8.98		9.15	11.25		13.25
brazilin	9.20			9.68		13.40
robinetinidol		8.81		9.65	11.2	
leucofisetinidin	9.00			9.55		13.20
fustin	8.99(244)[b]			7.08		13.25(270)
dihydrorobinetin		8.79(261)		7.09	11.2(235)	
dihydroquercetin	9.03(260)		11.56	6.78		

a. Assignments, (the C_5 and C_7 assignments for catechin could also be the reverse of those given above).

b. Values in parentheses are the analytical wavelengths nm.

(2) Fustin, dihydrorobinetin and dihydroquercetin : The structure of dihydroquercetin[112] is shown on page 15.

It was evident from the extinction curves of these polyphenols that the ionisation of the B-ring hydroxyl groups had no effect on the absorption spectra, at wavelengths greater than 320 nm. Therefore the dissociation constants for the phenolic groups on the A-ring were calculated at wavelengths in this region of the spectrum with the aid of equation (24). The results of the calculation for dihydroquercetin are given in Table 25.

The determination of the dissociation constants for the phenolic groups on the B-ring required careful selection of the analytical wavelength. Isosbestic points were observed in the absorption spectra recorded at various pH values for the A-ring dissociations. The wavelengths at these points

(Table 6) were chosen for the determination of the B-ring dissociation constants. The results of the calculation using equation (24) for fustin are given in Table 28.

The very high pKa value for the $C_{4'}$ or $_{3'}$ hydroxyl group of fustin was calculated using equation (25). This constant could not be calculated for dihydroquercetin because a suitable analytical wavelength was not available.

Table 6 lists the assignments and the dissociation constants obtained for the three polyphenols of this class.

(d) Wattle tannins.

Due to the continuous nature of the extinction curve for wattle tannin (Fig. 6) and the absence of isosbestic points in the absorption spectra at different pH values, dissociation constants could not be calculated by spectrophotometric means. Neither could the method using the Ge(IV) complex be used because of the insolubility of the wattle tannin complex.

3. The effect of substitution on the phenolic dissociation constants.

The dissociation constants of the o-dihydroxybenzene grouping are those which are necessary for determining the stability constants of metal complexes of o-diphenols. The average values obtained from both above methods are listed in Table 7. In order to avoid confusion with the symbols used above for the polyphenols, the constants have been referred to as Ka and Kb for the first and second dissociations, respectively. Due to the limited accuracy in determining the second dissociation constant, the values of pKb and pKaKb have been rounded off to the nearest half or whole number.

A comparison of the pKa value for pyrocatechol viz. 9.36 with that for

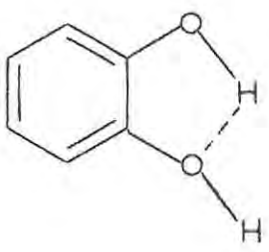
TABLE 7.

Dissociation constants, Ka and Kb, for the o-dihydroxyl group of o-diphenols.

Phenol	pKa	pKb	pKaKb	σ average
4-methylcatechol	9.55	14.05	23.6	-.12
4-tert.-butylcatechol	9.55	14.05	23.6	-.15
pyrocatechol	9.36	13.65	23.0	-
3-methoxycatechol	9.30	13.60	22.90	.04
4-hydroxycatechol	9.10	-	(23.4)[a]	-.12
pyrogallol	9.05	-	(22.65)	.06
catechin	8.99	13.25	22.25	.08
protocatechuic acid	8.82	13.20	22.0	.15
fustin	9.00	13.25	22.25	.08
brazilin	9.20	13.4	22.6	-
dihydroquercetin	9.03	-	(22.25)	.08
leucofisetinidin	9.00	13.2	22.2	.08
robinetinidol	8.81	-	(22.05)	.14
dihydrorobinetin	8.79	-	(22.05)	.14
wattle tannin	8.80	-	(22.05)	.14
gallic acid	8.68	-	(19.9)	.20
2,3-dihydroxynaphthalene	8.55	12.4	20.95	-
3,4-dihydroxybenzenesulfonate	8.39	12.4	20.8	.34
DHNS	8.18	12.15	20.35	-
propyl gallate	7.88	-	(20.0)	.56
Tiron	7.65	12.6	20.25	-
4-chloroacetylcatechol	7.40	12.0	19.4	-
protocatechuic aldehyde	7.21	11.8	19.0	.75
4-nitrocatechol	6.75	10.9	17.65	.98

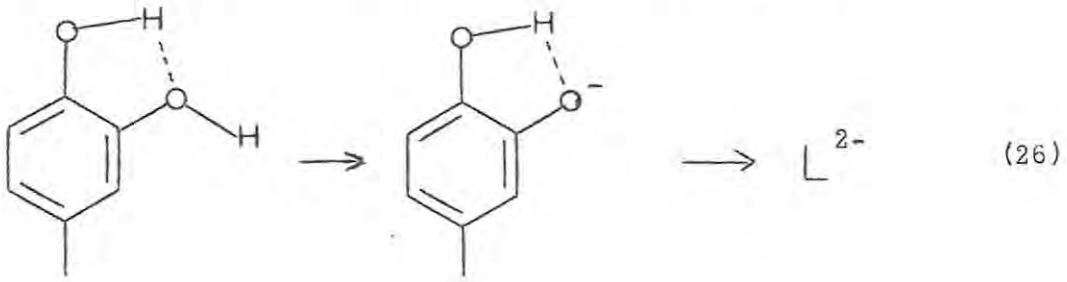
a. Values in parentheses refer to proposed dissociation constants - see text.

phenol viz. 9.6 (Table 5) shows that the ortho-hydroxyl group of the former lowers the pKa value relative to the latter compound. This has been explained[113] on the basis of an intramolecular hydrogen-bond :

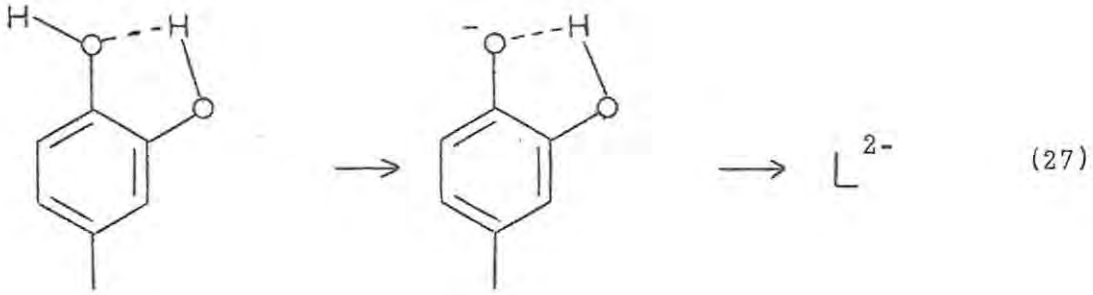


which lowers the bond order and therefore the pKa value of the free hydroxyl group, relative to phenol.

For the 4-substituted o-dihydroxybenzene derivatives, there are two processes by which the dissociation may proceed as shown below :



(26)



(27)

It has been assumed[114] that the substituent effect which produces the lowest value of pKa, determines which of the two processes will take place. The electron density on the phenolic oxygen has been shown[115] to be the main factor which determines the value of the monohydric phenolic dissociation constants. An electron-releasing substituent was found to increase the electron density and the pKa value relative to the unsubstituted analogue and vice versa. The Hammet σ^- function is a measure of the electronic effects of substituents. The relavent values[116,117,127] are listed in Table 8.

Linear relationships have been found[114] to exist between the dissociation constants (pKa) for 4-substituted pyrocatechol derivatives determined in

TABLE 8.

Hammet σ^- values for phenolic substituents.

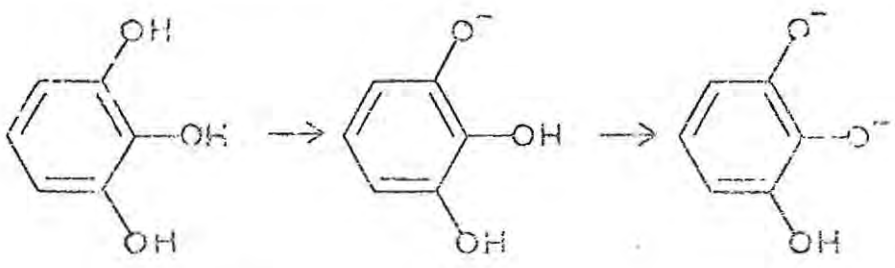
Substituent	σ^-_m	σ^-_p	σ^-_o
Me	-0.07	-0.17	-0.13
t-Bu	-0.1	-0.2	
MeO	0.08	-0.11	0.00
H	-	-	
OH	0.12	-0.37	0.00
O^-	-0.17	-0.52	
COO^-	-0.02	0.31	
COOH	0.37	0.73	
SO_3^-	0.28	0.40	
CHO	0.48	1.03	
CH_3CO	0.38	0.84	
$HCCH_2$	0.08	0.08	
COOEt	0.37	0.64	
NO_2	0.71	1.24	

40 percent dioxane solutions and the substituent constants, σ^-. Similar graphs were plotted in order to establish whether the relationships are also valid for dissociation constants determined in aqueous solution. The above assumption concerning the dissociation process requires the algebraically highest σ^- value to be plotted against the pKa values as illustrated in Fig. 7. In order to include the B-ring dissociation constants of the flavanoid compounds, the σ^- value for the related $-CH_2OH$ substituent was used. The linear relationship which is observed is similar to that obtained previously.[114] Also, a linear relationship was found in a plot of the algebraically lowest σ^- value and the second dissociant constants (pKb) as illustrated in Fig. 7. It has, however, been found[114] that a better fit is obtained in this type of correlation, if the average value of σ^-_p and σ^-_m is used instead. This was explained on the basis of the intramolecular H-bond which causes strong interaction between the oxygen atoms. Hence both o-hydroxyl groups are equally affected by the substituent. The result of a

similar correlation with the pKa values determined in this investigation also gave a slightly better linear fit, as illustrated in Fig. 8.

In order to relate the overall dissociation constants, Ka_1b, for the 4-substituted pyrocatechol derivatives, the average of the para- and meta- σ values (Table 8) were used as illustrated in Fig. 8. The existence of the observed linear relationship allowed unknown dissociation constants to be estimated and also enabled proposed values to be checked.

The dissociation order for pyrogallol has been established[103] (cf. reaction (22)) viz. the first two hydroxyl groups to ionise are those meta to each other. It would be expected that the other 1,2,3-trihydroxybenzene derivatives behave similarly. Therefore the second dissociation constants for these derivatives cannot be compared to those for the o-dihydroxybenzene derivatives. The third dissociation constant, Ka_3, for the 1,2,3-trihydroxybenzene derivatives could not be determined, because of its very low value. The acidity of the third hydroxyl group will of necessity be very low, due to the electronic influences of the two adjacent ionised hydroxyl groups. Even if the constant, Ka_3, could be obtained, it could not be used to determine the stability constants of the 1,2,3-trihydroxybenzene complexes. These complexes were generally found to consist of a co-ordinated o-dihydroxo group with the third hydroxyl group free and undissociated. Therefore the dissociation constants required are those for the dissociation order :



(28)

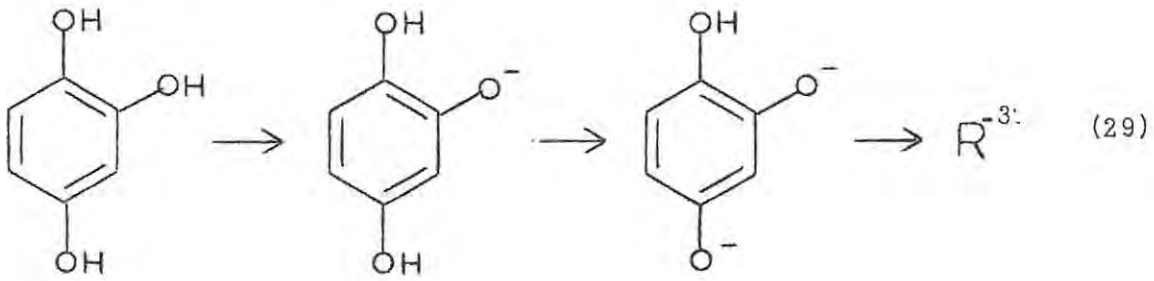
Since the σ_o values for the -OH and -OMe substituents have been found[118] to be the same, the value of the dissociation constant, Kb, for 3-methoxycatechol was used to obtain the combined dissociation constant, KaKb, for pyrogallol (Table 7). This pKaKb value was found to fit the linear relationship observed in Fig. 8, if the value of σ_o for the -OH substituent was taken as zero, as for the -OMe substituent.

Due to the similarity in pKb values for 3-methoxycatechol and pyrocatechol, the pKaKb values for the 1,2,3-trihydroxybenzene derivatives were obtained using the pKb value for the corresponding o-dihydroxybenzene derivative, if available. Thus the pKaKb value for gallic acid (Table 7) was obtained using the pKb value for protocatechuic acid. The σ^- average value for gallic acid (Table 7), used to check the accuracy of this method, was calculated as the sum of the average σ^- value for the para and meta $-COO^-$ substituent and the average value for the ortho and meta -OH substituent. The position of the point for gallic acid in the σ^- average vs. pKaKb correlation (Fig. 8) was found to correspond exactly to the linear relationship observed. In a similar manner the pKaKb values for the wattle tannin monomers with a 1,2,3-trihydroxybenzene B-ring and for wattle tannin (cf. Table 7), were obtained using the pKb value for catechin. The σ^- values for the $-CH_2OH$ substituent were used to determine the sum of the σ^- average values (Table 7) for these compounds. Again the values appear to be of the correct order since they were found to fit the above linear relationship.

The pKaKb value for propyl gallate (Table 7) was estimated directly from the σ^- average vs. pKaKb correlation. The σ^- values for the EtOCO- substituent were used to determine the sum of the σ^- average value (Table 7). Also the average σ^- values for the 1,2,3-trihydroxybenzene derivatives

were checked by including them in the σ average vs. pKa correlation (Fig. 8). All the points were found to fit the observed linear relationship.

The dissociation order for 4-hydroxycatechol was assumed to be similar to that for pyrogallol, viz :



(29)

The similarity of the pKa_1 values for pyrogallol and 4-hydroxycatechol (Table 7) supports the first step, because in both cases the first hydroxyl group to ionise has two hydroxyl groups, ortho and meta, to it. The larger value of pKa_2 = 11.55 for 4-hydroxycatechol relative to that for pyrogallol viz. 11.2 may be ascribed to the higher σ_p value of the HO-substituent in the former, relative to the σ_o in the latter phenol. The final dissociation constant, Ka_3, could not be determined, but it is not relevant in the determination of the metal complex stability constants, as was the case for pyrogallol. The required value of pKaKb for this phenol (Table 7) was estimated directly from the linear relationship of pKaKb and σ average (Fig. 8).

A comparison of the dissociation constants for Tiron (4,5-dihydroxybenzene-1,3-disulfonate) with those for 3,4-dihydroxybenzenesulfonate given in Table 7, shows that the double influence of the electron-withdrawing sulfonic acid substituent lowers the value of pKa for Tiron relative to that for 3,4-dihydroxybenzenesulfonate, as would be expected. However, the

value of the second constant, pKb, for Tiron is relatively higher, the reverse of that expected. The presence of the ortho-sulfonic acid to an hydroxyl group in Tiron, makes it possible for a strong intramolecular H-bond to form. This would explain the observed anomality.

The dissociation constants for the flavanoid A-ring phenolics were correlated with the sum of the substituent σ values (Table 9) as illustrated in Fig. 9. The individual substituent σ values which were used to determine the sum of the σ values are as follows : The substituent $-OCHR_2$ on carbon atom C_9, $\sigma_m = 0.08$ as for -CMe; the substituent -COR on C_3, $\sigma_p = 0.84$ as for -COMe and the substituent -R on C_3, $\sigma_p = -0.17$ and $\sigma_o = -0.13$ as for -Me. The linear relationship observed (Fig.9) also held for the dissociation constants of the related phenols, resorcinol and phenol.

The dissociation order for the catechin A-ring meta-dihydroxyl group could be either of two processes viz. the hydroxyl on carbon atom C_5 dissociates first and then the hydroxyl on C_7, or vice versa. The best fit with the linear relationship (Fig. 9) was obtained with the σ values calculated for the former of these two possibilities, suggesting that this is the dissociation order.

For the A-ring meta-dihydroxyl group of dihydroquercetin the dissociation order proposed is the reverse of the above. The H-bond formation between the C_5 hydroxyl and the C_6 carbonyl group will favour the C_7 hydroxyl group to dissociate first. This order is supported by the fact that the value of the second constant, $pKa_2 = 11.56$, was found to be much higher than expected if no H-bonding is taken into account.

TABLE 9.

Dissociation constants, Ka, for the flavanoid A-ring phenolic groups and related compounds.

Phenol	pKa	Sum of σ
catechin	9.16	0.07
	11.23	-0.80
robinetinidol	9.64	-0.09
brazilin	9.69	-0.09
fustin	7.05	0.92
dihydrorobinetin	7.06	0.92
dihydroquercetin	6.78	1.04
resorcinol	9.30	0.12
	11.22	-0.71
phenol	9.6	-

4. The ultraviolet spectra of the phenolic compounds.

The ultraviolet spectra were recorded for the spectrophotometric determination of the phenolic dissociation constants (Fig. 5). The wavelengths of maximum absorption, the molar extinction coefficients and the proposed assignments for the main absorption bands of the undissociated phenolic compounds investigated are listed in Table 10.

The assignments were based on those for the parent compounds.[120] The spectrum of phenol[119] shows two absorption bands, at 270 nm (1450) and 211 nm (6200) which have been assigned[120] to the transitions, $\pi \longrightarrow \pi^*$ of the phenyl nucleus and electron transfer from unshared electron pair on the phenolic oxygen to the phenyl nucleus respectively. The absorption bands of benzene derivatives with the substituents, -COOR and $-NO_2$, have also been assigned[120] to the above transitions, but the electron transfer is now in the opposite direction. In addition, the unsaturated derivatives show weak $n \longrightarrow \pi^*$ absorption bands.[120] In substituted phenolic compounds with the

TABLE 10.

Spectral data for the o-diphenol derivatives.

Phenol	Local excitation of phenyl nucleus	Electron transfer
4-tert.-butylcatechol	279[a](2760)[b]	
4-methylcatechol	280(2700)	
pyrocatechol	276(2360)	
3-methoxycatechol	267(855)	
pyrogallol	266(670)	
protocatechuic acid	259(10,100)	293(5330)
protocatechuic acid (mono-anion)	250(8800)	287(4130)
2,3-dihydroxynaphthalene	272,281(4130) 311(2200),324(3200)	
3,4-dihydroxybenzenesulfonate	281(3100),234(6500)	
Tiron	233(6500),291(3800)	
gallic acid		271(9600)
gallic acid (mono-anion)		258(8330)
propyl gallate		271(9800)
DHNS	280(4900),331(2330) 360(2870)	
protocatechuic aldehyde	229(12,500)	278(10,250),307(8250)
4-chloroacetylcatechol	230(11,830)	280(9330),309(7930)
4-nitrocatechol	242(6700)	345(7000)

a. Wavelength of maximum absorption, nm.

b. Values in parentheses are the molar extinction coefficients.

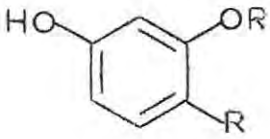
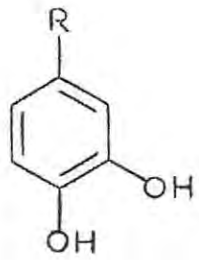
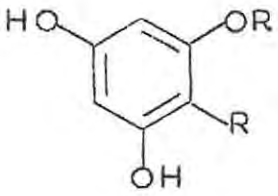
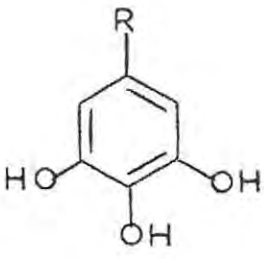
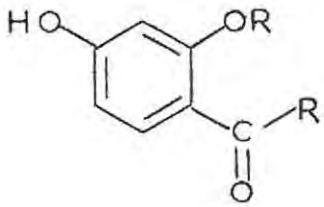
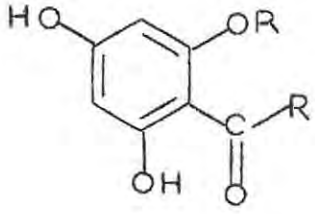
above substituents, the electron transfer band is shifted to lower energies (higher wavelengths), because the electronic effects are complimentary.[119]

From Table 10, it may be seen that the $\pi \longrightarrow \pi^*$ (phenyl nucleus) absorption bands for the phenolic derivatives with saturated substituents and the higher energy electron transfer bands with the unsaturated substituent, -CRO, occur in the same spectral region viz. 270 - 290 nm. The extinction coefficients for these bands may therefore be related. A set of extinction coefficients for the absorption bands in this spectral region was derived for the A- and B-nuclei of the flavanoid molecules and are listed in Table 11. The values were derived from Table 10 and from published

spectra.[121]

TABLE 11.

Approximate extinction coefficients for the absorption bands in the wavelength region 270 - 290 nm for the A- and B-nuclei of flavanoid molecules.

B-nuclei	Extinction coefficient	A-nuclei	Extinction coefficient
	2000		2800
	2600		1000
	900		13,400
			14,700

Using the values given in Table 11, the extinction coefficients for the absorption bands of flavanoid compounds were calculated and related to the observed values, as illustrated in Table 12.

TABLE 12.

Calculated and observed extinction coefficients for absorption bands in the region 270 - 290 nm of flavanoid compounds.

Flavanoid	wavelength maximum nm	Extinction coefficient found	calculated	References
catechin	279	3800	3600	a
	280	3830	3600	122
robinetinidol	280	4000	3700	a
	282	3992	3700	122
epicatechin	280	3580	3600	123
leucofisetinidin	279	5600	5400	a
gallocatechin[x]	271	1820	1900	122
	271	1734	1900	124
7,3',4',5'-tetra-hydroxyflavan-3,4-diol	279	3860	3700	125
fustin	280	16,150	16,000	a
dihydrorobinetin	278	14,180	14,300	a
4',7-dihydroxyflavanone	277	15,500	15,400	a
dihydroquercetin	288	17,500	17,300	126
naringenin[y]	288	17,000	16,700	126
wattle tannin dimer, D[z]	280	5,400	5600	122

a. Present investigation.

x. 5,7,3',4',5'-pentahydroxyflavan-3-ol.

y. 5,7,4'-trihydroxyflavanone.

z. Dimer of robinetinidol and gallocatechin.

The extinction coefficient for the 279 nm absorption band of wattle tannin was calculated from the spectrophotometric data used in the spectrophotometric method of tannin analysis.[15] A value of 3800 was obtained, if the molecular weight of the flavanoid monomer is assumed to be 288 ($C_{15}H_{12}O_6$). Using the percentages[7] of the various A- and B-nuclei found in wattle tannin, a calculated value of 4000 was obtained. It therefore appears that the wattle tannin chromophores are additive, as was found (Table 12) for the monomeric and dimeric flavanoid compounds.

TABLE 13.

Determination of the dissociations constants, Ka_1, for 4-chloroacetylcatechol and 2,3-dihydroxynaphthalene.

4-chloroacetylcatechol :				2,3-dihydroxynaphthalene :				
pH	v''	$\bar{n}_a$	pKa_1	pH	v''	v'	$\bar{n}_a$	pKa_1
6.4	3.35	1.913	7.418	7.6	3.31	3.00	1.897	8.539
6.6	3.54	1.865	7.407	7.8	3.45	3.00	1.850	8.553
6.8	3.80	1.800	7.402	8.0	3.66	3.00	1.780	8.550
7.0	4.14	1.715	7.400	8.2	3.94	3.00	1.687	8.541
7.2	4.55	1.613	7.399	8.4	4.25	3.00	1.583	8.546
7.4	5.00	1.500	7.400	8.6	4.57	3.00	1.477	8.559
7.6	5.46	1.385	7.397	8.8	4.91	3.00	1.363	8.556
7.8	5.86	1.285	7.401	9.0	5.20	3.005	1.268	8.565
8.0	6.21	1.198	7.391	9.2	5.46	3.01	1.183	8.552

Data used in equations (6) and (8) :

$T_L^o = 0.008$ M, $V^o = 50$ ml, $T_L^o = 0.006$ M, $V^o = 50$ ml,

$E^o = 0.006$ M, $N = 0.1$ N, $v' = 3$ ml. $E^o = 0.006$ M, $N = 0.1$ N.

TABLE 14.

Determination of dissociations constants, Ka_2, for 4-nitrocatechol and protocatechuic aldehyde.

4-nitrocatechol :					protocatechuic aldehyde :				
pH	v''	v'	$\bar{n}_a$	pKa_2	pH	v''	v'	$\bar{n}_a$	pKa_2
10.0	7.50	3.05	.889	10.902	10.4	7.31	3.14	.960	11.783
10.4	8.10	3.14	.763	10.908	10.6	7.47	3.22	.942	11.810
10.6	8.53	3.21	.675	10.918	10.8	7.73	3.33	.907	11.788
10.8	9.12	3.33	.561	10.907	11.0	8.10	3.51	.963	11.801
11.0	9.80	3.51	.442	10.900	11.2	8.72	3.82	.794	11.785

Data used in equations (6) and (9) :

$T_L^o = 0.008$ M, $V^o = 50$ ml, $E^o = 0.006$ M, $N = 0.1$ N.

TABLE 15.

Determination of the dissociation constants, Ka_1 and Ka_2, for pyrogallol according to method (2).

pH_1	v_1''	v_1'	pH_2	v_2''	v_2'	pKa_1	pKa_2
9.6	6.23	3.02	10.4	7.51	3.14	9.052	11.207
9.4	5.82	3.01	10.6	7.88	3.21	9.055	11.218
9.2	5.38	3.01	10.8	8.39	3.35	9.052	11.218
9.0	4.91	3.00	11.0	9.00	3.51	9.047	11.209
8.8	4.46	3.00	10.8	8.39	3.35	9.045	11.219
8.6	4.08	3.00	10.6	7.88	3.21	9.034	11.221
8.4	3.76	3.00	10.4	7.51	3.14	9.031	11.214

Data used in equations (12) - (18) :

$T_L^o = 0.008$ M, $V^o = 50$ ml, $E^o = 0.006$ M, $N = 0.1$ N.

TABLE 16.

Determination of dissociation constants, Ka_1 and Ka_2, for pyrogallol according to method (3) [equations (19) - (21)].

d	pH_{2+d}	pH_{2-d}	z	pKa_1	pKa_2
.50	9.04	11.21	-.009	9.049	11.201
.45	9.13	11.13	.076	9.054	11.206
.40	9.21	11.06	.162	9.048	11.222
.35	9.30	10.99	.250	9.050	11.240
.30	9.39	10.90	.342	9.048	11.242
.25	9.49	10.79	.439	9.051	11.229
.20	9.59	10.69	.547	9.043	11.237
.15	9.71	10.57	.664	9.046	11.234

Experimental data from Fig. 4.

TABLE 17.

Determination of $\bar{n}_a$ and dissociation constants, Ka, by the least squares method for the A-ring phenolic groups of catechin.

pH	v''	v'	$\bar{n}_a$	pKa_1	pH	v''	v'	$\bar{n}_a$	pKa_2
8.4	2.44	2.00	1.853	9.165	10.4	5.39	2.14	0.920	11.458
8.6	2.63	2.00	1.790	9.175	10.6	5.69	2.20	0.841	11.324
8.8	2.86	2.00	1.713	9.196	10.8	6.12	2.33	0.745	11.265
9.0	3.20	2.005	1.602	9.179	11.0	6.62	2.51	0.643	11.256
9.2	3.56	2.01	1.483	9.171	11.2	7.30	2.80	0.523	11.240
9.4	3.93	2.015	1.362	9.154	From equation (11) : correlation coefficient = 0.99, pKa_1 = 9.18, pKa_2 = 11.22.				
9.6	4.27	2.03	1.254	9.132					
9.8	4.58	2.04	1.154	9.060					
10.0	4.83	2.06	1.078	8.926					

Data used in equations (6) - (9) :
T_L^o = 0.006 M, V^o = 50 ml, E^o= 0.004 M, N = 0.1 N; v' = volume of alkali added to reach same pH as v'' in a titration of 0.004 N HCl, v'' = data from the Ge(IV)-catechin (T_M^o = 0.002 M, T_L^o = 0.006 M) titration curve.

TABLE 18.

Determination of dissociation constants, Ka, of the uncomplexes phenolic groups by method (2) for robinetinidol (equations (12) - (18)).

pH_1	v_1''	v_1'	pH_2	v_2''	v_2'	pKa_2	pKa_3
10.0	4.34	2.06	10.6	5.46	2.13	9.624	11.193
9.8	3.92	2.04	10.8	6.00	2.32	9.635	11.196
9.7	3.72	2.04	10.9	6.34	2.40	9.637	11.213
9.6	3.50	3.03	11.0	6.59	2.50	9.650	11.176
9.5	3.30	3.03	10.9	6.24	2.40	9.657	11.209
9.4	3.12	3.02	10.8	6.00	2.32	9.655	11.191
9.2	2.82	3.01	10.6	5.46	2.13	9.643	11.183

Experimental data as for Table 17.

TABLE 19.

Determination of dissociation constant, Ka, of the most acidic hydroxyl group on the B-ring of robinetinidol by the difference method using equations (7) and (8).

pH	v''	v'	$\bar{n}_a$	pKa
7.6	2.37	2.19	1.940	8.795
7.8	2.52	2.25	1.910	8.805
8.0	2.75	2.33	1.860	8.788
8.2	3.05	2.45	1.800	8.802
8.4	3.45	2.60	1.717	8.803
8.6	3.95	2.80	1.617	8.806
8.8	4.56	3.06	1.500	8.800
9.0	5.22	3.37	1.383	8.794
9.2	5.93	3.77	1.280	8.790
9.4	6.66	4.25	1.197	8.789
9.6	7.40	4.80	1.133	8.787
9.8	8.13	5.40	1.090	8.795

T_L^o = 0.006 M, V^o = 50 ml, N = 0.1 N, v'' from titration of 0.008 M robinetinidol + 0.004 N HCl, v' from titration of 0.002 M Ge(IV) + 0.008 M robinetinidol.

TABLE 20.

Determination of dissociation constants, Ka, for fustin by method (3) using equations (19) - (21).

d	pH_{2+d}	pH_{2-d}	z	pKa_1	pKa_2
0.9	6.10	9.97	-.955	7.055	9.015
0.8	6.44	9.61	-.605	7.045	9.005
0.7	6.68	9.37	-.373	7.053	8.997
0.6	6.87	9.185	-.185	7.055	9.000
0.5	7.04	9.01	-.014	7.054	8.996
0.4	7.20	8.84	.152	7.048	8.992
0.3	7.375	8.665	.325	7.050	8.990
0.2	7.56	8.47	.513	7.047	8.983
0.1	7.77	8.25	.729	7.041	8.879

Experimental data from Fig. 4.

TABLE 21.

Determination of dissociation constant, Ka, for wattle tannin by the difference method using equations (7) and (8).

pH	v''	v'	$\bar{n}_a$	pKa
8.2	4.55	4.24	1.793	8.784
8.3	5.00	4.63	1.753	8.785
8.4	5.46	5.025	1.710	8.789
8.5	5.95	5.45	1.667	8.801
8.6	6.49	5.92	1.620	8.813
8.7	7.05	6.40	1.567	8.817
8.8	7.67	6.93	1.507	8.812
8.9	8.25	7.425	1.450	8.813
9.0	8.94	8.02	1.387	8.800
9.1	9.60	8.60	1.333	8.799
9.2	10.30	9.23	1.287	8.804

V^o = 50 ml, N = 0.1 N, T_L^o = 0.003 M, v'' = volume of alkali required to reach same pH as v' in a titration of 0.02 M wattle tannin + 0.002 M HCl, v' = volumetric data from Ge(IV)-wattle tannin complex, titration curve (T_M^o = 0.001 M, T_L^o = 0.02 M).

TABLE 22.

Determination of dissociation constants, Ka_1 and Ka_2, for 4-methylcatechol and protocatechuic aldehyde, respectively, using equation (24).

4-methylcatechol :			protocatechuic aldehyde :		
pH	A	pKa_1	pH	A	pKa_2
8.82	.128	9.569	11.30	.130	11.794
9.08	.187	9.564	11.53	.183	11.799
9.37	.275	9.564	11.63	.210	11.797
9.56	.335	9.581	11.81	.258	11.806
9.77	.420	9.546	11.90	.288	11.801
9.87	.442	9.578	12.07	.332	11.797
10.10	.510	9.569	12.30	.385	11.799
wavelength = 245 nm, A_O^o = 0.035			wavelength = 400 nm, A_1^o = 0.010		
A_1^o = 0.650, T_L = 1.25 x 10^{-4} M.			A_2^o = .504, T_L = 4.0 x 10^{-5} M		
l = 1 cm			l = 1 cm		

TABLE 23.

Determination of dissociation constants, Ka_2, for the less acidic o-dihydroxyl groups of Tiron and protocatechuic acid using equation (25).

Phenol : (1) Tiron				(2) protocatechuic acid			
pH	A	$[H](A - A_1^o)$	pKa_2	pH	A	$[H](A - A_1^o)$	pKa_2
12.03	.258	1.661×10^{-13}	12.57	12.32	.120	3.829×10^{-14}	13.19
12.49	.450	1.199×10^{-13}	12.56	12.61	.183	3.510×10^{-14}	13.18
12.77	.565	8.245×10^{-14}	12.58	12.80	.246	3.265×10^{-14}	13.15
12.95	.630	6.160×10^{-14}	12.61	12.95	.282	2.715×10^{-14}	13.20
13.05	.695	5.48×10^{-14}	12.53	13.05	.328	2.566×10^{-14}	13.17

(1) $T_L = 1.5 \times 10^{-4}$ M, $A_1^o = 0.08$; (2) $T_L = 7.5 \times 10^{-5}$ M, $A_1^o = 0.04$; (1) and (2) I = 0.1 N, wavelength = 330 nm, l = 1 cm. Least squares applied to columns 2 and 3 gave $A_2^o = 0.88$, $pKa_2 = 12.57$ and to columns 6 and 7 gave $A_2^o = 0.71$, $pKa_2 = 13.18$.

TABLE 24.

Dissociation constants, Ka_1, for propyl gallate and pyrogallol, using equation (24).

pyrogallol :			propyl gallate :		
pH	A	pKa_1	pH	A	pKa_1
8.43	.236	9.051	6.60	.112	7.900
8.64	.260	9.059	7.18	.187	7.901
8.82	.286	9.060	7.74	.356	7.895
9.02	.319	9.056	8.34	.570	7.905
9.32	.368	9.054	8.45	.602	7.903
9.50	.395	9.043	8.63	.645	7.899
9.72	.420	9.040			
9.88	.432	9.058			

wavelength = 270 nm, $A_0^o = 0.180$, $A_1^o = 0.470$, $T_L = 0.0003$ M, l = 1 cm.

wavelength = 310 nm, $A_0^o = 0.08$, $A_1^o = .750$, $T_L = 6.0 \times 10^{-5}$ M, l = 1 cm.

TABLE 25.

Determination of dissociation constants, Ka, for the C_7 hydroxyl group of brazilin and dihydroquercetin using equation (24).

brazilin :			dihydroquercetin :		
pH	A	pKa	pH	A	pKa
8.93	.710	9.683	6.18	.158	6.776
9.20	.730	9.677	6.42	.201	6.786
9.65	.775	9.694	6.60	.245	6.772
9.75	.790	9.663	6.92	.327	6.760
10.04	.820	9.672	7.13	.370	6.783
10.22	.835	9.683	7.32	.408	6.778
10.42	.850	9.667	7.56	.443	6.781

wavelength = 289 nm, A_O^o = .68, A_1^o = 0.88, T_L = 1.125 x 10^{-4} M, T_M = 3.75 x 10^{-5}M, l = 1 cm.

wavelength = 330 nm, A_O^o = 0.070, A_1^o = 0.505, T_L = 4 x 10^{-5} M, l = 1 cm.

TABLE 26.

Determination of dissociation constant,, Ka, for the $C_{3'\ or\ 4'}$ hydroxyl group of leucofisetinidin using equation (24).

pH	A_1	A_2	ΔA	pKa
8.33	.166	.025	.141	8.979
8.63	.233	.045	.188	9.005
8.87	.310	.070	.240	9.007
8.98	.350	.090	.260	9.032
9.18	.428	.115	.313	9.008
9.38	.508	.155	.353	9.024
9.57	.590	.200	.390	9.013
9.78	.660	.240	.420	9.003

wavelength = 295 nm, T_L = 0.0001 M, A_O^o = 0.065, A_1^o = A_1^o free phenolic - (A_1^o - A_O^o)Ge(IV) complex = .480, A_1 = free phenolic absorbance, A_2 = (A - A_O^o)Ge(IV) complex; T_M =3.33 x 10^{-5} M.

TABLE 27.

Determination of dissociation constant, Ka, for the $C_{4'}$ or $_{3'}$ hydroxyl group of leucofisetinidin using equation (25).

pH	A	$[H^+](A - A_1^o)$	pKa
12.59	0.218	1.491×10^{-14}	13.18
12.74	0.232	1.310×10^{-14}	13.21
12.83	0.245	1.258×10^{-14}	13.20
12.92	0.262	1.224×10^{-14}	13.17
13.05	0.280	1.069×10^{-14}	13.18

wavelength = 310 nm, $A_1^o = 0.160$, $T_L = 1 \times 10^{-4}$ M, l = 1 cm.

Least squares applied to columns 2 and 3 gave, $A_2^o = 0.443$, $pKa_2 = 13.19$.

TABLE 28.

Determination of dissociation constant, Ka, for the $C_{3'}$ or $_{4'}$ hydroxyl group of fustin using equation (24).

pH	A	pKa
8.51	.440	8.979
8.80	.490	9.000
9.08	.550	8.999
9.22	.583	8.980
9.55	.635	9.017
9.77	.665	9.005

wavelength = 244 nm, $A_0^o = .345$, $A_1^o = .720$, $T_L = 5.0 \times 10^{-5}$ M, l = 1 cm.

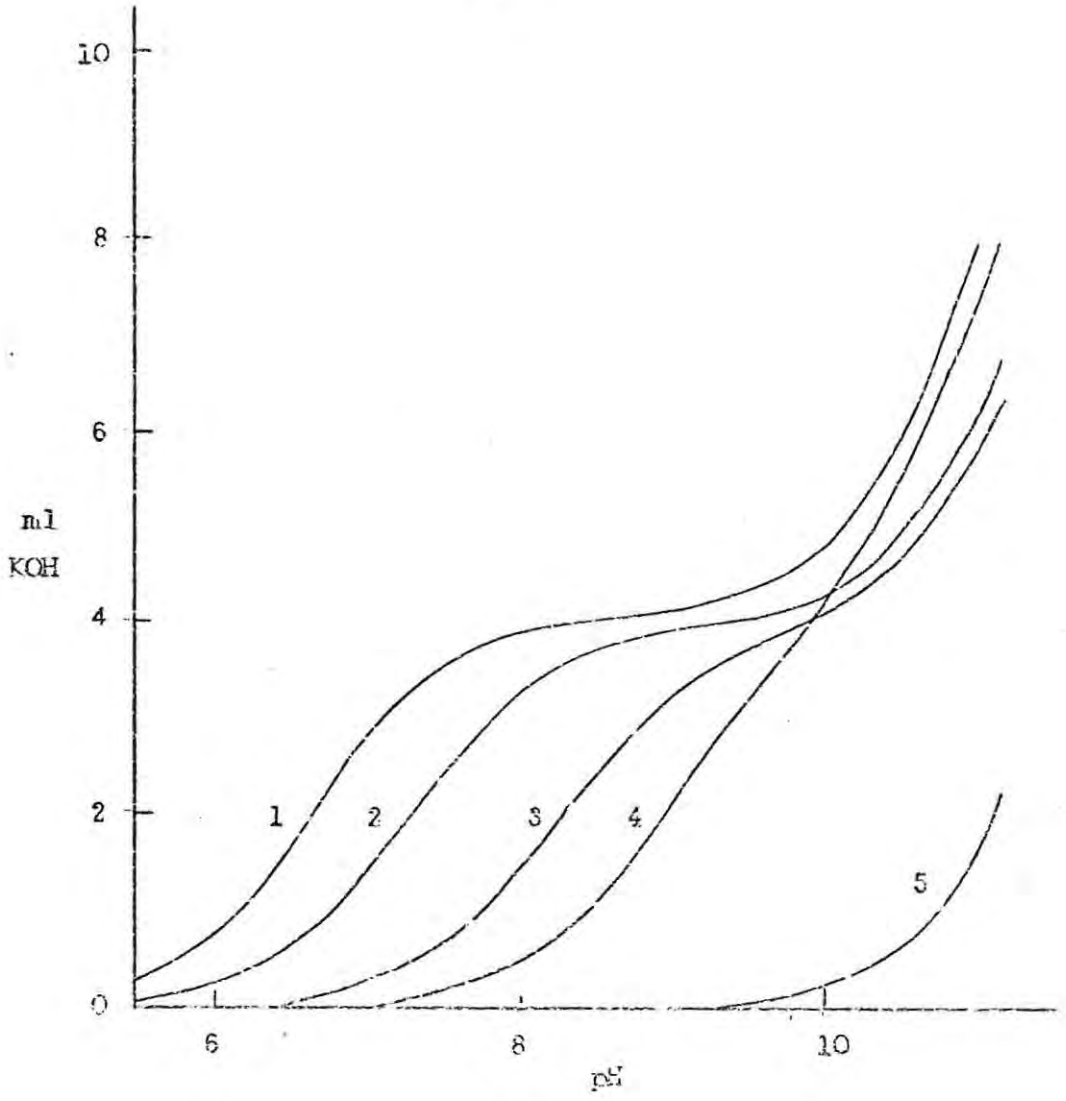


FIG. 1. Potentiometric titration curves for (1) 4-nitrocatechol, (2) 4-chloroacetylcatechol, (3) DHNS (see below) (4) pyrogallol, (5) water; $T_L^o = 0.008$ M, $V^o = 50$ ml, N = 0.1 N KOH, I = 0.1 N KCl. DHNS = 2,3-dihydroxynaphthalene-6-sulfonate.

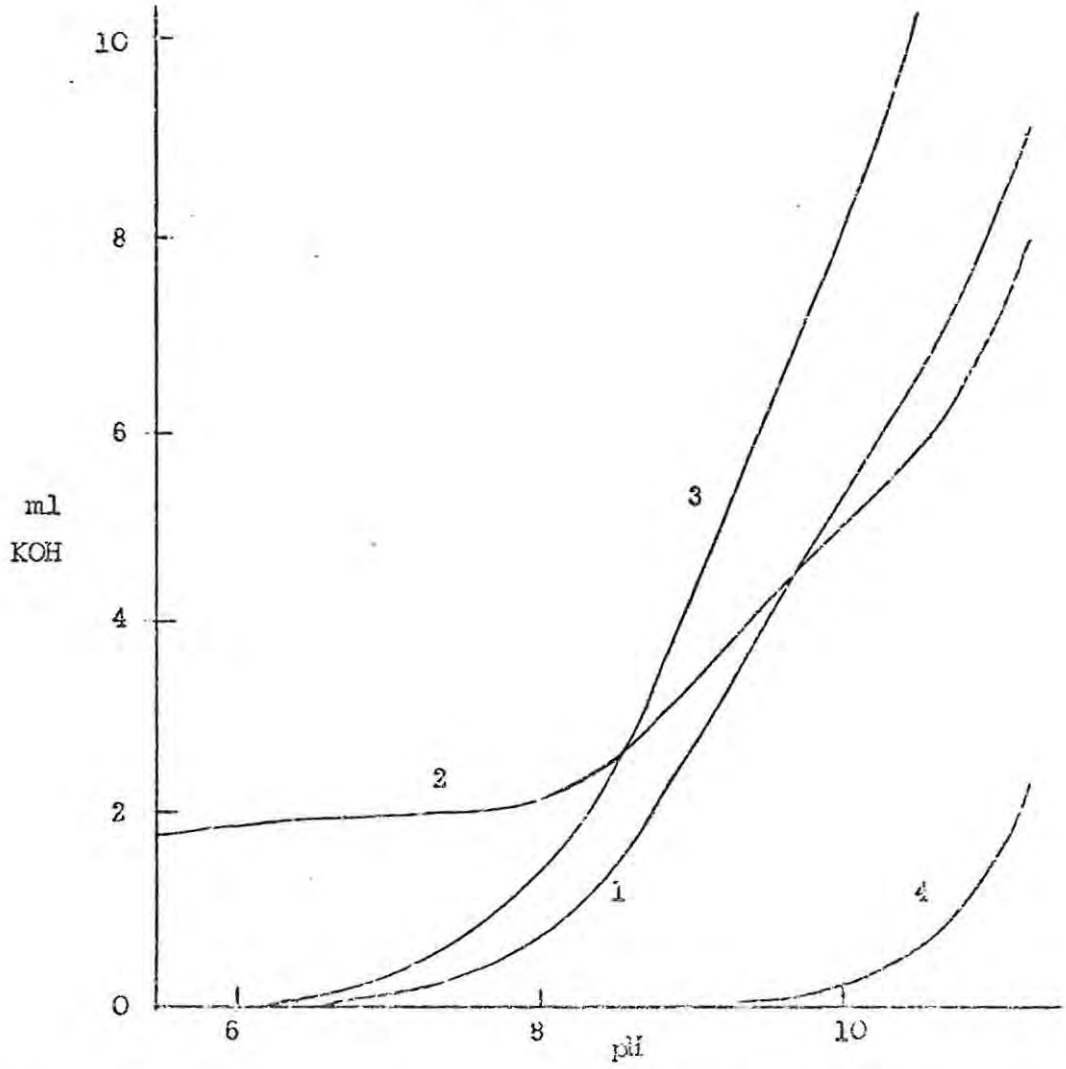


FIG. 2. Potentiometric titration curves for (1) 0.006 M robinetinidol, (2) 0.006 M catechin + 0.002 M GeO_2, (3) 0.01 M wattle tannin, (4) water; V^o = 50 ml, N = 0.1 N KOH, I = 0.1 N KCl.

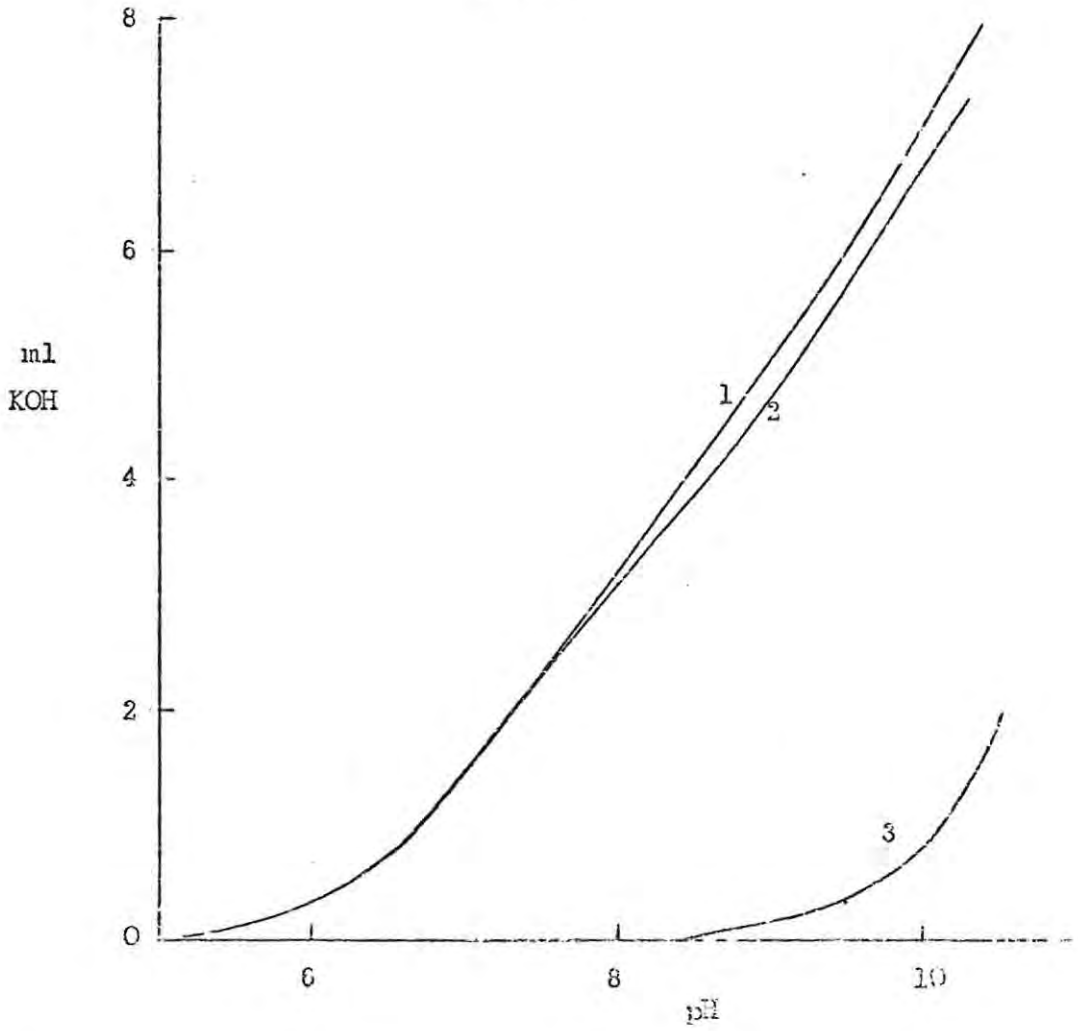


FIG. 3. Potentiometric titration curves for (1) dihydrorobinetin, (2) fustin, (3) water; $T_L^o = 6.0 \times 10^{-4} M$, $V^o = 50$ ml, N = 0.01 N KOH, I = 0.1 N KCl.

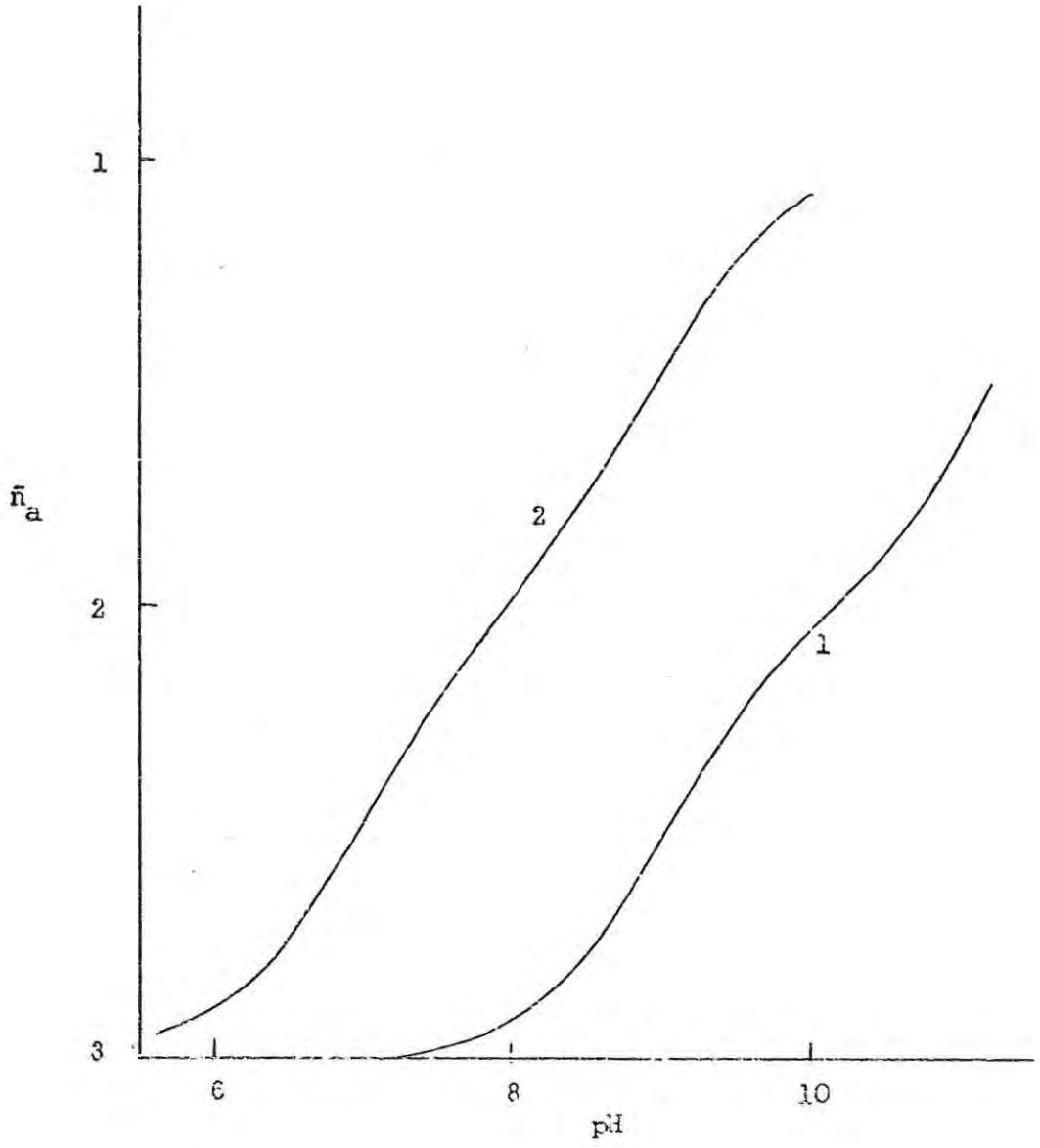


FIG. 4. $\bar{n}_a$ vs pH Plots for (1) pyrocallol
(2) fustin.

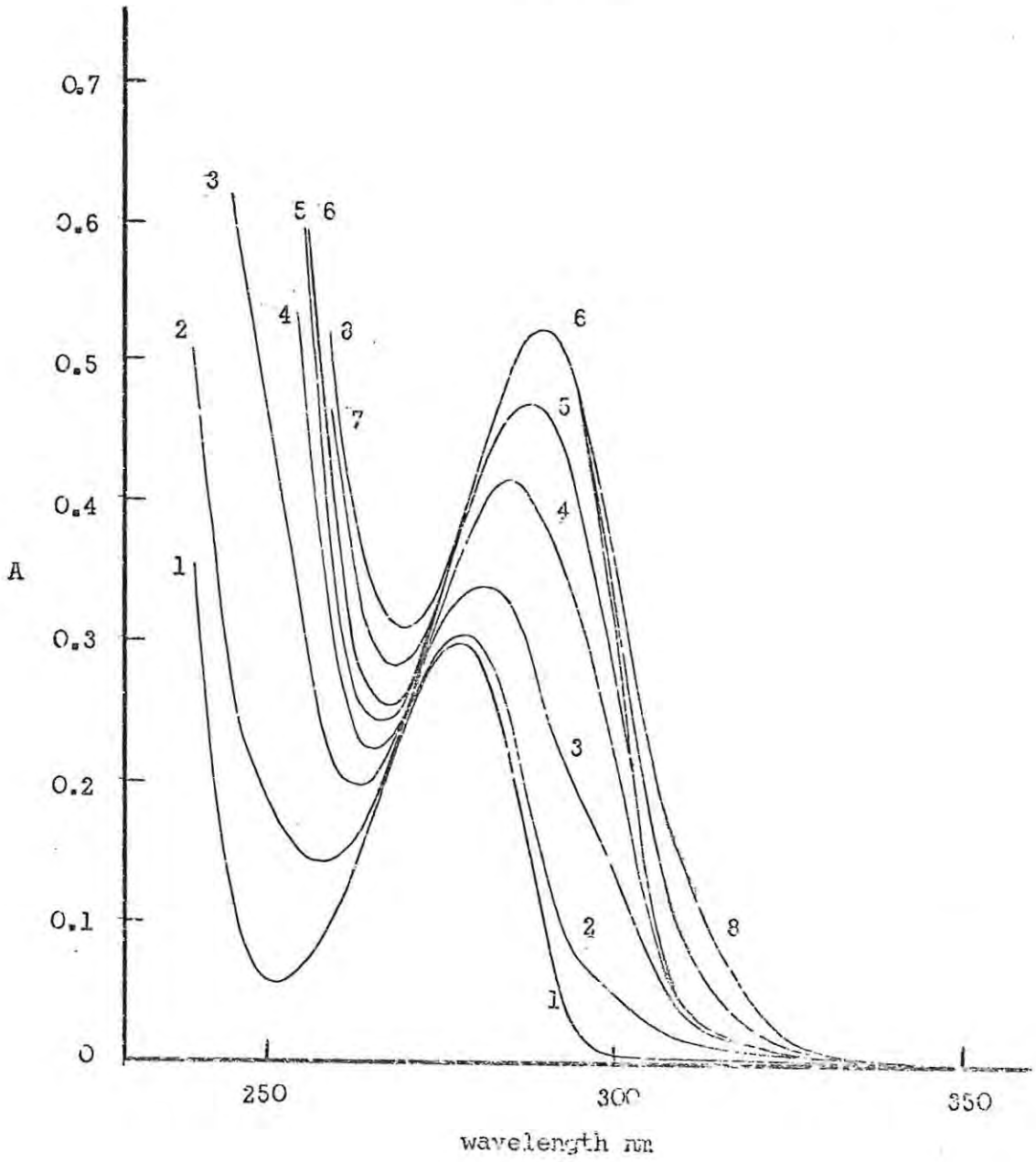


FIG. 5. Absorption spectra of catechin at pH values (1) 5.00, (2) 8.34, (3) 8.96, (4) 9.62, (5) 10.03, (6) 11.00 (7) 12.58, (8) 12.93; $I = 0.1$, $T_L = 7.8 \times 10^{-5}$M, $l = 1$ cm.

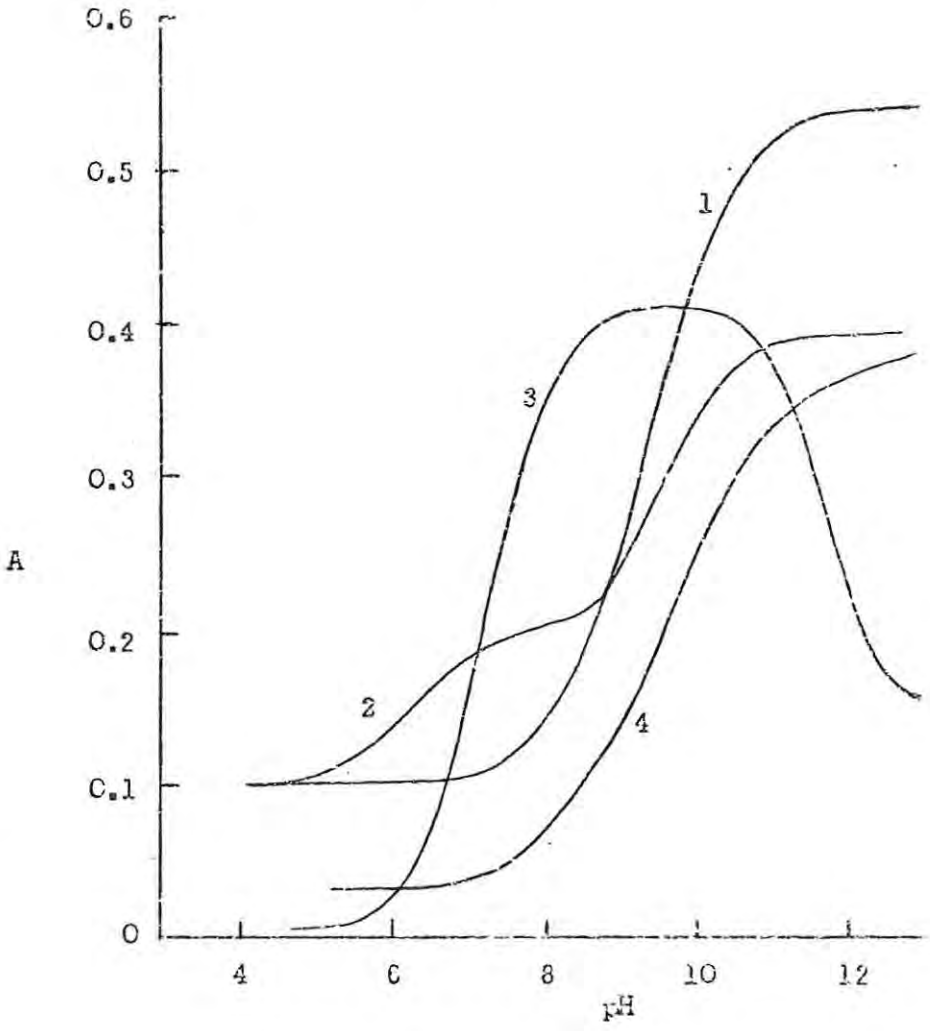


FIG. 6. Extinction curves for (1) brazilin 1.125×10^{-4}M, wavelength = 258 nm, (2) brazilin 1.125×10^{-4}M + GeO_2 3.75×10^{-5}M, wavelength = 258 nm, (3) protocatechuic aldehyde 2.0×10^{-5}M, wavelength = 340 nm, (4) wattle tannin 8.5×10^{-5}M, wavelength = 300 nm; I = 0.1, l = 1 cm.

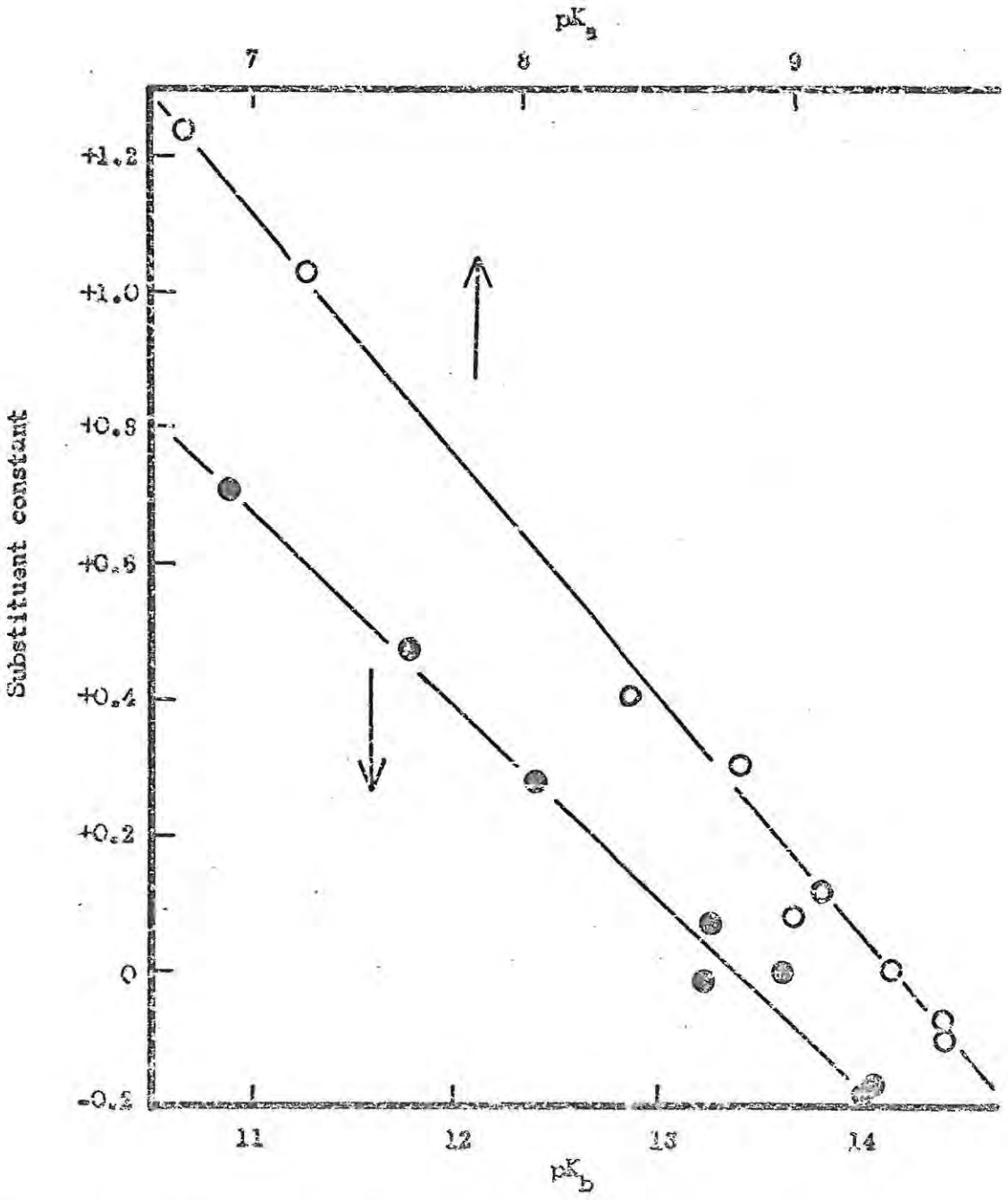


FIG. 7. Plots of pK_a (top scale) and pK_b (bottom scale) against substituent constants, σ^-, for 4-substituted pyrocatechol derivatives.

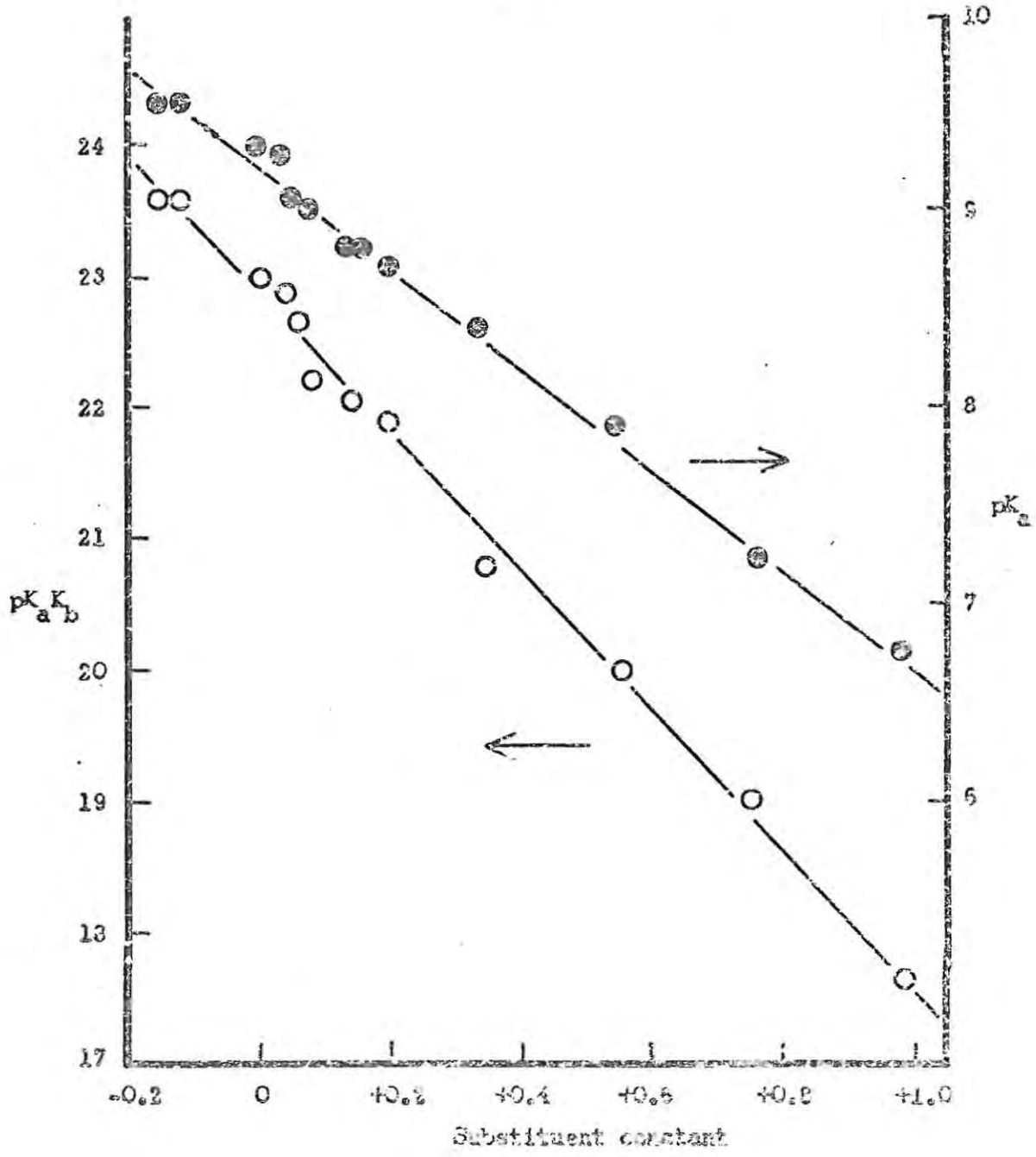


FIG. 3. Plots of pK_aK_b (left scale) and pK_a (right scale) against the average substituent constants for g-diphenols.

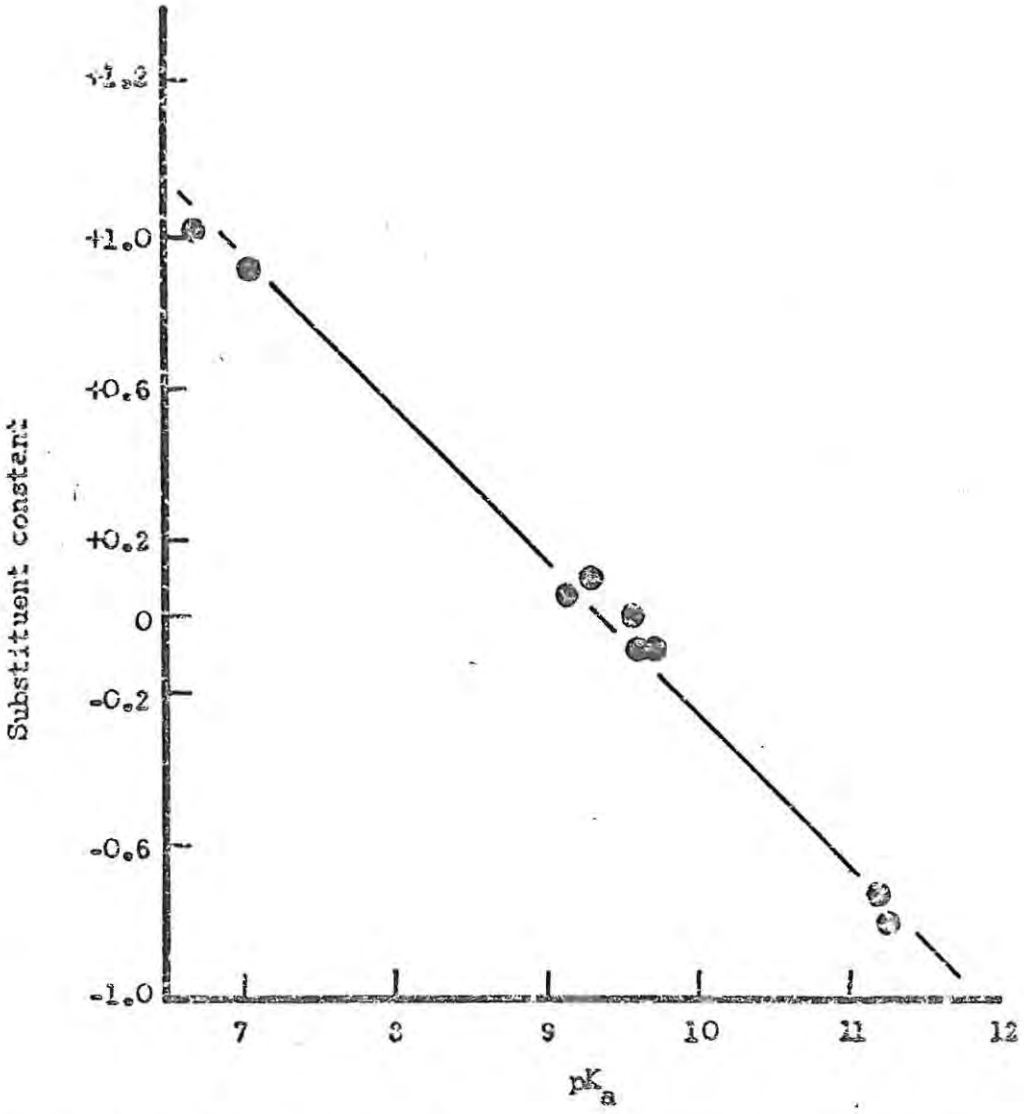


FIG. 9. Plot of dissociation constants, K_a, against the sum of the substituent constants, σ^-, for the flavanoid A-ring phenolic groups and related phenolic compounds.

B. IRON(III) COMPLEXES OF POLYPHENOLS

Pyrocatechol, pyrogallol, resorcinol and phloroglucinol nuclei have been found to be the main polyphenolic constitutents of wattle tannin molecules.[7] Therefore, initially the complexes of these polyphenols and their derivatives were studied as model compounds for the more complicated tannin complexes.

The reaction of ferric ions with mono- and polyphenols is well known.[137] The intense colours produced in these reactions is a definite indication of complex formation.[138] Resorcinol and phloroglucinol were however found to be only weakly bound because on increasing the pH of the solution, the colour disappeared and ferric oxide precipitated. Pyrocatechol and pyrogallol on the other hand were found to produce intense, stable colours with Fe(III) ions, even at high pH values. Resorcinol and phloroglucinol nuclei are therefore unimportant in the Fe(III)-tannin complexes and further studies with these compounds were not carried out.

In view of the different Fe(III) complex species that formed with the o-dihydroxybenzene (pyrocatechol) derivatives and the 1,2,3-trihydroxybenzene (pyrogallol) derivatives, these systems have been dealt with separately.

1. o-Dihydroxybenzene complexes.

The Fe(III) complexes with fifteen o-dihydroxybenzene derivatives were studied, including the wattle tannin monomers catechin and fustin.

The hue and the intensity of the coloured complexes in aqueous media were found to be pH dependent, indicating that hydrogen ions are involved

in the reaction. In general, the colours ranged from green in acid, to blue in neutral and red in alkaline solutions. Because of the pH dependence of colour formation, visible absorption spectra of the Fe(III) complexes of o-diphenols were recorded at various pH values. Fig. 1 illustrates the general form of the curves. The wavelength of maximum absorption can be seen to decrease with increasing pH. This is the reason for the changes in colour observed.

The variations of absorbance with pH at various fixed wavelengths (extinction curves) for some of the complexes are shown in Fig. 2. Three distinct absorption maxima are observed, indicating that three different species are formed. The presence of isosbestic points between each species in the visible spectra, indicates that the three species are formed separately and that they are in equilibrium with each other.

Extinction curves for the pyrocatechol, 4-methylcatechol, 3-methoxycatechol and catechin complexes could only be determined after the formation of the first species, because at pH values lower than this, absorbance was found to decrease rapidly with time. The reason for this will be discussed later (p. 79).

Table 1 lists the wavelength and the extinction coefficient of the maximum absorption of each species and the wavelengths at the isosbestic points for the complexes. The absorption maxima of the higher species for the 4-nitrocatechol, protocatechuic aldehyde and 4-chloroacetylcatechol complexes could not be determined because of optical interference from the coloured phenols. The fustin, brazilin and 4-t-butylcatechol complexes precipitated in solution and therefore these complexes could not be investigated by the available methods.

TABLE 1.

Spectral data of the Fe(III) complexes of o-dihydroxybenzene derivatives.

Ligand	Wavelength maxima nm			Isosbestic points nm		Extinction coefficients		
	FeL	FeL_2	FeL_3	1st	2nd	FeL	FeL_2	FeL_3
4-methylcatechol	710	585	500	730	565	1360	3440	4600
3-methoxycatechol	710	590	500	725	570	1400	3480	4680
pyrocatechol	700	575	495	710	550	1480	3400	4400
catechin	690	575	495	700	550	1750	4000	5150
protocatechuic acid	670	570	490	700	545	1780	4250	5450
3,4-dihydroxybenzenesulfonate	670	565	485	680	535	1900	4000	5200
4-chloroacetylcatechol	655	550	-	675	540	2100	4850	-
Tiron	655	555	480	675	530	1980	4650	6000
protocatechuic aldehyde	650	555	-	670	-	2100	4800	-
4-nitrocatechol	640	-	-	670	-	2250	-	-
2,3-dihydroxynaphthalene	600	525	455	600	510	3140	6950	9400
DHNS	580	515	450	580	500	3480	7700	10600

In order to determine the Fe(III) to ligand ratios of the three species, the methods of continuous variation (Job's method),[139] molar ratio,[16] and slope ratio[17] were used. These methods have been used[17] to determine the component ratios of the Fe(III)-Tiron system; it was found that the blue-green complex had a 1 : 1 ratio, the violet a 1 : 2 ratio and the red a 1 : 3 molar ratio of Fe(III) to Tiron. However, in order to establish whether the results are general for o-dihydroxybenzene complexes, these methods have been applied to a number of the complexes.

It is essential that the pH values of the solutions be fixed over a narrow range, corresponding to the region where each species exists separately. This information is obtained from the extinction curves (Fig.2), the ideal pH being at the centre of the plateau. The results of the above methods are illustrated in Figs. 3 - 6. It may be seen from the molar ratio results that the plots all break sharply from the linear at Fe to

ligand ratios of 1 : 1, 1 : 2 and 1 : 3 for the green, blue and red species, respectively. The same result may be deduced from the Job's plots with sharp peaks occurring at values of 0.5, 0.66 and 0.75 for the ratio $\left[\text{ligand}\right]$ to $\left[\text{Fe}\right] + \left[\text{ligand}\right]$. Similarly the slope ratios of 1, 2 and 3 calculated according to the slope ratio method indicate that the three species can be represented by FeL_1, FeL_2 and FeL_3, where L is the phenolic ligand. These results are thus in agreement with those obtained for the Fe(III)-Tiron system[17] and it appears that ratios of 1, 2, 3 are generally valid for all the o-dihydroxybenzene derivatives.

The number of hydrogen ions liberated on formation of the complexes has been calculated from the slopes of the extinction curves.[25] The slopes of all three species are equal to 2 indicating that both hydroxyl protons are liberated from the o-dihydroxybenzene ligand on successive complex formation as follows :

$$Fe^{3+} + xH_2L \rightleftharpoons FeL_x^{3-2x} + 2xH^+ \qquad (1)$$

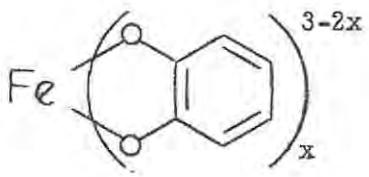
where x = 1, 2 or 3.

Paper electrophoresis was used to determine the overall charge on the complexes. Results show that the 1 : 1 Fe(III)-pyrocatechol complex is cationic since it migrated to the negative pole. The 1 : 2 and 1 : 3 pyrocatechol complexes migrate in the opposite direction, indicating anionic complexes. These results were generally true for all the o-dihydroxybenzene derivatives without ionic substituents. This is in accordance with the formulae proposed above viz. FeL^+, FeL_2^- and FeL_3^{3-}. For the sulfonic acid substituted derivatives the overall charges were found to be cationic for all three species - as expected. The 1 : 1 protocatechuic acid complex proved to be cationic, thus the carboxyl substituent must necessarily be

undissociated. The 1 : 2 and 1 : 3 complexes, were highly anionic suggesting that the carboxyl groups are in the ionic form.

The above formulae have been confirmed[21,22] by the isolation of the solid pyrocatechol complexes, $Na\left[Fe(C_6H_4O_2)_2\right].H_2O$ and $K_3\left[Fe(C_6H_4O_2)_3\right]$.

The crystal structure of the closely related tris(oxalato)iron(III) ion has been shown to have three 5-membered rings with six oxygen ions octahedrally co-ordinated.[140] A similar situation probably exists in the o-dihydroxybenzene complexes. The structure of these octahedral complexes is thus :



where x is 1, 2 or 3.

In the lower complexes, water molecules probably occupy the remaining octahedral positions, since it has been shown[21] that the solid, catechol complex, FeL_2 is always isolated with associated water molecules. The stable chelates formed by the o-dihydroxybenzene derivatives explains the unimportance of resorcinol and phloroglucinol in complexation.

Potentiometric titrations have also been used[20,141] to study the Fe(III) complexes of Tiron and DHNS. The results of these treatments indicated that it is possible to follow the successive formation of the complexes potentiometrically. Therefore a potentiometric study on the complex formation of the o-dihydroxybenzene derivatives with Fe(III) ions was carried out to supplement the spectrophotometric observations.

Fig. 9 illustrates the general type of titration curve obtained with various ratios of metal and ligand. The curves with a 1 : 3 molar ratio were found to have inflection points, at $\bar{z} = 2$, 4 and 6 (where $\bar{z}$ = the number of moles of alkali added per mole of metal ion present). These values correspond to the complete formation of the FeL, FeL_2 and FeL_3 complexes, with two hydrogen ions being liberated on each successive formation.

The number of ligand molecules bound per metal ion can be inferred from the titration curves at lower molar ratios. Inflections occur at $\bar{z} = 2$, 4 and 6 with minimum molar ratios of 1 : 1, 1 : 2 and 1 : 3 respectively. These results are in agreement with those obtained from the spectrophotometric treatments.

Titrations of pyrocatechol, 4-methylcatechol, 3-methoxycatechol and catechin complexes were started only at $\bar{z} = 2$. When the titration was started at $\bar{z} = 0$, the position of the first inflection ($\bar{z}$ inflection) was found to be less than two, indicating incomplete complex formation of the FeL species. Also, the $\bar{z}$ inflection value was dependent on the speed of the titration. This suggests that there is some form of decomposition at these low pH values. This corresponds to the fade in colour at low pH observed with these ligands in the spectrophotometric investigation.

It has been shown[142] that a product of reaction between pyrocatechol and ferric ions at low pH, is ferrous ions. The reaction also produced a brown coloration generally associated with oxidation products of phenolics.[25] A redox process must occur :

$$Fe^{3+} + ROH \longrightarrow Fe^{2+} + \dot{R}OH \qquad (2)$$

where ROH is a phenol.

The radical produced would be unstable and react further to give oxidation products.

Thus free ferric ions and the readily oxidisable phenolics mentioned above cannot exist together in solution without oxidation and reduction taking place. In the formation of the first Fe(III) complex, shown in reaction (1), the redox process will remove both reactants and result in the observed dissociation of the complex.

The potentiometric titration curves with 1 : 2 molar ratios illustrated in Fig. 7 were found to have additional inflections at $\bar{z} = 5$. This could either be due to the formation of a hydroxo compound :

$$FeL_2 \underset{H_2O}{\rightleftharpoons} FeL_2(OH)^{2-} + H^+ \qquad (3)$$

or to the formation of the FeL_3 species, with dissociation of some of the FeL_2 species to provide the additional ligand :

$$FeL_2^- \rightleftharpoons \tfrac{2}{3} FeL_3^{2-} + \tfrac{1}{3} Fe^{3+} \qquad (4)$$

The Fe^{3+} ions would not remain in solution in this form because of the high pH, but would form the trihydroxide :

$$\tfrac{1}{3} Fe^{3+} \longrightarrow \tfrac{1}{3} Fe(OH)_3 + H^+ \qquad (5)$$

Also, the hydroxide would not remain in solution, ferric oxide being formed[143] and precipitated because of the expected high concentration.

The fact that no immediate precipitate of ferric oxide occurred suggests that reaction (3) occurs. Similar hydroxo species have been found to form in pyrocatechol complexes of aluminium(III)[39] and tin(IV)[144] and more

generally in amine complexes.[145]

The non-formation of the FeL_3 species at lower molar ratios was confirmed by spectrophotometric evidence. The wavelengths of maximum absorption of the red species, at high pH values, with molar ratios of 1 : 1, 1 : 2 and 1 : 3 were found to be different. The wavelengths of maximum absorption at molar ratios less than 1 : 3 were found to occur at lower wavelengths than the maximum of the FeL_3 species. This can only mean that another species is formed because the maximum cannot be associated with incomplete formation of the FeL_3 species, otherwise it would exhibit a maximum at higher wavelength.

In the spectrophotometric methods used to determine the component ratios of the red species, a pre-requisite is the formation of the same complex.[146] Thus if it is proposed that at low molar ratios the species is not FeL_3, but FeL_2OH, then the results obtained are anomalous. However it will be shown later that the intensity of the absorbance is dependent on the number of co-ordinated phenolic ligands. The extinction coefficient of the FeL_2OH species will therefore be $\frac{2}{3}$ the value of the FeL_3 species. Therefore the situation remains unaltered and the result obtained for the red species is still valid.

The equilibrium constants, K', for reaction (3):

$$K' = \frac{\left[FeL_2OH\right]\left[H\right]}{\left[FeL_2\right]} \qquad (6)$$

were calculated from the potentiometric data for the titration curves with a 1 : 2 molar ratio. The following equations were adapted from those normally used to calculate dissociation constants.[89] The value of n, the

mean number of hydroxo groups bound per FeL_2 complex present was calculated thus :

$$n = \frac{(v''' - v')N}{V^{o}T^{o}_{M}} \qquad (7)$$

where v''' and v' denote the respective volumes of alkali required to reach the same pH in titration of the metal ion plus ligand and free mineral acid of concentration equal to 4 T^{o}_{M}; N, V^{o} and T^{o}_{M} have been previously defined (Section A). Then :

$$pK' = \log \frac{1 - n}{n} + pH \qquad (8)$$

Examples of the calculations using equations (7) and (8) are given in Table 11.

For the catechin complex it was necessary to allow for the dissociation of the unco-ordinated hydroxyl groups on the A-ring of the flavanoid molecule. The values of n were calculated from the equation :

$$n = \frac{(v''' - v' - v)N}{V^{o}T^{o}_{M}} \qquad (9)$$

where v is the volume of alkali required to reach the same pH corresponding to v''' and v', in a titration of the unco-ordinated A-ring hydroxyl groups and was calculated from the equation :

$$v = \frac{V^{o}\,T^{o}_{L}}{N\left[\text{antilog}\,(pKa - pH) + 1\right]} \qquad (10)$$

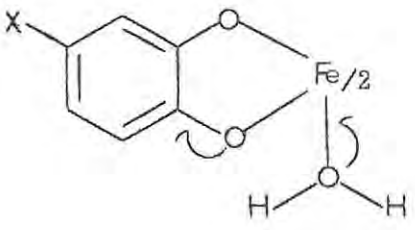
where Ka is the dissociation constant of the more acidic A-ring hydroxyl

group (for catechin, pKa = 9.15). Results of the calculation for catechin using equations (8) - (10) are given in Table 12. The constancy of pK' in Tables 11 and 12 supports the above reasoning. Table 2 lists the constants for the other o-dihydroxybenzene complexes.

Table 2 shows that the constant is dependent on the acidity of the phenol - the more acid the phenol, the lower the value of pK' and vice versa. If it is assumed that the reaction is an acid dissociation of a bound H_2O molecule which make up the octahedral co-ordination :

$$FeL_2(H_2O)_2^- \rightleftharpoons FeL_2(OH)(H_2O)^{2-} + H^+ \qquad (11)$$

and if the electronic effect of the substituents on the benzene ring is transmitted through the metal ion, thus :



(where X is an electron-withdrawing substituent)

then the strength of the O-H bond will be affected in a manner similar to that in the uncomplexed phenol. Plots of pK' for reaction (3) against the dissociation constants of the phenols are shown in Fig. 8. Except for the points for Tiron and 4-chloroacetylcatechol, the best linear correlation is with the combined phenolic dissociation constant, KaKb. This is expected because the electronic process illustrated above has two ways in which it may operate and both the phenolic constants must be used to give the overall

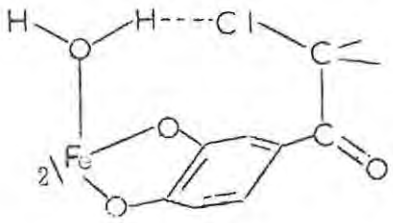
TABLE 2.

Hydrolysis constants, K', for the o-dihydroxybenzene complexes, FeL_2.

Ligand	pK'
4-methylcatechol	9.40
pyrocatechol	9.20
3-methoxycatechol	9.10
catechin	8.81
protocatechuic acid	8.78
3,4-dihydroxybenzenesulfonate	8.28
DHNS	8.35
Tiron	8.59
4-chloroacetylcatechol	8.25
protocatechuic aldehyde	7.75
4-nitrocatechol	7.18

effect. The slope of the plot with pKa (Fig. 8) shows that the effect of the substituent is stronger in the phenol than in the complex, probably due to the fact that the relative distances involved for the electronic effect are much less in the former case.

The anomalous positions of the points for 4-chloroacetylcatechol indicate there is some other factor involved in the complex which is absent in the uncomplexed phenol, making it more difficult for the bound H_2O to be hydrolysed. This is ascribed to the presence of an intramolecular hydrogen bond between the phenolic substituent and a bound water molecule, thus :



The deviation of the points for Tiron from the linear correlations could be due to a number of reasons. It was observed in Section A that the values of the dissociation constants for Tiron are anomalous. The values of complex formation constants for Tiron have also been shown to be dependent on the ionic strength of the solution to a much greater extent than for other phenolic complexes.[34] It is also possible for intramolecular H-bonds to form between an oxygen ion on the ortho-sulfonate substituent and a bound water hydrogen. This would affect the value of pK' in a manner similar to that found for the 4-chloroacetylcatechol complex.

The titration curves with a 1 : 1 molar ratio (Fig. 7) of Fe(III) to ligand were found to have additional inflections at $\bar{z} = 3.5$ and 4.0. The former is proposed to correspond to the formation of the FeL_2 complex from the FeL complex, with dissociation of some of the latter complex to provide the extra ligand molecules, thus :

$$2\ FeL^{+} \longrightarrow FeL_2^{-} + Fe_2O_3\downarrow + 3H^{+} \qquad (12)$$

This is similar to the alternative reaction described above, and has also

been observed in copper (II) complexes of o-dihydroxybenzene derivatives.[232] Equilibrium constants for reaction (12) could not be determined because of the presence of the precipitated ferric oxide.

The inflection at $\bar{z} = 4$ in titrations with 1 : 1 molar ratios (Fig. 7) corresponds to the complete formation of the hydroxo species, $FeL_2(OH)$, from the FeL_2 complex formed in reaction (12).

The stepwise equilibrium constants, k, for the following reactions :

$$Fe^{3+} + H_2L \rightleftharpoons FeL^+ + 2H^+ \qquad k_1 = \frac{[FeL][H]^2}{[Fe][H_2L]} \tag{13a}$$

$$FeL^+ + H_2L \rightleftharpoons FeL_2^- + 2H^+ \qquad k_2 = \frac{[FeL_2][H]^2}{[FeL][H_2L]} \tag{13b}$$

$$FeL_2^- + H_2L \rightleftharpoons FeL_3^{3-} + 2H^+ \qquad k_3 = \frac{[FeL_3][H]^2}{[FeL_2][H_2L]} \tag{13c}$$

were calculated from potentiometric data, according to the equations (14)-(17) which follow. The value of $\bar{n}$, the mean number of ligands bound per metal ion present was calculated by the electro-neutrality equation[89] :

$$\bar{n} = \frac{(v''' - v'')\left[N + E^o + T_L^o(c - \bar{n}_a)\right]}{(V^o + v'')T_M^o\,\bar{n}_a} \tag{14}$$

where v''' and v'' are the respective volumes of alkali required to reach the same pH in titrations of the metal complex plus mineral acid and the ligand plus free acid; $\bar{n}_a$, c, N and T_M^o as defined previously. Then for the general reaction :

$$ML_a + H_cL \rightleftharpoons ML_b + h\,H \qquad (15)$$

$$k_b = \frac{(\bar{n} - a)\left[H\right]^h (V^o + v''')}{(b - \bar{n})(T_L^o - \bar{n}T_M^o)(\bar{n}_a - 1)\,V^o} \qquad (16)$$

Equation (14) may be simplified[89] if $N \gg E^o$ and $V^o \gg v''$, thus :

$$\bar{n} = \frac{(v''' - v'')N}{V^o T_M^o \bar{n}_a} \qquad (17)$$

Solutions of excess of ligand were used in the potentiometric titrations to ensure that only the above three species were formed. The general form of the titration curves is shown in Fig. 9.

For pyrocatechol, 4-methylcatechol, 3-methoxycatechol and catechin only the constants, k_2 and k_3, could be determined because of non-equilibrium conditions at low pH values. For the 4-nitrocatechol, 4-chloracetylcatechol, Tiron and protocatechuic aldehyde complexes the first constant, k_1, could not be determined, because it was found that the FeL species was formed completely at the start of the titrations. In calculations involving the flavanoid compounds the $\bar{n}_a$ values used are those for the B-ring hydroxyl groups.

Worked examples of the calculations using equations (14) - (17) are given in Table 13. The complete list of equilibrium constants is shown in Table 3. The values of the constants, k_2 and k_3, for the 4-chloroacetylcatechol complex were found to be dependent on the concentration of the complex (Table 3).

The above equilibrium constants were also calculated from the spectro-

TABLE 3.

The equilibrium constants, k, for the Fe(III) complexes of o-dihydroxybenzene derivatives.

Ligand	pk_1		pk_2		pk_3	
	*P	S	P	S	P	S
4-methylcatechol	-	-	8.30	8.25	13.74	13.6
3-methoxycatechol	-	-	7.98	7.9	13.06	13.0
pyrocatechol	-	-	7.97	7.95	13.16	13.1
catechin	-	-	7.40	7.4	12.50	12.45
protocatechuic acid	-	1.55	-	-	12.30	12.25
3,4-dihydroxybenzenesulfonate	1.75	1.7	6.58	6.55	11.21	11.2
2,3-dihydroxynaphthalene	-	1.7	-	6.5	-	11.4
DHNS	1.43	0.85	5.96	6.05	10.55	10.5
Tiron	-	-0.10	5.08	5.1	9.19	9.25
4-chloroacetylcatechol[a]	-	1.1	4.50(1) 4.82(2)	5.2(3)	10.32(1) 9.99(2)	9.7(3)
protocatechuic aldehyde	-	1.00	5.18	5.2	9.04	9.1
4-nitrocatechol	-	0.45	4.53	4.5	8.16	-

* P and S represent potentiometrically and spectrophotometrically determined values respectively.

a. Concentration of complex (1) $T_M^o = 0.002$ M, (2) $T_M^o = 0.001$ M (3) $T_M^o = 0.0002$ M.

photometrically determined extinction curves (Fig. 2). The constants, k_1, could not be determined for pyrocatechol, 4-methylcatechol, 3-methoxycatechol and catechin due to interfering factors mentioned previously. For the 4-nitrocatechol complex also the constant, k_3, could not be determined because of the optical interference of the phenolic absorbance.

The following equations were derived for the calculations involving spectrophotometric data :

$$\bar{n} = a + \frac{A - A_a^o}{A_b^o - A_a^o} \qquad (18a)$$

where a and b are as in reaction (15), A is the absorbance observed for a

particular pH at a fixed wavelength, A_a^o and A_b^o are the respective absorbances at complete formation of the FeL_a and FeL_b species. Then for reaction (15) :

$$k_b = \frac{(\bar{n} - a)\left[H\right]^h}{(b - \bar{n})\left[\frac{T_L^o - \bar{n}T_M^o}{1 + \frac{1}{\text{antilog}(pKa - pH)}}\right]} \qquad (18b)$$

where Ka is the first phenolic dissociation constant.

The spectrophotometric data used to calculate a few representative constants and the results are given in Table 14. The other equilibrium constants are incorporated in Table 3. Except for the 4-chloroacetylcatechol complex, good correlation was generally found between the spectrophotometrically and potentiometrically determined constants.

The variation of the successive equilibrium constants, k, for the complexes with the phenolic dissociation constants is shown in Figs. 10 and 11. The direct correlations observed illustrate the dependence of complex formation (reactions 13) on the acidity of the ligand. The fact that the catechin complex does not deviate from the linear correlation indicates that the rest of the flavanoid molecule does not interfere with complex formation. The position of the points for Tiron were found to deviate from the linear correlation. This can be ascribed to the factors which have been mentioned previously.

The spectrophotometrically determined constants, k_2 and k_3, for the 4-chloroacetylcatechol complex were found to fit the linear correlations, whereas the potentiometrically determined values deviated quite markedly.

In addition, the deviations increased with increasing concentration of the complex. The only difference between the two methods is that in the former the concentration of the complex is much lower. Hydrogen bonding, such as that proposed in the FeL_2 species, could cause the observed differences. The situation shown in the diagram on page 84 approximates the ideal, since there will be rapid exchange between the bound and unbound water molecules. Thus it would be expected that in the extreme case, where this exchange is very rapid, the effect of the hydrogen bond will be negligible. This would occur at very low concentrations of the complex where the large excess of water molecules will promote the exchange. Also, as the concentration is increased, so the exchange will decrease and the effect of the hydrogen bond will increase. In the FeL_2 species the more pronounced the hydrogen bond is, the more favourable will be complex formation. This is reflected in the value of the constant, pk_2, which decreases as the concentration of the complex increases (Table 3).

In the fully co-ordinated FeL_3 complex no hydrogen bonding is possible. Therefore the hydrogen bond in the FeL_2 complex will have to be broken in forming the FeL_3 complex and the stronger the hydrogen bond, the more difficult will be the transformation. This is reflected in the value of the constant, pk_3, which increases as the concentration of the complex increases (Table 3).

The spectrophotometrically determined values probably correspond to the extreme situation, with little or no effect due to the hydrogen bond, because they fit the linear correlations (Figs. 10 and 11).

In the protocatechuic acid complex, FeL, the carboxyl group was shown to be undissociated. Therefore the constant, k_1, cannot be correlated with

the dissociation constants determined for this phenol, because the values are related to the ionised carboxyl form. An estimation of the pKaKb value for this phenol in the undissociated form may be made from Fig. 10, where the value corresponding to pk_1 for the complex was found to be 20.2. This decrease from 22.0, the value for the ionised form, seems reasonable in view of the fact that it has been shown[116] that the electron-withdrawing character of the carboxyl group is much stronger in the undissociated form. The FeL_3 species was found to form only after complete carboxyl ionisation, therefore the constant, k_3, may be correlated with the normal dissociation constants of this ligand. An accurate value of the constant, k_2, for the protocatechuic acid complex could not be determined because it was found that the value of pk_2 was dependent on the pH. This is due to the fact that the FeL_2 species formed in the pH region in which the carboxyl group ionised. Therefore the constant, k_2, will be dependent on whether the carboxyl group is ionised or not.

It is normal,[147-149] however, to relate the acidity of the ligand with the stability constants, K, and not the equilibrium constants, k, of the complex. This enables correlations to be made between the bonding in the protonated ligands and in the metal complexes.

The stability constants, K, for the reactions :

$$Fe^{3+} + L^{2-} \rightleftharpoons FeL^{+} \qquad K_1 = \frac{[FeL]}{[Fe][L]} \tag{19}$$

$$FeL^{+} + L^{2-} \rightleftharpoons FeL_2^{-} \qquad K_2 = \frac{[FeL_2]}{[FeL][L]} \tag{20}$$

$$FeL_2^- + L^{2-} \rightleftharpoons FeL_3^- \qquad K_3 = \frac{[FeL_3]}{[FeL_2][L]} \tag{21}$$

were calculated from the formation constants with the aid of the equation :

$$K_{1,2 \text{ or } 3} = \frac{k_{1,2 \text{ or } 3}}{KaKb} \tag{22}$$

and are listed in Table 4. The stability constants for the Tiron[141] and DHNS[20] compare favourably with the published values. The values quoted for the 4-chloroacetylcatechol complex are the spectrophotometrically determined constants.

The relationships between the overall stability constants of the complexes and the association constants of the phenols are shown in Figs. 12 and 13. The association constants for the equilibrium :

$$L^{2-} + 2H^+ \rightleftharpoons H_2L \tag{23}$$

were used so that they are in the same form as reactions (19) - (21). The points for Tiron have not been included in these plots, because of the anomalous behaviour of this ligand.

The existence of the observed direct correlation enabled the quantatative prediction of unknown constants. Log K_1 (log β_1) values for the more oxidisable phenolic complexes could not be determined. These values are necessary for determining the overall stability constants, β_2 and β_3. However they could be estimated (by the least squares method) from the extrapolated straight line in Fig. 12. K_1 Values were also obtained from a similar extrapolation of the linear correlation observed between the log K_1 values for the Fe(III) and Al(III) complexes (to be discussed later,

Section C) as shown in Fig. 14. The values obtained from both these methods are given in Table 5.

TABLE 4.

Stability constants for the o-dihydroxybenzene complexes of iron(III).

Ligand	log K_1 (log β_1)	log K_2	log β_2	log K_3	log β_3
4-methylcatechol	(20.85)	15.3	36.15	9.9	46.05
pyrocatechol	(20.5)	15.05	35.55	9.9	45.45
3-methoxycatechol	(20.35)	15.05	35.4	9.8	45.2
catechin	(20.0)	14.85	34.85	9.9	44.75
4-protocatechuic acid	18.8	-	-	9.7	-
3,4-dihydroxybenzenesulfonate	19.05	14.25	33.3	9.6	42.9
2,3-dihydroxynaphthalene	19.25	14.45	33.7	9.55	43.25
DHNS	18.9	14.35	33.25	9.8	43.05
Tiron	20.35	15.15	35.5	11.05	46.55
4-chloroacetycatechol	18.3	14.2	32.5	9.7	42.2
protocatechuic aldehyde	18.0	13.8	31.8	9.9	41.7
4-nitrocatechol	17.2	13.15	30.35	9.5	39.85

TABLE 5.

Estimation of stability constants, log K_1, from Figs. 12 and 14 for the Fe(III) complexes of pyrocatechol, 4-methylcatechol, 3-methoxycatechol and catechin.

Ligand	log K_1 from Fig. 12	log K_1 from Fig. 14
4-methylcatechol	20.9	20.8
pyrocatechol	20.5	20.5
3-methoxycatechol	20.3	20.4
catechin	20.0	20.0

The direct correlations observed in Figs. 12 and 13 illustrate that the factors which influence the bonding of the hydrogen in the phenols have a similar influence on the bonding of the metal in the complexes. The strengths of the O-H bond in the phenols have been shown to be increased by electron-releasing substituents and weakened by electron-withdrawing

substituents. Therefore similar deductions may be made for the M-O bonding in the complexes. Similar linear relationships have been found for a series of closely related ligands by many workers.[150-157]

2. 1,2,3-Trihydroxybenzene complexes.

Fe(III) complexes with four 1,2,3-trihydroxybenzene derivatives were studied, including the wattle tannin monomers robinetinidol and dihydrorobinetin.

Only two coloured species were formed with phenols of this class. In general, the colours were blue to violet in slightly acid to neutral solutions and red in alkaline solutions. In order to follow complex formation the visible absorption spectra of the Fe(III) complexes were recorded at various pH values. Fig. 15 illustrates the general form of these curves. The variation of absorbance with pH (extinction curves) at various fixed wavelengths is shown in Fig. 16.

Spectra and extinction curves for all these complexes could not be obtained at low pH values, because the colours, especially for the pyrogallol complex, faded rapidly with time. The reason for this has been discussed previously (p. 79).

Although the general form of the spectra (Fig. 15) appears to be similar to those of the o-dihydroxybenzene complexes (Fig. 1), the successive complex formation and the type of 1,2,3-trihydroxybenzene complex formed were found to be much more complicated.

(a) Pyrogallol and propyl gallate complexes : In order to determine the Fe(III) to ligand stoichiometry of what appeared to be the "normal" blue and

the red species ("normal" denoting those found for the o-dihydroxybenzene complexes), the continuous variation (Job's) and molar ratio methods were used. The pH values at which these methods were applied were those at the centre of the plateau observed in the extinction curves (Fig. 16).

The molar ratio plots showed no sharp breaks, but rather a gradual sloping away of the curve. No definite formulae could be assigned to the complexes on the basis of these measurements. Although rounded maxima were observed in the Job's plots, they were not found to correspond to any definite ratio as in the o-dihydroxybenzene complexes. There are two probable reasons for the above results. Either the complexes are appreciably dissociated in solution or there is more than one complex formed. If the former possibility occurred, then it would be expected that the wavelength of maximum absorption should remain constant no matter what mole ratio was used. In order to distinguish between the two possibilities, the visible absorption spectra of the blue and the red Fe(III)-pyrogallol complexes with various mole ratios were recorded. It was found that the blue species had absorption maxima at 575 and 560 nm with respective mole ratios of 1 : 1 and 1 : 2 (Fe to ligand) and the red species at 510, 500 and 495 nm with respective mole ratios of 1 : 1, 1 : 2 and 1 : 3. This indicates that the latter possibility probably occurs.

As a direct comparison it was found that the wavelength maxima of the violet pyrocatechol complex remained unchanged with variation in the mole ratios, suggesting that only one complex is formed. Although the wavelength maxima of the red pyrocatechol species were found to vary with the mole ratio, the changes were in the opposite direction to the above values, indicating different complexes being formed in the two cases.

The extra hydroxyl group in the 1,2,3-trihydroxybenzene derivatives can only be responsible for the differences observed between pyrocatechol and pyrogallol complexes. The cause cannot be steric in character because it was found that 3-methoxycatechol behaved as a normal o-dihydroxybenzene derivative in Fe(III) complex formation.

The molar ratio and Job's methods were also applied at a pH slightly lower than the first plateau observed in the extinction curves for pyrogallol (Fig. 16). The results are shown in Figs. 17 and 18. The sharp break in the molar ratio plot at a 1 : 1 mole ratio and the sharp maximum in the Job's plot at 0.5 for the ratio $\left[\text{ligand}\right]$ to $\left[\text{Fe}\right] + \left[\text{ligand}\right]$, suggests that only one blue complex is formed viz. FeR. The reason for the non-formation of any higher species is that the lower pH value prohibits their formation as in the case of o-dihydroxybenzene complexes, even with an excess of ligand.

The absorption spectrum of the 1 : 1 Fe(III)-pyrogallol species at these lower pH values was found to have a maximum at 575 nm (Extinction coefficient = 2,600), suggesting that it is the same species (wavelength maximum = 570 nm, extinction coefficient = 2,600) which is formed with low mole ratios at the higher pH values of the first plateau.

Electrophoresis applied to the FeR species of pyrogallol showed that it has a neutral overall charge as no migration was observed.

Potentiometric titrations were also recorded in order to supplement the spectrophotometric results. Titrations of the pyrogallol complex were only started at $\bar{z} = 2$ because of the complicating redox reactions at very low pH values. From the potentiometric titration curve for the Fe(III)-

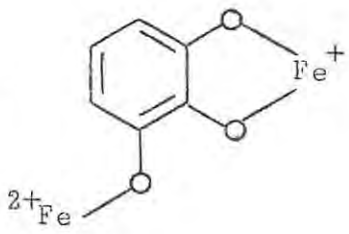
pyrogallol system in a 1 : 1 mole ratio (Fig. 19) it was found that an inflection occurred at $\bar{z} = 3$, indicating that three hydroxyl ions are involved in the formation of the blue FeR species. This inflection was found to be absent in solutions with excess pyrogallol (Fig. 19) and in Fe(III)-o-dihydroxybenzene titration curves with a 1 : 1 mole ratio (Fig. 9).

The Fe(III)-propyl gallate complexes proved to be more interesting than those of pyrogallol, because this ligand is less susceptible to oxidation. The potentiometric titration curves of Fe(III) ions and propyl gallate in a 1 : 1 mole ratio also showed an inflection at $\bar{z} = 3$ (Fig. 20). However, the results with excess of ligand solution were different from those of the pyrogallol complex, in that an inflection was still observed at $\bar{z} = 3$ (Fig. 20), indicating that separation of the successive complexation occurred. The steep rise in the spectrophotometrically determined extinction curves (Fig. 16) for propyl gallate, between pH 3.0 and 4.8 was found to correspond to the formation of this species. The results of the molar ratio and Job's methods for this species are shown in Figs. 17 and 18 and indicate that this blue species has a 1 : 1 mole ratio, similar to that of pyrogallol. Electrophoretic studies established that this species (FeR) is neutral.

The first propyl gallate species which was formed at very low pH values was found to have a very broad absorption spectrum (Fig. 15) with no definite maximum. The mole ratio of this species could not be determined by spectrophotometric methods because precipitates tended to form in solutions with excess of metal ions. Electrophoretic measurements on this species were also unsatisfactory as the complex formed a precipitate on the paper. However, the potentiometric titration curve (Fig. 20) showed an inflection at $\bar{z} = 1.5$, corresponding to the complete formation of this species.

If two of the ortho hydroxyl groups of pyrogallol or propyl gallate are co-ordinated to an Fe(III) ion, as in the o-dihydroxybenzene complexes, then the remaining hydroxyl group cannot combine with the central metal ion, because of its spacial arrangement. Such a 1 : 1 complex with an undissociated adjacent hydroxyl group was not observed. It should produce an absorption band in the region of 700 nm, as for a 1 : 1 o-dihydroxybenzene derivative. No such absorption band was observed.

The third hydroxyl group in the above species could combine with another metal ion :

$$2\ Fe^{3+} + H_3R \rightleftharpoons$$  $$+\ 3\ H^+ \qquad (24)$$

A similar structure has been postulated[102] for the first uranyl(VI)-pyrogallol species formed. This structure satisfies the potentiometric results for the first Fe(III)-propyl gallate species formed at low pH. The absorption spectrum of this species can be explained on the basis of this formula as well. The broad absorption band observed could be due to a combination of a band at about 700 nm, due to the o-dihydroxo group co-ordinated to one of the Fe(III) ions, as in the pyrocatechol derivatives, and a band at approximately 550 nm due to the Fe(III) ion attached to the third hydroxo ion, as in the Fe(III)-monohydric phenol compounds.[171]

At higher pH values the second Fe(III) ion, which is less strongly bound, could dissociate and react with another ligand molecule :

$$Fe_2R^{3+} + H_3R \rightleftharpoons 2 \text{ [chelate ring with } Fe^{+} \text{ and } O^{-}\text{]} + 3\,H^{+} \qquad (25)$$

where H_3R is a pyrogallol derivative.

A similar reaction has been postulated in a study of the uranyl(VI)-pyrogallol system.[102] This formula satisfies the spectrophotometric, potentiometric and electrophoretic results of the blue, 1 : 1 Fe(III)-pyrogallol and -propyl gallate complexes. An hydroxo species, FeRH(OH), can be ruled out because the equilibria were found to be dependant on the concentration of the ligand.

The formation constant for the first Fe(III)-propyl gallate species, Fe_2R, could not be calculated from the potentiometric results since the complex was found to be completely formed at the start of the titration. Also the constant could not be determined from the spectrophotometric data as it was found that the colour faded rapidly at pH less than 3.

The formation constant, k', for the second propyl gallate complex according to the equilibrium :

$$\tfrac{1}{2}\,M_2R^{3+} + \tfrac{1}{2}\,H_3R \rightleftharpoons MR + 1\tfrac{1}{2}\,H^{+} \qquad (26)$$

was calculated from the potentiometric data with the aid of the equations below.

For the general reaction :

$$x\,M_dR_a + y\,H_cR \rightleftharpoons z\,ML_b + h\,H \qquad (27)$$

$$n = \frac{\left[(v''' - v'') - v\right](N + E^{o})}{(V^{o} + v'')\, h\, T_{M}^{o}} \qquad (28)$$

(this equation is only valid for $\bar{n}_a = 3$ when $c = 3$)

where v''' and v'' are the respective volumes of alkali required to reach the same pH in titrations of the metal complex plus free acid and ligand plus free acid, and v is the volume of alkali required to reach $\bar{z} = 1.5$ in a titration with no free acid.

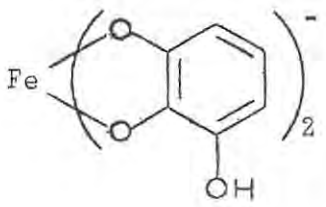
Then :

$$K' = \frac{(n\, T_{M}^{o})^{z} \left[H\right]^{h}}{\left[\frac{(1 - n)T_{M}^{o}}{d}\right]^{x} \left[\frac{\left[T_{L}^{o} - T_{M}^{o}(a/d + yn)\right] V^{o}}{(V^{o} + v'')}\right]^{y}} \qquad (29)$$

The symbols have been defined in equation (14).

The results and the experimental data used in the calculation are given in Table 15. The equilibrium constant, k', for the propyl gallate complex, FeR, could not be determined from the spectrophotometric data because an accurate value of the lower absorbance limit, A_1^o, was unavailable. The constant for the equivalent pyrogallol complex could also not be determined because of the non-equilibrium at low pH.

The violet Fe(III)-pyrogallol species formed at higher pH values and in excess of ligand solutions, has been established to be different from the above species by virtue of its different wavelength of maximum absorption. From an electrophoretic treatment it was established that the violet pyrogallol complex has a negative overall charge. For the complex to be anionic it is necessary for at least four hydroxyl groups, per metal ion, to be ionised. The following formula would satisfy this requirement :



This formula was confirmed by the potentiometric results obtained in titrations of Fe(III) ions and excess of pyrogallol (Fig. 19). On complete formation of the violet complex an inflection occurred at $\bar{z} = 4$. The minimum mole ratio of metal to ligand required to produce the inflection was found to be 1 : 2, i.e. $\bar{n} = 2$.

The corresponding propyl gallate complex also gave an inflection at $\bar{z} = 4$ and $\bar{n} = 2$ in titrations with excess of ligand (Fig. 20) and a 1 : 2 molar ratio of metal to ligand. The sloping plateau observed in the extinction curves (Fig. 16) between pH values 4.5 and 6.5 corresponds to the formation of this species. The wavelengths of maximum absorption and the extinction coefficients of the 1 : 1 and 1 : 2 complexes are obviously very similar. Electrophoretic measurements established that the complex is anionic as expected.

The formation constantfor the violet Fe(III)-pyrogallol species could not be determined because of the simultaneous formation of both the blue and the violet species.

The formation constant, k", for the propyl gallate complex, $Fe(HR)_2^-$, according to the equilibrium :

$$FeR + H_3R \rightleftharpoons Fe(HR)_2^- + H^+ \qquad (30)$$

was calculated from the potentiometric data with the aid of equations (28) and (29). The results of the calculation are given in Table 16. The spectrophotometric data could not be used to calculate this constant because the formation of the $Fe(HR)_2$ species had only a slight effect on the absorbance values.

The anomalous results of the molar ratio and Job's methods for the red Fe(III)-pyrogallol and -propyl gallate systems must obviously be due to the formation of different species dependent on the mole ratio of the reactants. Also the visible absorption spectra at various pH values for the Fe(III)-pyrogallol system, showed that the formation of the red species was not a simple one-step process, as in the o-dihydroxybenzene complexes, since no isosbestic points were observed. A detailed analysis of the various species was not attempted, because the situation was even further complicated by the ionisation of the uncomplexed phenolic ligands at the high pH values necessary for complex formation of the red species. However, it was established from the potentiometric results that the final red species formed in solutions of excess of ligand is similar to those of the o-dihydroxybenzene derivatives, viz. $Fe(HR)_3^{3-}$ with the third hydroxyl group not co-ordinated and undissociated. This was established from calculations using equation (14). Consistent values of $\bar{n} = 3$ obtained at high pH values for both the pyrogallol and propyl gallate complexes.

The visible absorption spectra at various pH values for the Fe(III)-propyl gallate system (Fig. 15) gave only one isosbestic point at 560 nm on formation of the $Fe(HR)_3$ species. This suggests there is only one complex being formed in solutions of excess of ligand :

$$Fe(HR)_2^- + H_3R \rightleftharpoons Fe(HR)_3^{3-} + 2H^+ \qquad (31)$$

The formation constant, k_3, was calculated from the spectrophotometric data using equations (18a) and (18b). Results are given in Table 17. The constancy of the value of k_3 confirms the proposed one-step process.

(b) Robinetinidol and dihydrorobinetin complexes : Robinetinidol and dihydrorobinetin both have 1,2,3-trihydroxybenzene B-rings (cf. p. 14).

The Fe(III) complex of dihydrorobinetin precipitated in solution and therefore could not be investigated by the available methods.

Robinetinidol formed similar complex species with Fe(III) to those of pyrogallol. Potentiometric titrations of Fe(III) with an excess of ligand, gave a sharp inflection at $\bar{z} = 4$ and $\bar{n} = 2$, corresponding to the violet FeL_2 complex. The absorption spectrum of this species had a maximum at 555 nm and extinction coefficient of 3700, very similar to that of pyrogallol (Table 6). A detailed study of the other blue species that could be formed in solutions of lower mole ratios was not performed due to the limited quantity of robinetinidol.

The potentiometric results indicated that the final red species had the usual formula, FeL_3, and again the absorption spectrum was found to be similar to that of pyrogallol, with a maximum at 495 nm (extinction coefficient = 5000). It can therefore be assumed that this compound reacts as a 5-substituted derivative of pyrogallol and that the rest of the flavanoid molecule does not interfere with complex formation.

(c) Wattle tannin complexes : The Fe(III)-wattle tannin systen caused some complication because a blue species precipitated under the conditions used. However, this difficulty could be overcome if a sulfited derivative of wattle was used. Sulfitation has been assumed[158] to attack the aliphatic

portion of the flavanoid molecule and therefore should not interfere with the complexing groups on the B-ring. This was verified in the study of the boric acid complexes, (to be discussed later, Section C) where it was found that the equilibrium constants for both the sulfited and unsulfited wattle tannin complexes were identical.

The absorption spectra at various pH values for the Fe(III)-wattle tannin system are illustrated in Fig. 22. The spectra at low pH values could not be obtained because of rapid fading in colour, similar to the other Fe(III) complexes with more oxidisable phenolic ligands.

A comparison of the visible absorption spectra of the o-dihydroxybenzene with the 1,2,3-trihydroxybenzene complexes showed that the general form of the curves for the two classes were different. In the former complexes, the tail of the red band, due to the FeL_3 species, was found to cross the violet band, due to the FeL_2 species, at lower wavelengths than the maximum, as indiacted by the isosbestic points in Table 1. In the latter complexes, however, the tail of the red band was found to cross the violet band on the higher wavelength side of the maximum. The fact that the wattle tannin complex follows the latter rule, suggests that it reacts as a pyrogallol derivative. This was supported by the similarity of the wavelengths of maximum absorption at 555 nm (extinction coefficient = 3650) and 495 nm (extinction coefficient = 5000) for the wattle tannin complex with those for pyrogallol (Table 6). Thus, although wattle tannins are known to contain both o-dihydroxybenzene and 1,2,3-trihydroxybenzene rings,[17] it appears that the latter are more prominent in Fe(III) complex formation.

The formation of the Fe(III)-wattle tannin complexes could also be

TABLE 6.

Experimental results for the Fe(III) complexes of 1,2,3-trihydroxybenzene derivatives.

Ligand	*Species	Absorption maximum nm	Extinction coefficient	-log of the equilibrium constant	Symbol
pyrogallol	FeR	575	2600	-	
	$Fe(RH)_2^-$	560	3350	-	
	$Fe(RH)_3^{3-}$	495	4850	-	
propyl gallate	Fe_2R^{3+}	-	1500	-	
	FeR	550	3900	5.85	k'
	$Fe(RH)_2^-$	545	4200	2.82	k''
	$Fe(RH)_3^{3-}$	485	5950	10.77	k_3
Robinetinidol	$Fe(RH)_2^-$	555	3700	-	
	$Fe(RH)_3^{3-}$	495	5000	-	
wattle tannin	$Fe(RH)_2^-$	555	3650	-	
	$Fe(RH)_3^{3-}$	495	5000	-	

* where H_3R is a 1,2,3-trihydroxybenzene derivative.

followed by means of potentiometric titrations. The titration curve with a large excess of wattle tannin, illustrated in Fig. 21, was found to have a sharp inflection at $\bar{z} = 4$, corresponding to the complete formation of the violet, FeL_2 species. A large excess of wattle tannin was necessary for complete complex formation, because of the polymeric nature of the ligand.

It was hoped that the spectrophotometric methods used to determine component ratios would indicate the number of polymeric tannin units which would be necessary for complete complex formation. However, the complicated nature of the results applied to known simpler 1,2,3-trihydroxybenzene derivatives precluded any definite conclusions to be reached.

Unfortunately, equilibrium constants for the formation of the various wattle tannin and robinetinidol complexes could not be determined for the same reasons as those for the pyrogallol complex.

The various species and their related formation constants, wavelengths of maximum absorption and extinction coefficients for the Fe(III) complexes of 1,2,3-trihydroxybenzene derivatives are summerised in Table 6.

The only formation constant which can be related to those of the o-dihydroxybenzene complexes, is the constant, k_3, for the propyl gallate complex. None of the other constants could be related because of the different equilibria which are involved. The position of the point for propyl gallate (pKaKb = 20.0) in the pk_3 vs. pKaKb correlation (Fig. 11) was found to correspond to the linear relationship. Thus it appears that when the extra hydroxyl group of the 1,2,3-trihydroxybenzene derivatives is not involved in complex formation, then the phenolic ligand reacts as a 3-substituted derivative of o-dihydroxybenzene.

3. Interpretation of the visible absorption spectra for the Fe(III) complexes of o-diphenols.

(a) The nature of the intense colours.

The magnetic moment of 5.93 B.M. at 25° for the complex, tris(tetrachlorocatecholato)iron(III) ion shows[24] that Fe(III) complexes of o-diphenols are high-spin. The electronic spectra of high-spin Fe(III) complexes have a number of absorption bands spread over the visible region, but because the d-d transitions are all spin-forbidden, the intensity of these bands are all very low (extinction coefficient = 0.01).[160]

The intense nature of the absorption bands of the o-diphenol complexes rules out the possibility that they are associated with d-d transitions (Table 1).

The phenolic ligands are known to have very intense bands in the ultraviolet region of the spectrum. The absorption band for pyrocatechol, with a maximum at 36,000 cm^{-1}, was found to shift slightly (1000 cm^{-1}) to lower energy on formation of the colourless Ge(IV) complex. However a shift of the order of 15,000 - 20,000 cm^{-1} for this absorption, to correspond to the Fe(III)-pyrocatechol absorption bands, seems very unlikely.

Thus the strong visible absorption bands must be due to transitions of electrons which take place as a result of complex formation. The intense colours of the Fe(III) complexes of o- diphenols suggests[161] that the absorption bands are due to charge transfer transitions.

Charge transfer complexes have been interpreted on the basis of an electron donor D and an electron acceptor A.[10] The energy required for transition to the electronically excited state was shown to be dependent on the ionisation potential of D and the electron affinity of A. The charge transfer spectra of the Fe(III) halides have been shown[162] to be in quantative agreement with the following equation based on an electrostatic model :

$$U = \Delta + I - E \qquad (32)$$

where U is the energy required for charge transfer, Δ assumed to be constant for a set of related compounds,[163] is the difference of electrostatic formation energies for the ground and excited state, I is the ionisation potential of the donor and E is the electron affinity of the

acceptor. This equation is similar to the one used for interpreting the energies for electronic transitions in alkali halides.[164]

The strong absorption band in the spectrum of hexa-aquoiron(III)[165] and the yellow colours of Fe(III) hydrolysis products[166] have also been assigned to charge transfer processes. In oxides containing trivalent iron both charge transfer from oxygen to iron and $3d^5 \longrightarrow 3d^4\ 4p$ transitions were considered as possible sources for the intense absorption bands.[167] However, it was found that the charge transfer model best suited all the experimental results.

The blue colours produced between solutions of ferric chloride and monohydric phenols is a well known diagnostic test for phenols,[168-169] and have also been assigned to a charge transfer process.[71] Thus the generally found[166] charge transfer nature of Fe(III) complexes was expected and has been found[25,170] to apply to the o-diphenol complexes.

(b) The effect of ring substitution.

The wavelengths and wave numbers of the maxima of the main absorption bands for the Fe(III) complexes of o-diphenols are given in Table 7. Ring substitution can be seen to have an appreciable effect on the values of the wave numbers of maximum absorption for all three species. In order to correlate these two functions according to equation (32), the ionisation potentials of the ligands need to be known. Unfortunately these values for the o-diphenol ligands are not known. However, it has been shown that in a set of related substances, the ionisation potentials are directly related to the oxidation potentials.[174] Oxidation potentials of phenols are difficult to determine[175] because of the labile nature of the radical. However, the

TABLE 7.

Absorption maxima for the charge transfer of Fe(III) complexes of o-diphenols.

Ligand	FeL_1 Absorption maxima		FeL_2 Absorption maxima		FeL_3 Absorption maxima	
	nm	kK	nm	kK	nm	kK
4-methylcatechol	710	14.08	585	17.09	500	20.00
3-methoxycatechol	710	14.08	590	16.95	500	20.00
pyrocatechol	700	14.29	575	17.39	495	20.20
catechin	690	14.49	575	17.39	495	20.41
protocatechuic acid	670	14.93	570	17.54	490	20.41
3,4-dihydroxybenzene-sulfonate	670	14.93	565	17.70	485	20.62
pyrogallol	-	-	560	17.86	495	20.20
robinetinidol	-	-	555	18.02	495	20.20
wattle tannin	-	-	555	18.02	495	20.20
4-chloroacetylcatechol	655	15.27	550	18.18	-	-
Tiron	655	15.27	555	18.02	480	20.83
protocatechuic aldehyde	650	15.38	555	18.02	-	-
4-nitrocatechol	640	15.63	-	-	-	-
propyl gallate	-	-	545	18.35	485	20.62
2,3-dihydroxynaphthalene	600	16.67	525	19.05	455	21.98
DHNS	580	17.24	515	19.42	450	22.22

"critical" oxidation potentials, E_c, of a number of related compounds including phenols have been determined.[176] The effect of substitution on the oxidation potentials, ΔE_c, of these compounds was also determined.[176] A plot of these values against the energies required for charge transfer for the FeL complex species (Table 7) is illustrated in Fig. 23. The direct correlation which is observed indicates that the less oxidisable the ligand, the higher is the energy of the charge transfer band relative to the unsubstituted ligand and vice versa; cf. equation (32). This result is in accordance with a charge transfer process from the oxidisable phenolic ligand to the reducible metal ion. Similar correlations were found for the FeL_2 and FeL_3 species.

(c) The effect of the increasing number of ligands.

From Table 7 it may be seen that on successive formation of the Fe(III) complexes of o-diphenols, the wave numbers of maximum absorption are shifted to higher energies. This may be interpreted using the electrostatic model for charge transfer (equation (32)). It has been shown[177] that the electron affinity of the acceptor in a charge transfer process is proportional to its oxidation potential. Thus the higher the oxidation potential of the Fe^{3+}/Fe^{2+} couple, the lower will be the energy for charge transfer and vice versa. Although it would be expected that the oxidation potential of the Fe^{3+}/Fe^{2+} couple and thus the electron affinity would increase on successive formation of the o-diphenol complexes, due to the readily oxidisable nature of the ligand, the reverse in fact occurs. In general it has been found[178] that on complex formation the higher valency state will be stabilised relative to the lower and that the degree of stabilisation ($E^{o}_{aquo} - E^{o}_{complex}$) will increase with increased polarisability of the ligand. Thus for the redox reaction[178]:

$$ML_x^{m+} + n\bar{e} \rightleftharpoons ML_y^{(m-n)+} + (x - y)L \qquad (33)$$

where n is the number of electrons involved, x and y the number of ligands and m the higher oxidation state, it was shown that :

$$E^{o}_{complex} = E^{o}_{aquo} - \frac{RT}{nF} \ln \frac{K_m}{K_{m-n}} \qquad (34)$$

where K_m and K_{m-n} are the respective overall stability constants of the higher and lower valency complexes. Thus $E^{o}_{complex} < E^{o}_{aquo}$ if $K_{m-n} < K_m$.

The equilibrium constants for the formation of the Fe(II) -pyrocatechol

complexes have been determined[53] and found to be $pk_1 = 14.33$, $pk_2 = 16.74$. The stability constants calculated from these values are $\log \beta_1 = 8.67$ $\log \beta_2 = 14.93$. Using the stability constants for the Fe(III)-pyrocatechol complexes (Table 4) of $\log \beta_1 = 20.5$, $\log \beta_2 = 35.55$ and $\log \beta_3 = 45.45$, the following oxidation potentials for the Fe^{3+}/Fe^{2+} system were calculated from equations (34), with n = 1, R = 8.3143 $JK^{-1}mole^{-1}$, F = 96,487 C/mole , E^{o}_{aquo} [178] = 0.77 v and T = 293°K.

If x = y = 1, then for the FeL^{+}/FeL couple, $E^{o}_{complex} = +0.08$

If x = y = 2, then for the FeL_2^{-}/FeL_2^{2-} couple, $E^{o}_{complex} = -0.43$

If x = 3, y = 2, then for the FeL_3^{3-}/FeL_2^{2-} couple, $E^{o}_{complex} = -1.00$

Consequently on successive formation of the o-diphenol complexes, the oxidation potential and thus the electron affinity of the acceptor decreases and, from equation (32), the energy required for charge transfer increases, as observed.

(d) Molecular orbital approach.

Charge transfer spectra have been successfully interpreted on a molecular orbital model.[12,13] This gives a more flexible description of the results. From the simplified molecular orbital diagram[13] (Fig. 24), four types of transitions can be expected for ligand to metal charge transfer, viz. ν_1, $\pi \longrightarrow t_{2g}$; ν_2, $\pi \longrightarrow eg$; ν_3, $\sigma \longrightarrow t_{2g}$ and ν_4, $\sigma \longrightarrow e_g$. It is also expected that the energy of the transitions increases in the order $\nu_1 < \nu_2$ and $\nu_3 < \nu_4$. The relative order of ν_3 and ν_4 will depend on whether the energy difference between the π- and σ-orbitals is smaller or larger than 10Dq.

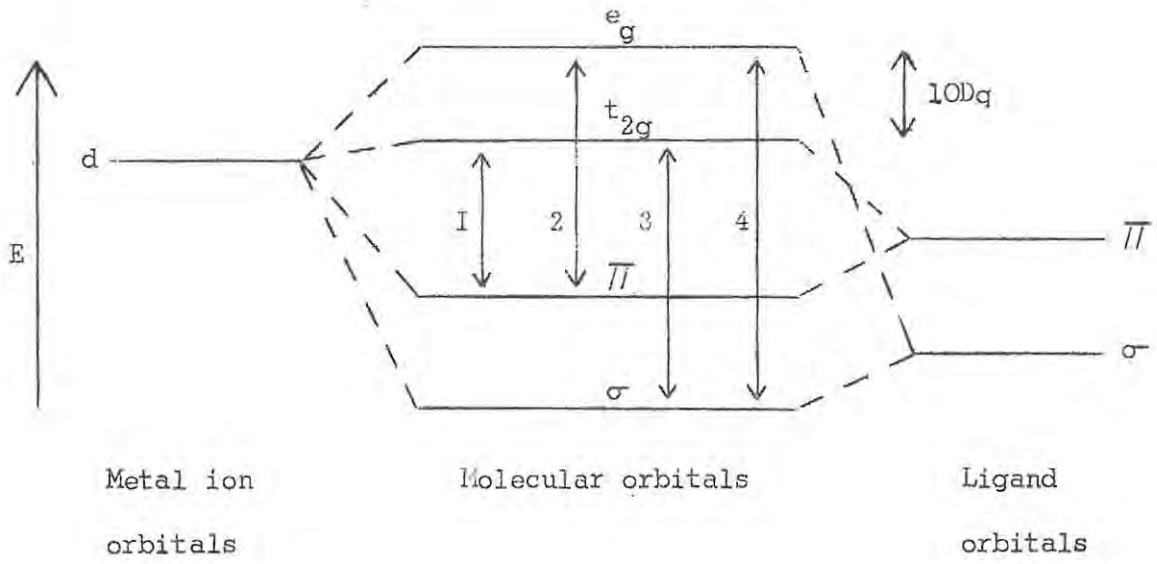


Fig. 24. Simplified molecular orbital energy level diagram for octahedral nd metal complexes with π ligand donor orbitals.

Charge transfer transitions from spin-paired ligand orbitals to high-spin d^5 metal orbitals result in no change in the overall spin state and are thus all spin-allowed. They are also Laporte-allowed because the wave functions involved are u $\longrightarrow$ g.[180,185] The probability of the transition and thus the extinction coefficient are therefore very large.

In order to interpret the charge transfer bands of the Fe(III) complexes of o-diphenols on a molecular orbital basis a closer examination of the absorption spectra of these complexes was made. The spectra (Fig. 25) show in addition to the main charge transfer absorption bands further bands at much higher energies than the main bands for the FeL and FeL_2 complexes. In the FeL_3 spectrum, only a shoulder may be observed on the lower wave number side of the phenolic ligand absorption, also at much higher energy than the main band. It is obvious that the higher energy bands are not due to the d-d transitions of the metal ion because of their large extinction coeffic-

ients. The possibility that they might be due to phenolic absorption was ruled out, since they were found to absent from absorption spectra of the free phenols and the colourless Ge(IV) complexes of o-diphenols.

The absorption maxima and extinction coefficients of all the higher energy bands for the Fe(III) complexes of o-diphenols are listed in Table 8. Unfortunately the close proximity of the strong phenolic absorption made detection of some of the high energy bands impossible. This applied to all the 1,2,3-trihydroxybenzene complexes and the 4-nitrocatechol, 3-methoxy-catechol and 4-chloracetylcatechol complexes.

The high energy bands for the Fe(III)-Tiron complex may be observed in the published spectra,[17] but no comment was made concerning them. Similar bands may be observed[179] in the Fe(III)-salicylate complexes as shoulders on the low energy side of the ligand absorption band.

The higher energy absorption bands, ν_2, are clearly due to charge transfer, because they follow the main charge transfer bands up to higher energies on successive complex formation. They also show the same shifts in absorption maxima with the various substituted o-diphenols as observed in Table 8.

The charge transfer absorption bands of metal-phenolic complexes have been assigned to an electronic transition from the ligand π-orbital to a metal orbital.[25] Therefore the lowest energy bands, ν_1, of the Fe(III) complexes of o-diphenols can be similarly assigned viz. $\pi \longrightarrow t_{2g}$. The assignment of the higher energy bands, ν_2, to a $\pi \rightarrow e_g$ transition was proposed as in the heavy metal halides,[12] tris(oxalato)iron(III)[180] and other Fe(III) compounds.[181]

The substituent effect on the energy for charge transfer can also be

TABLE 8.

Absorption maxima for the charge transfer Fe(III) complexes of o-diphenols.

Species	Ligand	ν_1	Extinction coefficient	ν_2	Extinction coefficient
FeL_1	4-methylcatechol	14.08	1360	22.73	1,040
	pyrocatechol	14.29	1480	23.00	1,080
	catechin	14.49	1750	23.00	1,460
	protocatechuic acid	14.93	1780	(25.32)	1,380
	3,4-dihydroxybenzene-sulfonate	14.93	1900	23.50	1,250
	Tiron	15.27	1980	23.81	1,200
	protocatechuic aldehyde	15.38	2100	24.10	2,000
	2,3-dihydroxynaphthalene	16.67	3140	(28.17)	1,600
	DHNS	17.24	3480	(27.40)	1,800
FeL_2	4-methylcatechol	17.09	3440	26.32	2,160
				(29.85)	2.260
	pyrocatechol	17.39	3400	26.67	1,380
				(29.85)	1,960
	catechin	17.39	4000	26.67	2,500
				(29.85)	2,660
	3,4-dihydroxybenzene-sulfonate	17.70	4000	28.57	2,600
	Tiron	18.02	4650	28.99	3,200
FeL_3	4-methylcatechol	20.00	4600	(30.77)	
	pyrocatechol	20.20	4400	(31.25)	
	catechin	20.20	5150	(31.25)	

interpreted on a molecular orbital model. The energy of the bands will depend on the energy level differences between the π ligand orbitals and the metal d ligand orbitals. It has been shown[182] that the ionisation and oxidation potentials in a series of related compounds are inversely related to the energy levels of the highest occupied molecular orbital. Thus a substituted o-diphenol with a higher oxidation potential (electron-withdrawing substituent) relative to the unsubstituted phenol would have its highest occupied molecular orbital (π ligand orbital) at a relatively lower energy. From Fig. 24 the energy necessary for charge transfer would thus be higher and vice versa, as observed in Table 8.

From Table 8 it may be seen that for the FeL_2 species of 4-methylcatechol, pyrocatechol and catechin, two ν_2 bands were assigned to a $\pi \longrightarrow e_g$ transition. The occurrence of two bands in the ν_2 class could be due to a number of reasons :

(i) The presence of dissimilar phenolic and water ligand molecules could result in the splitting of the metal e_g orbitals.[13]

(ii) The transitions could be from non-degenerate ligand π-orbitals.[12]

(iii) In the excited state with electronic configuration, $t_{2g}^3 e_g^3$, Jahn-Teller (dynamic) distortion could split the e_g orbitals.[183]

It would be expected that the energy difference between the $\pi \longrightarrow t_{2g}$ (ν_1) and $\pi \longrightarrow e_g$ (ν_2) transitions would be of the order of $10Dq$. The values obtained are given in Table 9.

TABLE 9.

$\Delta\nu$ values for the Fe(III) complexes of o-diphenols.

Ligand	$\nu_2 - \nu_1$ FeL (kK)	$\nu_2 - \nu_1$ FeL_2 (kK)	$\nu_2 - \nu_1$ FeL_3 (kK)
4-methylcatechol	8.65	11.00	10.77
pyrocatechol	8.71	10.87	11.05
catechin	8.51	10.87	11.05
3,4-dihydroxybenzenesulfonate	8.57	10.87	
Tiron	8.54	10.97	
protocatechuic aldehyde	8.72		

As seen from Table 9 the values obtained for each species are approximately all of the same order. This provides some justification for the above assignments. The lower difference value for the FeL_1 species is probably a result of the lower symmetry[180] of this system, relative to the others.

The $\Delta\bar{\nu}$ value of 11,050 cm^{-1} for tris(pyrocatecholato)iron(III) compared with 10Dq for hexa-aquoiron(III)[186] of 13,700 cm^{-1} and for tris(oxalato)-iron(III)[180] of 12,600 cm^{-1}, is somewhat lower than expected because similar values of 10Dq were found for aquo and o-diphenol complexes of nickel(II) (Section D). However, $\Delta\bar{\nu}$ values which were lower than the expected 10Dq, have been found for other charge transfer complexes.[12,180]

(e) The intensities of the charge transfer bands.

The half band widths, δ, and the oscillator strengths, f, were determined with the aid of the equations :

$$\delta = 2(\bar{\nu}_{max} - \bar{\nu}_{\frac{1}{2}}) \qquad (35)$$

where $\bar{\nu}_{\frac{1}{2}}$ is the wave number on the lower energy side at half the extinction coefficient of the maxima, and[184]:

$$f = 4.6 \times 10^{-9} . \delta \varepsilon \qquad (36)$$

(ε values from Table 1) for the main charge transfer absorption bands. The results are shown in Table 10.

From Tables 1 and 10 it may be seen that the extinction coefficients and the oscillator strengths are as expected[185] for charge transfer bands.

The increase in the extinction coefficients observed on successive formation of the o-diphenol complexes is probably due to the increasing number of co-ordinated ligands which increase the probability of the charge transfer from ligand to metal taking place.

From Table 1 it may be seen that the various phenolic ligands have considerable effect on the extinction coefficients. An interesting correlation was found to exist between the wavelengths of maximum absorption and the

TABLE 10.

Halfband widths and oscillator strengths for the Fe(II) o-diphenol charge transfer absorption bands.

Ligand	FeL_1		FeL_2		FeL_3	
	$\delta/2$ kK	f	$\delta/2$ kK	f	$\delta/2$ kK	f
4-methylcatechol	2.72	.034	3.01	.095	3.19	.135
4-methoxycatechol	-	-	3.06	.098	3.30	.142
pyrocatechol	2.80	.038	3.00	.094	2.96	.120
catechin	3.00	.048	2.90	.107	2.96	.140
protocatechuic acid	3.15	.052	3.05	.118	2.90	.146
3,4-dihydroxybenzenesulfonate	3.03	.053	2.99	.110	3.08	.147
4-chloroacetylcatechol	3.00	.058	3.03	.135	-	-
Tiron	3.00	.055	3.03	.130	2.97	.164
protocatechuic aldehyde	2.85	.055	2.87	.128	-	-
4-nitrocatechol	3.13	.065	-	-	-	-
pyrogallol	-	-	3.87	.119	3.33	.150
robinetinidol	-	-	3.70	.126	3.30	.152
wattle tannin	-	-	3.66	.124	3.30	.152
propyl gallate	-	-	3.64	.141	3.38	.185
2,3-dihydroxynaphthalene	3.06	.089	2.92	.186	2.93	.253
DHNS	3.16	.102	3.03	.215	3.35	.326

corresponding extinction coefficients of the bands as illustrated in Fig. 26. A similar correlation has been found for charge transfer complexes of iodine with aromatic hydrocarbons.[172] The explanation which was given, that the intensities are dependent on the stability constant of the complex i.e. the more stable the lower the intensity, does not hold for the Fe(III) complexes of o-diphenols. Although the 2,3-dihydroxynaphthalene complexes are not the least stable, they have the highest extinction coefficients. However, an alternative explanation for the observed correlations could not be formulated.

The different correlation which may be drawn for the FeL_2, 1,2,3-trihydroxybenzene complexes, as illustrated in Fig. 26, is useful because a

distinction may be made between these complexes and those of the o-dihydroxybenzene derivatives. The fact that in the graphical representation the point for wattle tannin corresponds to this correlation, again illustrates that it belongs to the 1,2,3-trihydroxybenzene class.

Correlations with extinction coefficients are, however, only valid if the band widths are the same. From Table 10 it may be seen that the band widths for all the o-dihydroxybenzene complexes and the FeL_3, 1,2,3-trihydroxybenzene complexes are of approximately the same order. However, the FeL_2 species of the latter complexes all have broader bands relative to the above. Therefore the oscillator strengths, f, should actually be used in correlating data. A plot of the wave numbers of maximum absorption for the FeL_2 species against the corresponding oscillator strengths gave a linear relationship for both the o-dihydroxybenzene and 1,2,3-trihydroxybenzene complexes.

4. "Ferrous" tartrate complexes of o-diphenols.

The complexes of wattle tannins with ferrous tartrate solutions form the basis of a colorimetric method of tannin analysis.[15] In the light of the results obtained for the Fe(III) complexes of o-diphenols, the nature of the complexes formed according to the above method should be reviewed.

Although ferrous salts are used to make up the iron solutions, on addition of the Rochelle salt (sodium potassium tartrate) the pH is raised sufficiently for oxidation by molecular oxygen of Fe(II).[187] Thus the coloured metal-polyphenol complexes produced according to the above method in fact contain Fe(III) and not Fe(II), as previously thought.[15] The tartrate is added as a sequestering agent to prevent the precipitation of

ferric oxide, because the analysis is carried out at pH 7 (ammonium acetate buffer).

The pyrogallol and pyrocatechol complexes which are formed with ferric tartrate solutions were investigated by spectrophotometric methods. The experimental conditions were the same as those used in the analytical method. The results of the Job's method applied to the pyrocatechol complex at pH 7 is illustrated in Fig. 17. The maximum observed at a 1 : 2 molar ratio of Fe(III) to ligand for the blue complex formed, indicates that the tartrate does not interfere with the complex formation, since this is the same molar ratio found previously for the blue pyrocatechol species.

The same method applied to the blue pyrogallol complex produced a similar plot, with a maximum at a 1 : 1 molar ratio, as previously obtained without the tartrate present at a much lower pH value cf. Fig. 17. The presence of the tartrate therefore prevents the formation of the higher FeL_2 complex.

The significance of these results is that in large excess of ferric tartrate, as used in the analytical method, there would be complete formation of the FeL_1 species with three ionised hydroxyl groups. The possibility of higher complexes being formed would be small. Resulting from the similarity which has been found between the pyrogallol and wattle tannin complexes, it is expected that the wattle tannin species formed in such an analytical method would follow a similar trend.

These results may be used to interpret the comparisons which have been made between pyrocatechol, pyrogallol and wattle tannin complexes, formed with excess of ferric tartrate.[189] It was found that the absorbance value

at complete complex formation was larger for pyrogallol than for an equivalent molar concentration of pyrocatechol. The extinction coefficients, based on the concentration of the phenol, were shown to be 2500 and 1650 respectively. However the respective complexes were found in the present investigation to have molar ratios of 1 : 1 and 1 : 2 (Fe to ligand), hence such a comparison is not valid. The extinction coefficients should be determined on the basis of the complex concentration and thus the above value for pyrocatechol should actually be 3300. A comparison of these values with those listed in Tables 1 and 6 show close agreement.

The assumption[189] that wattle tannins react similarly to pyrogallol moeities in Fe(III) complex formation, has been confirmed in the present investigation.

TABLE 11.

Determination of hydrolysis constants, K', for the 4-nitrocatechol and 3,4-dihydroxybenzenesulfonate complexes, $Fe(OH)L_2$.

Ligand : 4-nitrocatechol				3,4-dihydroxybenzenesulfonate			
pH	v'''	n	pK'	pH	v'''	n	pK'
6.2	4.09	0.09	7.205	7.4	4.12	0.12	8.265
6.4	4.14	0.14	7.188	7.6	4.17	0.17	8.289
6.6	4.21	0.21	7.175	7.8	4.25	0.25	8.277
6.8	4.30	0.30	7.168	8.0	4.34	0.34	8.288
7.0	4.40	0.40	7.176	8.2	4.45	0.45	8.287
7.2	4.50	0.50	7.200	8.4	4.56	0.56	8.295
7.4	4.60	0.60	7.224	8.6	4.67	0.67	8.292
7.6	4.70	0.70	7.232	8.8	4.77	0.77	8.275
7.8	4.79	0.79	7.225	9.0	4.84	0.84	8.280

Experimental data used in equations (7) and (8) :

V^o = 50 ml H_2O, T_L^o = 0.004 M, T_M^o = 0.002 M, N = 0.1 N KOH

TABLE 12.

Determination of pK' values for the catechin complex, $Fe(OH)L_2^{2-}$.

pH	v'''	v'	v	n	pK'
8.2	4.41	4.00	0.20	0.21	8.775
8.4	4.59	4.00	0.30	0.29	8.789
8.6	4.84	4.00	0.44	0.40	8.776
8.8	5.12	4.00	0.62	0.50	8.800
9.0	5.43	4.00	0.83	0.60	8.824
9.2	5.77	4.01	1.06	0.70	8.832
9.4	6.09	4.02	1.28	0.79	8.825

Experimental data used in equations (9) and (10) :
V^o = 50 ml, T_L^o = 0.004 M, T_M^o = 0.002 M, N = 0.1 N.

TABLE 13.

Determination of the successive equilibrium constants, k, for the 4-nitrocatechol and catechin complexes of Fe(III).

Ligand : (1) 4-nitrocatechol						(2) catechin :					
pH	v'''	v''	$\bar{n}_a$	$\bar{n}$	pk	pH	v'''	v''	$\bar{n}_a$	$\bar{n}$	pk
a = 1, b = 2											
3.2	3.84	2.68	2	1.167	4.518	4.6	1.23	0	2	1.23	7.393
3.4	4.10	2.79	2	1.315	4.531	4.7	1.32	0	2	1.32	7.386
3.6	4.38	2.86	2	1.524	4.515	4.8	1.41	0	2	1.41	7.408
3.8	4.62	2.91	2	1.713	4.525	5.0	1.62	0	2	1.62	7.415
4.0	4.79	2.94	2	1.852	4.531	5.2	1.79	0	2	1.79	7.434
a = 2, b = 3											
5.2	5.23	3.05	1.970	2.214	8.163	7.2	2.31	0.10	1.965	2.227	12.483
5.4	5.40	3.08	1.955	2.374	8.172	7.4	2.52	0.16	1.975	2.390	12.520
5.6	5.60	3.125	1.935	2.569	8.160	7.5	2.65	0.19	1.968	2.50	12.508
5.8	5.80	3.20	1.900	2.737	8.160	7.6	2.80	0.23	1.96	2.62	12.471
6.0	5.94	3.30	1.850	2.854	8.172	7.8	3.05	0.36	1.94	2.773	12.524
6.2	6.05	3.45	1.775	2.930	8.152	8	3.29	0.53	1.91	2.890	12.515

Experimental data used in equations (14) - (17) :
T_L^o = (1) 0.004 M, (2) 0.006 M, T_M^o = 0.001 M, N = 0.1 N, E^o = (1)0.006 M, (2) 0, V^o = 50 ml, I = 0.1 N, c = 2.

TABLE 14.

Determination of equilibrium constants, k, for the 2,3-dihydroxynaphthalene, 4-chloroacetylcatechol and pyrocatechol complexes of Fe(III).

Ligand : (1)2,3-dihydroxynaphthalene				(2)4-chloroacetylcatechol				(3)pyrocatechol.			
pH	A	$\bar{n}$	pk_1	pH	A	$\bar{n}$	pk_2	pH	A	$\bar{n}$	pk_3
a = 0, b = 1				a = 1, b = 2				a = 2, b = 3			
2.45	.144	0.42	1.69	3.98	.515	1.32	5.16	7.70	.500	2.21	13.12
2.55	.175	0.52	1.72	4.14	.580	1.45	5.21	7.86	.425	2.37	13.08
2.62	.200	0.59	1.73	4.25	.64	1.58	5.20	7.98	.365	2.50	13.08
2.70	.230	0.68	1.71	4.50	.745	1.80	5.20	8.25	.253	2.74	13.14

Data used in equations (18a) and (18b) :

Wavelength = 600 nm,	Wavelength = 600 nm,	Wavelength = 660 nm,
$A_0^\circ = 0$, $A_1^\circ = 0.34$,	$A_1^\circ = 0.365$, $A_2^\circ = 0.84$,	$A_2^\circ = 0.60$, $A_3^\circ = 0.13$,
$T_M = 1.05 \times 10^{-4}$ M,	$T_M = 2 \times 10^{-4}$ M,	$T_M = 2.5 \times 10^{-4}$ M,
$T_L = 5 \times 10^{-4}$ M,	$T_L = 1 \times 10^{-3}$ M,	$T_L = 2 \times 10^{-3}$ M,
pKa = 8.55	pKa = 7.4	pKa = 9.4

For (1), (2) and (3) : ionic strength = 0.1 M and l = 1 cm.

TABLE 15.

Determination of equilibrium constant, k', for the propyl gallate complex, FeR.

(1)pH	v'''	v''	pk'	(2)pH	v'''	v''	pk'
3.4	2.75	1.79	5.85	3.4	3.68	2.78	5.85
3.5	2.88	1.84	5.82	3.5	3.79	2.83	5.83
3.6	2.98	1.88	5.86	3.6	3.9	2.87	5.82
3.7	3.07	1.90	5.89	3.7	4.0	2.90	5.83
3.8	3.17	1.91	5.88	3.8	4.07	2.91	5.88

Data used in equations (28) and (29) :

(1)$T_L^\circ = 0.008$ M, $E^\circ = 0.004$ M (2)$T_L^\circ = 0.004$ M, $E^\circ = 0.006$ M

For (1) and (2): $V^\circ = 50$ ml, $T_M^\circ = 0.001$ M, N = 0.1 N, I = 0.1 M, x = y = 0.5, z = 1, a = 1, d = 2, v = 0.75 ml and h = 1.5.

TABLE 16.

Determination of the equilibrium constant, k'', for the propyl gallate complex, $Fe(HR)_2$.

pH	v''	v'''	n	pk''
5.0	2.0	3.73	.46	2.854
5.1	2.0	3.76	.52	2.845
5.2	2.0	3.80	.60	2.798
5.3	2.0	3.82	.64	2.822
5.4	2.0	3.85	.70	2.799

Experimental data used in equations (28) and (29) :

T_M^o = 0.001 M, T_L^o = 0.008 M, E^o = 0.004 M, V^o = 50 ml, N = 0.1 N, v = 1.5 ml, x = y = z = h = a = d = 1.

TABLE 17.

Determination of the equilibrium constant, k_3, for the Fe(III)-propyl gallate system.

pH	A	$\bar{n}$	pk_3
6.75	.285	2.214	10.774
7.0	.22	2.433	10.776
7.2	.166	2.617	10.792
7.5	.095	2.850	10.736

Experimental data used in equations (18a) and (18b) :

Wavelength = 700 nm, A_2^o = .35, A_3^o = .05, a = 2, b = 3, T_M^o = 0.0002 M, T_L^o = 0.001 M and l = 1 cm.

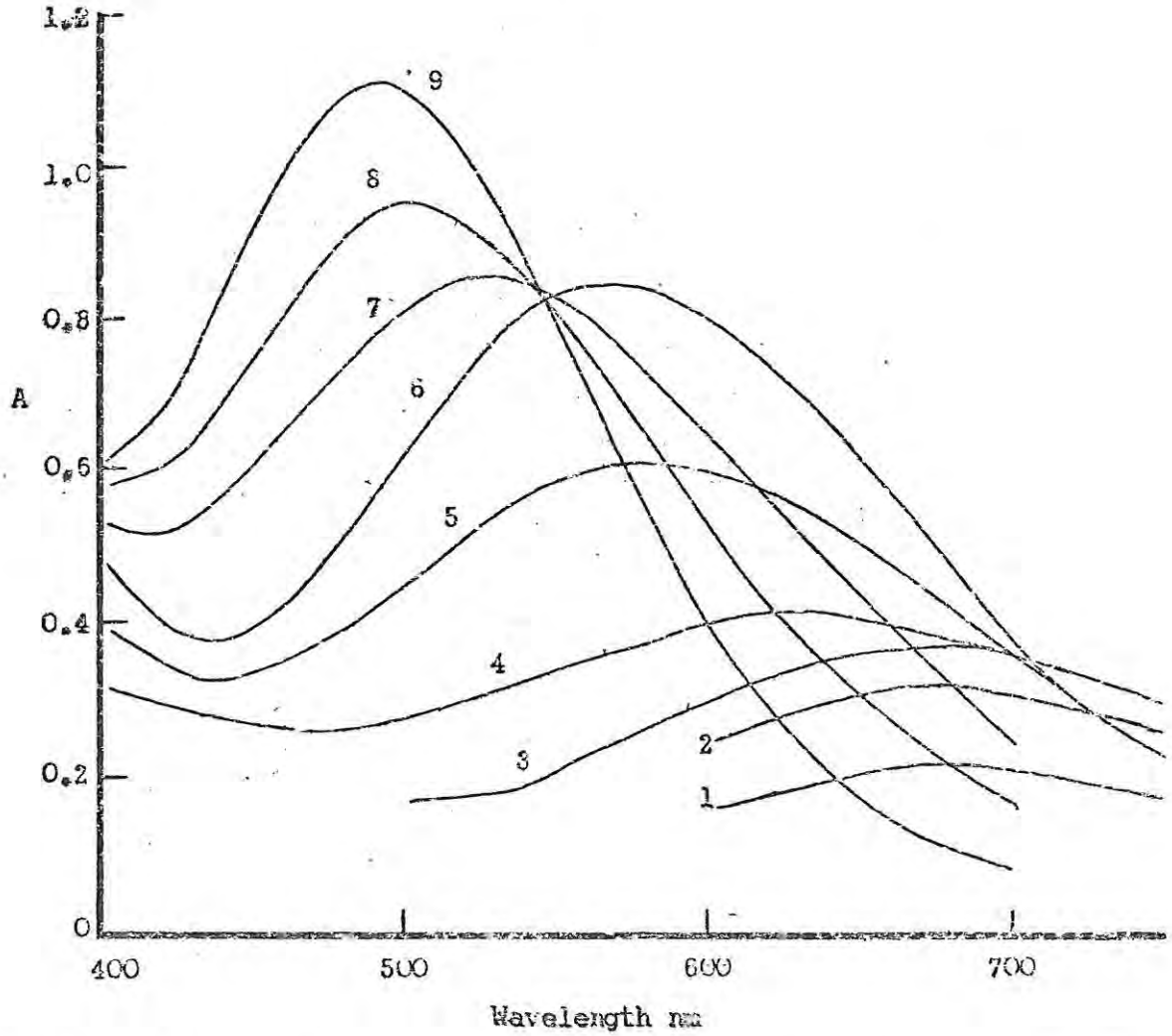


FIG. 1. Visible absorption spectra of Fe(III)-protocatechuic acid at pH values : (1) 2.42, (2) 2.83, (3) 3.60, (4) 4.48, (5) 4.95, (6) 5.10 - 7.0, (7) 7.68, (8) 8.0 and (9) 8.4 - 9.1; T_M = 0.0002M, T_L = 0.001M, I = 0.1, l = 1 cm.

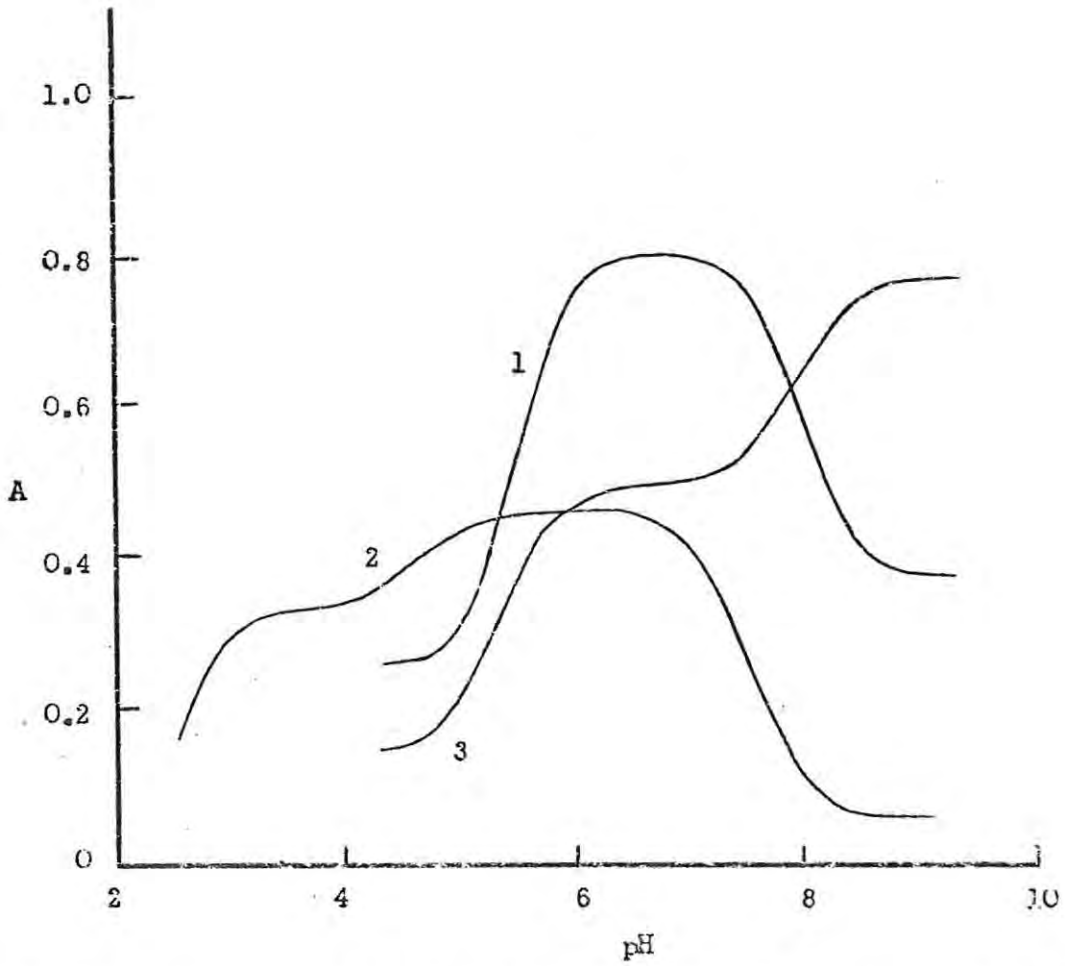


FIG. 2. Extinction curves for Fe(III) complexes of (1)pyrocatechol at 600 nm with $T_M^o = 2.5 \times 10^{-4}$ M, $T_L^o = 1.25 \times 10^{-3}$ M, (2)2,3-dihydroxynaphthalene at 600 nm with $T_M^o = 1.05 \times 10^{-4}$ M, $T_L^o = 5 \times 10^{-4}$ M, (3)catechin at 500 nm with $T_M^o = 1.5 \times 10^{-4}$ M, $T_L^o = 7.5 \times 10^{-4}$ M, Ionic strength = 0.1, T = 20°C, l = 1 cm.

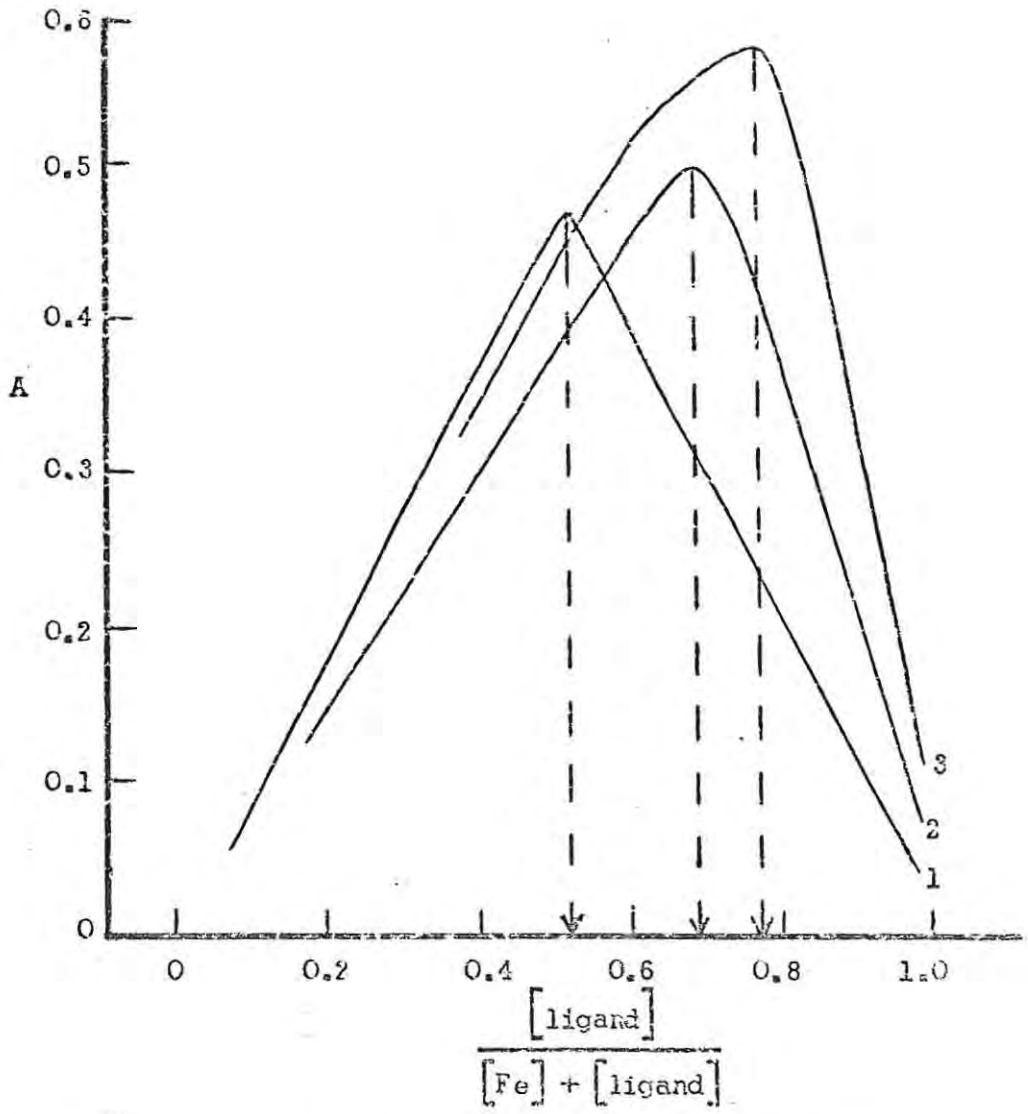


FIG. 3. Continuous variation method applied to Fe(III)-o-dihydroxybenzene complexes of (1) 3,4-dihydroxybenzenesulfonate at pH = 3.5, wavelength = 670 nm; (2) pyrocatechol at pH = 6.4, wavelength = 570 nm; (3) protocatechuic acid at pH = 9.6, wavelength = 490 nm with $[Fe] + [ligand] = 0.0005$ M.

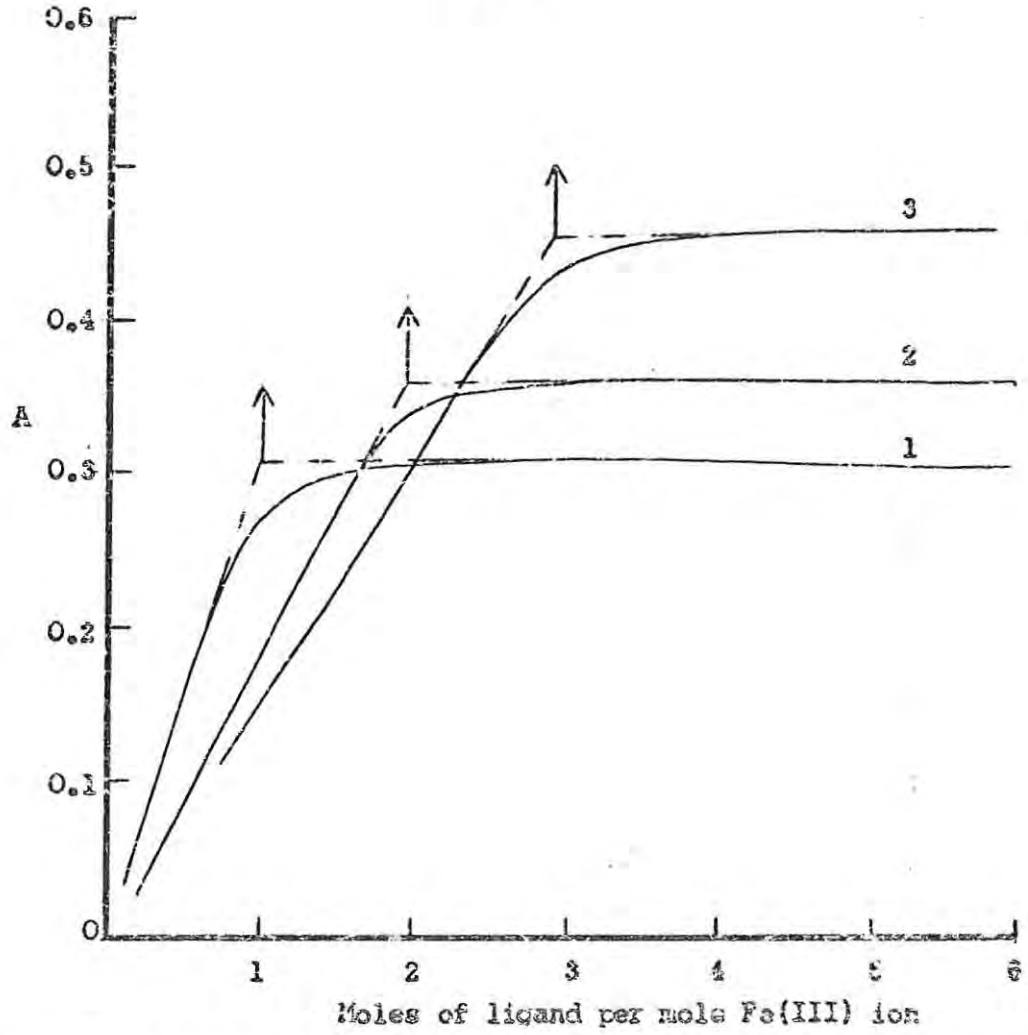


FIG. 4. Molar ratio method applied to o-dihydroxybenzene complexes of Fe(III) : (1) 4-chloroacetylcatechol at pH = 3.1 with $[Fe] = 0.00015M$, wavelength = 650 nm; (2) protocatechuic aldehyde at pH = 5.9 with $[Fe] = 0.000075M$, wavelength = 560 nm; (3) 4-methylcatechol at pH = 9.0 with $[Fe] = 0.0001M$, wavelength = 500 nm. l = 1 cm.

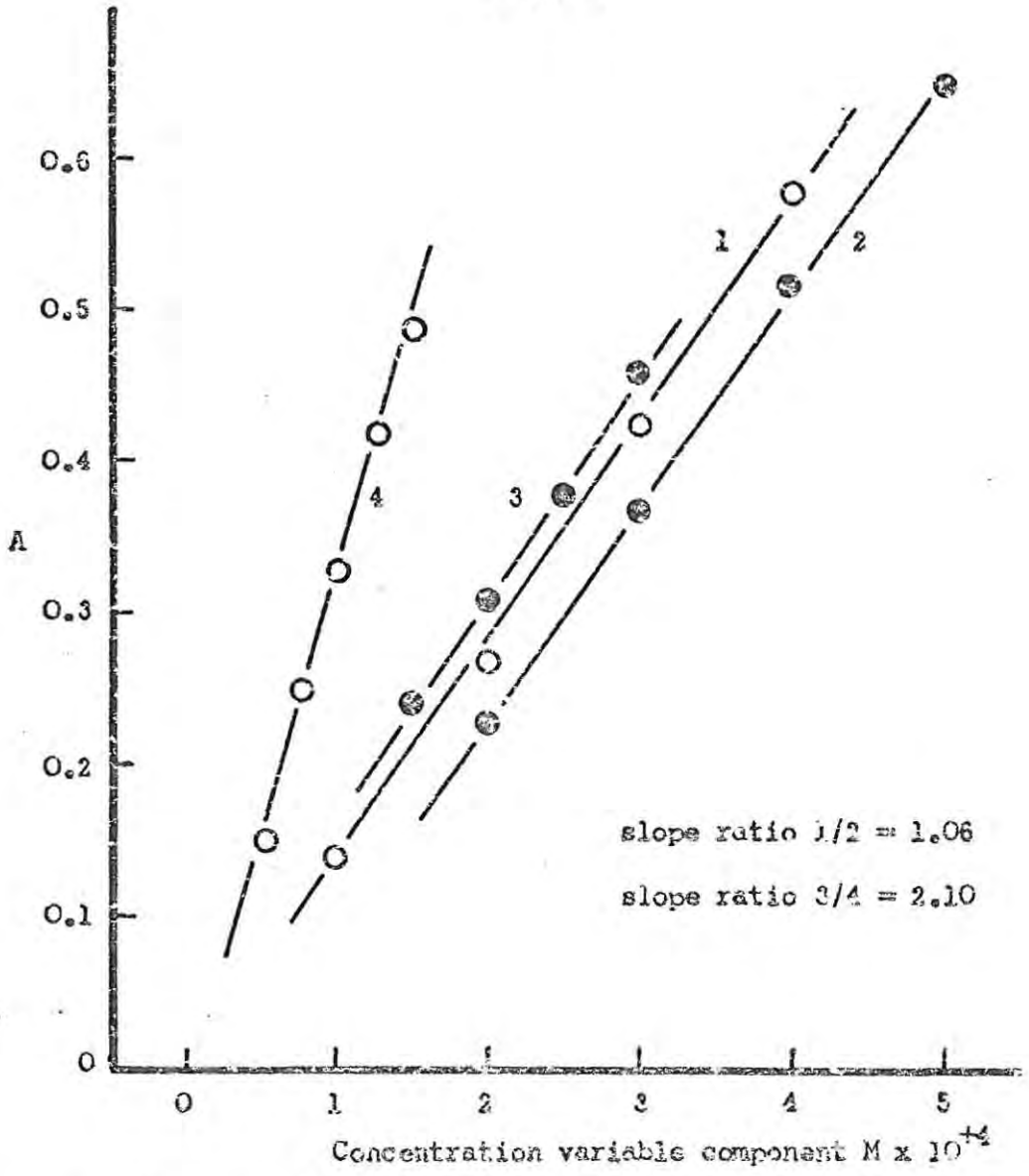


FIG. 5. Slope ratio method applied to the Fe(III)-pyrocatechol complex: ● pyrocatechol varying, ○ Fe varying; (1) and (2) at pH 4.5, wavelength = 700 nm; (3) and (4) at pH 8.4, wavelength = 570 nm; constant component = 0.001M.

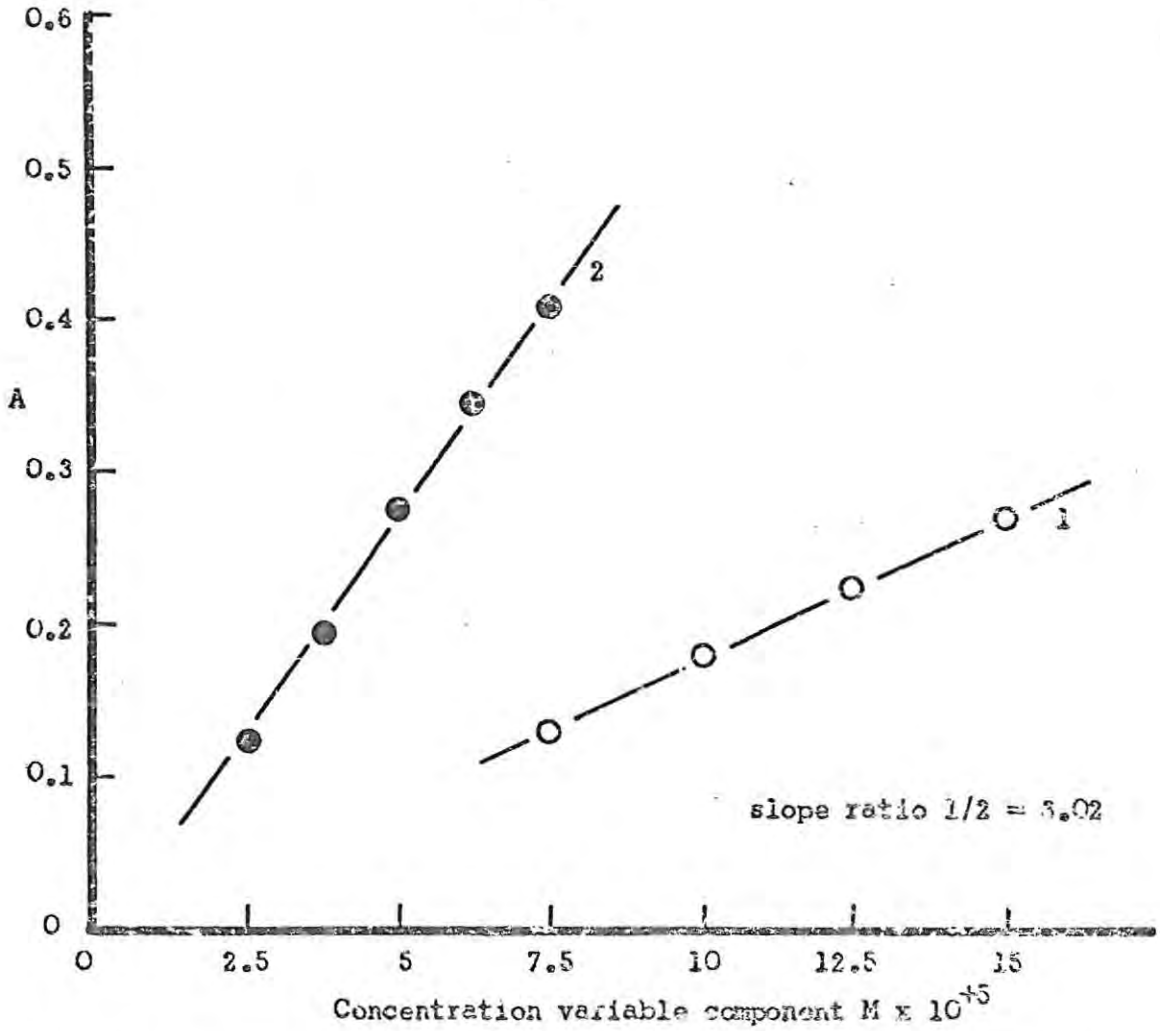


FIG. 6. Slope ratio method applied to the Fe(III)-protocatechuic acid complex : ○ ligand varying, ◉ Fe varying; (1) and (2) at pH 9.6 wavelength = 490 nm; constant component = 0.0004M.

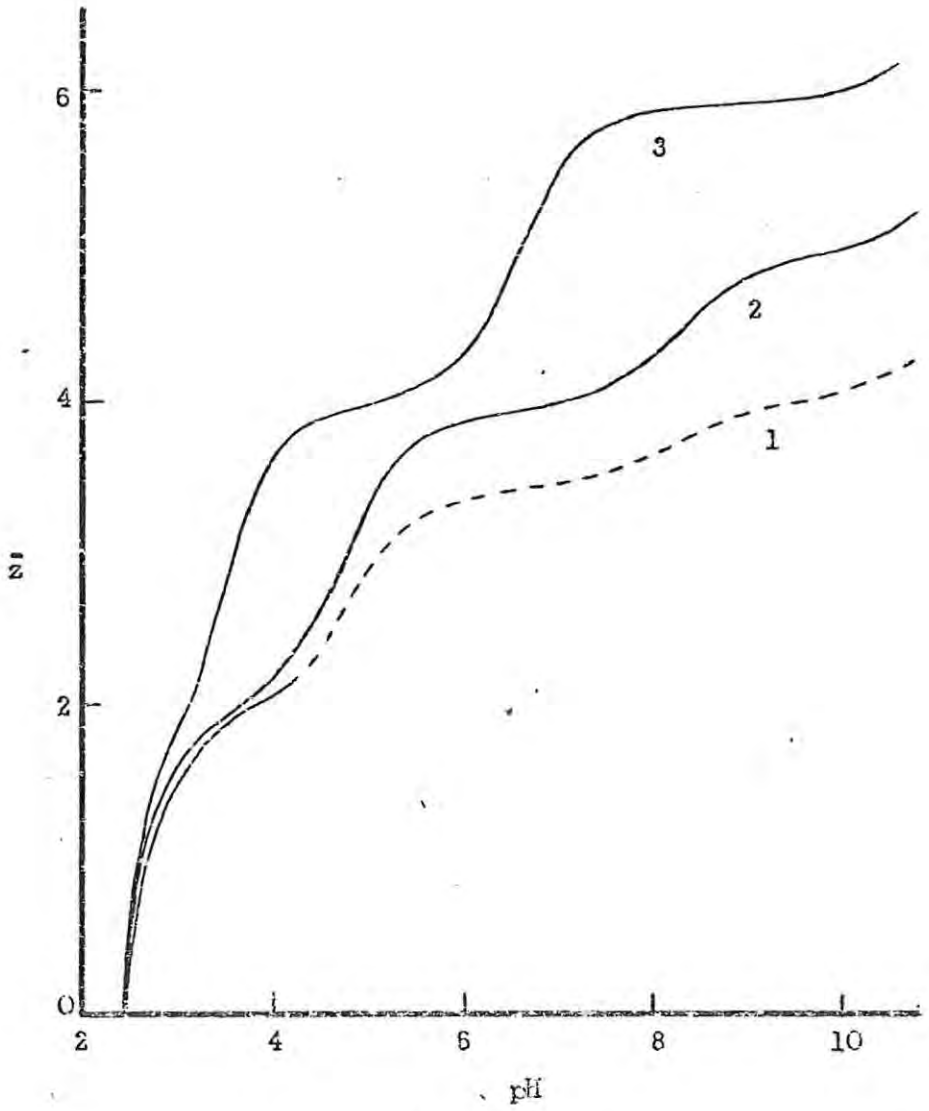


FIG. 7. Potentiometric titration curves for the Fe(III) complexes of (1) DHFS, $T_M^o = T_L^o = 0.002$ M, (2) 3,4-dihydroxybenzenesulfonate, $T_M^o = 0.002$ M, $T_L^o = 0.004$ M, (3) 4-chloroacetylcatechol, $T_M^o = 0.002$ M, $T_L^o = 0.006$ M; $V^o = 50$ ml, N = 0.1 N KOH, I = 0.1 N KCl. (Dotted line represents presence of a precipitate).

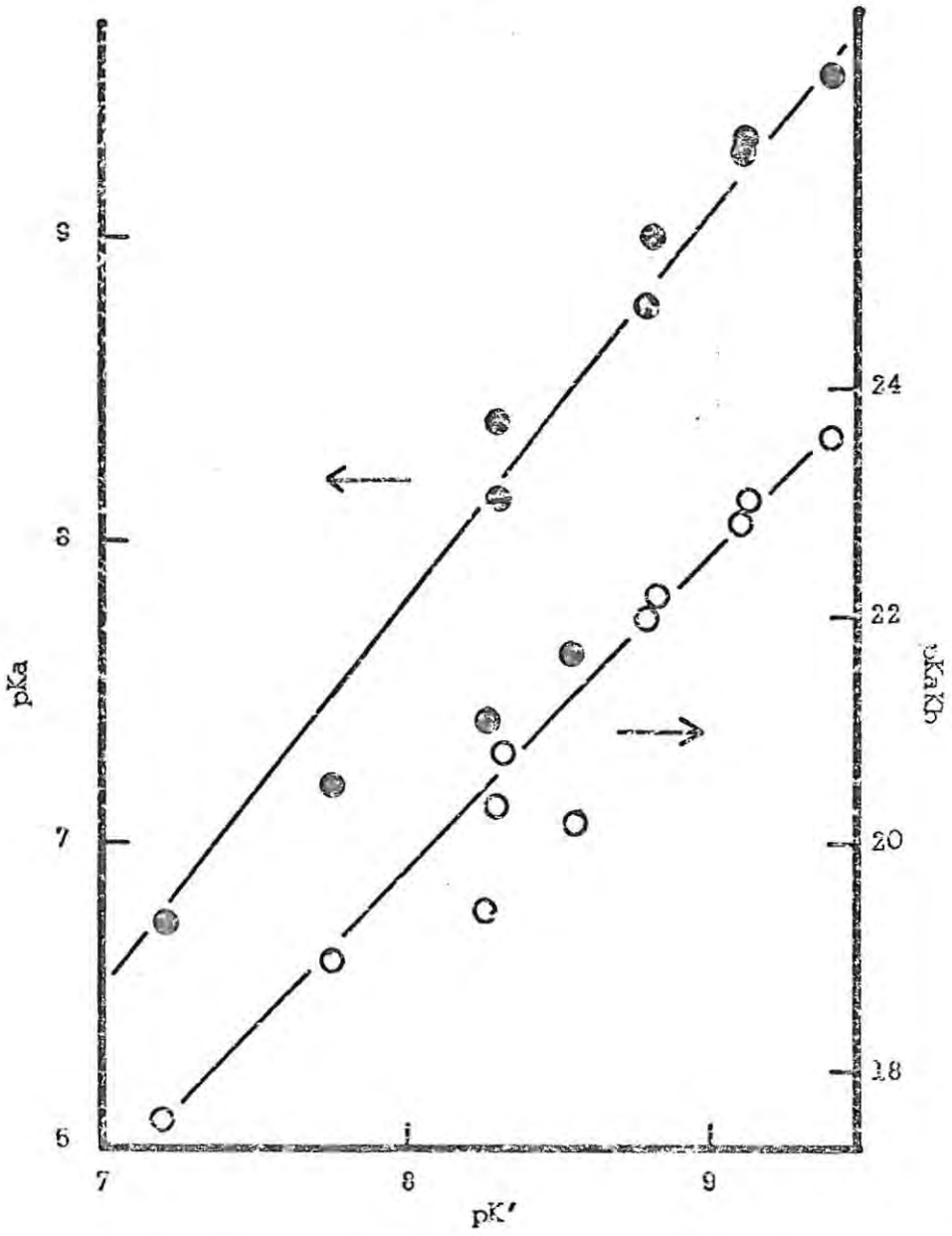


FIG. 8. Plots of the ligand dissociation contants, Ka (left scale ●) and KaKb (right scale ○), against the hydrolisis contants, K', for the FeL_2 complexes of o-dihydroxybenzene derivatives.

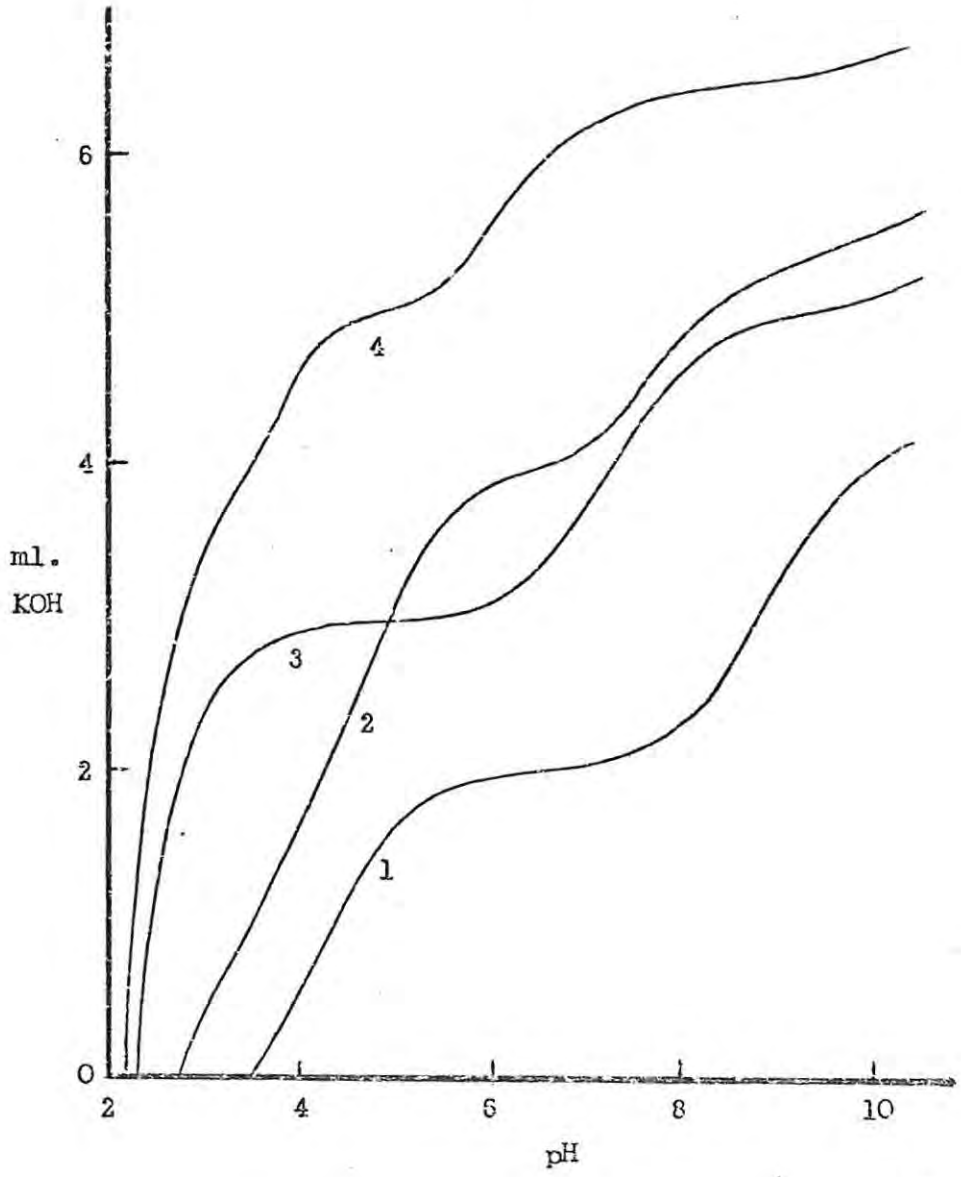


FIG. 9. Potentiometric titration curves for (1) 0.004 M protocatechuic acid, (2) 0.004 M protocatechuic acid + 0.001 M Fe(III), (3) 0.004 M protocatechuic aldehyde + 0.006 N HCl, (4)0.004 M protocatechuic aldehyde + 0.006 N HCl + 0.001 M Fe(III); V^{o} = 50 ml, N = 0.1 N KOH, I = 0.1 N KCl, T = 20° .

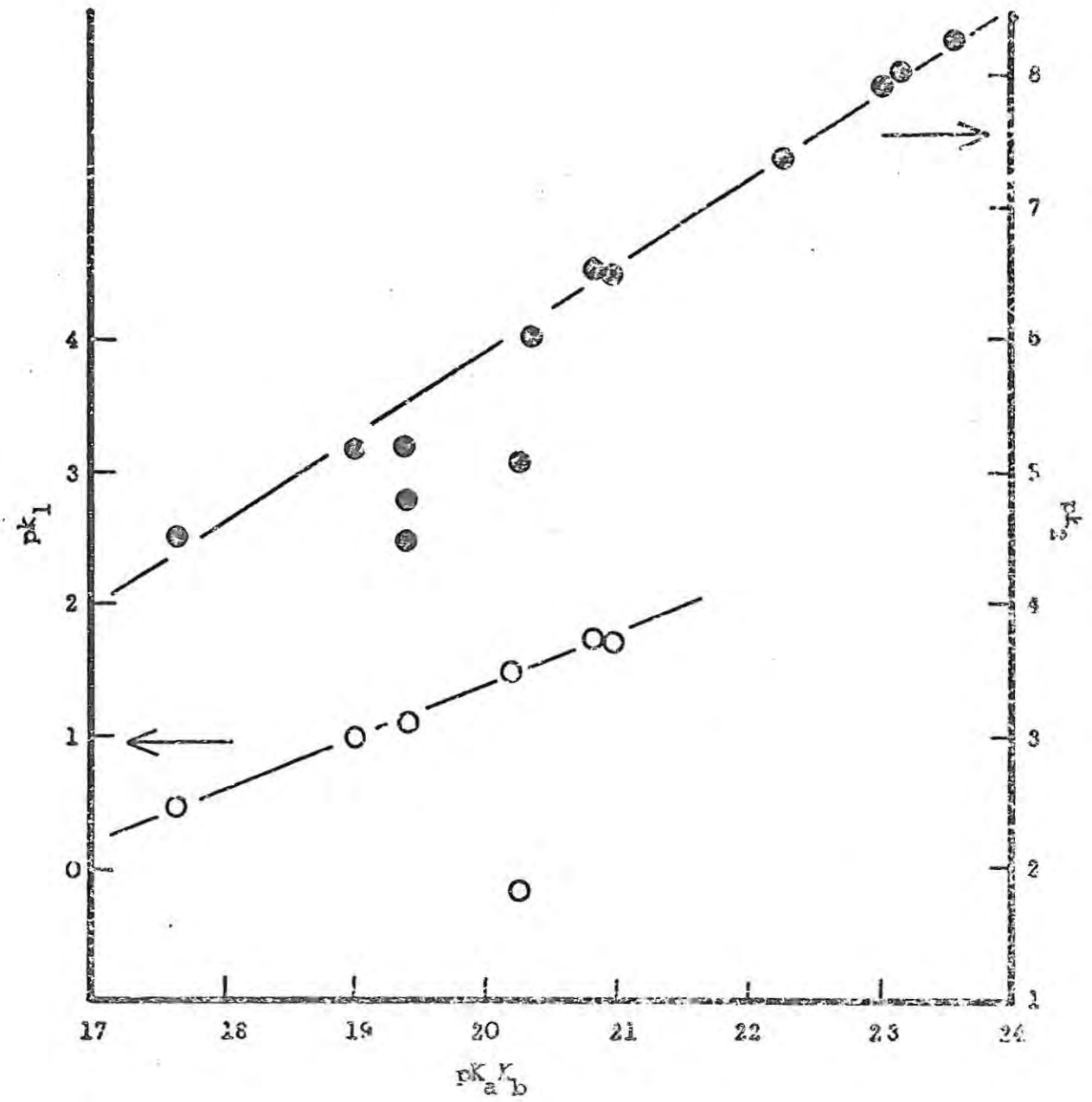


FIG. 10. Relation between equilibrium constants, k_1 and k_2, for o-dihydroxybenzene complexes of Fe(III) and acidity constants, $K_a K_b$, for the ligands.

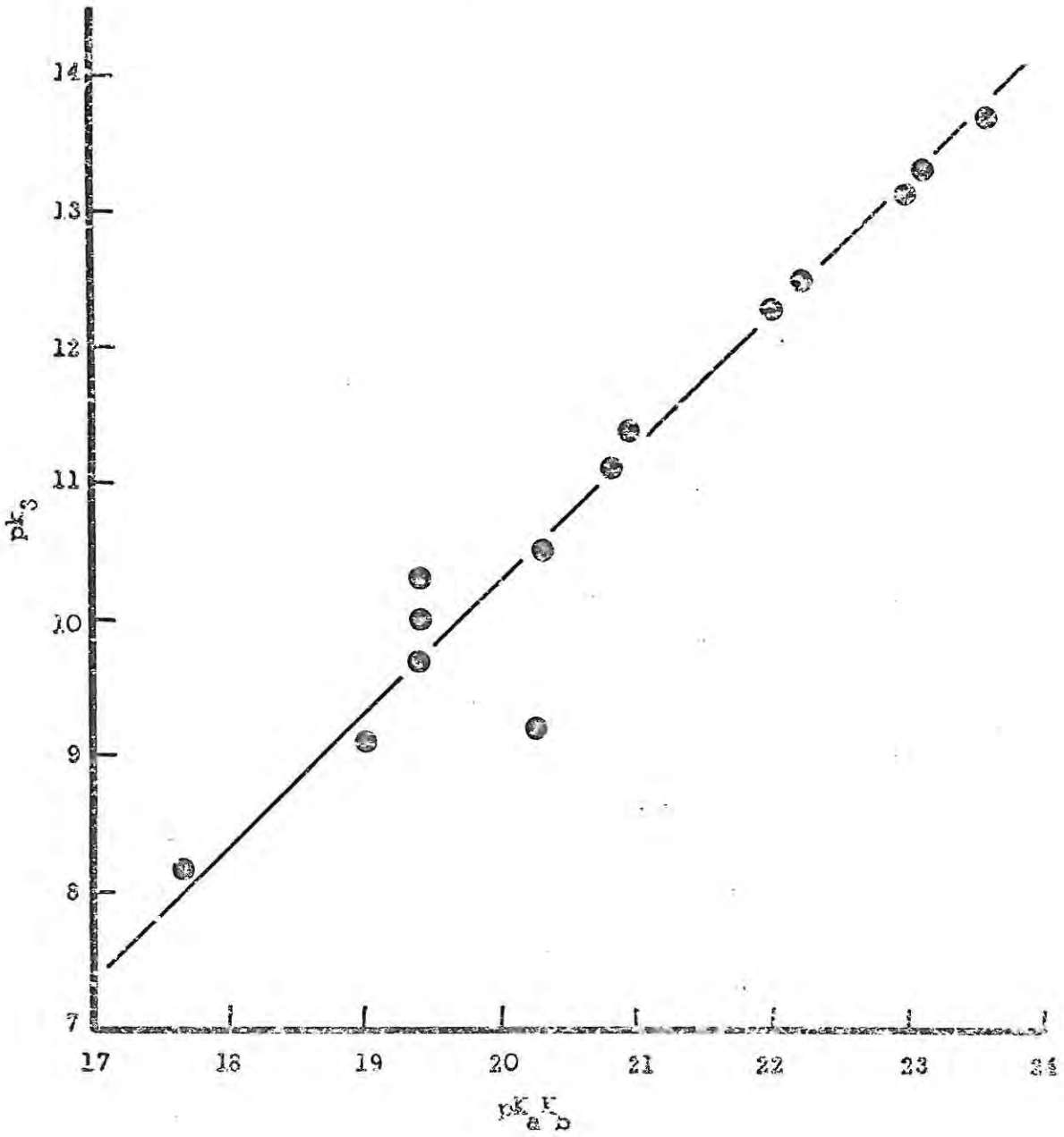


FIG. 11. Relation between equilibrium constants, k_3, for o-dihydroxybenzene complexes of Fe(III) and acidity constants, K_aK_b, for the ligands.

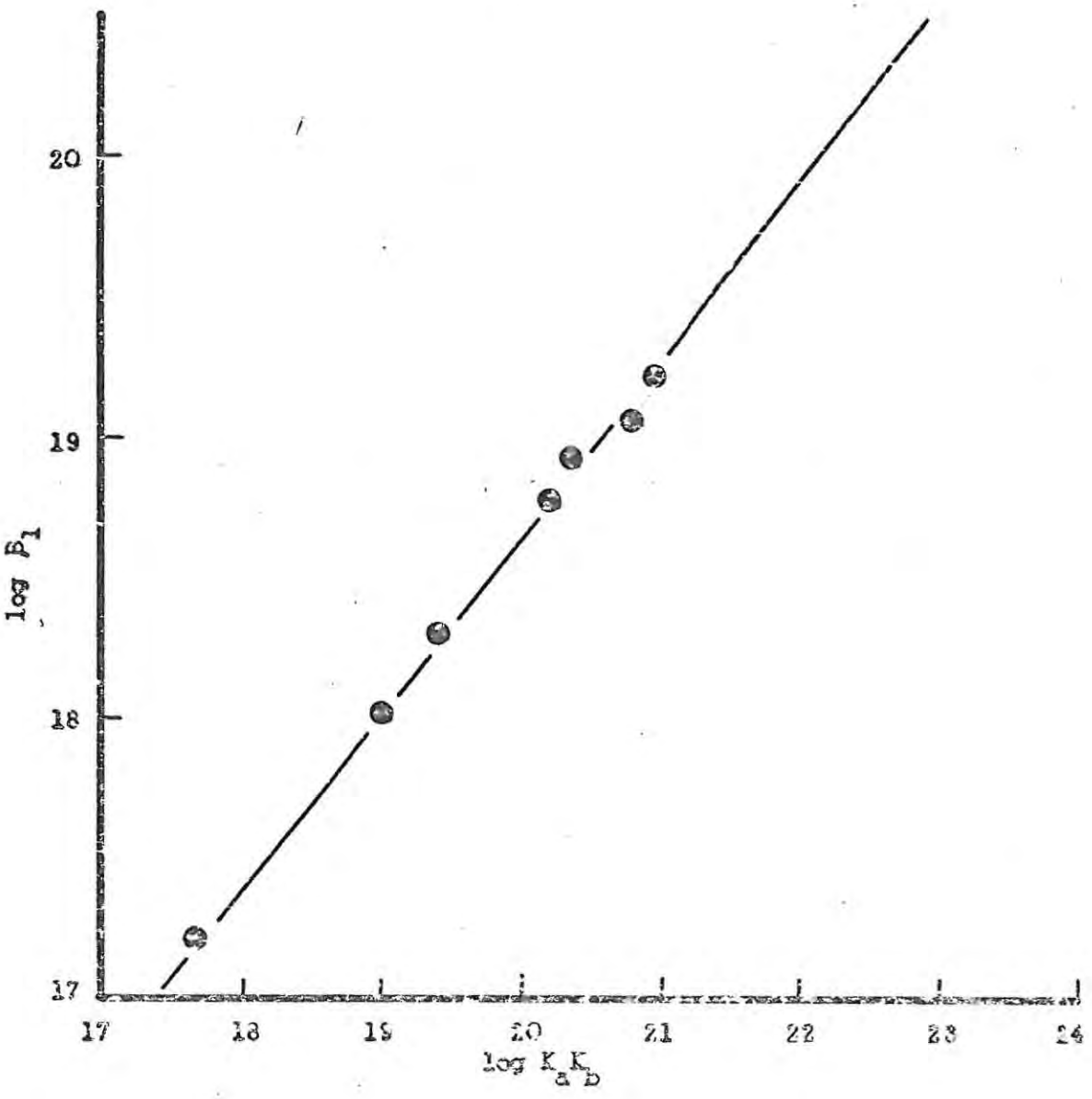


FIG. 12. Relation between stability constants, β_1, for o-dihydroxybenzene complexes of Fe(III) and association constants, $K_a K_b$, for the ligands.

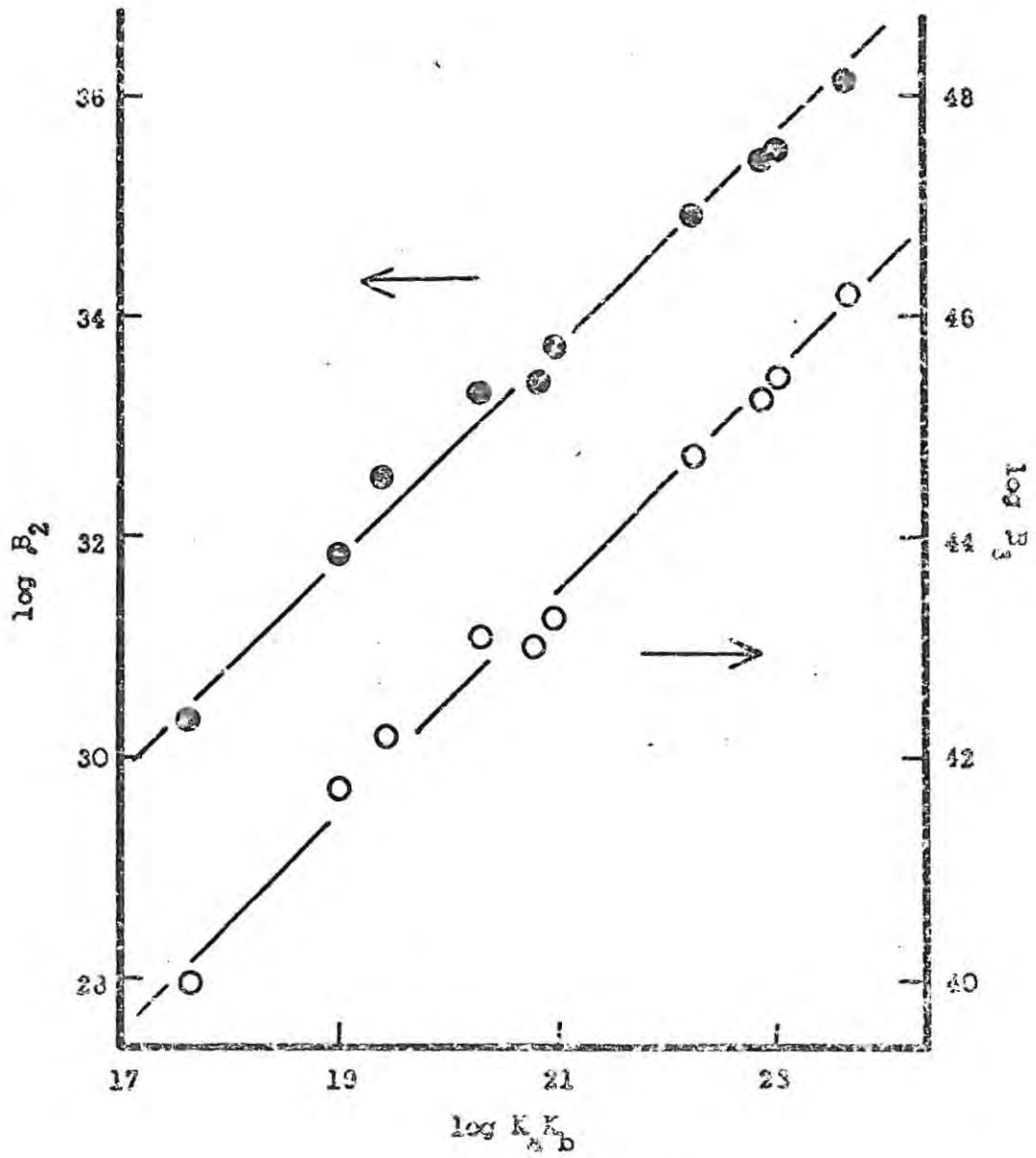


FIG. 13. Relation between stability constants, β_2 and β_3, for o-dihydroxybenzene complexes of Fe(III) and association constants, $K_a K_b$, for the ligands.

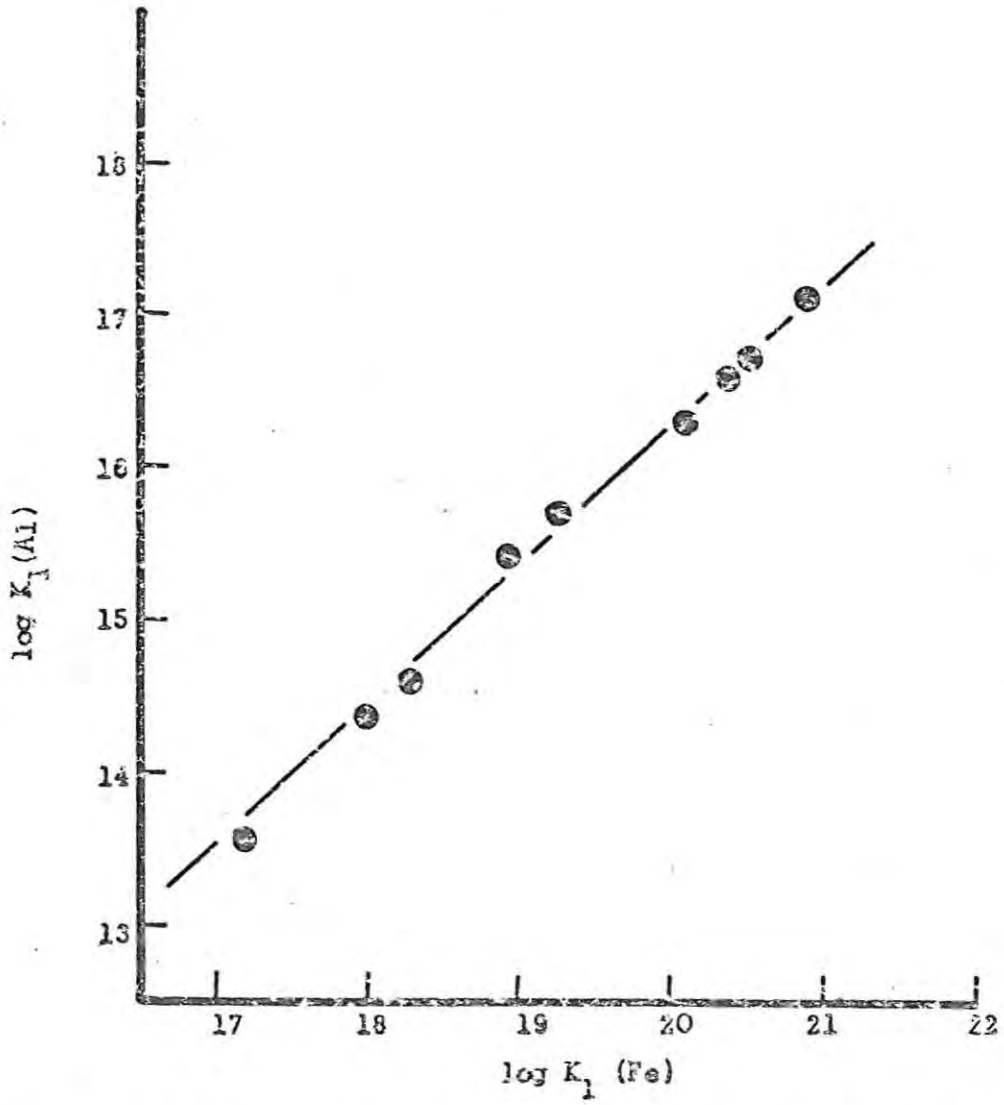


FIG. 14. Relation between stability constants, K_1, for o-diphenol complexes of Al(III) and Fe(III).

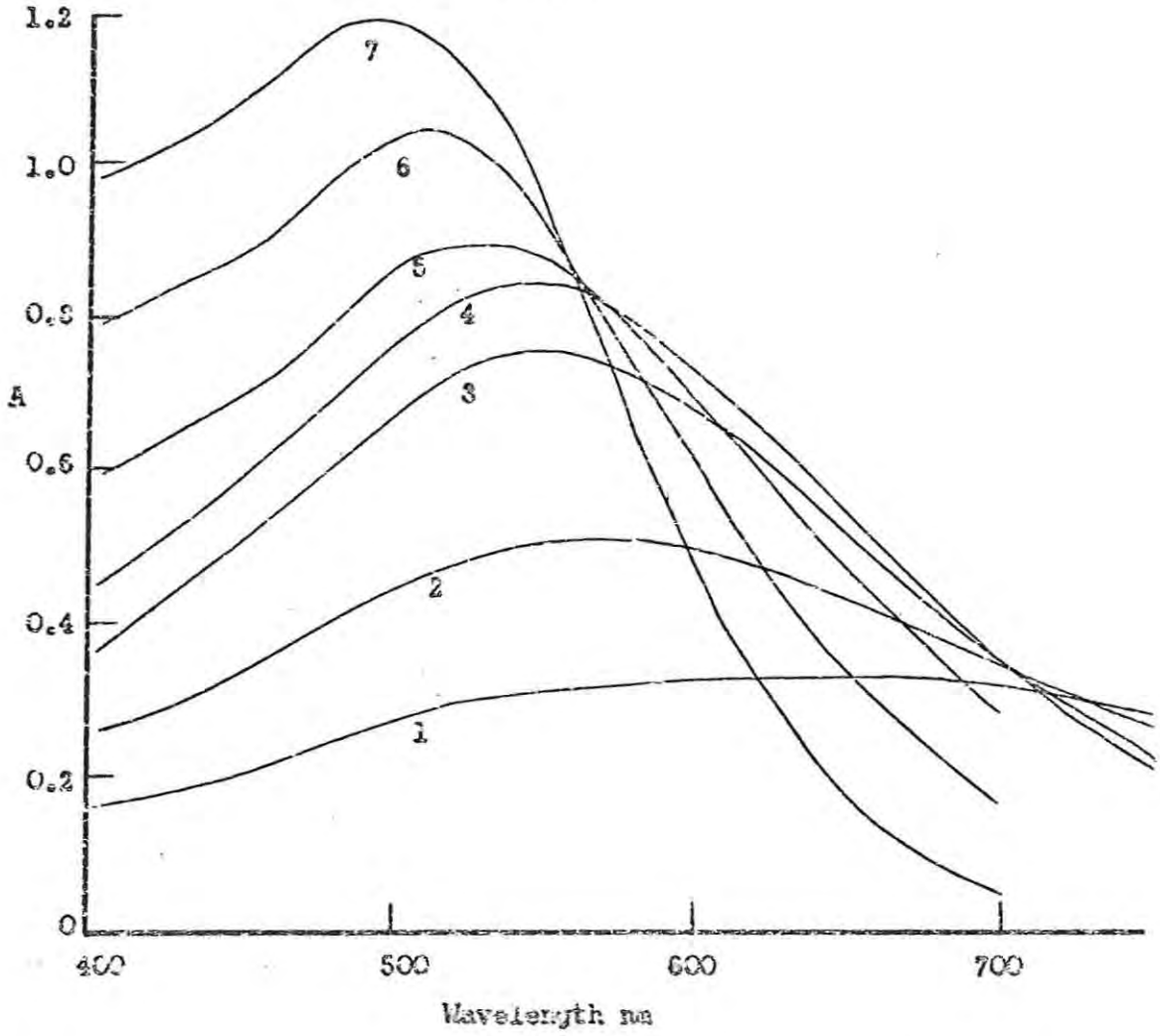


FIG. 15. Visible absorption spectra of Fe(III)-propyl gallate at pH values of (1) 3.40, (2) 3.89, (3) 4.54, (4) 5.80, (5) 6.75, (6) 7.20 and (7) 9.6; T_M = 0.0002 M, T_L = 0.001 M, I = 0.1, l = 1 cm.

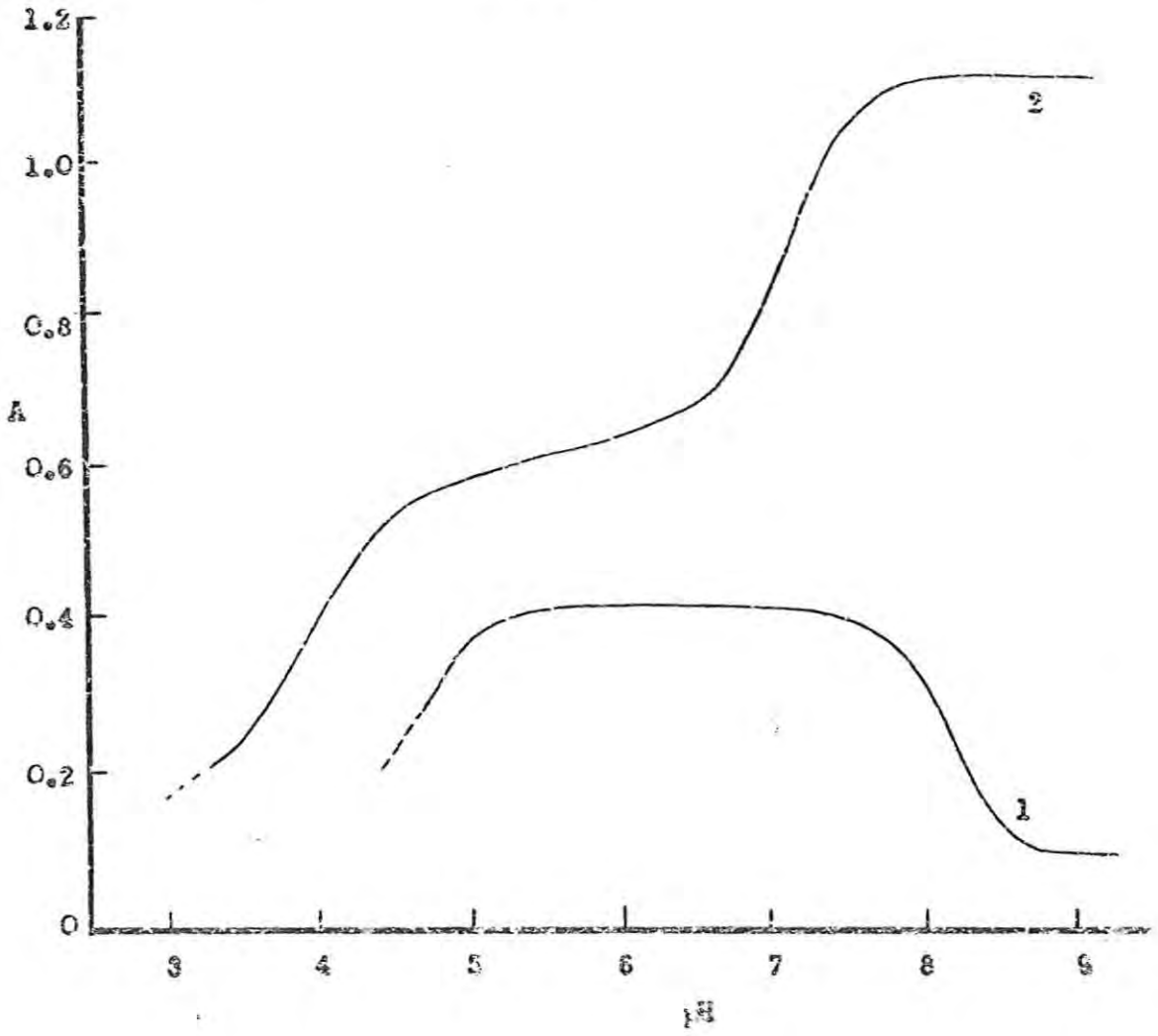


FIG. 16. Extinction curves for the Fe(III) complexes of :

(1) pyrogallol, T_M = 0.000225M, T_L = 0.0015M, wavelength = 700 nm.

(2) propylgallate, T_M = 0.0002M, T_L = 0.001M, wavelength = 460 nm.

l = 1 cm.

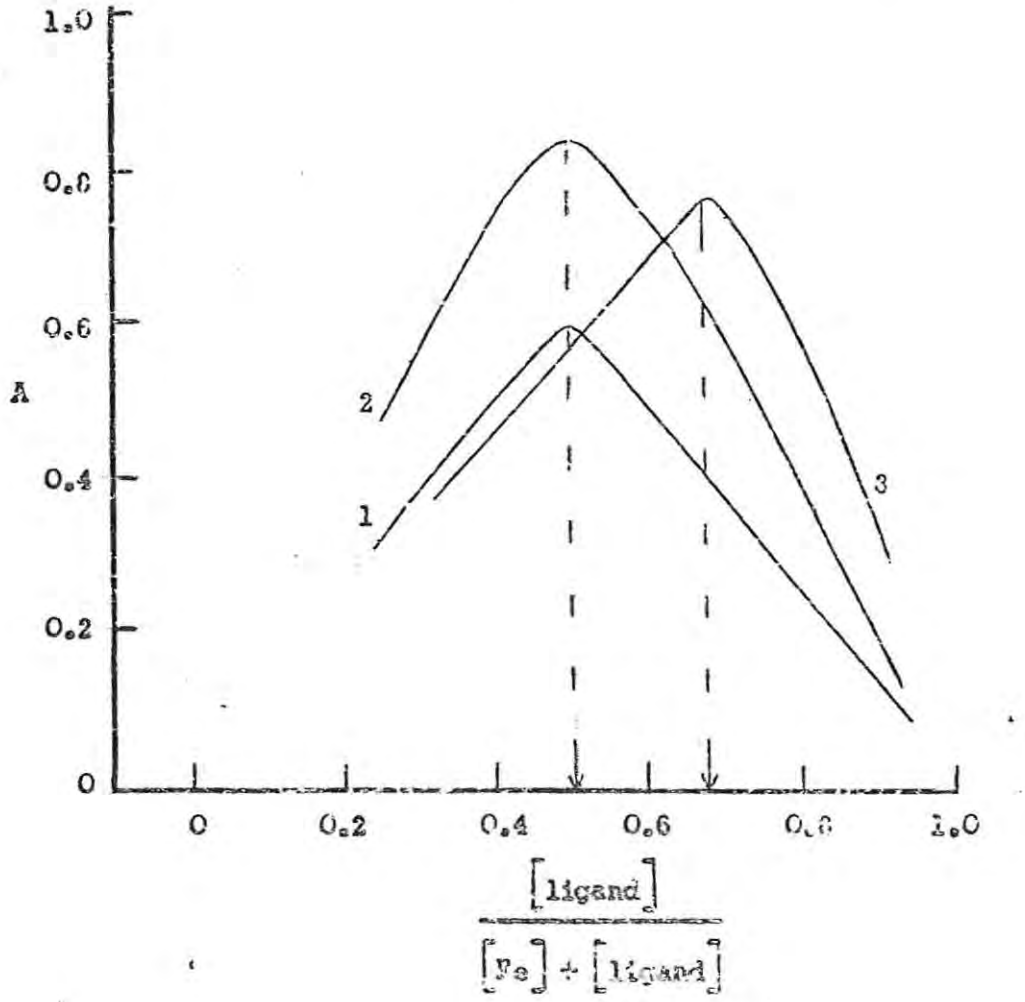


FIG. 17. Continuous variation method applied to 1,2,3-trihydroxybenzene complexes of Fe(III) : (1) pyrogallol at pH 5.0, wavelength = 570 nm, (2) propyl gallate at pH 4.8, wavelength = 550 nm; $[Fe] + [ligand] = 0.0005M$; and to the Fe(III)–pyrocatechol tartrate system, (3) at pH 7.0, wavelength = 570 nm; $[Fe] + [ligand] = 0.001M$. l = 1 cm.

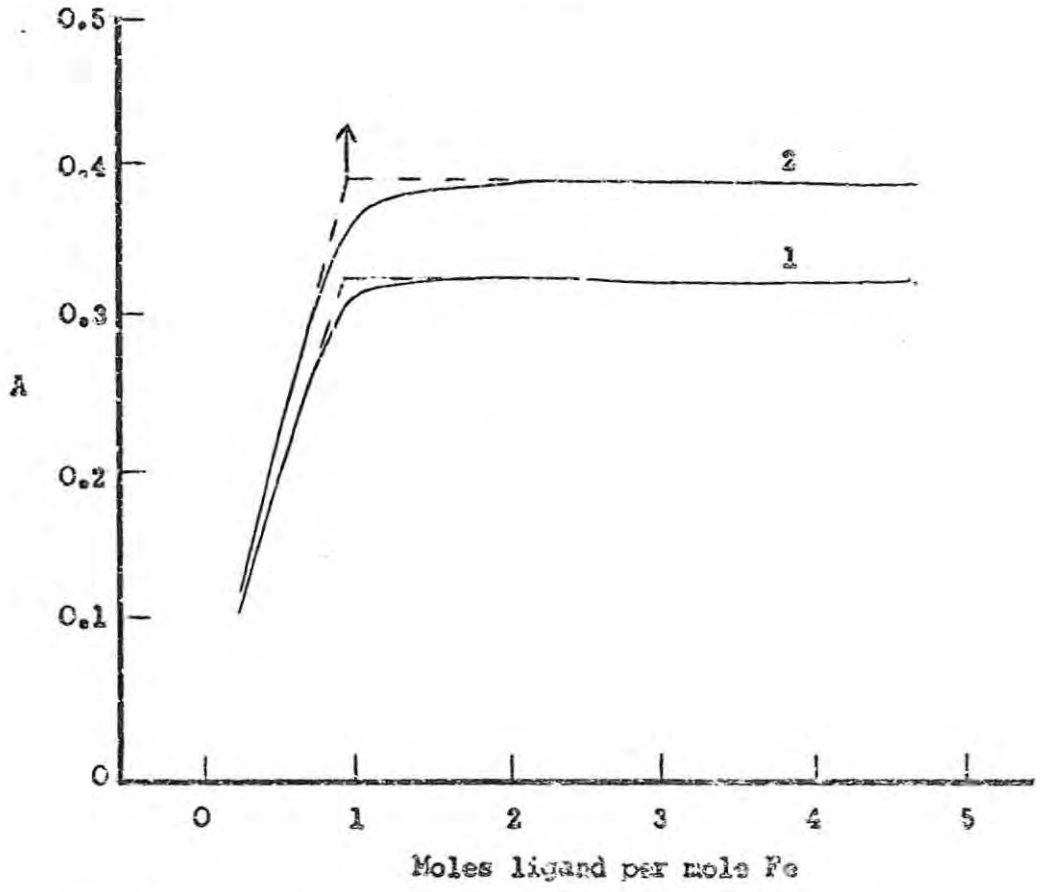


FIG. 18. Molar ratio method applied to 1,2,3-trihydroxybenzene complexes of Fe(III): (1) pyrogallol at pH 5.0, wavelength = 570 nm $[Fe]$ = 0.00012M, (2) propyl gallate at pH 4.8, wavelength = 530 nm $[Fe]$ = 0.0002M. l = 1 cm.

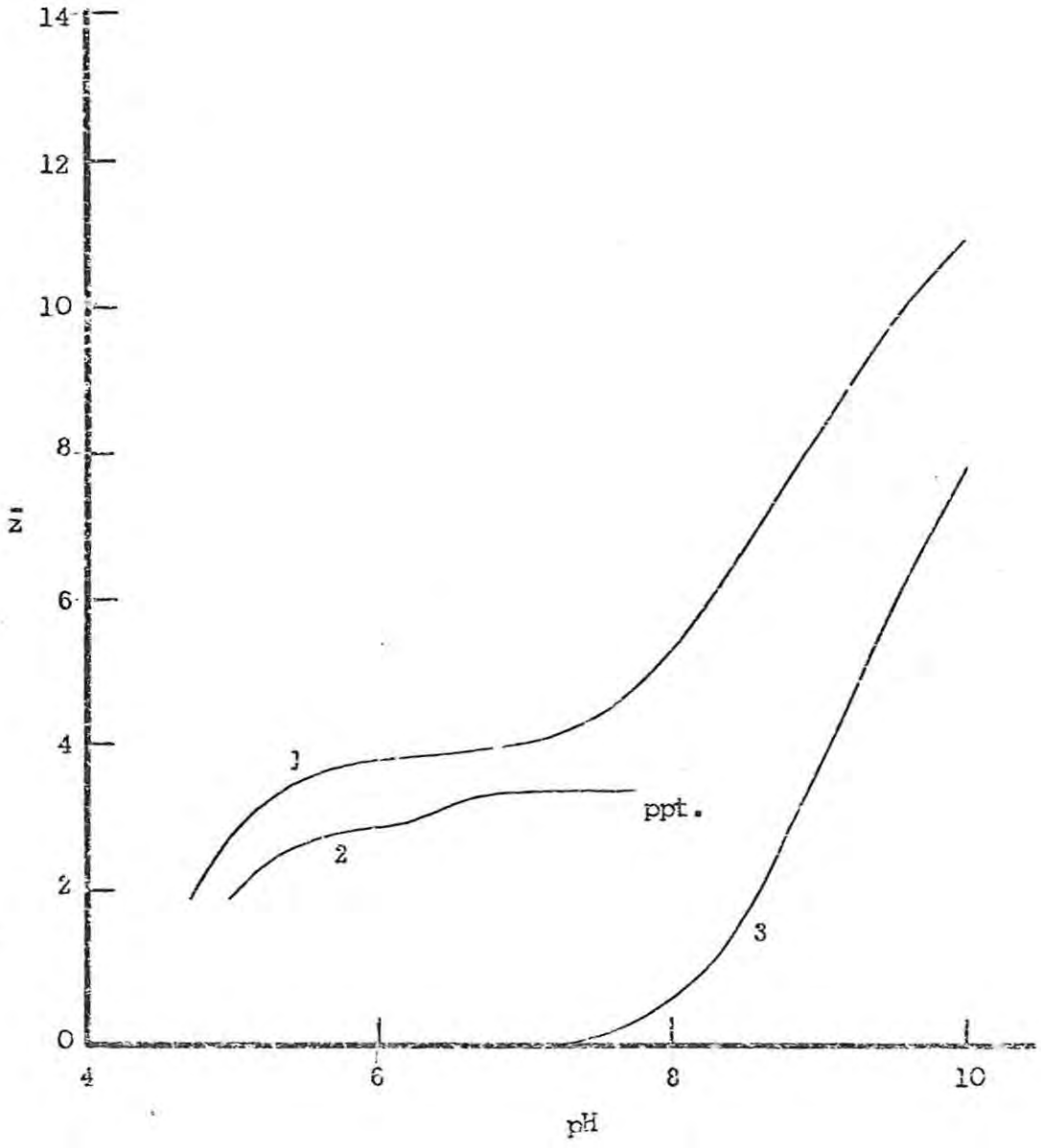


FIG. 19. Potentiometric titration curves for Fe(III)-pyrogallol : (1) T_N^o = 0.001 M, T_L^o = 0.008 M, (2) $T_M^o = T_L^o$ = 0.001 M, (3) T_L^o = 0.008 M; V^o = 50 ml, N = 0.1 M KOH and I = 0.1.

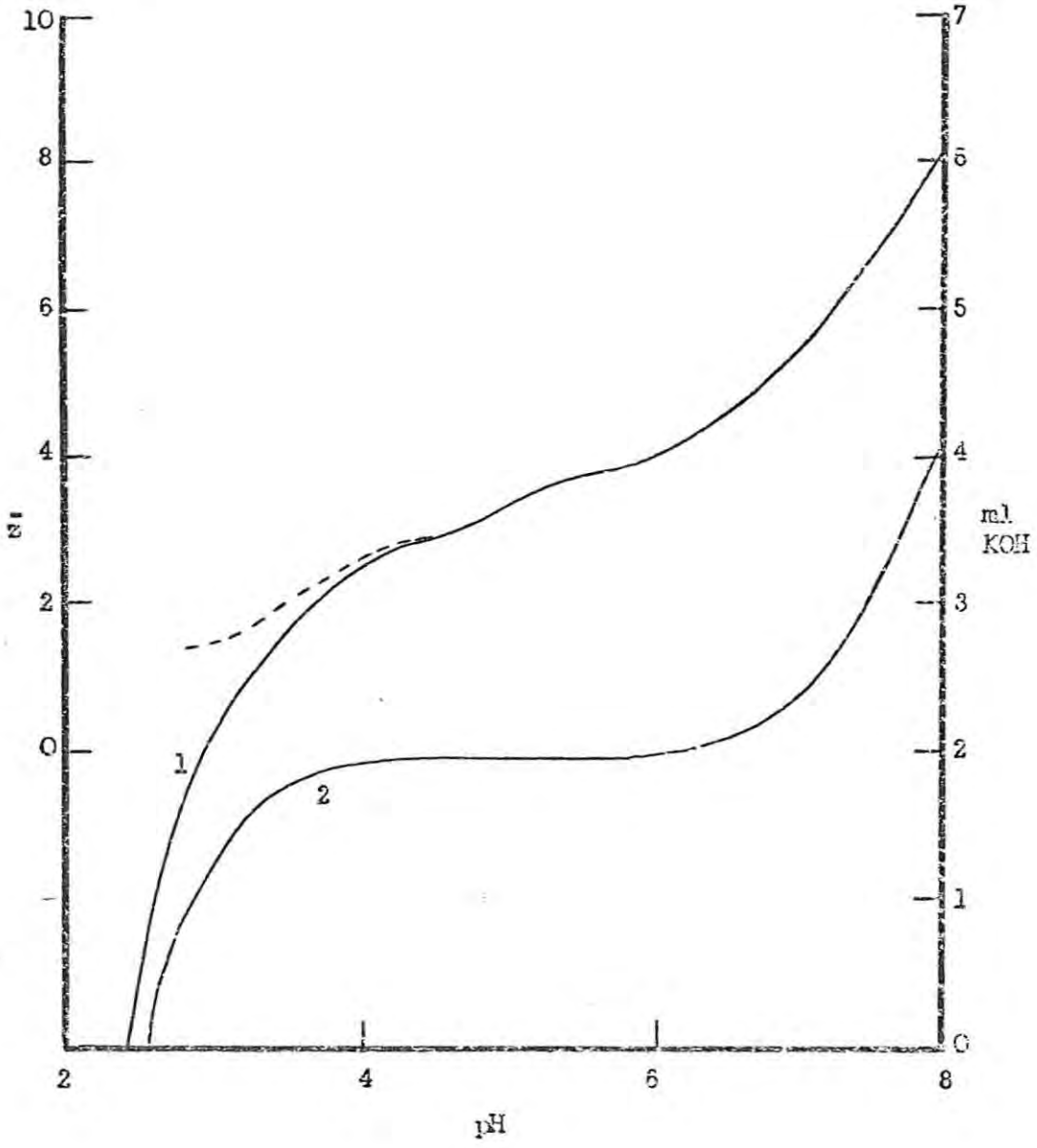


FIG. 20. Potentiometric titration curves for Fe(III)-propyl gallate : (1) T_M° = 0.002 M, T_L° = 0.008 M, E° = 0.004 N HCl, (2) T_L° = 0.008 M, E° = 0.004 N HCl; V° = 50 ml, N = 0.1 N KOH and I = 0.1.

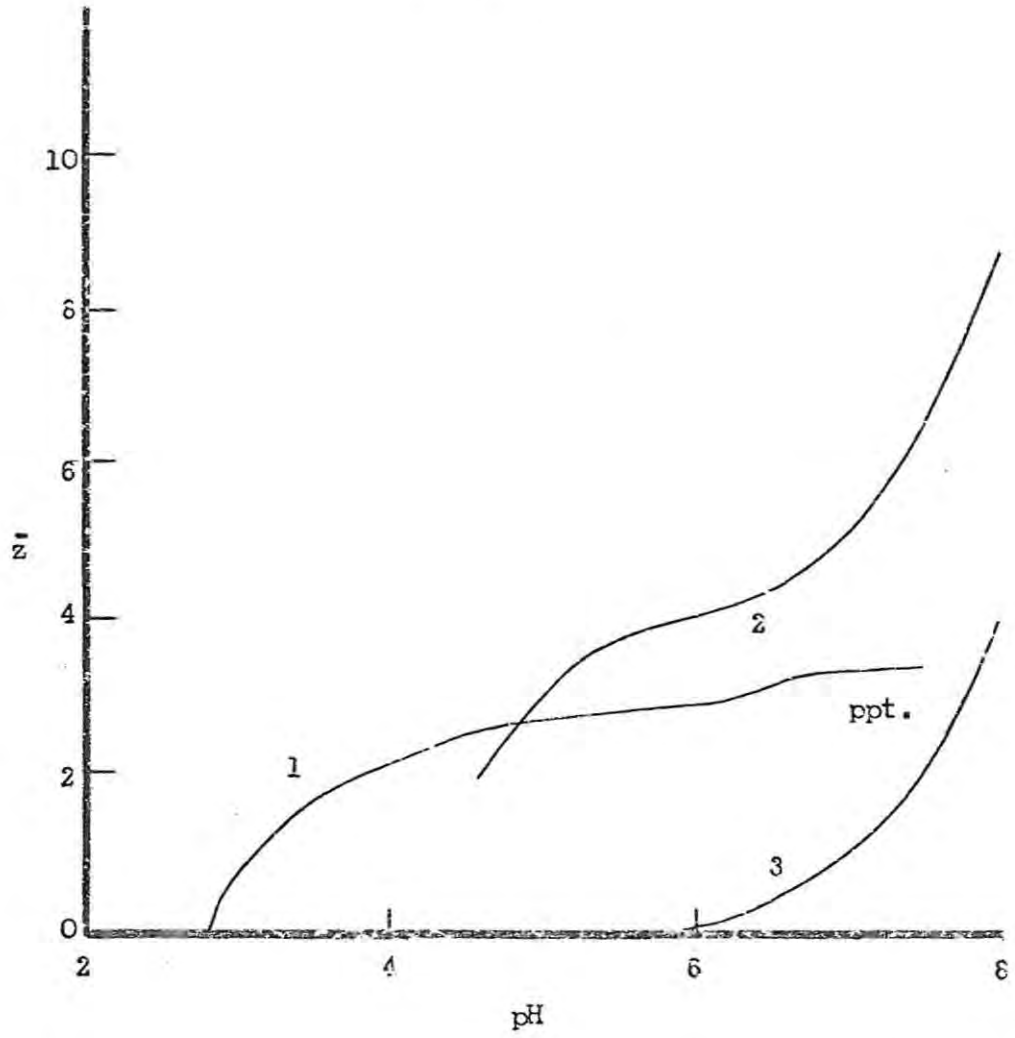


FIG. 21. Potentiometric titration curves for Fe(III)–propyl gallate, (1) $T_M^o = T_L^o = 0.001$ M; and Fe(III)-wattle tannin complexes, (2) $T_M^o = 0.001$ M, $T_L^o = 0.02$ M, (3) $T_L^o = 0.02$ M; $V^o = 50$ ml H_2O, N = 0.1 N KOH and I = 0.1 N (KCl).

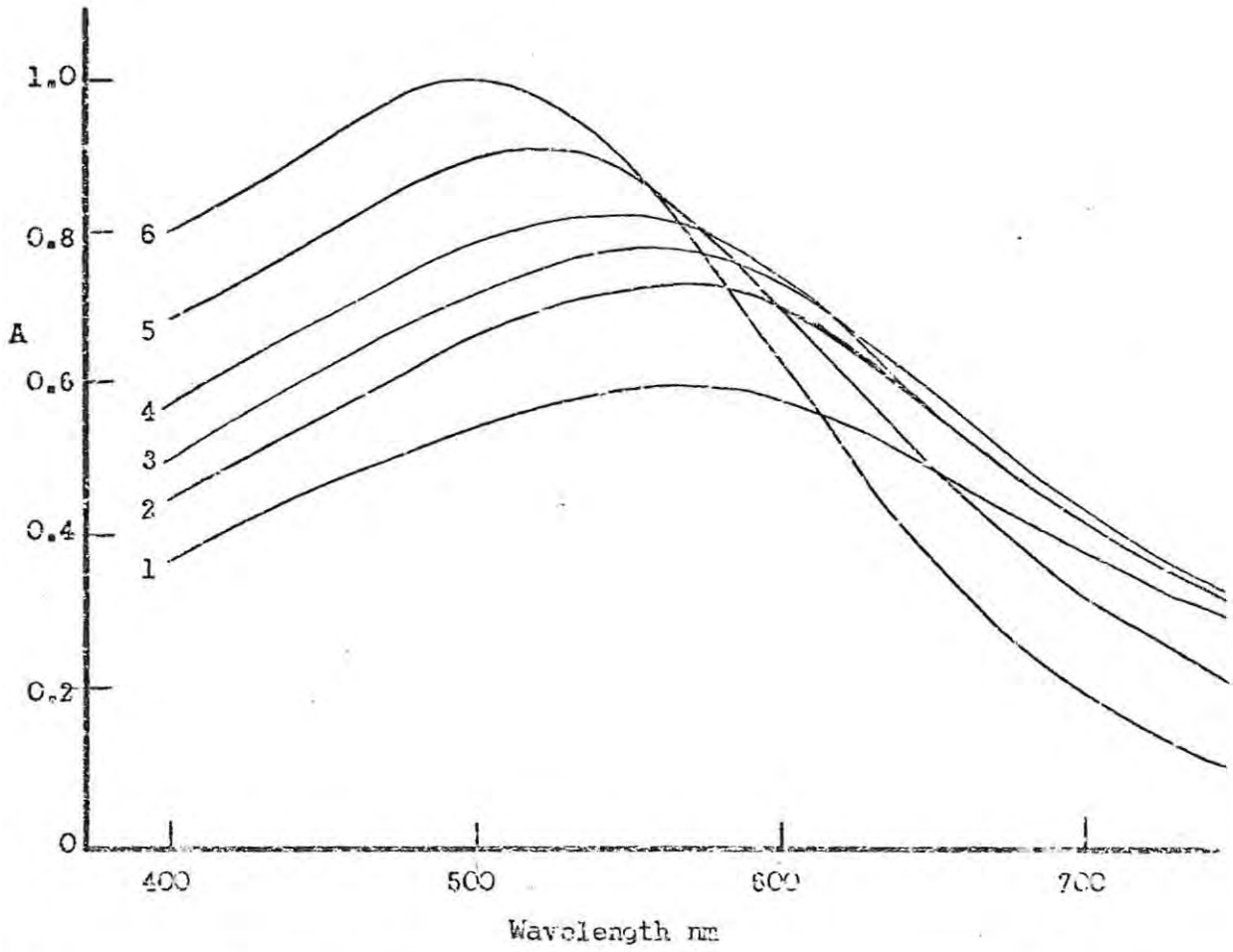


FIG. 22. Visible absorption spectra of Fe(III)-wattle tannin at pH values of (1) 5.0, (2) 5.4, (3) 6.2, (4) 7.1, (5) 7.5 and (6) 8.9; T_M = 0.0002 M, T_L = 0.004 M, l = 1 cm.

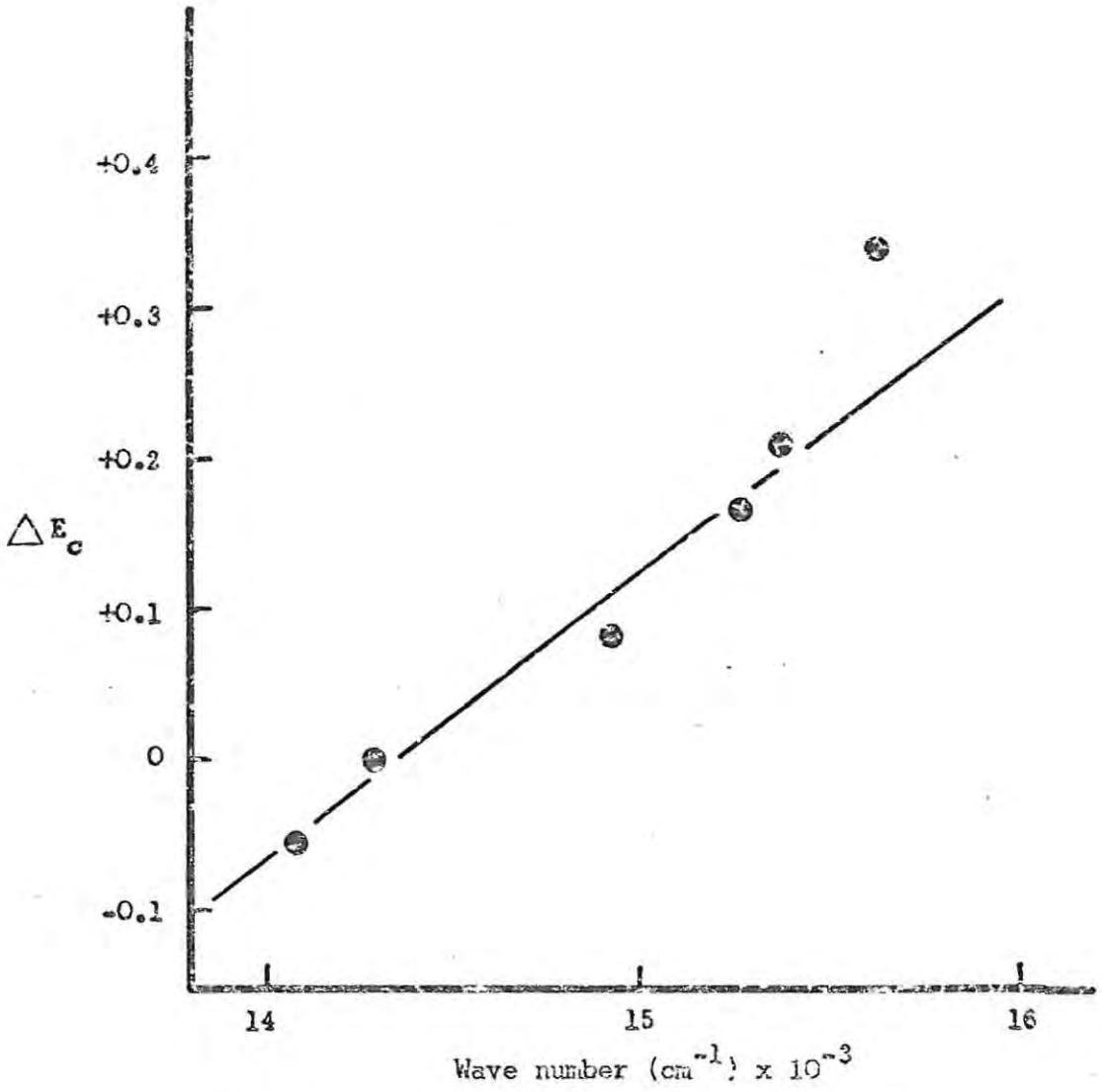


FIG. 23. Relation between $\triangle E_c$ and the wave numbers of maximum absorption for the FeL complexes.

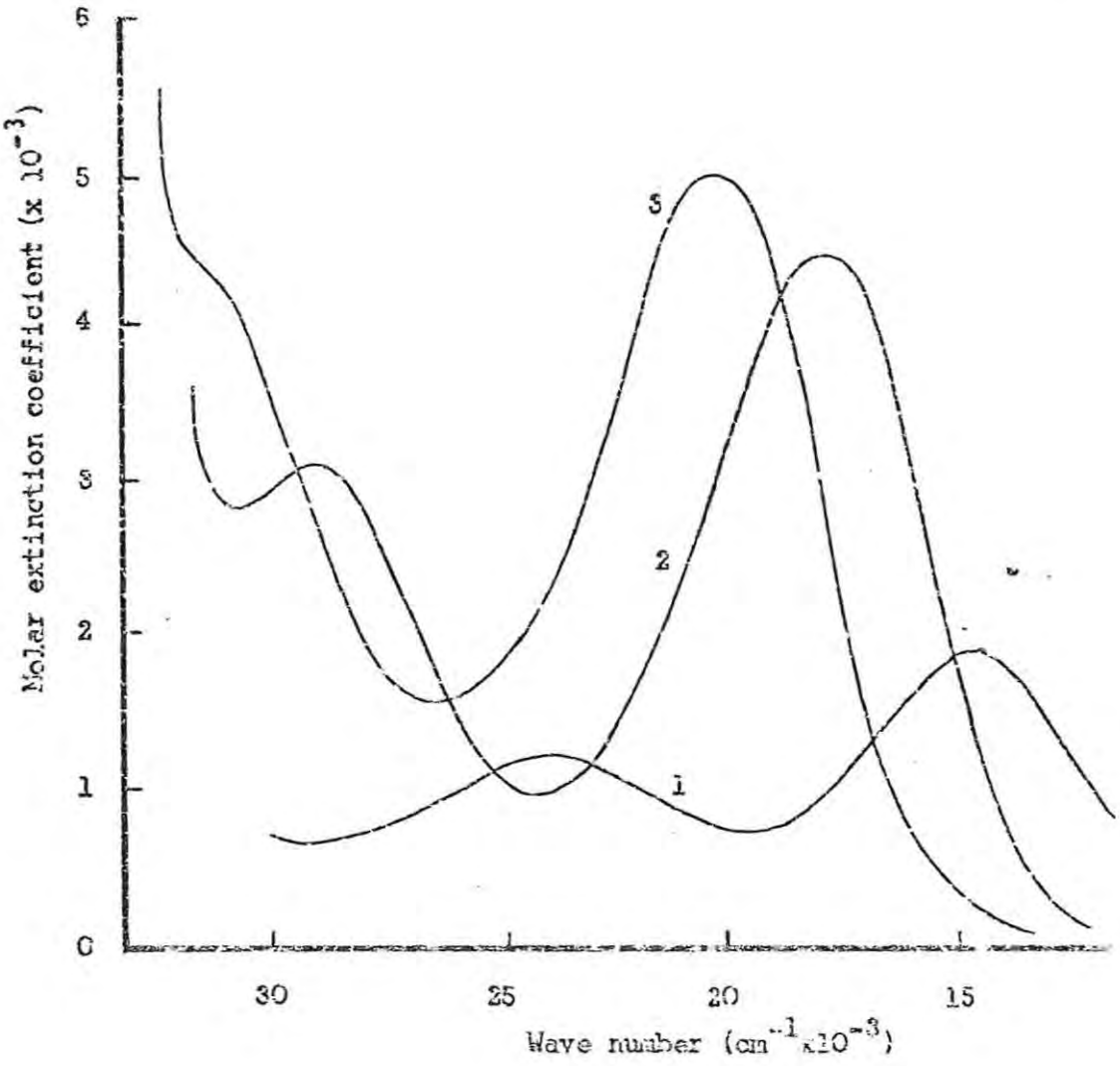


FIG. 25. Visible absorption spectra of (1) FeL_1 species of 3,4-dihydroxybenzenesulfonate, (2) FeL_2 species of Tiron and (3) FeL_3 species of catechin.

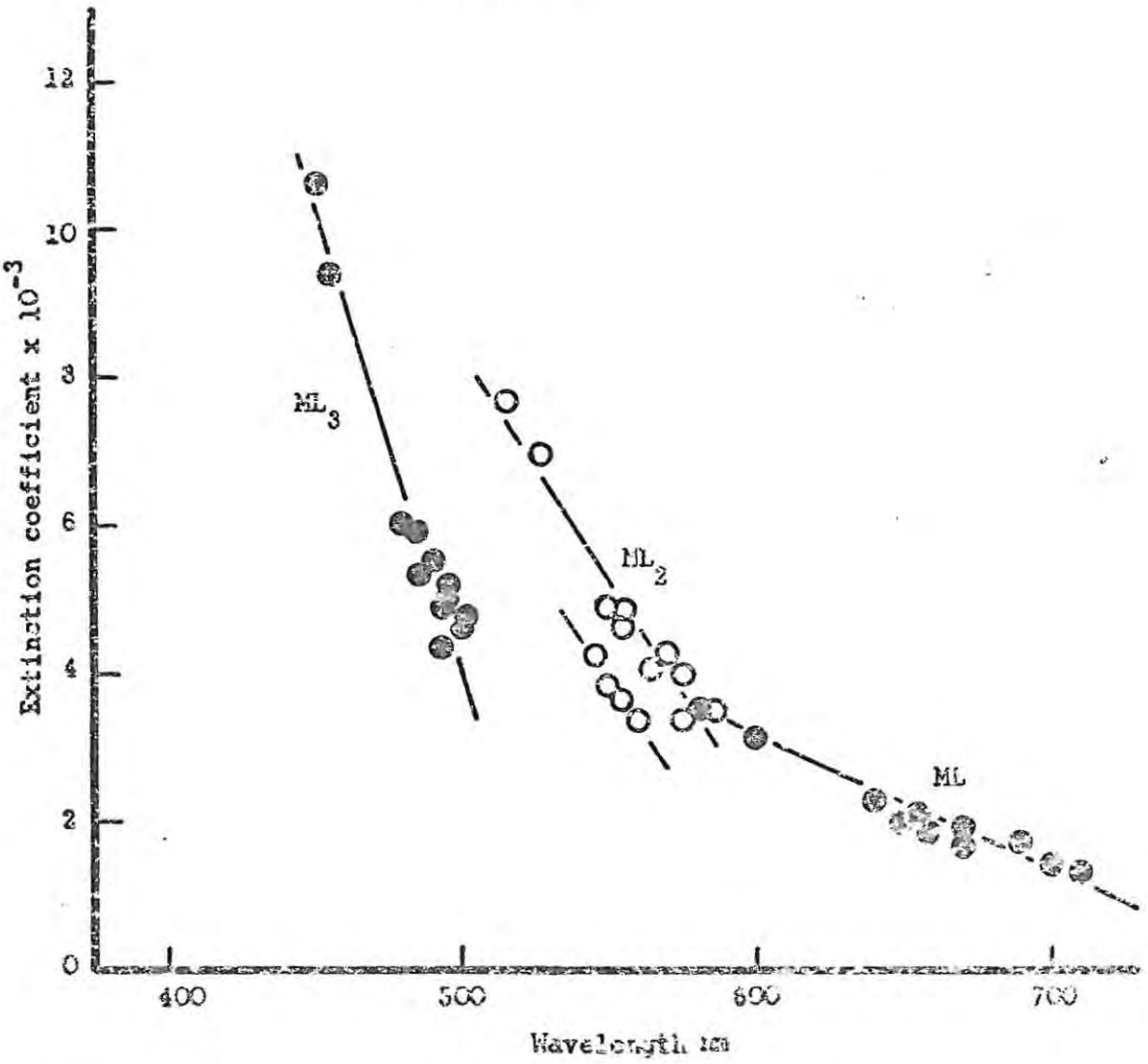


FIG. 26. Relation between the extinction coefficients of the main charge transfer bands and the wavelengths of maximum absorption for the o-diphenol complexes of Fe(III).

C. GERMANIUM(IV), ALUMINIUM(III) AND BORON(III) COMPLEXES OF o-DIPHENOLS.

Although the chemistry of germanium(IV) complexes is not related to that of aluminium(III) and boron(III) complexes, the o-diphenol complexes of Ge(IV), Al(III) and B(III) are here discussed together firstly, because of the colourless nature of the complexes and secondly, because the formation constants for the wattle tannin complexes could be determined for all three metals.

1. Germanium(IV) complexes.

Germanium(IV) salts, eg. $GeCl_4$, could not be used as a source of metal ion because of the very rapid hydrolysis of Ge(IV).[190] In addition acid could not be used to suppress the hydrolysis because it has been found that the addition of acid merely decreases the solubility of the hydrolosis product.[191] The hydrolysis product, GeO_2, exists in two forms; one, with a quartz lattice, is moderately soluble in aqueous media and the other, with a rutile lattice, is insoluble.[192] The former is the more common and has been used as the source of Ge(IV) in this investigation.

Germanium dioxide, GeO_2, has been shown to exist in aqueous solutions as an uncharged mononuclear species.[193] It is a weak acid and the first hydrolysis constant, K_1^*, according to the equilibrium :

$$GeO_2 \underset{H_2O}{\rightleftharpoons} GeO_2(OH)^- + H^+ \qquad (1)$$

was calculated from potentiometric titration data (Fig. 1) with the aid of equations (7) and (9), Section A. The value of $pK_1^* = 9.12$ compares

favourably with the previously determined[194] value of 9.08.

It is known from earlier investigations[32,195] that o-diphenols have a marked tendency to form chelates with GeO_2. The stoichiometry of the o-diphenol complexes of Ge(IV) has been determined by the continuous variation(Job's) method, utilising the ultraviolet absorption band of the phenolic ligand.[32] It was found that 3 moles of the o-diphenolato ligand are bound to one Ge(IV) ion. A similar result has also been obtained using conductiometric[196] and potentiometric[197] methods.

On the basis of the above results, the reaction taking place between GeO_2 and o-diphenols in aqueous solution at pH $>$ 2, has been shown[34] to be :

$$GeO_2 + 3H_2L \rightleftharpoons GeL_3^{2-} + 2H^+ \qquad (2)$$

It has, however, been established that at high acidity the bis-chelate is formed.[36,198] But since this complex formation only takes place at very low pH, it has not been studied in the present investigation.

Both potentiometric and spectrophotometric methods were used to determine the equilibrium constants for the o-diphenol complexes of Ge(IV).

(a) Potentiometric investigation : The general type of potentiometric titration curve obtained in titrations of GeO_2 with presence of excess of ligand is illustrated in Fig. 1. The distinct inflection which may be observed after addition of two moles of alkali per mole of metal ($\bar{z} = 2$) is in agreement with reaction (2).

In order to establish whether the only species formed is GeL_3,

solutions containing less than the stoichiometric concentration of ligand were studied. The potentiometric titration curves obtained under this condition are illustrated in Fig. 1. The inflection at $\bar{z} = 1.33$ for the solution with a 1 : 2 molar ratio of metal to ligand is also in accordance with reaction (2), since in this the end point will be determined by the concentration of ligand present. The excess of GeO_2, after complete complex formation may be observed (Fig. 1) to hydrolyse at higher pH values, as required by (p)hydrolysis constant of 9.12. The final inflection at $\bar{z} = 1.66$ for the titration with a 1 : 2 molar ratio is in agreement with both reactions (1) and (2), thus :

$$GeO_2 + 2H_2L \rightleftharpoons \tfrac{2}{3} GeL_3^{2-} + \tfrac{1}{3} GeO_2 + 1\tfrac{1}{3} H^+ \qquad (3)$$

$$\tfrac{1}{3} GeO_2 \rightleftharpoons \tfrac{1}{3} GeO_2(OH)^- + \tfrac{1}{3} H^+ \qquad (4)$$

The titration curves for the Ge(IV)-polyphenolic flavanoid complexes are shown in Fig. 2, Section A. It was shown that Ge(IV) only co-ordinates with the B-ring o-dihydroxo group. Use was made of this fact to calculate the dissociation constants of the uncomplexed A-ring hydroxyl groups.

The nature of the titration curves for the 1,2,3-trihydroxybenzene complexes were found to have the same form as those for the o-dihydroxybenzene complexes. This indicates that the former phenols react with GeO_2 as 3-hydroxycatechol derivatives. This has been confirmed by the isolation[32] of the pyrogallol complex, $\left[Ge(C_6H_4O_3)_3\right](C_5H_5NH)_2$.

Solutions of wattle tannin and GeO_2 formed an immediate white precipitate. Complexation was obvious because of the marked decrease in the

pH of the above solution relative to solutions containing only metal or tannin. The potentiometric titration curve for the Ge(IV)-wattle tannin system with excess of ligand is illustrated in Fig. 2. The sharp inflection at $\bar{z} = 2$ indicates that although precipitation occurs, the complexation is still in agreement with reaction (2). Use was made of this fact to determine the minimum molar concentration of wattle tannin necessary for complete complex formation. From reaction (2) the theoretical number of moles of alkali per mole of ligand at the end point is 0.66. Titration curves obtained with excess of GeO_2 and varying amounts of wattle tannin are illustrated in Fig. 2. It was found that the average number of moles of alkali per mole of wattle tannin required to reach the end point was 0.45. Comparison of this value with that required by theory, indicates that one-third of the B-ring o-dihydroxyl groups are not available for complex formation because of the plymeric nature of wattle tannin.

The precipitated Ge(IV)-wattle tannin complex was found to dissolve at pH greater than 10. This may be ascribed to the ionisation of the uncomplexed A-ring phenolic groups, making the complex more hydrophilic. The solubility of the Ge(IV)-wattle tannin complex also was found to be dependent on the ionic strength of the solution - at zero ionic strength the complex is completely soluble whereas with increasing ionic strength (KCl) the solubility decreases - indicative of a salting-out effect.[199] When the potentiometric titration of the Ge(IV)-wattle tannin system was conducted in the absence of KCl no precipitate formed. If the KCl was only added after complete complexation, to give I = 0.1, then still no precipitate formed. This also may be ascribed to the ionisation of the uncomplexed A-ring phenolic groups increasing the solubility of the wattle

tannin complex. Use was made of this procedure to determine the dissociation constants of the B-ring phenolic groups (Section A).

The equilibrium constants, k'_3, for reaction (2) were calculated with the aid of equations (14) and (17) Section B, and the equation :

$$k'_3 = \frac{\bar{n}\left[H\right]^2}{(1 - \bar{n})\left[\frac{(T_L^o - 3\bar{n}T_H^o)V^o}{V^o + v'''}\right]^3} \qquad (5)$$

Worked examples of the calculations are given in Table 7.

Owing to the insolubility of the Ge(IV)-wattle tannin complex in aqueous solution of I = 0.1, the equilibrium constant could not be determined. However the sulfited derivative of wattle tannin was found to form a soluble complex with GeO_2 and the equilibrium constant was determined from the potentiometric results. In calculating the equilibrium constants of complexes the total concentration of the ligand is required. It has been shown above that only two-thirds of the complexing B-ring o-dihydroxyl groups of wattle tannin are available for complex formation, hence it is necessary to multiply the concentration of wattle tannin used by a factor of 0.66 in order to obtain the true ligand concentration. Results of the calculations of the equilibrium constant, k'_3, for the Ge(IV)-wattle tannin complex are given in Table 8. The close agreement between the values of log k'_3 with different concentrations of wattle tannin supports the above reasoning.

Potentiometrically determined values of log k'_3 for the o-diphenol complexes of Ge(IV) are listed in Table 1.

TABLE 1.

Log k'_3 and log $\beta_3 K_{Ge}^{-1}$ values for the Ge(IV) complexes of o-diphenols.

Ligand	log k'_3			log $\beta_3 K_{Ge}^{-1}$
	*P	S	L	
4-tert.-butylcatechol	-1.39			69.41
4-methylcatechol	-1.32			69.48
4-hydroxycatechol	-1.08			69.12
pyrocatechol	-0.63	-0.68	-0.77(201)	68.35
3-methylcatechol	-1.03			67.67
pyrogallol	-0.15	-0.18	-0.22(201)	67.78
brazilin	0.02	0.04		67.83
catechin	0.39	0.41		67.15
leucofisetinidin	-	0.42		67.02
fustin	0.43			67.18
robinetinidol	0.94	0.96		67.10
dihydrorobinetin	0.98			67.13
wattle tannin	1.02			67.17
2,3-dihydroxynaphthalene	1.67			64.52
3,4-dihydroxybenzenesulfonate	1.60			64.0
DHNS	2.17		2.0(34)	63.22
Tiron	2.79		2.74(201)	63.57
protocatechuic acid	2.55			63.30
gallic acid	2.68			62.68
propyl gallate	2.66	2.62		62.64
4-chloroacetylcatechol	2.89			61.09
protocatechuic aldehyde	3.35	3.41		60.38
4-nitrocatechol	4.13	4.22	3.90(34)	57.23

*P represents potentiometrically determined values.

S represents spectrophotometrically determined values.

L represents published values I = 0.1, T = 25°C, references given in parenthesis.

The formation of the Ge(IV)-protocatechuic acid and -gallic acid complexes was found to take place at pH values below the ionisation of the carboxyl substituent. Hence, the equilibrium constants (Table 1) for these complexes are related to the complexes with the carboxyl groups in the undissociated form.

Since the Ge(IV)-prctocatechuic and -gallic acid complexes form before carboxyl ionisation, the subsequent ionisation and the corresponding dissociation constants of this group will not be related to those of the uncomplexed, protonated phenols. The dissociation constants were determined from the titration curve of GeO_2 and ligand in stoichiometric concentrations, with the aid of equations (6) and (9), Section A. It has been shown that the electronic influence of the substituent in substituted benzoic acids (and phenols) has a direct bearing on the value of the dissociation constant[116] - the more electron-releasing the substituent, the higher the value of pK and vice versa relative to the unsubstituted benzoic acid (and phenol). The increase in the pK (carboxyl group) values of 5.10 and 5.01 for the Ge(IV)-protocatechuic acid and -gallic acid complexes respectively, relative to the uncomplexed respective values of 4.35 and 4.25 (Tables 3 and 6, Section A), indicates that the electron-releasing character of the Ge(IV) complexed o-dihydroxo group is greater than that of the protonated species. This can be ascribed to the overall dinegative character of the tris-complex, GeL_3^{2-}, as will be shown below.

The dissociation constants of the third uncomplexed hydroxyl group in the Ge(IV)-trihydroxybenzene complexes were determined in a similar manner to that described above. The values obtained are compared to those for the corresponding protonated species (Section A) in Table 2. A comparison of the values in columns 1 and 2 (Table 2) reveals that the electron-releasing effect of the Ge(IV) complexed o-dihydroxo group is greater than that of the fully protonated species, H_3R. This is similar to that obtained for the carboxyl dissociation constants. However the values in column 3 indicate that the electron-releasing effect of the

TABLE 2.

Dissociation constants, K, for the uncomplexed hydroxyl groups of the Ge(IV)-trihydroxybenzene complexes and the dissociation constants, Ka_1 and Ka_2, for the free phenolic ligands.

Ligand	pK	pKa_1	pKa_2
	Ge(IV) complex	free phenolic groups	
pyrogallol	11.18	9.05	11.23
gallic acid	11.15	8.68	11.30
propyl gallate	10.82	7.88	11.04
robinetinidol	11.2	8.81	11.25
4-hydroxycatechol	11.05	9.10	11.55

complexed group is less than the singly ionised species, H_2R^-. On the basis of electroneutrality, the residual dinegative charge in the GeL_3^{2-} complex will result in the electron-releasing character of the complexed groups being greater than the fully protonated phenol. But as the dinegative charge of the complex must be divided amongst three ligand molecules (i.e. six hydroxo groups) the electronic effect will be less than for the singly ionised species, H_2R^-.

(b) Spectrophotometric investigation : Changes that occur in the ultraviolet absorption spectra of the phenolic ligand on complexation of Ge(IV) form the basis of this method. Absorption spectra of solutions containing stoichiometric concentrations of GeO_2 and ligand were recorded at various pH values as illustrated in Fig. 3. Spectral data of o-diphenol complexes are given in Table 6. The following equation for the spectrophotometric determination of the equilibrium constants, k_3', has been derived[34] :

$$k'_3 = \frac{(\Delta A/\Delta An)\left[H\right]^2}{(T_M - \Delta A/\Delta An)(T_L - 3\Delta A/\Delta An)^3} \qquad (6)$$

where $\Delta A = A - A^o_O$ and $\Delta An = (A^o_1 - A^o_O)/\left[GeL_3\right]$

Examples of the calculations are given in Table 3. The spectrophotometrically determined equilibrium constants, k'_3, for the o-diphenol complexes are listed in Table 1. Not all of the o-diphenol complexes were studied spectrophotometrically.

From Table 1 it may be seen that the value of k'_3 for the Ge(IV)-wattle tannin complex is very similar to those for the robinetinidol and dihydrorobinetin complexes. This suggests that wattle tannin reacts with GeO_2 as a 1,2,3-trihydroxybenzene derivative. This result is similar to that found for the Fe(III) complex.

The equilibrium constants, k'_3, determined in the present investigation are generally in good agreement with published values as shown in Table 1.

The effect of changing the substituent on the benzene ring may be seen in Table 1 to have an appreciable effect on the values of log k'_3. A plot of the combined ligand dissociation constants, KaKb, against the complex equilibrium constants, k'_3, is illustrated in Fig. 4. The k'_3 value for the Ge(IV)-protocatechuic acid complex was correlated with the KaKb value for the ligand in the undissociated (carboxyl group) form, viz. pKaKb = 20.2 (Section B). The KaKb value used for gallic acid in the undissociated form was that for the related ligand, propyl gallate. The

non-linear relationship observed (Fig. 4) illustrates the direct dependence of complex formation (reaction 2) on the acidity of the ligand.

It has been shown[34] that the equilibrium constant, k_3', is related to the stability constant, β_3,

$$\beta_3 = \frac{\left[GeL_3^{2-}\right]}{\left[Ge^{4+}\right]\left[L^{2-}\right]} \qquad (7)$$

thus :

$$\log \beta_3 K_{Ge}^{-1} = \log k_3' + 3(pKaKb) \qquad (8)$$

where $K_{Ge} = \left[GeO_2\right]\left[H^+\right]^4 \Big/ \left[Ge^{4+}\right]$ is the hypothetical hydrolysis constant of Ge(IV). The values of $\log \beta_3 K_{Ge}^{-1}$ for the o-diphenol complexes are listed in Table 1, and a plot of these values against those for the ligand association constants (KaKb) is illustrated in Fig. 5. The direct linear relationship observed is similar to that obtained previously[34] with five o-diphenol complexes. The fact that the points for the 1,2,3-trihydroxybenzene derivatives correspond to the linear relationship indicates that the third, adjacent hydroxyl group does not interfere with complex formation. The point for 3-methoxycatechol was found to deviate from the linear in a manner which suggests that the bulkier methoxyl group reduces the stability of the complex by steric interference. The fact that the point for wattle tannin falls on the straight line is noteworthy as it shows that the Ge(IV)-wattle tannin complex conforms to the normal complexation behaviour of o-diphenol compounds.

2. Aluminium(III) complexes.

The hydrolysis of Al(III) ions in aqueous media has been shown[40] to occur at pH greater than 4. At lower pH values the Al(III) ions exist as octahedral hexa-aquo species[202], $\left[Al(H_2O)_6\right]^{3+}$.

It has been established that the stoichiometries of the Al(III)-o-diphenol complex species in acid, neutral and alkaline media are 1 : 1, 1 : 2 and 1 : 3 (metal to ligand) respectively, by potentiometric[39,41,204] and calorimetric[203] methods. The number of hydrogen ions liberated, from the o-diphenol ligand, on successive complex formation has been shown[40] to be equal to two, according to the general reaction :

$$AlL_{x-1}^{5-2x} + H_2L \rightleftharpoons AlL_x^{3-2x} + 2H^+ \qquad (9)$$

with x = 1, 2 and 3.

o-Diphenol complexes of Al(III) are colourless if the ligand itself is not coloured. Hence potentiometric methods were used to study the complex formation. Figs. 6 and 7 illustrate the general form of potentiometric titration curves for the o-diphenol complexes. Excess of ligand was used to prevent any hydrolytic reactions in alkaline media.[40] Free mineral acid was also used to enable the low pH region to be interpreted. Inflections observed (Figs. 6 and 7) at $\bar{z} = 2$ and 4 correspond to the complete formation of the AlL and AlL_2 species. The final species, AlL_3, forms in the region of the ligand dissociation, hence no inflection is observed at complete complex formation.

The titration curve for the Al(III)-pyrogallol system was found to be different from those of the o-dihydroxybenzene derivatives, in that an

inflection was not observed at $\bar{z} = 4$ but at $\bar{z}$ values ranging from 3.6 - 3.9 depending on the concentration of the ligand. This indicates that more complicated complex formation occurs than shown in reaction (9). However an inflection was always observed at $\bar{z} = 2$ as required by reaction (9). Therefore the first species, AlL, is similar to those of the o-dihydroxybenzene derivatives. The above results also apply to the Al(III)-robinetinidol and -dihydrorobinetin systems.

Stability constants of the o-diphenol complexes of Al(III) were determined directly from the potentiometric results by the method of Irvine and Rossotti.[89] For the reaction :

$$AlL_{x-1}^{5-2x} + L^{2-} \rightleftharpoons AlL_{x}^{3-2x} \qquad (10)$$

where x = 1, 2 and 3

the successive stability constants, K_x, were determined by first calculating the value of $\bar{n}$ with the aid of equations (14) and (17) Section B and then the concentration of the ionised ligand, L^{2-}, thus :

$$pL = \log \frac{\sum_{j=o}^{j=J} \beta_j^H \left[H\right]^j}{T_L^o - \bar{n} T_M^o} \times \frac{(V^o + v''')}{V^o} \qquad (11)$$

where β_j^H is the overall ligand association constant. For o-diphenol ligands :

$$\sum_{j=o}^{j=J} \beta_j^H \left[H\right]^j = KaKb\left[H\right]^2 + Kb\left[H\right] + 1 \qquad (11a)$$

The values of pL at $\bar{n} = 0.5$, 1.5 and 2.5 correspond to the values of log K_1, log K_2 , and log K_3, respectively. However this is only

valid[90] if K_1/K_2 and $K_2/K_3 > 10^{2.5}$. In order to use all the experimental results the following equation[90] was also used to determine the stability constants :

$$\log K_x = pL - \log \frac{x - \bar{n}}{\bar{n} - x + 1} \qquad (12)$$

Use of equation (12) over the whole range is only justified[90] if K_1/K_2 and $K_2/K_3 > 10^4$.

Examples of the formation curves ($\bar{n}$ vs. pL plots) for the o-diphenol complexes of Al(III) are illustrated in Fig. 8. From the stability constants determined by interpolation at the half-$\bar{n}$ values, it was found that the requirement of $K_2/K_3 > 10^4$ only held for the less acidic o-diphenol ligands. However, the requirement $K_2/K_3 > 10^{2.5}$ held for all the complexes. Therefore the stability constants, K_3, were determined from the half-$\bar{n}$ values. The values obtained are listed in Table 3.

The requirement $K_1/K_2 > 10^{2.5}$ was only met by the less acidic o-diphenols, indicating overlap of the formation curves. This was confirmed by the drift of the K_1 and K_2 values calculated with the aid of equation (12), especially in the region of $\bar{n} = 1$. Accurate values of K_1 and K_2 were obtained by two methods :

(a) Least squares treatment[90] : Values of $\bar{n}$ and $[L]$ were used to determine the stability constants, K_1 and K_2, by means of a least squares treatment of the following equation for a straight line :

$$\frac{\bar{n}}{(\bar{n} - 1)[L]} = \frac{(2 - \bar{n})[L]}{(\bar{n} - 1)} K_1K_2 - K_1 \qquad (13)$$

(b) Correction term method[90] : The correction term, y, is given by :

$$y = \log \frac{1 - d}{d} + \log \left[1 - \frac{(1 + d) \left[L\right]_{1-d}}{(1 - d) \left[L\right]_{1+d}} \right] \qquad (14)$$

where d = 0 at the mid points ($\bar{n} = 1$) of the formation curves (Fig. 8) for systems where N = 2 i.e. for K_1 and K_2; d = 0.5 at $\bar{n} = 0.5$ and 1.5 and $\left[L\right]_{1-d}$ and $\left[L\right]_{1+d}$ are obtained from the formation curves at $\bar{n} = 1-d$ and $\bar{n} = 1+d$ respectively.

$\bar{n}$ Values of less than 1.5 were used in methods (a) and (b) to avoid interference from the possible overlap of the AlL_3 complex formation. Examples of the calculations using methods (a) and (b) are given in Tables 10 and 11. The average value obtained by these methods for the constants K_1 and K_2 are listed in Table 3. For the cases where only the calculation of K_1 was possible (Table 3), the value was obtained by interpolation at half-$\bar{n}$ values.

A white precipitate formed immediately on adding wattle tannin to a solution of Al(III). Even using the more soluble sulfited derivative of wattle tannin only the stability constant for the first species, AlL, could be determined because a precipitate still formed at $\bar{z} = 2.0$. The inflection observed at $\bar{n} = 1$ in the formation curve (Fig. 8) indicates that the AlL species is completely formed before precipitation occurred.

The K_1 and K_3 values in Table 3 for the protocatechuic acid complex are related to the carboxyl substituent of the ligand in the undissociated and dissociated forms respectively. The AlL_2 species was found to form in the region of the carboxyl ionisation and the value of log K_2 was found

TABLE 3.

Stability constants, K_1, K_2 and K_3, and equilibrium constants, k_1, k_2 and k_3, for the o-diphenol complexes of Al(III).

Ligand	log K_1	log K_2	log K_3	pk_1	pk_2	pk_3
4-tert.-butylcatechol	17.15	-	-	6.45		
4-methylcatechol	17.11	13.90	9.25	6.49	9.70	14.35
4-hydroxycatechol	17.02	13.85	9.2	6.38	9.55	14.2
pyrocatechol	16.75	13.60	9.0	6.25	9.40	14.0
3-methoxycatechol	16.59	13.43	9.05	6.31	9.47	13.85
pyrogallol	16.60	-	-	5.95		
brazilin	16.50	13.60	9.0	5.9	8.80	13.6
catechin	16.32	13.5	9.2	5.93	8.75	13.05
fustin	16.38	13.58	9.2	5.87	8.67	13.05
robinetinidol	16.30	-	-	5.75		
dihydrorobinetin	16.35	-	-	5.70		
wattle tannin	16.30	-	-	5.75		
2,3-dihydroxynaphthalene	15.64	13.12	9.0	5.31	7.83	11.15
3,4-dihydroxybenzenesulfonate	15.80	12.75	8.90	5.0	8.05	11.9
DHNS	15.47	12.98	9.35	4.88	7.37	11.0
protocatechuic acid	15.18	-	9.00	5.02		13.0
propyl gallate	15.05	12.61	9.05	4.95	7.39	10.95
gallic acid	15.00	-	-	5.0		
Tiron	16.62	13.68	9.8	3.63	6.57	10.45
4-chloroacetylcatechol	14.59	12.50	9.3	4.81	6.90	10.1
protocatechuic aldehyde	14.37	12.31	9.25	4.63	6.69	9.75
4-nitrocatechol	13.54	11.60	8.85	4.11	6.05	8.8

to be dependent on the pH. Obviously the state of the carboxyl group affects the complex formation, due to the different electronic effects of the carboxyl group in the dissociated and undissociated forms. This is similar to the observations on the Fe(III)-protocatechuic acid complex.

The values of the equilibrium constants, k_1, k_2 and k_3, for reaction (9) were obtained from the stability constants using equation (22), Section B and are listed in Table 3.

Values of the equilibrium constants, k, for the pyrocatechol,

3,4-dihydroxybenzenesulfonate and Tiron complexes of Al(III) (Table 3) compare favourably with those obtained by Havelkova and Bartusek.[40] Values quoted by Dubey and Mehrotra[39,204] for the Al(III)-pyrocatechol and -Tiron systems have been shown to be erroneous.[40] However, the reason given[40] that the error lay in the fact that the constants were determined from potentiometric titrations with only a small excess of ligand is incorrect since the ligand concentrations used in the present investigation are similar to those used by Dubey and Mehrotra yet equilibrium constants comparable with those of Havelkova and Bartusek were obtained. Equilibrium constants were recalculated from the potentiometric results of Dubey and Mehrotra. It was found that the error in fact lay in the calculation - the values of $\bar{n}$ should be half the values quoted. The recalculated equilibrium constants were found to compare favourably with those quoted by Havelkova and Bartusek[40] and with those in Table 3.

Stability constants, K_1 and K_2, were correlated with the combined ligand association constants, KaKb, and the result is given in Fig. 9. The linear relationships observed in this figure are similar to those obtained for the o-diphenol complexes of Fe(III) and Ge(IV). The only points that deviated from the straight line are those for Tiron. However a similar observation was made for the Fe(III) complex and the same reasons apply. The fact that the points for 4-chloroacetylcatechol do not deviate indicates that the hydrogen bonding that was proposed for the Fe(III) complex is not an important factor in this case. The o-diphenol complexes, AlL_1 and AlL_2, therefore follow the general relationship[151-157] between ligand acidity and complex stability. This refutes the observat-

ion that has been made,[40] that there is no correlation between these two functions for the Al(III) complexes. However as only three o-diphenols were compared and the fact that Tiron was included in the correlation explains the converse observation.

From Fig. 9, it may be observed that the slope of the linear relationship is less for the K_2 correlation relative to that for K_1. Thus the effect of ligand acidity on the successive stability constants decreases and from Table 3 it is apparent that the final constant, K_3, is almost independent of the ligand acidity. This may be ascribed to the electrostatic nature of the bonding. On formation of the first species, AlL^+ the effect of the ligand acidity will be greatest. However on further complex formation, the species AlL_2^- and AlL_3^{3-} become progressively oversaturated with negative charge and the effect of the ligand acidity decreases correspondingly.

The values of the successive stability constants, K_1, K_2, and K_3, (Table 3) for a single ligand decrease in the above order. This is a general result[206] due to the statistical decrease in frequency of co-ordination because of repulsion of the incoming ligand by the co-ordinated ligand or ligands.

The values of the equilibrium constants, k_1, k_2, and k_3, for reaction (9), listed in Table 3, may be observed to be directly dependent on the acidity of the ligand. This is expected, as the reaction involves displacement of the phenolic protons by the metal ion. In correlations of these constants with the ligand dissociation constants, linear relation-

ships were obtained similar to those for the Fe(III) complexes of o-diphenols (Figs. 10 and 11, Section B).

Stability constants of a few o-diphenol complexes of Ga(III) were compared with those of the corresponding Al(III) complexes. Both metals belong to the Group III b. The general form of the potentiometric titration curves for the Ga(III) complexes were found to be similar to those for Al(III). This indicates the same successive formation of the ML, ML_2, and ML_3 complexes. Stability constants were calculated in the manner described above and the values of K_2 and K_3 which were obtained are listed in Table 4. Values of K_1 could not be determined because the GaL_1 species was completely formed at the start of the potentiometric titration.

From the values of K_2 and K_3 for the Al(III) complexes (Table 3) and the Ga(III) complexes (Table 4) the stability order Ga $>$ Al holds for a particular o-diphenol ligand. A similar order has been found for the acetylacetonate complexes of these metals.[214] It has been proposed that the ability of a metal ion to accept electrons from co-ordinated ligands is related to the gaseous ionisation potentials of the cations, since these are a measure of the energy involved in the reverse process.[56] Therefore this will also determine the stability of the complex. The above stability order is in agreement with this since it is also the order of the third ionisation potential.[215]

TABLE 4.

Stability constants, K_2 and K_3, for o-diphenol complexes of Ga(III).

Ligand	log K_2	log K_3
pyrocatechol	16.05	10.2
catechin	15.83	10.2
Tiron	15.75	11.1
4-nitrocatechol	13.54	10.0

3. Boron(III) complexes.

The source of B(III) used in the present investigation was boric acid. At concentrations of less than 0.025 M, boric acid is essentially a mononuclear species, $B(OH)_3$, but at higher concentrations polymeric species form.[207] As the concentrations of boric acid used were less than the above value, only the former species need be considered.

The weak acidic nature of boric acid is illustrated in Fig. 6 which shows the potentiometric titration curve for the reaction[207] :

$$H_3BO_3 \underset{H_2O}{\rightleftharpoons} B(OH)_4^- + H^+ \qquad (15)$$

The hydrolysis constant, K*, was calculated with the aid of equations (7) and (9), Section A. A value of $pK^* = 9.08$ (lit.[208] 9.00) was obtained.

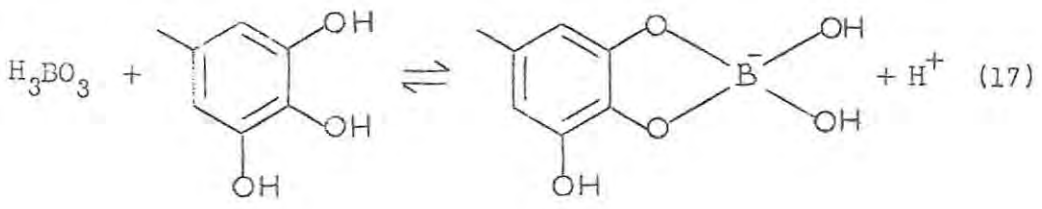
The ability of boric acid to form complexes with polyhydroxo compounds is well known.[209] o-Diphenols including 1,2,3-trihydroxybenzene derivatives have been shown, by potentiometric[46,47,210,211] and calorimetric[49] methods, to react with boric acid to form a mono-chelated complex in

aqueous media, thus :

$$H_3BO_3 + H_2L \rightleftharpoons BL(OH)_2^- + H^+ \qquad (16)$$

. The bis(pyrocatecholato)boron(III) anion has been isolated from concentrated aqueous solutions.[48] In general however, only the mono-chelated species, $BL(OH)_2^-$, have been detected in dilute solutions.[46,49] B(III) complexes with bidentate oxygen ligands have been shown to have tetrahedral symmetry.[212] This is based on the ability of these complexes to form optical isomers with asymmetric ligands, eg. salicylic acid.

The boric acid-wattle tannin complex was found to be completely soluble in aqueous solutions of I = 0.1 and the use of the sulfited derivative was not necessary. A possible reason for the solubility of the boric acid-wattle tannin complex, as opposed to the insolubility of the Fe(III), Ge(IV) and Al(III) complexes, is the nature of the boric acid complex formed,



(17)

results in there being no change in the number of hydrophilic hydroxyl groups. Increasing complexation also appears to decrease the solubility of the wattle tannin complexes. The 1 : 1 boric acid and Al(III) complexes are soluble whereas the higher Al(III) species and the tri-nuclear Ge(IV) complex are insoluble. In addition, it has been found that the

Fe(III)-wattle tannin complex is soluble in tartrate solutions, if the wattle tannin is added to a solution, at pH 7, containing excess of Fe(III) tartrate, whereas the complex is insoluble for the reverse process.[213] It was shown in Section B that the mono-nuclear species, FeR (RH_3 = pyrogallol derivative), is formed in the former process, whereas in the latter process the initial excess of wattle tannin would result in the formation of the dinuclear species, $Fe(RH)_2$.

Figs. 6 and 7 illustrate the general type of potentiometric titration curve of solutions containing boric acid and excess of ligand. Because the boric acid complexes form in the same pH region as the acid dissociation of the ligand, both the titration curves of the complex and the free ligand are necessary to determine the equilibrium constants.

The equilibrium constants, k_1', for reaction (16) were calculated with the aid of the following equations :

$$\bar{n} = \frac{(v''' - v'')N}{V^oT_M^o(\bar{n}_a - 1)} \qquad (18)$$

and

$$k_1' = \frac{\bar{n}\left[H\right](V^o + v''')}{(1 - \bar{n})(T_L^o - \bar{n}T_M^o)(\bar{n}_a - 1)V^o} \qquad (19)$$

(the symbols have been defined previously).

Examples of the calculations are given in Table 12. The values of k_1' were calculated at pH < 7.5 to avoid any interference from the hydrolysis of the uncomplexed boric acid.

The equilibrium constants, k_1', for the o-diphenol complexes of boric acid are listed in Table 5. Equilibrium constants for a number of o-diphenol complexes have been determined.[46,47,210] Generally it was found that there was good agreement between the published values of pk_1' and those determined in the present investigation as shown in Table 5.

TABLE 5.

pk_1' and log K_1' values for o-diphenol complexes of boric acid.

Ligand	pk_1'	pk_1' (lit.)*	log K_1'
4-tert.-butylcatechol	5.26		4.29
4-methylcatechol	5.23		4.32
4-hydroxycatechol	5.15		3.95
pyrocatechol	5.15	5.17(46)	4.21
3-methoxycatechol	5.10		4.20
pyrogallol	4.98	4.98(46)	4.07
brazilin	4.95		4.25
catechin	4.89		4.10
robinetinidol	4.81		4.00
wattle tannin	4.83		3.97
wattle tannin (sulfited)	4.82		3.98
protocatechuic acid	4.85		3.97
gallic acid	4.75		3.93
2,3-dihydroxynaphthalene	4.10	4.13(46)	4.45
3,4-dihydroxybenzenesulfonate	4.48	4.6 (46)	3.91
DHNS	3.94	3.98(46)	4.24
propyl gallate	4.26		3.64
4-chloroacetylcatechol	4.06		3.34
protocatechuic aldehyde	3.93	3.95(47)	3.27
Tiron	3.68	3.73(46)	3.97
4-nitrocatechol	3.75	4.0 (218)	3.00

* Published values, I = 0.1, T = 20 - 25°; references given in parentheses.

In order to determine whether sulfitation of wattle tannin had any effect on the complex formation, the equilibrium constant, k_1', for the boric acid complex of this derivative was determined. From Table 5 it is

seen that sulfitation has no effect on the value of pk_1' for the wattle tannin complex.

The equilibrium constants, k_1', for the boric acid complexes were correlated with the ligand dissociation constant, Ka, and the result illustrated in Fig. 10. The linear relationship observed in this figure is similar to that found previously [46] and illustrates the generally found dependence of the equilibrium constant on the acidity of the phenol. Three points were found to deviate from the straight line (Fig. 6) viz. Tiron which is generally anomalous and the two o-dihydroxynaphthalene derivatives. An explanation for the deviation of the two o-dihydroxy-naphthalene derivatives could not be formulated. It is again noteworthy that the point for wattle tannin lies on the straight line.

In order to convert the equilibrium constants, k_1', for the o-diphenol complexes of boric acid into a form similar to the stability constants of the other metal complexes of o-diphenols, a reaction independent of hydrogen ions is required. The following two reactions satisfy this requirement :

$$B(OH)_4^- + H_2L \rightleftharpoons BL(OH)_2^- \qquad (20)$$

$$H_3BO_3 + HL^- \rightleftharpoons BL(OH)_2^- \qquad (21)$$

The constants, K_1', for reaction (21) were calculated by the equation,

$$\log K_1' = pKa - pk_1' \qquad (22)$$

where Ka is the first ligand dissociation constant. The values obtained

are listed in Table 5. The constant for reaction (20) can be similarly calculated by substituting the hydrolysis constant of boric acid in place of the ligand dissociation constant in equation (22). From Table 5 it may be observed that the ligand acidity affects the constants, K_1', in a similar manner as it does the constants, k_1'.

Neither of the constants for reaction (20) nor (21) can be related to the other Group III b metals, because of the different equilibria.

4. Correlations between metal complexes of o-diphenols.

The limitations of comparing the complex stability constants with the ligand acidity constants have been pointed out.[216] It was shown that stability correlations involving pairs of metal ions are more advantageous. If the metal ions have the same valency and can assume the same co-ordination number, then the properties affecting the stabilities of the complexes can be assessed.

Although the metal ions, Al(III) and Fe(III) do not belong to the same period, they do satisfy the above requirements of charge and co-ordination. Correlations of the stability constants, K_1 and K_2, for the o-diphenol complexes of Al(III) and Fe(III) are shown in Fig. 11 Section B, and Fig. 11, respectively. The linear relationships obtained indicate that the factors which influence the stabilities of the Al(III) complexes have a similar effect on those of the Fe(III) complexes. Furthermore, the slopes of approximately unity show that the ring substituent affects the stabilities of the two sets of complexes to the same extent. A

similar result has been found for the related Si(IV) and Ge(IV) complexes of o-diphenols.[34]

The advantages of this type of correlation is shown by the fact that the position of the points for the Tiron complexes correspond to the above linear relationships. Whereas in correlations with the ligand association constants, the position of the points for Tiron were found to be anomalous.

In similar correlations between the o-diphenol complexes of Al(III) and boric acid (Fig. 12); and Ge(IV) and Al(III) (Fig. 13), linear relationships were also obtained. In these correlations, the equilibrium constants, k, and not the stability constants are used. The position of the point for Tiron in the Ge(IV) correlation (Fig. 13) was found to deviate markedly from the straight line. This shows that for the successful application of this type of correlation the metal ions should have the same valency and the equilibrium reactions should also be similar. In the boric acid correlation (Fig. 12), the previously observed anomalous behaviour of the two o-dihydroxynaphthalene derivatives (cf. Fig. 10) was confirmed by the deviation of the points for these phenols from the straight line in Fig. 12.

Because the complex formation involve different equilibria, the slopes of the straight lines in Figs. 12 and 13 cannot be interpreted as above.

In conclusion, it is significant that the flavanoid monomers and the wattle tannin complexes of Ge(IV), Al(III) and boric acid conform to the

normal complexation behaviour of o-diphenol compounds, in that they all correspond to the linear relationships in Figs. 4, 5, 9 - 13.

TABLE 6.

Spectral data for the GeL_3 complexes of o-diphenols.

Ligand	Absorption maxima nm	Extinction coefficient x 10^{-3}
pyrocatechol	286	14.5
3-methoxycatechol	278	7.7
catechin	290	22.0
leucofisetinidin	286	24.3
robinetinidol	280	19.8
pyrogallol	276	5.8
brazilin	303	24.5
propyl gallate	302	36.0
4-chloroacetylcatechol	247	40.0
	345	37.5
protocatechuic aldehyde	245	44.3
	294	24.0
	338	44.3
4-nitrocatechol	258	30.0
	392	29.0

TABLE 7.

Determination of log k_3' for the 4-methylcatechol and robinetinidol complexes, GeL_3^{2-} .

Ligand : (1) 4-methylcatechol					(2) robinetinidol				
pH	v'''	v''	$\bar{n}$	log k_3'	pH	v'''	v''	$\bar{n}$	log k_3'
3.6	3.21	2.87	.170	-1.337	3.0	1.30	.40	.455	0.946
3.7	3.335	2.89	.223	-1.329	3.2	1.78	.64	.574	0.954
3.8	3.47	2.91	.280	-1.323	3.4	2.14	.79	.677	0.947
3.9	3.61	2.93	.340	-1.322	3.6	2.39	.86	.767	0.938
4.0	3.74	2.94	.400	-1.325	3.8	2.59	.91	.841	0.934
4.2	4.0	2.95	.526	-1.312	4.0	2.73	.93	.901	0.940
4.3	4.12	2.96	.580	-1.321	4.2	2.835	.95	.943	0.938

Data used in equation (14) Section B, and equation (5) Section D :

(1) $T_M^o = 0.002$ M, $T_L^o = 0.008$ M
$E^o = 0.006$ M, $V^o = 50$ ml
N = 0.1 N, c = 2 and $\bar{n}_a = 2$.

(2) $T_M^o = 1.767 \times 10^{-3}$ M,
$T_L^o = 7.067 \times 10^{-3}$ M,
$E^o = 1.767 \times 10^{-3}$ M, $V^o = 56.6$ ml
N = 0.1 N, c = 2 and $\bar{n}_a = 2$.

TABLE 8.

Determination of log k_3' for the wattle tannin complex, GeL_3^{2-}.

pH	v'''	v''	log k_3'	pH	v'''	v''	log k_3'
2.8	1.65	1.15	1.02	2.8	1.83	1.0	1.04
2.9	1.90	1.32	1.02	2.9	2.08	1.2	1.05
3.0	2.14	1.47	1.05	3	2.30	1.38	1.01
3.1	2.32	1.58	1.05				
3.2	2.47	1.68	1.00				

Data used in equations as for Table 3.

$T_M^o = 0.001$ M, $T_L^o = 0.008$ M
$E^o = 0.004$ M, $V^o = 50$ ml,
N = 0.1 N, c = 2, $\bar{n}_a = 2$.

$T_M^o = 8.33 \times 10^{-4}$ M,
$T_L^o = 1.33 \times 10^{-2}$ M, $V^o = 60$ ml,
$E^o = 3.33 \times 10^{-3}$ M, N = 0.1 N,
c = 2, $\bar{n}_a = 2$.

TABLE 9.

Determination of log k'_3 for the protocatechuic aldehyde and catechin complexes, GeL_3^{2-}.

Ligand : protocatechuic aldehyde :			catechin :		
pH	$\triangle A$	log k'_3	pH	$\triangle A$	log k'_3
3.02	0.058	3.394	5.1	0.028	0.424
3.15	0.087	3.421	5.48	0.074	0.416
3.30	0.122	3.410	5.76	0.114	0.393
3.43	0.154	3.393	6.08	0.160	0.412
3.66	0.220	3.384	6.35	0.191	0.406
3.96	0.293	3.415	6.6	0.215	0.419
4.18	0.340	3.423	6.95	0.240	0.427

Data used in equation (6) :

Wavelength = 340 nm, $A_0^o = 0.068$,
$A_1^o = 0.598$, $\triangle An = 3.975 \times 10^3$
$T_M = 1.33 \times 10^{-4}$ M, $T_L = 4 \times 10^{-4}$ M,
l = 1 cm, ionic strength = 0.1 N.

Wavelength = 255 nm, $A_0^o = 0.118$
$A_1^o = 0.412$, $\triangle An = 5.88 \times 10^3$
$T_M = 5 \times 10^{-5}$ M,
$T_L = 1.5 \times 10^{-4}$ M, l = 1 cm,
ionic strength = 0.1 N.

TABLE 10.

Determination of the stability constants, K_1 and K_2, for the Al(III)-protocatechuic aldehyde system by method (9) (least squares).

pH	v'''	v''	$\bar{n}$	pL	log K_x
3.0	1.73	1.46	0.136	15.143	14.342
3.1	1.98	1.58	0.202	14.953	14.355
3.2	2.25	1.68	0.287	14.765	14.369
3.3	2.51	1.75	0.382	14.578	14.369
3.4	2.76	1.79	0.487	14.393	14.370
3.5	3.02	1.83	0.597	14.209	14.379
3.6	3.25	1.86	0.697	14.024	14.385
3.7	3.46	1.89	0.787	13.837	14.404
3.8	3.66	1.91	0.876	13.651	14.502
4.2	4.31	1.94	1.136	12.901	12.261
4.3	4.50	1.95	1.276	12.717	12.299
4.4	4.70	1.96	1.371	12.534	12.305
4.5	4.92	1.97	1.476	12.353	12.311

Least squares treatment using the values in columns 4 and 5 in equation (13) : correlation coefficient = 1.00, log K_1 = 14.35 and log K_2 = 12.34

Values used in equation (14) Section B and equations (11) and (12) : T_M^o = 1.923 x 10^{-3} M, T_L^o = 7.692 x 10^{-3} M, E^o = 3.846 x 10^{-3} M, V^o = 52 ml, $\bar{n}_a$ = 2, c = 2, pKaKb = 14 and pKb = 11.8.

TABLE 11.

Determination of the stability constants, K_1 and K_2, for the Al(III)-4-nitrocatechol system by method (b) (correction term).

d	pL_{1-d}	pL_{1+d}	y	log K_1	log K_2
0.45	13.48	11.68	0.069	13.549	11.611
0.4	13.40	11.76	0.152	13.552	11.608
0.35	13.31	11.85	0.236	13.546	11.614
0.3	13.22	11.94	0.323	13.543	11.617
0.25	13.13	12.04	0.414	13.544	11.626
0.2	13.04	12.14	0.511	13.551	11.629
0.15	12.94	12.25	0.613	13.553	11.637
0.1	12.83	12.36	0.722	13.552	11.638
0.05	12.72	12.47	0.840	13.550	11.630

Data obtained from the formation curve, Fig. 8.

TABLE 12.

Determination of pk'_1 values for the catechin, wattle tannin, propyl gallate and robinetinidol complexes, $BL(OH)_2^-$

Ligand : catechin						wattle tannin					
pH	v''	v'''	$\bar{n}_a$	$\bar{n}$	pk'_1	pH	v''	v'''	$\bar{n}_a$	$\bar{n}$	pk'_1
6.2	0	0.10	2	.10	4.898	6.2	0.01	0.19	2.0	.180	4.823
6.4	0	0.15	2	.15	4.889	6.4	0.03	0.29	2.0	.260	4.810
6.6	0.01	0.225	2	.215	4.867	6.6	0.08	0.42	1.995	.342	4.830
6.8	0.04	0.33	1.995	.291	4.897	6.8	0.13	0.57	1.99	.444	4.829
7.0	0.06	0.44	1.99	.384	4.893	7.0	0.20	0.74	1.985	.548	4.834
7.2	0.10	0.59	1.985	.487	4.899	7.2	0.29	0.93	1.975	.656	4.821

Data used in equations (18) and (19) :

$T_M^o = 1.921 \times 10^{-3}$ M, $T_M^o = 1.916 \times 10^{-3}$ M,

$T_L^o = 5.764 \times 10^{-3}$ M, $V^o = 52.05$ ml, $T_L^o = 9.579 \times 10^{-3}$ M, $V^o = 52.2$ ml,

N = 0.1 N, c = 2. N = 0.1 N, c = 2.

Ligand : propyl gallate						robinetinidol					
pH	v''	v'''	$\bar{n}_a$	$\bar{n}$	pk'_1	pH	v''	v'''	$\bar{n}_a$	$\bar{n}$	pk'_1
5.8	2.03	2.23	1.995	.201	4.240	6.2	2.02	2.14	2.0	.12	4.806
6.0	2.05	2.33	1.987	.284	4.282	6.4	2.04	2.21	2.0	.17	4.821
6.2	2.08	2.44	1.98	.367	4.252	6.6	2.05	2.30	1.995	.251	4.792
6.4	2.12	2.58	1.97	.474	4.241	6.8	2.075	2.40	1.99	.328	4.814
6.6	2.2	2.75	1.95	.579	4.236	7.0	2.1	2.52	1.985	.426	4.812
6.8	2.3	2.93	1.925	.681	4.210	7.2	2.15	2.67	1.975	.533	4.802

Data used in equations (18) and (19) :

$T_L^o = 1.923 \times 10^{-3}$ M, $T_I^o = 0.002$ M, $T_L^o = 0.006$ M,

$T_L^o = 7.692 \times 10^{-3}$ M, $V^o = 50$ ml, $E^o = 0.004$ M,

$E^o = 3.846 \times 10^{-3}$ M, N = 0.1 N, N = 0.1 N, c = 2.

$V^o = 52$ ml, c = 2.

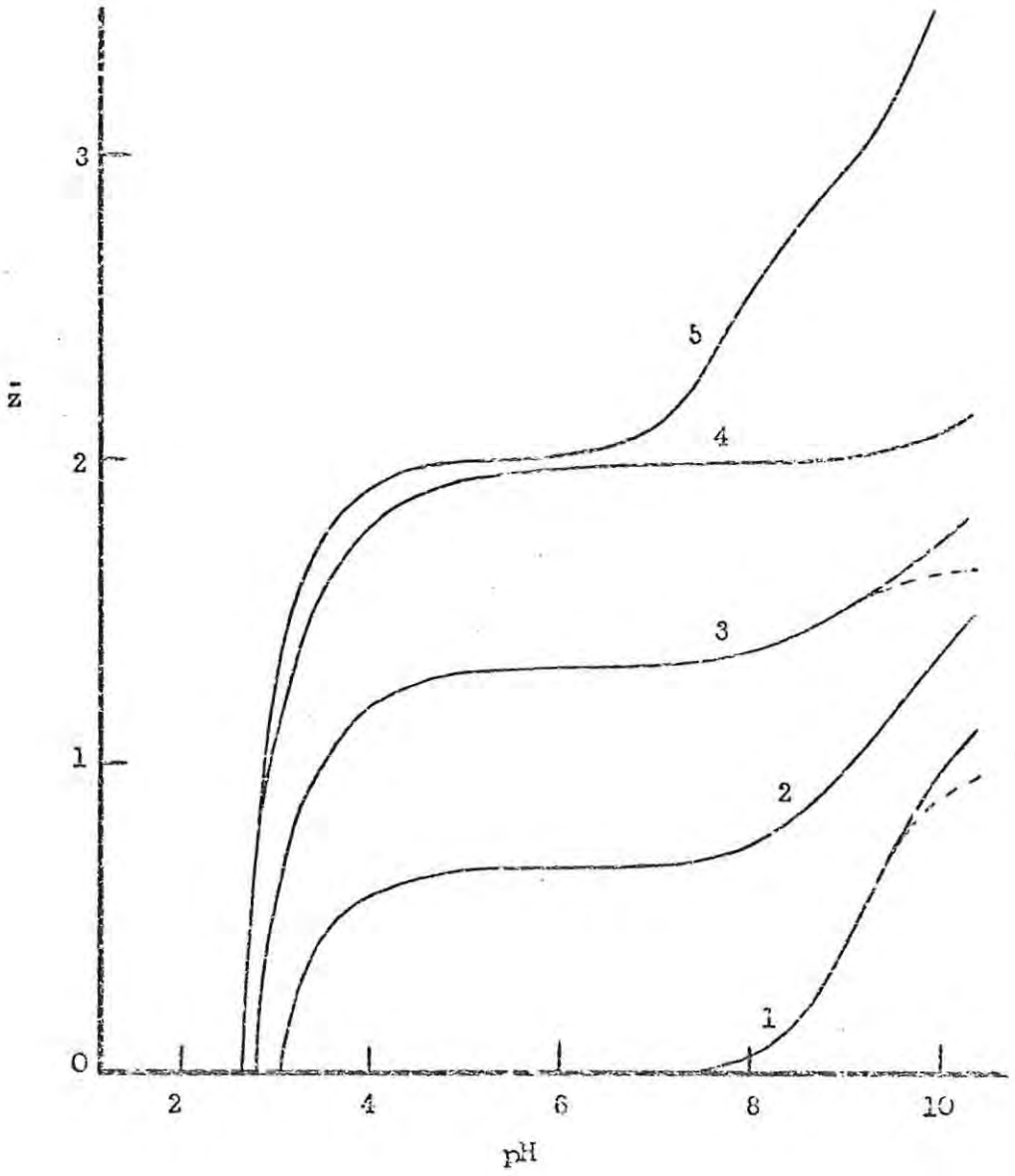


FIG. 1. Potentiometric titration curves for (1)0.002 M-GeO_2, (2)0.002 M-GeO_2 + 0.002 M-propyl gallate, (3)0.002 M-GeO_2 + 0.004 M 4-chloroacetylcatechol (4)0.002 M-GeO_2 + 0.006 M-Tiron, (5)0.002 M GeO_2 + 0.008 M-propyl gallate; N = 0.1 N-KOH, V° = 50 ml, and I = 0.1 N-KCl.

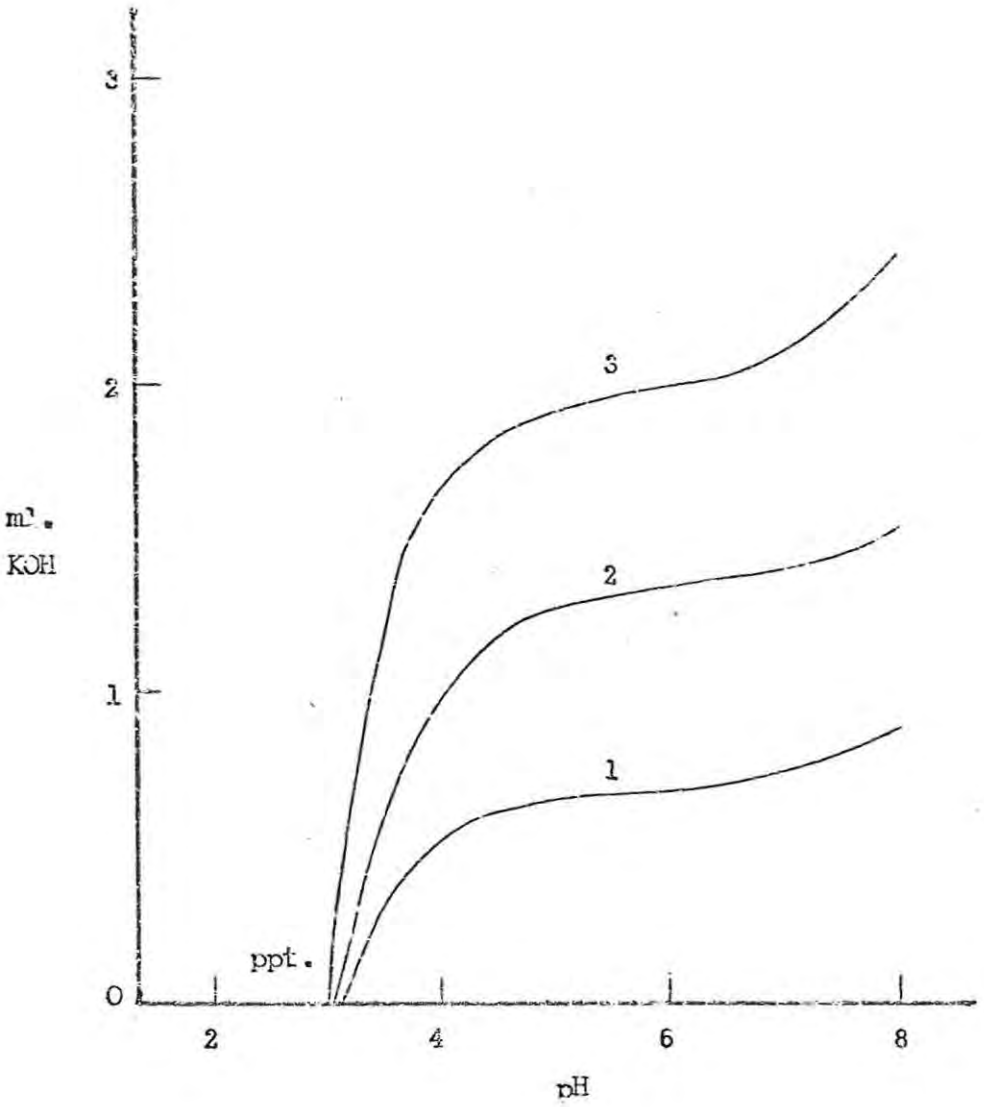


FIG. 2. Potentiometric titration curves for (1) 0.004 M GeO_2 + 0.003 M wattle tannin, (2) 0.001 M GeO_2 + 0.006 M wattle tannin, (3) 0.002 M GeO_2 + 0.024 M wattle tannin; N = 0.1 N KOH, V° = 50 ml. and I = 0.1 N KCl.

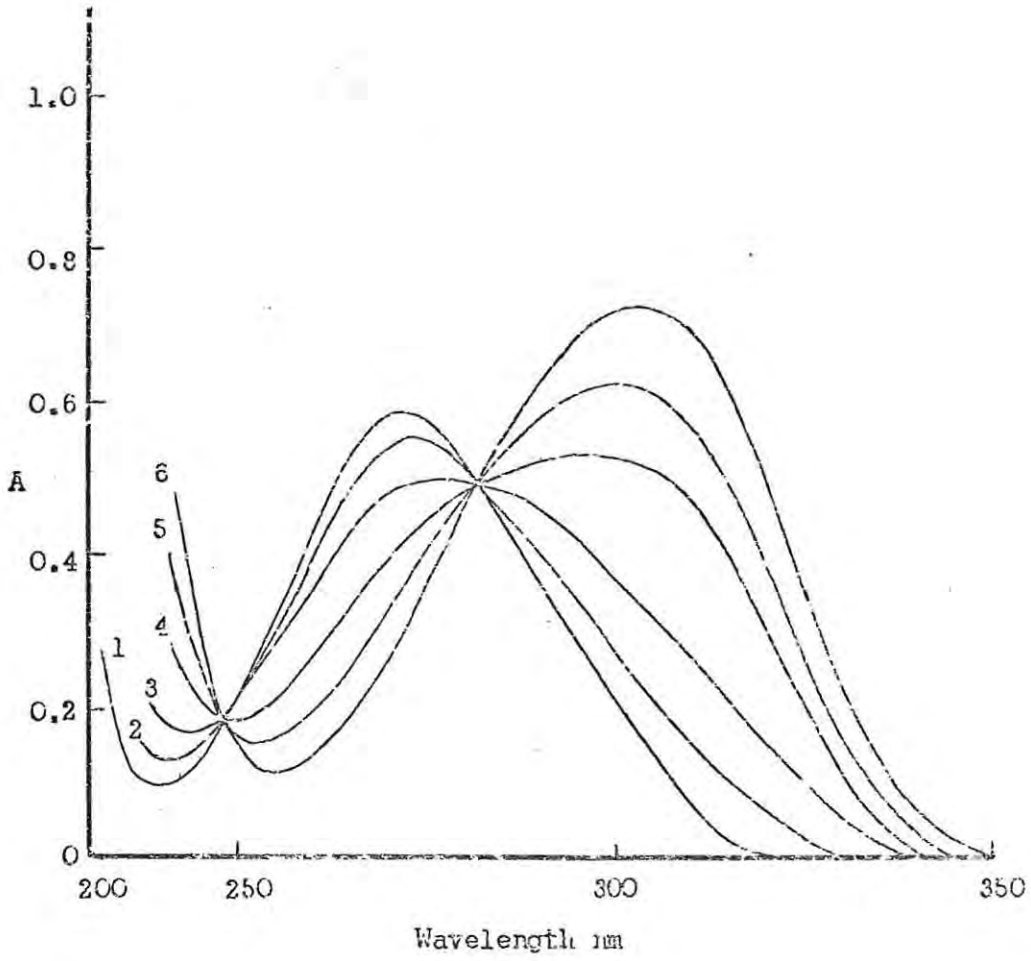


FIG. 3. Absorption spectra of the Ge(IV)-propyl gallate system at pH values : (1)3.0, (2) 4.72, (3)5.03, (4)5.65, (5)6.10, (6)7.5 - 8.5; I = 0.1, $T_M = 2 \times 10^{-5}$ M, $T_L = 6 \times 10^{-5}$ M, l = 1 cm.

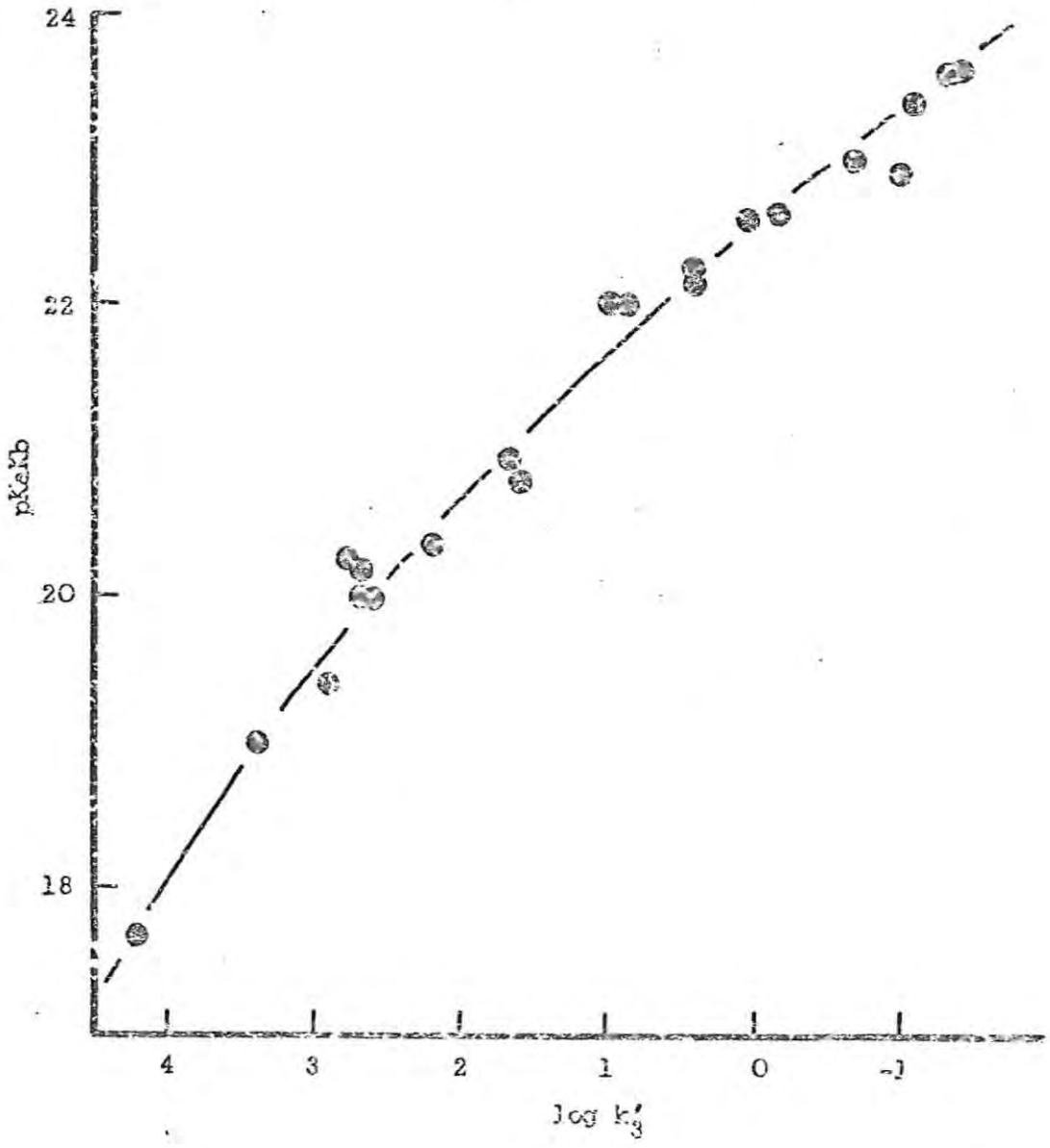


FIG. 4. Relation between the ligand dissociation constants, K_2K_b, and the equilibrium constants, k'_3, for Ce(IV) complexes of o-diphenols.

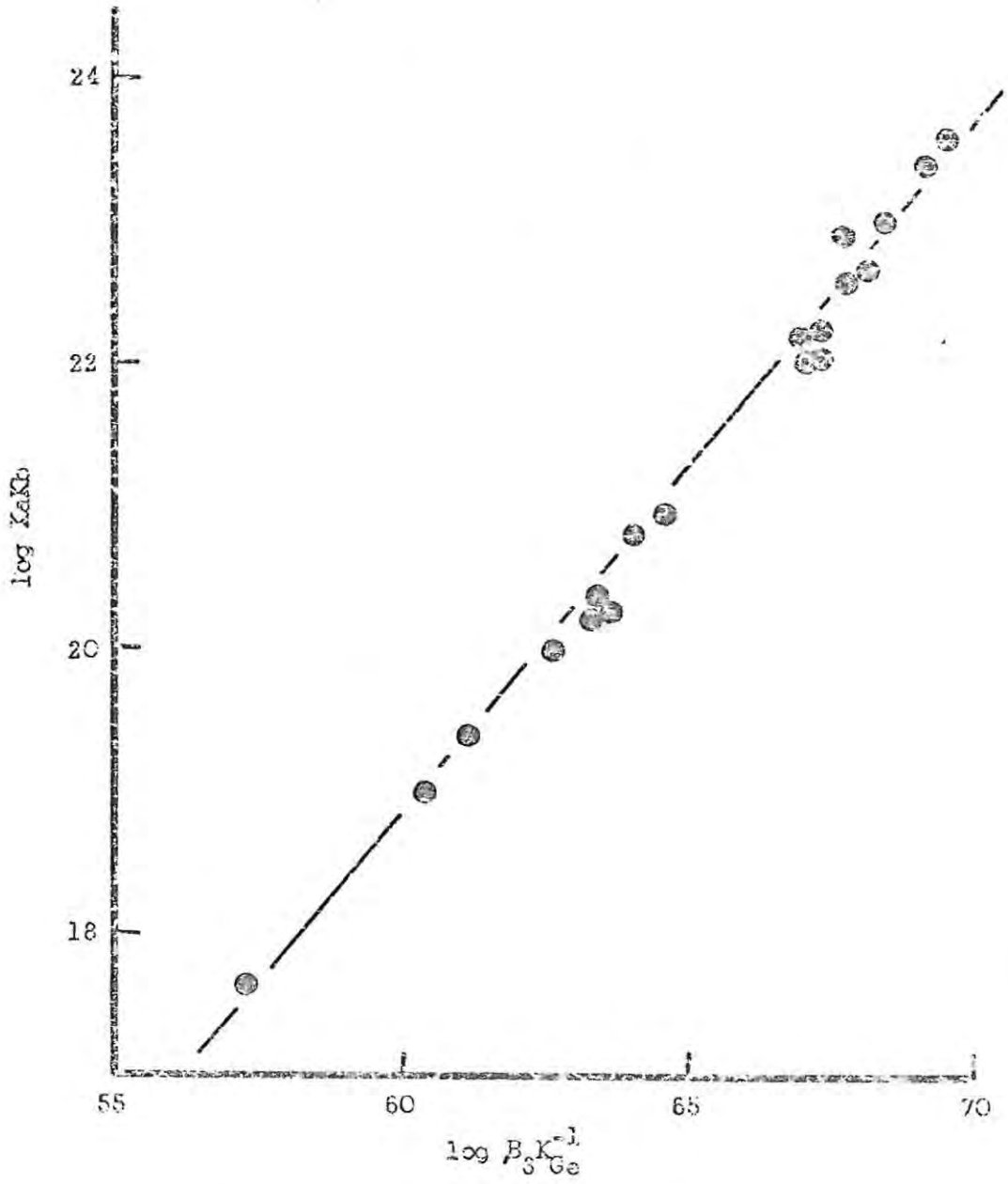


FIG. 5. Relation between the ligand association constants, KaKb, and the complex constants, $\beta_3 K_{Ge}^{-1}$, for the Ge(IV) complexes of o-diphenols.

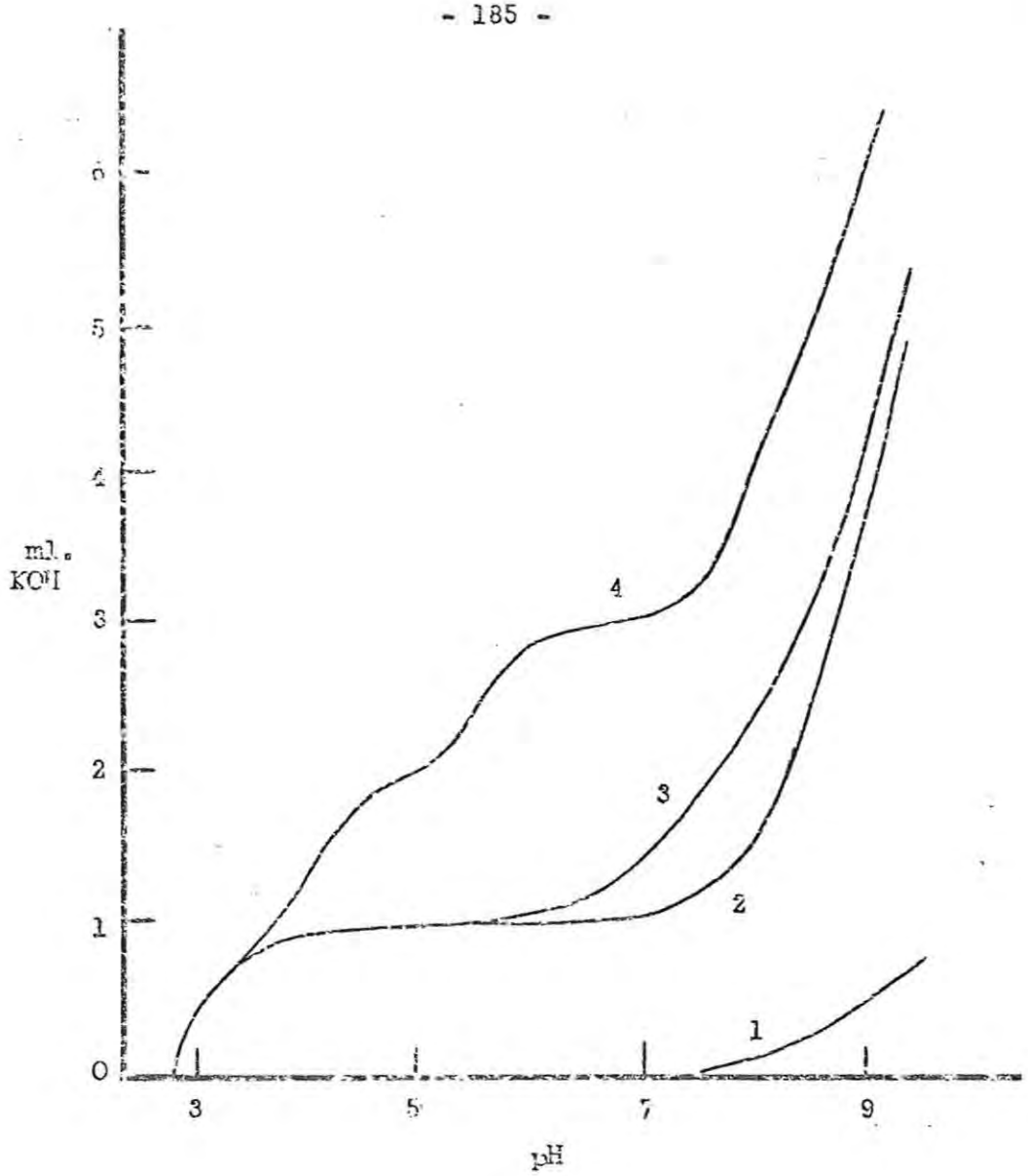


FIG. 6. Potentiometric titration curves of (1) 0.002 M boric acid, (2) 0.006 M catechin + 0.002 M HCl, (3) 0.006 M catechin + 0.002 M boric acid + 0.002 M HCl, (4) 0.006 M catechin + 0.001 M Al(III) + 0.002 M HCl; V^{o} = 50 ml., I = 0.1 N KCl and N = 0.1 N KOH.

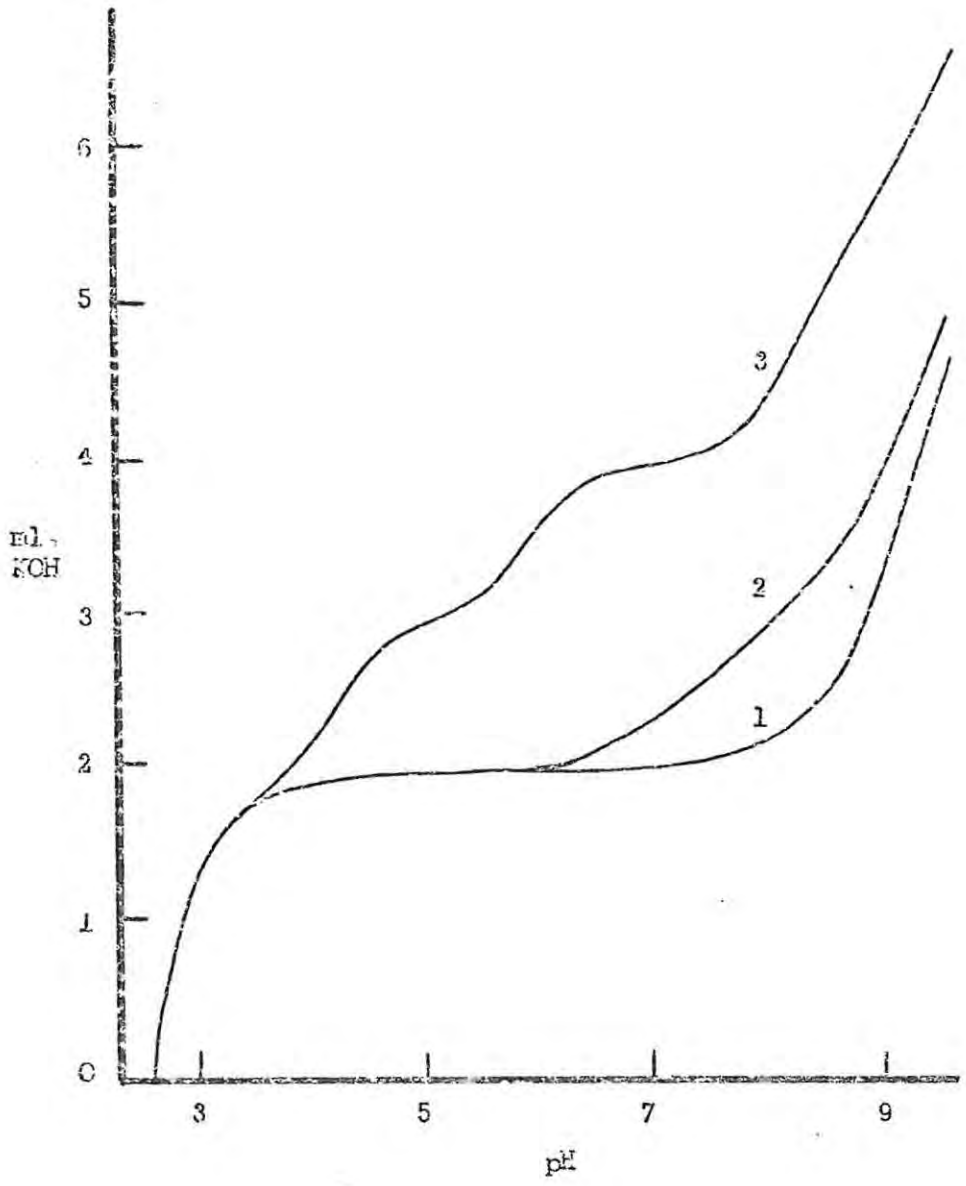


FIG. 7. Potentiometric titration curves of (1) 0.008 M 3-methoxycatechol, (2) 0.008 M 3-methoxycatechol + 0.002 M boric acid, (3) 0.008 M 3-methoxycatechol + 0.001 M Al(III); E^{o} = 0.004 N HCl, V^{o} = 50 ml., I = 0.1 N KCl and N = 0.1 N KOH.

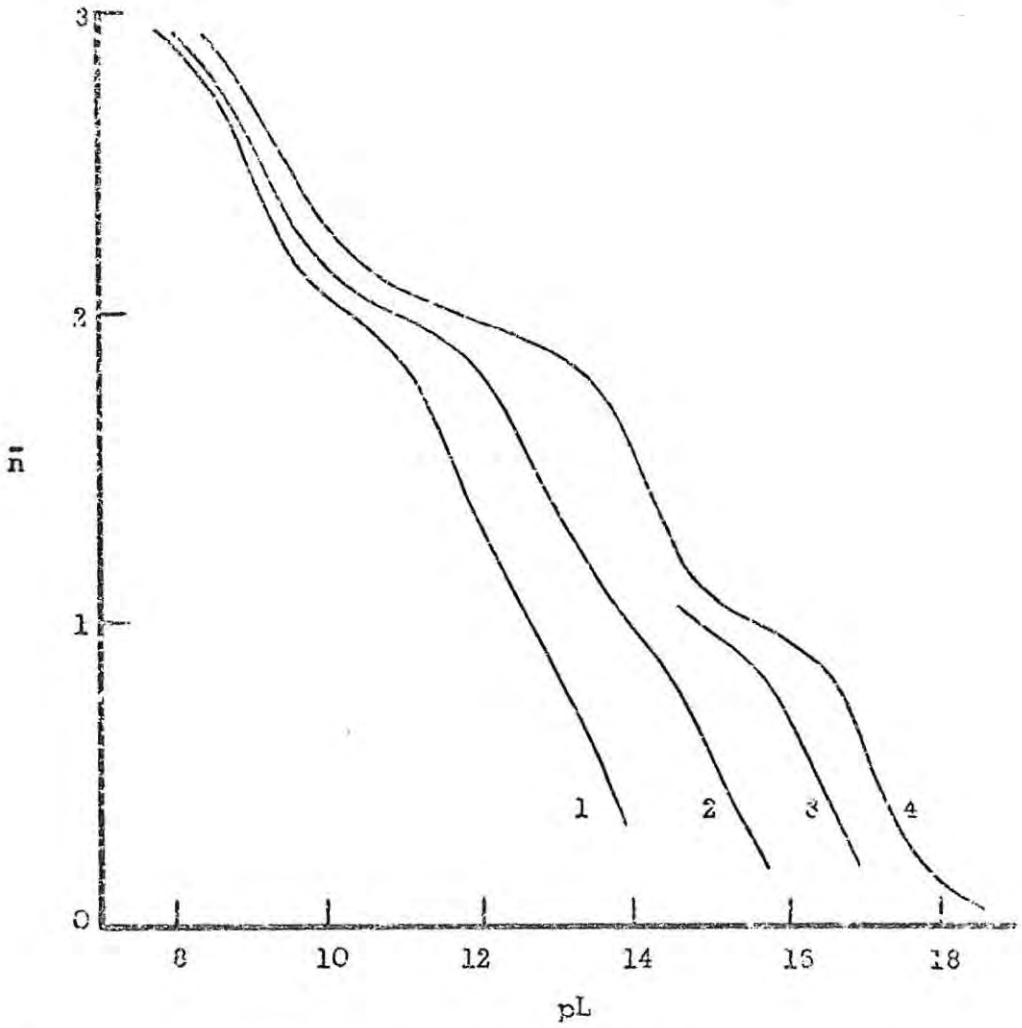


FIG. 8. Formation curves of the Al(III) complexes : (1) 4-nitrocatechol, (2) propyl gallate, (3) wattle tannin and (4) 4-methylcatechol.

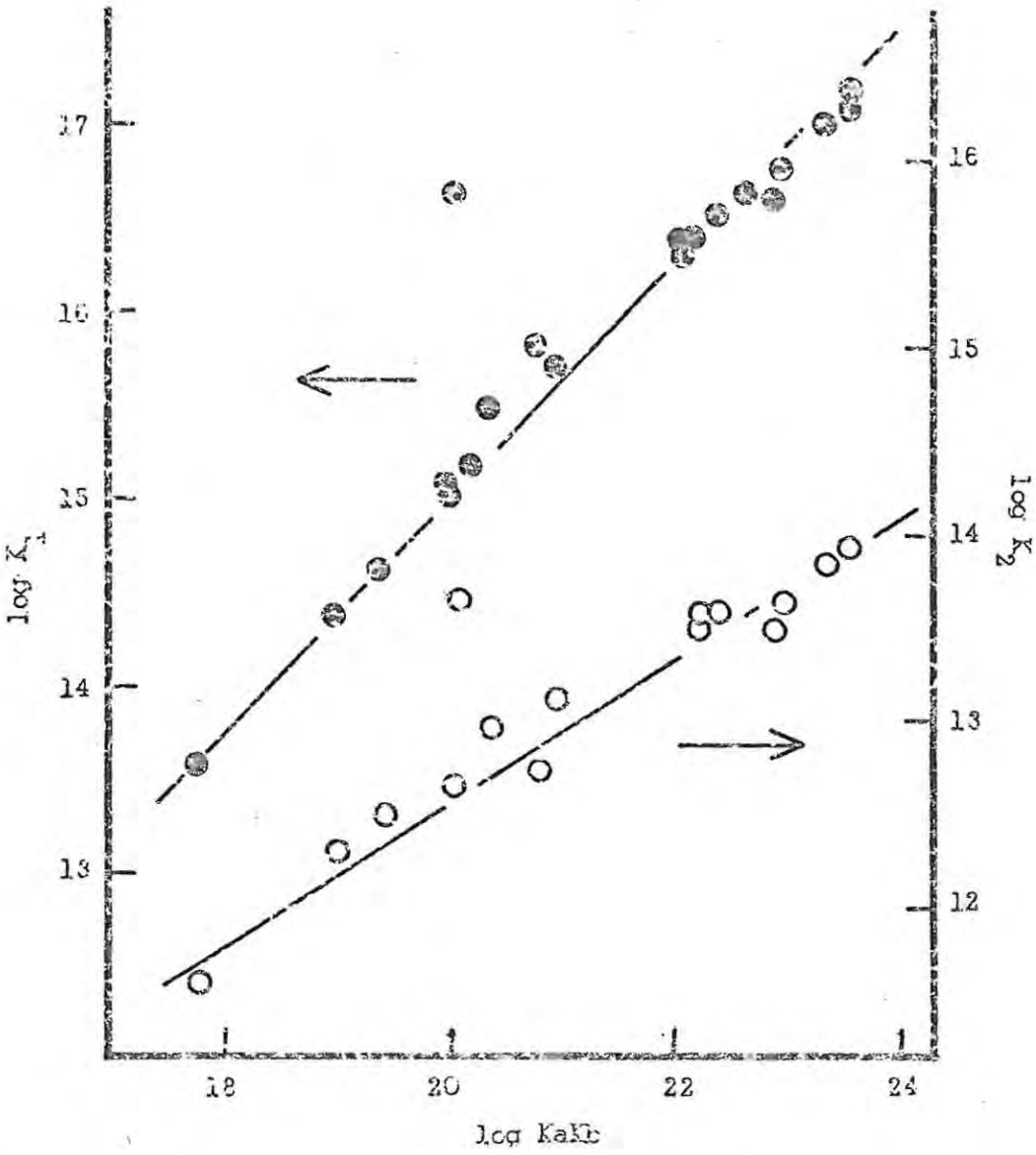


FIG. 9. Relation between stability constants, K_1 (left scale) and K_2 (right scale), of Al(III) complexes of o-diphenols and the ligand association constants, KaKb.

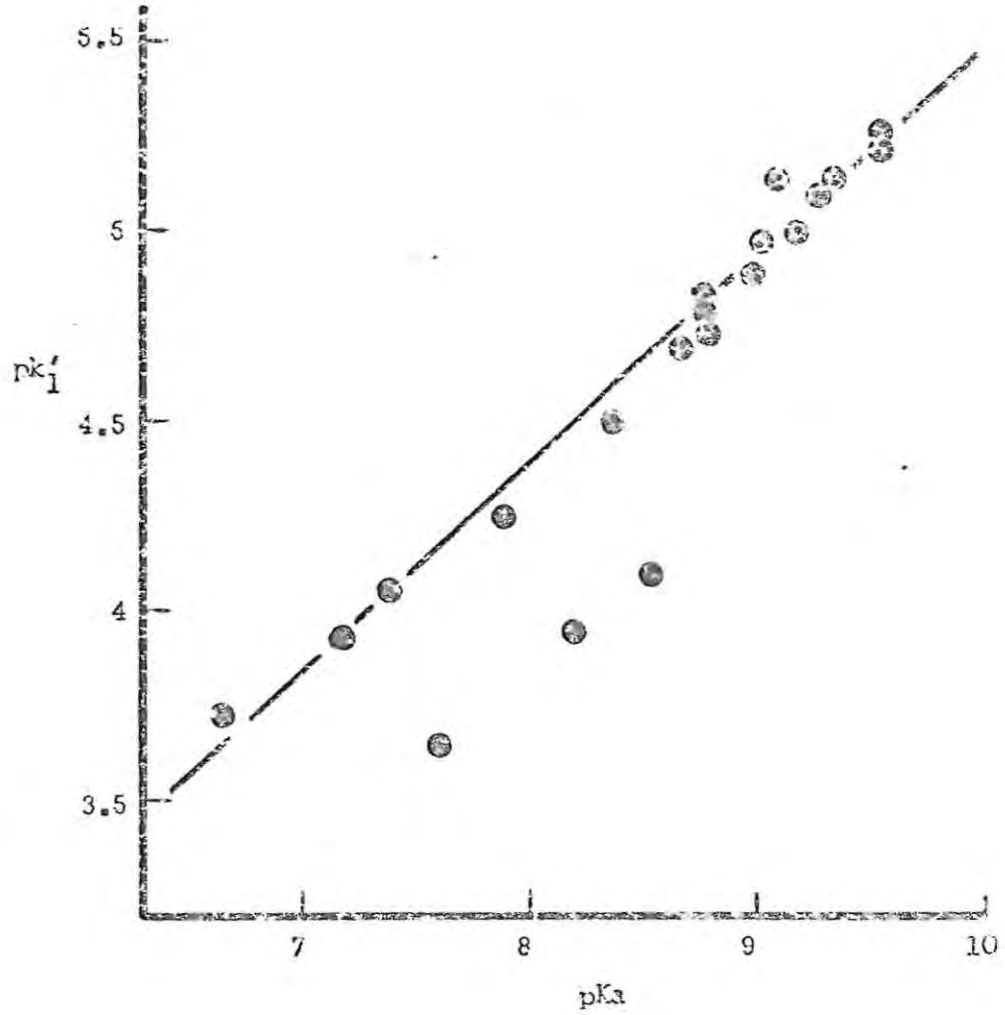


FIG. 10. Relation between equilibrium constants, k'_1, for boric acid complexes of o-diphenols and the ligand dissociation constants, Ka.

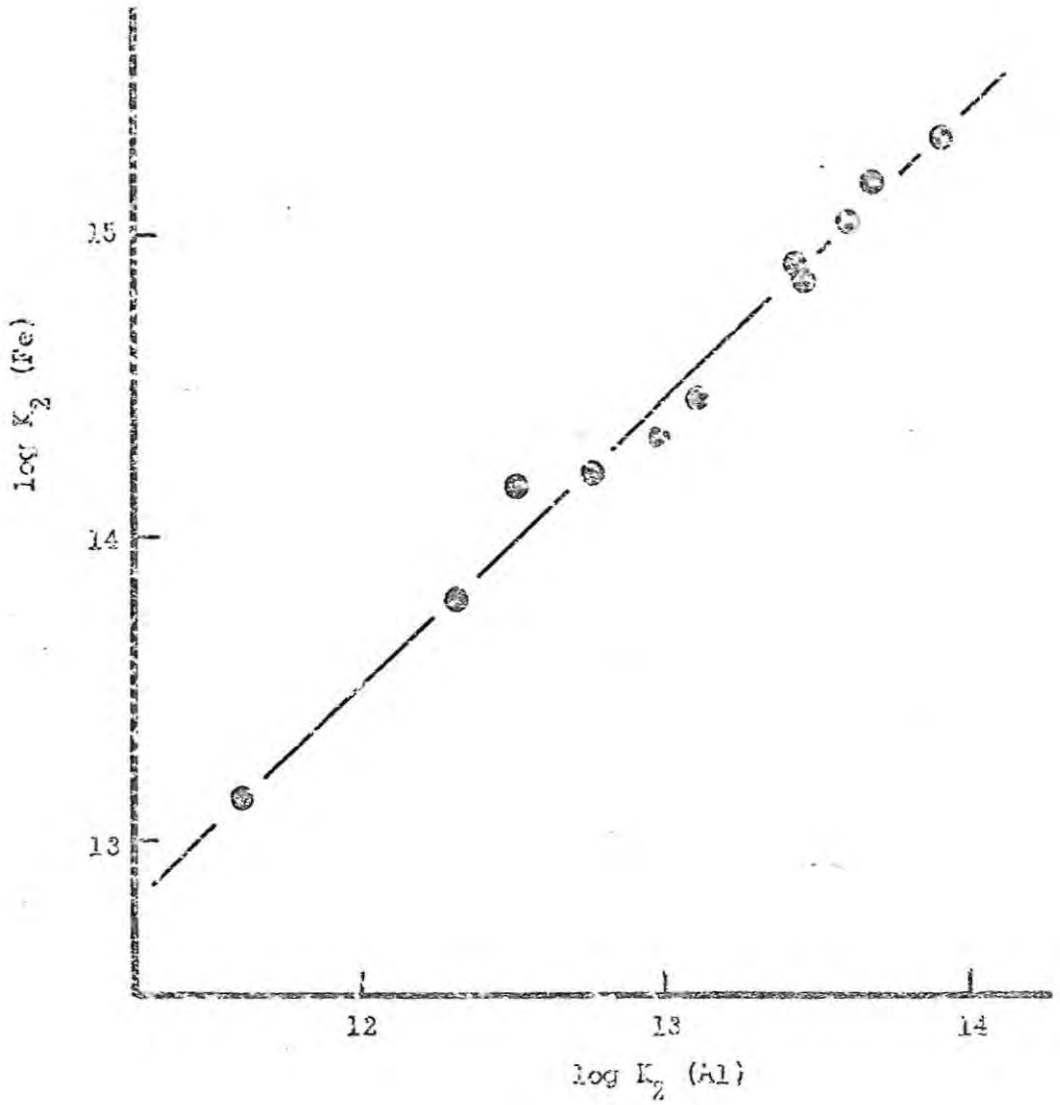


FIG. 11. Relation between the stability constants, K_2, for the Fe(III) and Al(III) complexes of p-diphenols.

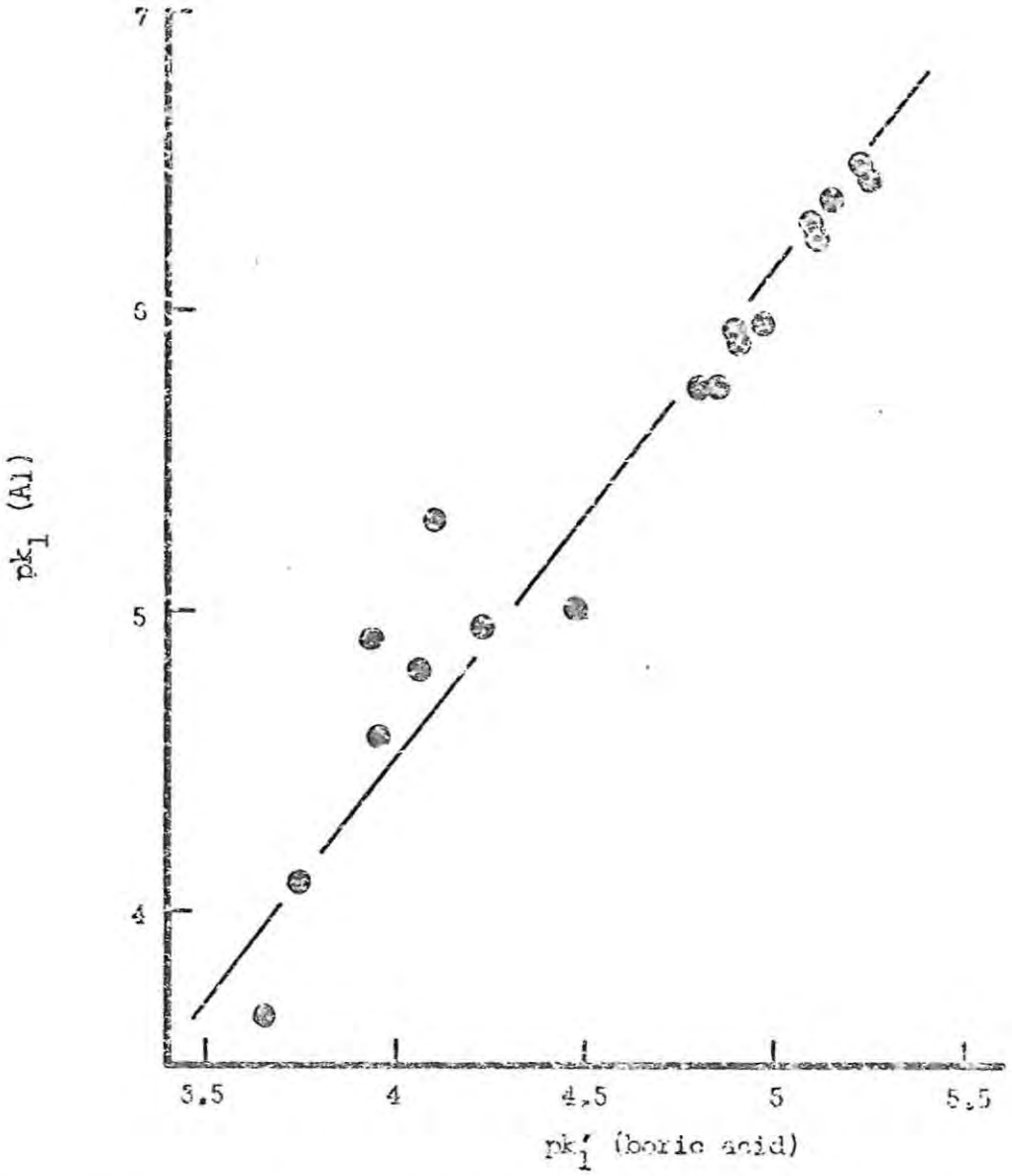


FIG. 12. Relation between the equilibrium constants, k_1, for the Al(III) complexes and k_1', for the boric acid complexes of o-dihydroxyls.

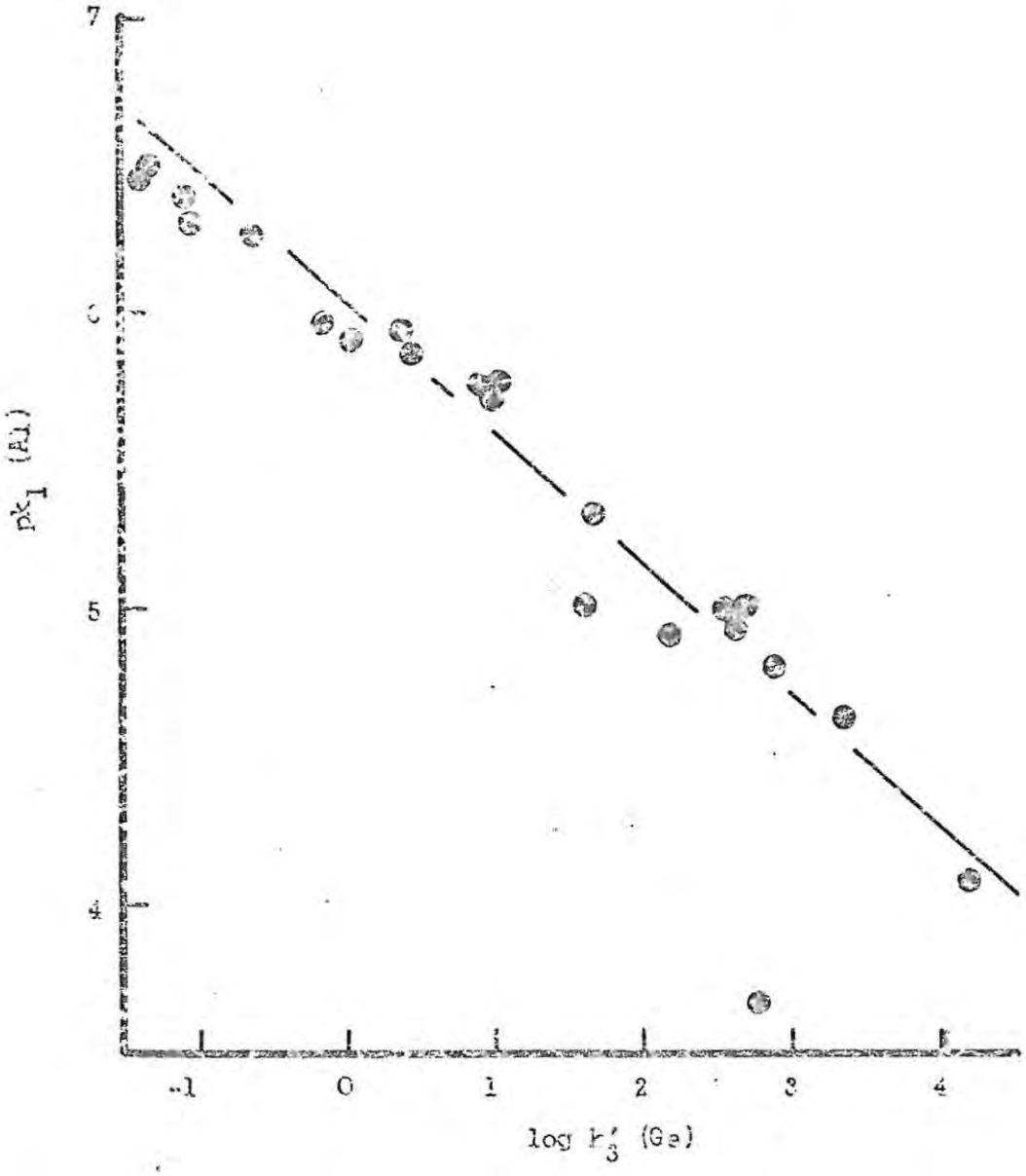


FIG. 13. Relation between equilibrium constants, k_1, for Al(III) complexes and, k'_3, for Ge(IV) complexes of o-dihenols.

D. DIVALENT METAL COMPLEXES OF o-DIPHENOLS.

The o-diphenol complexes investigated in this section are those of the divalent first transition metals, cobalt(II), nickel(II), copper(II), and zinc(II), the alkaline-earth metals, magnesium(II) and calcium(II) and two other divalent metals, lead(II) and vanadyl(IV).

1. Cobalt(II), nickel(II), copper(II), and zinc(II) complexes of o-diphenols.

Potentiometric and spectrophotometric methods were used to investigate the Co(II), Ni(II), Cu(II), and Zn(II) complexes.

(a) Potentiometric investigation :

The o-dihydroxybenzene and the 1,2,3-trihydroxybenzene complexes are dealt with separately, because different complex species are formed.

(i) o-Dihydroxybenzene complexes : It has been established[50-55] that Co(II), Ni(II), Cu(II) and Zn(II) ions and o-dihydroxybenzene derivatives form successive chelates in aqueous media according to the reactions :

$$M^{2+} + H_2L \rightleftharpoons ML + 2H^+ \qquad (1)$$

$$ML + H_2L \rightleftharpoons ML_2^{2-} + 2H^+ \qquad (2)$$

Potentiometric titration curves of the above metal ions and excess of ligand are illustrated in Fig. 1. For the Cu(II) complex the inflections observed at $\bar{z} = 2$ and 4 correspond to the complete formation of the ML and ML_2 species, in accordance with reactions (1) and (2). The minimum molar ratios of metal to ligand required to give the inflections at $\bar{z} = 2$ and 4 were 1 : 1 and 1 : 2, respectively. This corresponds to $\bar{n} = 1$ and 2

(cf. reactions (1) and (2)).

Titration curves for the copper(II) complexes with 1 : 1 molar ratios gave additional inflections at $\bar{z} = 3$. In addition, precipitates formed after the complete formation of the first complex species, ML_1. The formation of a precipitate suggests that the ML_2 species is formed with dissociation of the ML species to provide the extra ligand and precipitation of $Cu(OH)_2$, thus :

$$ML \rightleftharpoons \tfrac{1}{2} ML_2^{2-} + \tfrac{1}{2} M(OH)_2 + H^+ \qquad (3)$$

A similar reaction was found for the Fe(III) complexes of o-dihydroxybenzene derivatives (Section B) and has been shown to occur in a number of copper(II) complexes of o-diphenols.[232] Equilibrium constants for reaction (3) could not be determined, because of non-equilibria as a result of the precipitate.

Titration curves for the Co(II), Ni(II) and Zn(II) complexes of o-dihydroxybenzene derivatives (Fig. 1) gave no distinct inflections, because of the overlap of complexation and ligand dissociation. However, the stepwise formation of the ML and ML_2 species (reactions (1) and (2)) was established from the formation curves ($\bar{n}$ vs. pL plots) for these complexes, cf. below. In titrations with 1 : 1 molar ratios of metal ion and ligand, precipitates formed as found for the Cu(II) complexes. No precipitates formed if 1 : 2 molar ratios of metal to ligand were used. This suggests that reaction (3) also occurs for the Co(II), Ni(II) and Zn(II) complexes.

Values of $\bar{n}$ and pL for the Co(II), Ni(II), Cu(II) and Zn(II) complexes of o-dihydroxybenzene derivatives were calculated from the potentiometric

data with the aid of equations (14) and (17) Section B, and equation (11) Section C. Examples of the calculations and the formation curves ($\bar{n}$ vs. pL plots) are given in Tables 8 and 9 and Fig. 2, respectively. The inflections observed at $\bar{n} = 1$ and 2 (Fig. 2) for all the metal complexes are in agreement with the formation of the complex species, ML and ML_2. The formation of the higher Co(II) and Ni(II) complex species was evident from the formation curves (Fig. 2) and have been shown to be ML_3.[51,53,54]

Approximate values of the stability constants, K_1 and K_2, for reactions (4) and (5), respectively :

$$M^{2+} + L^{2-} \rightleftharpoons ML \qquad (4)$$

$$ML + L^{2-} \rightleftharpoons ML_2^{2-} \qquad (5)$$

were determined from the formation curves by interpolation at half-$\bar{n}$ values. Generally, it was found that $10^4 > K_1/K_2 > 10^{2.5}$ for the Cu(II) and Ni(II) complexes and that $K_1/K_2 < 10^{2.5}$ for the Co(II) and Zn(II) complexes. Therefore the method of least squares[90] was used to obtain accurate values of K_1 and K_2 for the last two metal complexes. Stability constants for the Cu(II) and Ni(II) complexes were determined as well, by the least squares method, since this enabled the use of all the experimental data and not only one point, as in the half-integral method. Examples of the results obtained using equation (13) Section C, by the least squares method, are given in Tables 8 and 9. The stability constants, K_3, for the Co(II) and Ni(II) complexes were not determined, because of the limited experimental data above $\bar{n} = 2$. The ML_3 species only form at very high pH and do not overlap with the formation of the ML_2 species.

Values of K_1, determined with the aid of equation (12) Section C,

were found to increase in the range $\bar{n} = 0.15$ to $\bar{n} = 0$. This indicates the formation of the MHL^+ species, as observed previously for the pyrocatechol system.[53] In order to avoid interference from this species, the above least squares calculations employed $\bar{n}$ values greater than 0.15. The equilibrium constants for the formation of the protonated species were not determined, because of their narrow formation range.

The stability constants, K_1 and K_2, for the Co(II), Ni(II), Cu(II) and Zn(II) complexes of o-dihydroxybenzene derivatives are listed in Table 1. Values quoted for the protocatechuic acid complex are related to the carboxyl substituent in the ionised form, because the complexes only form after complete ionisation of this substituent. Stability constants, K_2, for the Zn(II), Ni(II) and Co(II) complexes of 4-tert.-butylcatechol, the Ni(II) complex of 4-methylcatechol and the Ni(II) and Co(II) complexes of 3-methoxycatechol could not be determined because of precipitation at $\bar{n}$ values greater than 0.8.

From Table 1, the stability order (K_1) for a particular ligand is $Co < Ni < Cu > Zn$ and is in agreement with that of Irvine and Williams.[56] The above order has been established previously for a number of o-diphenol complexes.[51, 53,54] From Table 1, it is obvious that it is quite general for all the o-dihydroxybenzene complexes investigated, including the wattle tannin monomer, catechin. The above stability order has been related to a number of factors *viz*. ionisation potential of the metal[56,231] - the higher the ionisation potential, the greater the complex stability; ionic radius of the metal[56] - the smaller the radius, the greater the complex stability and crystal field stabilisation[233] with

TABLE 1.

Stability constants, K_1 and K_2, for the Cu(II), Zn(II), Ni(II) and Co(II) complexes of o- diphenols.

Ligand	Cu(II)		Zn(II)		Ni(II)		Co(II)	
	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2
4-methylcatechol	14.71	11.93	10.71	8.66	9.85	-	9.60	6.65
4-tert.-butyl-catechol	14.78	12.00	10.8	-	9.9	-	9.5	-
pyrocatechol	14.60	11.71	10.45	8.46	9.53	6.20	9.31	6.60
3-methoxycatechol	14.38	11.48	10.55	8.10	9.6	-	9.3	-
catechin	13.99	11.30	10.12	8.13	9.37	5.90	9.00	6.45
protocatechuic acid	13.70	11.02	10.10	7.89	9.44	5.85	9.08	6.30
2,3-dihydroxy-naphthalene	13.42	10.87	9.62	7.90	9.02	5.98	8.59	6.20
3,4-dihydroxybenzenesulfonate	13.46	10.65	9.60	7.56	9.05	5.75	8.65	6.18
DHNS	13.30	10.46	9.60	7.71	9.12	5.98	8.60	6.10
Tiron	12.62	10.22	10.30	8.53	9.90	7.12	9.41	6.91
4-chloroacetyl-catechol	12.41	10.05	9.06	7.50	8.57	5.90	8.12	6.04
protocatechuic aldehyde	11.61	9.32	8.91	7.33	8.45	5.76	8.04	5.87
4-nitrocatechol	14.38	11.56	8.26	6.85	7.90	5.38	7.42	5.50

Jahn-Teller distortion[234,235] to explain the higher stability of Cu(II) complexes. Crystal field stabilisations have generally[233] been used to explain the above stability order for amine complexes. Increased 10Dq produced by these ligands, relative to water, results in those metal complexes with the highest crystal field stabilisation energy to be the most stable as well. However, this cannot be applied to the o-dihydroxybenzene complexes, since it was found in the spectrophotometric investigation (p. 205) that o-diphenolato ligands occur in the same position as H_2O in the spectrochemical series.

The stability order Zn > Ni (Table 1) for the o- dihydroxybenzene

complexes is in disagreement with that of Mellor and Maley[57,236] who established the order Zn < Co < Ni < Cu for the divalent metal complexes of salicylaldehyde and ethylenediamine. However, it has been shown that the stability of Zn(II) complexes relative to those of Ni(II) and Co(II) is dependent on the nature of the ligand.[56] A similar stability order Zn > Ni has been found for a number of oxygen-type ligands capable of forming 5-membered chelates viz. tropolone derivatives,[217,237] kojic acid[58,220] and 2-hydroxynaphthoquinones.[58]

From Table 1, the stability order for the constants, K_2, (with the exception of those for Tiron) is Ni < Co < Cu > Zn. The order Ni < Co is in disagreement with that of Irvine and Williams.[56] However, for the Tiron complexes the stability order is the same as that for the constants, K_1, viz. Co < Ni < Cu > Zn. Although published[51,63] values of K_2 for a number of o-dihydroxybenzene complexes are in agreement with the order Ni < Co < Cu > Zn, no comment was made in the discussion concerning the anomalous stability order, Ni < Co. A possible explanation of the higher stabilities of the Co(II) complexes, ML_2, (except for Tiron), relative to those of Ni(II) will be given in the spectrophotometric investigation (p. 210).

The stability constants, K_1 and K_2, for the Co(II), Ni(II), Cu(II) and Zn(II) complexes of o-dihydroxybenzene derivatives were correlated with the ligand association constants, KaKb, and the results are shown in Figs. 3 and 4. The direct linear relationships are similar to those obtained previously (Sections B and C) and illustrate that the general relationship between ligand acidity and complex stability holds for the

above complexes. The position of the points for Tiron all deviate from the linear (Figs. 3 and 4), as found previously (Sections B and C). Various relationships have been found between the stabilities of the above metal complexes and the ligand acidities.[51,54,60,63] The reverse relationship[51] and the lack of correlation,[60] have been shown[34] to be due to erroneous values of the ligand dissociation constants. For this reason the stability constants obtained in the present investigation cannot be compared with the published values. Direct relationships have also been shown to exist between the stability constants and the ligand constants, Ka[63] and Kb[54]. However, since both hydroxyl groups of the o-dihydroxybenzene ligands are involved in complex formation, the combined ligand constants, KaKb, should be used rather than individual constants.

The slopes of the straight lines obtained in the correlations between the stability constants, K_1 and K_2, and the ligand association constants, KaKb, (Figs. 3 and 4) are higher for the K_1 plots relative to those of K_2. This indicates that the substituents affect the stabilities of the first species, ML, to a larger extent than those of the second species, ML_2. This is similar to that found for the Fe(III) and Al(III) complexes (Sections B and C, respectively).

From Figs. 3 and 4, the slopes of the straight lines for the Cu(II) complexes may be observed to be higher than for those of the Co(II), Ni(II) and Zn(II) complexes. A possible explanation of the greater effect of the substituents on the stabilities of the Cu(II) complexes will be given in the spectrophotometric investigation (p. 214).

The stability constants, K_1, of the Zn(II) and Ni(II) complexes were

correlated, as suggested[216] and the result is illustrated in Fig. 5. The linear relationship with slope of approximately unity is similar to that obtained previously.[54] The advantage of this type of correlation is shown by the fact that the point for Tiron falls on the straight line in Fig. 5, whereas in correlations with the ligand acidity (Figs. 3 and 4) its position is anomalous. This indicates that the influences (cf. p. 85) which result in the deviation of Tiron in the ligand acidity correlations, have similar influences on the stabilities of the Tiron complexes.

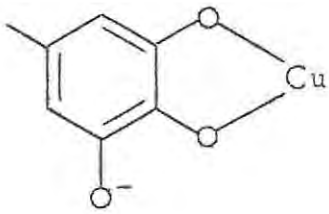
The fact that the points for the wattle tannin monomer, catechin, all correspond to the linear relationships observed in Figs. 3 - 5 indicates that the metal ions, Co(II), Ni(II), Cu(II) and Zn(II) react normally with catechin.

(ii)1,2,3-Trihydroxybenzene complexes : Results obtained from the potentiometric titrations for the Co(II), Ni(II), Cu(II) and Zn(II) complexes of 1,2,3-trihydroxybenzene derivatives were all complicated by the formation of precipitates during the course of the titration. That the precipitates were actually complex species and not metal hydroxides, was deduced from the lower pH values of solutions containing metal ions and ligand, relative to those containing these two components separately. Attempts to isolate pure samples of the precipitates for analysis failed, because of the extreme susceptibility of the 1,2,3-trihydroxybenzene ligands to oxidation.

A satisfactory interpretation of the potentiometric results was only possible for the Cu(II) complexes, because the results obtained for the Co(II), Ni(II) and Zn(II) complexes were even further complicated by the

overlap of complex formation and ligand dissociation.

Potentiometric titration curves for the Cu(II)-propyl gallate system with various molar ratios are shown in Fig. 6. In the titration of Cu(II) ions and ligand in a 1 : 1 molar ratio, the initial precipitated complex dissolved at $\bar{z}$ values greater than 2.9. This is the converse of that observed for the Cu(II) complexes of o-dihydroxybenzene derivatives. The extra hydroxyl group of the 1,2,3-trihydroxybenzene derivatives must therefore be responsible for the differences observed. The sharp inflection at $\bar{z} = 3$ in the 1 : 1 titration curve (Fig. 6) was proposed to correspond to the complete formation of the MR^- species (electrophoresis established that this species is anionic) thus :

$$Cu^{2+} + H_3R \rightleftharpoons$$  $$+ 3\,H^+ \qquad (6)$$

A similar reaction was proposed for the Fe(III) complex (Section B). The hydroxo species, $CuRH(OH)^-$, is another possible formula which would explain the inflection at $\bar{z} = 3$. However, this formula was ruled out, because in the 1 : 1 titration, no evidence was found for the ionisation of the third, undissociated hydroxyl group at high pH.

In titrations with excess of propyl gallate further complexation takes place, as is evident from the titration curves (Fig. 6). The formation of the complex species, $M(RH)_2^{2-}$, was deduced from the application of equation (14) (Section B) to the potentiometric data; consistent

values of $\bar{n} = 2$ were obtained at high pH. The reaction :

$$CuR^{-} + H_3R \rightleftharpoons Cu(RH)_2^{2-} + H^{+} \qquad (7)$$

satisfies the experimental results. The formation of this species was confirmed by the inflection at $\bar{z} = 4$ in the titration with a 1 : 2 molar ratio (metal to ligand) as shown in Fig. 6. The final species is thus similar to those of the o-dihydroxybenzene complexes, with the third hydroxyl group undissociated.

Similar results were obtained for the Cu(II)-pyrogallol system. Unfortunately, robinetinidol, dihydrorobinetin and gallic acid formed precipitates with Cu(II) ions which did not dissolve at higher pH, therefore an interpretation of the results was not possible.

Equilibrium constants for reaction (6) could not be determined because of the presence of a precipitate. Similarly the equilibrium constants for reaction (7) could not be determined from the potentiometric data with excess of ligand because a precipitated complex species was still present during the formation of the $Cu(RH)_2$ species as shown in Fig. 6.

The wattle tannin (sulfited and unsulfited) complexes of Co(II), Ni(II), Cu(II) and Zn(II) all formed precipitates in aqueous media ($I = 0.1$) as found for the 1,2,3-trihydroxybenzene complexes. The formation of precipitates was unaffected by the ionic strength of the solution since even in solutions of low ionic strength precipitation occurred. Although precipitation occurs, the order of complex stability can nevertheless be determined from the pH values at incipient precipitation. The lower the pH, the more stable is the complex.[238] The approximate pH

vlues at precipitation for the wattle tannin complexes are given in Table 2. These values established the stability order, Co < Ni < Cu > Zn, which is the same as that obtained for the o-dihydroxybenzene complexes and illustrate that the stabilities of the wattle tannin complexes are also in agreement with the order of Irvine and Williams.[56]

TABLE 2.

pH Values at incipient precipitation of metal-wattle tannin complexes.

Metal ion	Vanadyl(IV)	Cu(II)	Pb(II)	Zn(II)	Ni(II)	Co(II)	Mg(II)	Ca(II)
Incipient pH	3.4	4.2	4.3	6.1	6.4	6.5	8.8	9.2

($T_M^o = 0.001$ M, $T_L^o = 0.02$ M, $I = 0.1$).

(b) Spectrophotometric investigation :

The colours of the Co(II), Ni(II) and Cu(II) complexes of o-diphenols are generally pink, green and yellow-green, respectively. Transition metal complexes owe their colour to absorption bands in the visible region of the spectrum due to d-d transitions of the metal.

The spectrophotometric investigation of all the ML_1 complex species was not possible, because precipitates formed under the conditions required to obtain reasonable spectra, viz. high concentrations of metal ions and ligand. The close proximity of the strong phenolic absorption bands in the ultraviolet and visible region of the spectrum, prevented the detection of the high energy absorption bands of the metal complexes. Since large quantities of ligand were required in the investigation of the Co(II) and Ni(II) complexes, those phenols available in limited supply viz. the flavanoid monomers were not studied.

(i) Nickel(II) complexes : The light green colour of the Ni(II) complexes of o-diphenols is characteristic of octahedral nickel(II) complexes with ligands close to water in the spectrochemical series.[239] The electronic spectra shown in Fig. 7 for these complexes are similar to published spectra of the pyrocatechol and Tiron complexes.[23,64] Spectral data of the Ni(II) complexes are given in Table 3. Three absorption maxima were observed in the region of 8500, 14,000 and 25,000 cm^{-1}, corresponding to the spectra of typical octahedral Ni(II) complexes.[240] The absorption bands are due to the respective spin-allowed transitions, $^3A_{2g} \longrightarrow {}^3T_{2g}$, $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$.[240]

NiL_2 Complex species of pyrocatechol and Tiron have been isolated and were shown[23] to have octahedral symmetry with associated water molecules making up the octahedral co-ordination. The similarity between the spectra of the NiL and NiL_2 species (Table 3) indicates that the former species also has octahedral symmetry. Bis(pyrocatecholato)nickelate(II) has been isolated without associated water molecules.[24] This complex was shown[24] to be square planar on the basis of its diamagnetic character and its visible spectrum in a non-polar solvent. However, in a polar solvent (eg. water) this complex attains octahedral symmetry as shown by the spectral data in Table 3.

If the wave number of band ν_1 is taken as a measure of 10Dq (the transition $^3A_{2g} \longrightarrow {}^3T_{1g}$ of Ni(II) complexes (d^8) is mainly an electronic transition of $t_{2g}^6 e_g^2 \longrightarrow t_{2g}^5 e_g^3$)[241] then from Table 3 the similarity between the wave numbers of maximum absorption (ν_1) of hexa-aquonickel(II) ion and o-diphenol complexes indicates that the 10Dq values are also

TABLE 3.

Spectral data for Ni(II) complexes of o-diphenols.

Complex species	Ligand	$^3A_{2g} \rightarrow {}^3T_{2g}$ ν_1(kK)	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$ ν_2(kK)	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$ ν_3(kK)
NiL_1	Tiron	8.55(5.5)[a]	14.3(5.6)	(25.6)[b]
	DHNS	8.5 (5.3)	14.3(5.6)	(25.6)
	protocatechuic aldehyde	8.55(6.0)	14.5(5.9)	d
NiL_2	4-methylcatechol	8.5 (4.6)	14.2(6.5)	(25.0)
	pyrocatechol	8.55(4.0)	14.3(6.0)	(25.0)
	DHNS	8.55(6.9)	14.5(7.9)	d
	Tiron	8.6 (6.3)	14.4(7.5)	d
	protocatechuic aldehyde	8.55(7.1)	14.5(8.0)	d
	4-nitrocatechol	8.55(7.5)	d	d
$[Ni(H_2O)_6]^{2+}$		8.5	13.8	25.3[c]

[a] Extinction coefficients,

[b] Wave numbers in parenthesis refer to shoulders,

[c] References 267 and 268,

[d] Obscured by phenolic absorption.

similar. Therefore, applying the average environment rule,[242] the o-diphenolato ligands are placed close to water in the centre of the spectrochemical series, similar to the related oxalate ligand.[243] The close proximity of water and the o-diphenolato ligands in the spectrochemical series is the reason for band ν_1 remaining relatively unchanged on successive formation of the Ni(II) complexes of o- diphenols by replacement of the bound water molecules (Table 3).

From Table 3, a change of the phenolic substituent is seen to have little effect on the position of the absorption bands, indicating that the electronic influences of the substituents are not sufficiently

large to affect the energy levels of the metal ion.

(ii) Cobalt(II) complexes : The pink colour of the Co(II) complexes of o-diphenols is due to an absorption band in the blue region of the spectrum (Fig. 7). Two main absorption bands, typical of octahedral Co(II) complexes,[244] were observed in the spectra of the CoL_1 complexes in the region of 8000 and 19,000 cm^{-1}. This indicates that the remaining four co-ordination sites in the CoL_1 species are occupied by water molecules. The above two absorption bands, ν_1 and ν_3, are due to the spin-allowed (for d^7 high-spin) transitions, $^4T_{1g} \longrightarrow {}^4T_{2g}$ and $^4T_{1g} \longrightarrow {}^4T_{1g}(P)$, respectively.[244] The shoulder observed on the high energy side of band ν_3 has been proposed[245] to result from spin-orbit coupling in the $^4T_{1g}(P)$ state. The high-spin state of Co(II) complexes of o-diphenols has been established by the magnetic moment of 4.96 B.M. (25°C) for bis(tetrachlorocatecholato)cobaltate.[24] The higher value than required by the spin-only moment viz. 3.89 B.M. is associated with orbital contributions.[245]

The spectra of only three CoL_1 o-diphenol complexes could be obtained, because of interference from precipitation by the other complexes. Spectral data are listed in Table 4. The similarity between the wave numbers of band ν_1 (the transition $^4T_{1g} \longrightarrow {}^4T_{2g}$ is approximately equal to 8Dq)[246] for hexa-aquocobalt(II) ion and o- diphenol complexes, indicates that the values of 10Dq are also similar, as found for the Ni(II) complexes.

On formation of the second species, CoL_2, the low energy band, ν_1, was found to become very broad with no definite maximum. However, in

TABLE 4.

Spectral data for Co(II) complexes of o-diphenols.

Complex Species	*Ligand	$^4T_{1g} \rightarrow {}^4T_{2g}$ ν_1(kK)	$^4T_{1g} \rightarrow {}^4A_{2g}$ ν_2(kK)	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$ ν_3(kK)	
CoL_1	1	8.20(3.9)[a]	(15.8)[b]	18.9(20)	
	2	8.10(3.2)	-	19.0(20)	
	3	8.15(4.0)	-	d	
CoL_2	1	8.15(4.0)	-	18.8(25)	
$Co[(H_2O)_6]^{2+}$		8.1[c]	(16)	19.4	
		$^4A_2 \rightarrow {}^4E_2$	$^4A_2 \rightarrow {}^4A_2$	$^4A_2 \rightarrow {}^4E(P)$	$^4A_2 \rightarrow {}^4A_2(P)$
CoL_3	4	12.0(8.5)	(16.2)	18.0(38)	20.9(24)
	5	12.1(8.0)	(16.1)	17.9(36)	20.8(22)
	2	12.0(9.0)	(16.2)	18.0(40)	20.8(28)
	3	12.1(9.5)	d	d	d

*Ligand : (1) Tiron, (2) DHNS, (3) protocatechuic aldehyde, (4) 4-methylcatechol, (5) pyrocatechol.

[a]Extinction coefficients,

[b]Wave numbers in parentheses refer to shoulders,

[c]Reference 267,

[d]Obscured by phenolic absorption.

the absorption spectrum of the bis(tetrachlorocatecholato)cobalt(II) dianion, band ν_1 has been resolved[24] into a well defined doublet with bands at 7000 and 8700 cm^{-1}; whereas for the CoL_1 species bands ν_1 are in the region of 8100 cm^{-1} (Table 4). The splitting of band ν_1 is indicative[244] of some form of distortion in the CoL_2 species which is absent in the octahedral CoL_1 species.

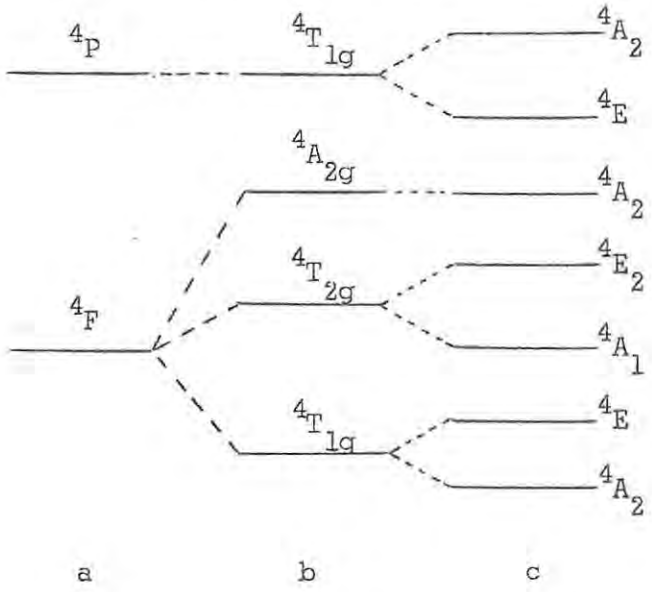
The CoL_2 species of Tiron is however an exception to the above spectral behaviour. The absorption spectrum of this species is indicative of a regular octahedral complex, as shown in Table 4. The presence of an ortho-sulfonic acid substituent probably prohibits the distortion of the octahedral symmetry in some manner.

The o-diphenol complexes, CoL_3, were shown, in the potentiometric investigation, to form at very high pH. The absorption spectra of these species were obtained by using stoichiometric concentrations of metal ion and ligand (1 : 3) and a high concentration of alkali (2 M). The spectrum of the pyrocatechol complex (Fig. 8) is similar to the published spectrum[23] of the complex, $K_4\left[Co(C_6H_4O_2)_3\right].4H_2O$. Spectral data for the other CoL_3 species are given in Table 4. The low energy bands in the region of 12,000 cm^{-1} cannot be associated with band ν_1 of the CoL_1 octahedral species, because they would place the o-diphenolato ligands far to the right of water in the spectrochemical series. It is proposed that these bands are associated with the higher energy band of the CoL_2 doublet, shifted to even higher energies as a result of further distortion of the octahedra.

Two forms of distortion commonly occur in pseudo-octahedral complexes viz. tetragonal and trigonal distortion.[247] The former may be ruled out, since it would not be expected in the tris-chelate, CoL_3. The latter distortion takes the form of compression or extention along an octahedral three-fold axis. Trigonal distortion has been proposed[248] to occur in complexes of the related toluene-3,4-ditholate ligand and has been shown[249] to occur in the rhenium(III) complex of the rigid, bidentate

ligand cis-1,2-diphenylethene-1,2-ditholate due to ring strain imposed by the 5-membered chelate.

The effect of trigonal distortion on the energy levels of a d^2 octahedral complex is known.[136] The published correlation diagram for a d^2 ion is also applicable to the Co(II) ion (d^7).[136] Fig. 9 illustrates the correlation diagram for a d^7 ion.



(a) spherically perturbed free ion, (b) octahedral (O_h) environment, and (c) trigonal (D_3) environment.

Fig. 9. Energy level scheme for a d^7 ion.

The assignments of the absorption bands of the o-diphenol complexes, CoL_3, given in Table 4 are proposed on the basis of a $^4A_2$ ground state in a trigonal (D_3) environment and the energy levels shown in Fig. 9. The lower energy bands of the $^4T_{2g}$ (in O_h) doublet were not observed probably because of their very low energy.

The proposed trigonal distortion of the CoL_2 o-diphenol complexes

would explain the anomalous stability order, Co > Ni for the constants, K_2, observed in the potentiometric investigation (p. 198). The presence of any ring strain imposed by the 5-membered chelate would result in the stabilities of the Ni(II) complexes (octahedral symmetry) being relatively lower than the Co(II) complexes, because in the latter complexes the ring strain would be relieved by distortion of the octahedra. This is supported by the fact that for the Co(II)-Tiron system, where no distortion was observed, the normal stability order Ni < Co holds (Table 1).

The interelectronic repulsion (Racah) parameter, B and 10Dq for the octahedral CoL_2 complex of Tiron were calculated from the ratio of bands ν_1 and ν_3 and the transition energy ratio diagrams given by Lever.[263] Values of 10Dq = 1300 cm^{-1} and B = 800 cm^{-1} were obtained. A comparison of the above 10Dq with that of 9200 cm^{-1} for the hexa-aquocobalt(II) ion,[244] again illustrates that the o-diphenolato ligands lie close to water in the spectrochemical series. From the above Racah B value, a value of β (the ratio of B in the complex to B in the free ion (Bo), for Co(II), Bo = 971 cm^{-1})[159] equal to 0.83 is obtained. This β value indicates that the metal to oxygen bonds in the o-diphenolato complexes are partially covalent since complexes with purely ionic ligands have values close to 1 and the greater the reduction of β, the greater the covalency in the metal ligand bonds.[159] A comparison of β = 0.83 for the Tiron complex with other β values for octahedral Co(II) complexes,[244] shows that the position of the o-diphenolato ligands in the nephelauxetic series[173] is between water and the halide ions, Cl^- and Br^-.

(iii) Copper(II) complexes : The spectral data for the o-diphenol

complexes of Cu(II) are given in Table 5. Typical absorption spectra for the CuL_1 and CuL_2 complexes are illustrated in Fig. 7. Two visible absorption bands, ν_1 and ν_2, were observed in the region 13,000 - 16,000 cm^{-1} and 23,000 - 26,000 cm^{-1}, respectively. These have been assigned to the d-d transitions of 6-co-ordinate Cu(II) and to charge transfer transitions respectively.[23]

The similarity of the spectral data for the o-dihydroxybenzene and 1,2,3-trihydroxybenzene complexes (Table 5) illustrates that the same, final species, CuL_2, is formed. This confirms the assumption which was made on the basis of the potentiometric results (p. 202).

From Table 5 it may be observed that for an electron-releasing phenolic substituent, the charge transfer band is at lower energy, relative to the unsubstituted phenol and vice versa. This established that the charge transfer is from ligand to metal as for the o-diphenol complexes of Fe(III) (Section B). In a molecular orbital interpretation of charge transfer the charge transfer transitions of lowest energy have been shown to be between a π ligand orbital and the lowest, vacant metal orbital.[13] Since Cu(II) has a d^9 configuration, with only one vacant d-orbital, the charge transfer can be assigned to the transition $\pi \rightarrow e_g$.

On successive formation of the CuL_1 and CuL_2 species, the charge transfer bands are shifted to higher energies (Table 5), as found for the Fe(III) complexes. The interpretations which were made on the charge transfer results of the Fe(III) complexes, based on an electrostatic model (p. 107) and a molecular orbital model (p. 111), also hold for the Cu(II)

TABLE 5.

Spectral data for Cu(II) complexes of o-diphenols.

Complex species	Ligand	d-d ν_1(kK)	$\frac{\sigma_{Cu}}{\sigma_{Ni}}$	charge transfer ν_2(kK)
CuL_1	Tiron	13.50(30)[b]	1.58	23.0(90)
	3,4-dihydroxy-benzenesulfonate	13.70(27)	-	23.3(85)
	DHNS	13.50(40)	1.59	25.3(150)
	protocatechuic aldehyde	13.45(38)	1.57	(23.5) -
CuL_2	4-methylcatechol	15.50(33)	1.82	24.4(190)
	pyrocatechol	15.38(31)	1.80	25.0(180)
	catechin	15.38(33)	-	25.3(210)
	protocatechuic acid	15.38(33)	-	25.6(240)
	pyrogallol	15.15(28)	-	25.3(170)
	Tiron	15.27(35)	1.78	26.3(200)
	2,3-dihydroxy-naphthalene	15.27(34)	-	d
	3,4-dihydroxy-benzenesulfonate	15.15(30)	-	25.6(220)
	DHNS	15.27(45)	1.79	d
	propyl gallate	14.93(32)	-	d
	protocatechuic aldehyde	14.93(40)	1.75	d
	4-nitrocatechol	(14.80)[a]	1.73	d
$[Cu(H_2O)_6]^{2+}$		12.60[c]	1.48	

[a] Wave numbers given in parentheses refer to shoulders

[b] Extinction coefficients

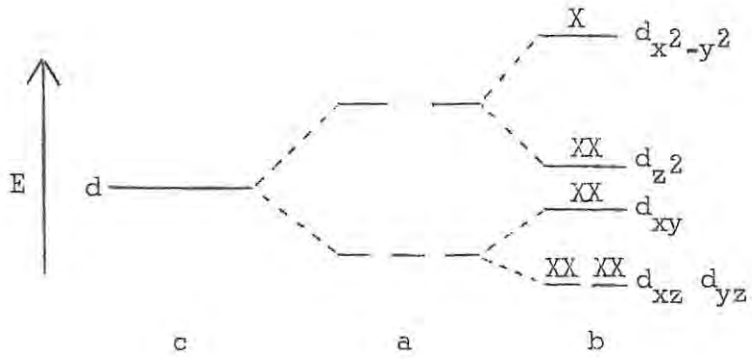
[c] Reference 262

[d] Obscured by phenolic absorption.

complexes of o-diphenols.

The d^9 configuration of Cu(II) results in considerable distortion due to the Jahn-Teller effect.[250] The majority of 6-co-ordinate Cu(II) complexes are tetragonally distorted with four short metal to ligand bonds in one plane (xy) and two longer bonds (z axis).[250] The energy

levels of such tetragonally distorted Cu(II) complexes are illustrated in Fig. 10.



(a) octahedral field, (b) tetragonal field, (c) spherically perturbed ion

Fig. 10. Effect of tetragonal distortion (elongation along z axis) on the energy levels of an octahedral complex (d^9 configuration).

From Fig. 10, three d-d transitions are expected viz. from the d_{z^2}, d_{xy} and d_{xz}, d_{yz} pair to the half-filled $d_{x^2-y^2}$ level. In general, however, the spectra of Cu(II) complexes show only one asymmetric absorption band in the region near 16,000 cm^{-1}.[250] This band has, however, been shown to be made up of two of three overlapping symmetrical bands.[250] If it is assumed that the band due to the d-d transition of the o-diphenol complexes of Cu(II), (Band ν_1, Table 5) is from an average of the d_{z^2}, d_{xy} and d_{xz}, d_{yz} levels, then from Fig. 10 an increase in tetragonal distortion will result in a shift to higher energy of the absorption band. Jorgensen[251] has defined the term σ_{Cu}/σ_{Ni}, as the ratio between the wave number σ_{Cu} of the principal band of a Cu(II) complex and σ_{Ni}, the wave number of the first, spin-allowed band of the high-spin, octahedral Ni(II) complex with the same ligand. This ratio varies from 1.0 to 1.8 depending on the extent of tetragonal distortion and consequently Cu(II)

complexes may be divided into three classes[251] : (i) the complexes with large tetragonal distortion with σ_{Cu}/σ_{Ni} = from 1.6 - 1.8, (ii) those with moderate distortion with σ_{Cu}/σ_{Ni} = 1.4 and (iii) those with low distortion with σ_{Cu}/σ_{Ni} = 1.1. The values of σ_{Cu}/σ_{Ni} obtained for the o-diphenol complexes are given in Table 5. The d-d absorption bands (ν_1) of the o-diphenol complexes of Cu(II) would be expected to be similar to that of hexa-aquocopper(II), as found for the Ni(II) complexes. From Table 5 it is seen that band ν_1 of the o-diphenol complexes are at higher energies relative to those of the hexa-aquo complex. This anomaly may be explained on the basis of a change to lower symmetry on formation of the o-diphenol complexes. From Table 5 the σ_{Cu}/σ_{Ni} values of 1.55 - 1.8 for the o-diphenol complexes, relative to that of 1.48 for the hexa-aquo complex, shows that the former complexes are highly tetragonally distorted. In addition, the increase in σ_{Cu}/σ_{Ni} on successive complex formation (Table 5) shows that the tetragonal distortion also increases on successive replacement of the bound water molecules by the phenolic ligands. This large tetragonal distortion also accounts for the relatively higher stabilities of the Cu(II) complexes (Table 1), because from Fig. 10 the larger the tetragonal distortion, the lower is the energy of the system and hence the more stable is the complex.

The effect of the phenolic substituents on the values of σ_{Cu}/σ_{Ni} (Table 5) shows a parallel relationship to the electronic character of the substituent - the more electron-releasing the substituent, the greater is the tetragonal distortion relative to the unsubstituted phenol and vice versa. This would account for the greater substituent effect on the stability constants of the Cu(II) complexes relative to those of Ni(II),

Co(II) and Zn(II) complexes (cf. slopes in Figs. 3 and 4 and p. 199) since in addition to the normal stabilisation by the electron-releasing substituent, the stabilities would be increased by the tetragonal distortion relative to the unsubstituted phenol and vice versa.

2. Magnesium(II) and calcium(II) complexes of o-diphenols.

Complexation of o-dihydroxybenzene derivatives with Mg(II) and Ca(II) ions have been shown to take place according to reactions (1) and (2).[51,54] Potentiometric titration curves for the Mg(II) and Ca(II) complexes illustrated in Fig. 1, show that these complexes are only formed at high pH. However, the formation of the MgL_1 and MgL_2 and the CaL_1 species was evident from the formation curves ($\bar{n}$ vs. pL plots), illustrated in Fig. 2. Values of $\bar{n}$ and pL were calculated using equations (14) and (17) Section B, and equation (11) Section C. Examples of the calculations are given in Table 10.

Similar MgL_1 complex species formed with the 1,2,3-trihydroxybenzene and o-dihydroxybenzene derivatives. This is shown by the similarity of their formation curves (Fig. 2). The 1,2,3-trihydroxybenzene complexes of Ca(II), however, formed precipitates in solution, similar to those of Co(II), Ni(II), Zn(II) and Cu(II).

The stability constants, K_1 and K_2, were calculated by the least squares method, using equation (13) Section C, as shown in Table 10. In the cases where the stability constants, K_2, were unobtainable because of the high pH of complexation, approximate values of K_1 were obtained from the formation curves by interpolation at half-$\bar{n}$ values. The

stability constants obtained by these methods are listed in Table 6.

TABLE 6.

Stability constants for o-diphenol complexes of Mg(II), Ca(II), and Pb(II).

Ligand	Mg(II)		Ca(II)	Pb(II)	
	log K_1	log K_2	log K_1	log K_1	log K_2
4-methylcatechol	7.06	4.49	4.8		
4-tert.-butylcatechol	7.10	-	4.85		
pyrocatechol	6.80	4.45	4.7		
3-methoxycatechol	6.47	4.33	4.55		
pyrogallol	6.6	-	-		
brazilin	6.65	-	-		
catechin	6.6	-	4.65		
robinetinidol	6.6	-	-		
protocatechuic acid	6.55	4.10	4.65		
gallic acid	6.5	-	-		
2,3-dihydroxynaphthalene	6.28	3.93	4.2		
3,4-dihydroxybenzenesulfonate	6.27	3.72	4.2	11.95	5.95
DHNS	6.32	3.70	4.15	11.9	-
propyl gallate	5.8	-			
4-chloroacetylcatechol	5.94	3.81	4.05		
Tiron	6.76	4.72	4.6	12.86	6.55
protocatechuic aldehyde	5.83	3.72	3.95		
4-nitrocatechol	5.26	3.38	3.6		

The stability order Mg > Ca (Table 6) is similar to that obtained previously.[51] This stability order is in agreement with the theoretical order based on the ionic radii of the alkaline-earth metals[252] and results from the smaller ionic radius of Mg(II) relative to that of Ca(II). A comparison of the stability constants of the Zn(II) complexes (Table 1) with those of Mg(II) (Table 6) shows that the stability order Zn > Mg holds for all the o-diphenol complexes. In general, this stability order has been found to hold for many complexes of these metals.[253]

The potentiometric investigation of the wattle tannin complexes of

Mg(II) and Ca(II) was hampered by the formation of precipitates. However, the above stability orders also hold for the wattle tannin complexes as shown by the pH at incipient precipitation, given in Table 2.

The stability constants of the Mg(II) and Ca(II) complexes were correlated with the ligand association constants and the results illustrated in Fig. 11. The observed linear relationships (except for Tiron) are similar to those obtained for the other o-diphenol complexes studied. In the correlation for Mg(II) complexes, the 1,2,3-trihydroxybenzene derivatives and the flavanoid compounds all follow a linear relationship.

3. Lead(II) complexes of o-diphenols.

In general, the o-diphenol complexes of Pb(II) were insoluble in aqueous media. The only exceptions were those phenolic derivatives with ionic substituents. Although precipitation occurred, the titration curves showed sharp inflections at $\bar{z} = 2$ and $\bar{n} = 1$ as illustrated in Fig. 1. This corresponds to the formation of the PbL complex species, according to reaction (1). It has been established that the precipitation of the 4-tert.-butylcatechol, 4-methylcatechol and pyrocatechol complexes of Pb(II) is quantitative and that complexes are only formed with phenolic ligands containing an o-dihydroxyl group.[254] The pyrocatechol complex was isolated as a white, amorphous solid. The infrared spectrum of the compound showed no O-H stretching vibrations, in accordance with the formula, $Pb(C_6H_4O_2)$, which has been established[255] for the pyrocatechol complex.

Solutions of Pb(II) ions and wattle tannin form an immediate white

precipitate. A potentiometric titration of Pb(II) ions and excess of wattle tannin also gave an inflection at approximately $\bar{z} = 2$, indicating that the same complex species, PbL_1, is formed as in the case of the other o-diphenol ligands listed in Table 6.

It was evident from the formation curves of the soluble o-diphenol complexes of Pb(II) that in addition to the PbL_1 species, the PbL_2 species form at high pH. The least squares method for determining the stability constants was unnecessary since the successive complexes form separately. The stability constants given in Table 6 for the soluble Pb(II) complexes were determined using equation (14) Section B, and equations (11) and (12) Section C. A comparison of the stability constants in Tables 1 and 6 shows that the stabilities of the ML_1 species increase in the order Co, Ni, Zn, Pb, Cu, whereas the stabilities of the ML_2 species increase in the order Pb, Ni, Co, Zn, Cu. It has, however, been shown[56] that the position of Pb(II) in such stability orders is dependent on the ligand and no general order could be established for Pb(II) complexes relative to other divalent metal complexes.

4. Vanadyl(IV) complexes of o-diphenols.

Vanadyl(IV) ions have been shown[63,65,256-258] to form successive complexes with o-dihydroxybenzene and 1,2,3-trihydroxybenzene derivatives in aqueous media, thus :

$$VO^{2+} + H_2L \rightleftharpoons VOL + 2\,H^+ \qquad (8)$$

$$VOL + H_2L \rightleftharpoons VOL_2^{2+} + 2\,H^+ \qquad (9)$$

The tris-pyrocatechol chelate, $Tl_2\left[V(C_6H_4O_2)_3\right]$ has been isolated[259]

as well. However, in dilute aqueous solutions only the VOL_1 and the VOL_2 species have been detected.[63,65] In vanadyl(IV) complexes with bidentate ligands, eg. acetylacetonate and oxalate, the VOL_2 complexes consist of two chelate rings in the xy plane and the V = O band perpendicular to the xy plane.[260] The o-diphenol complexes would be expected to be similar.

Potentiometric titration curves of vanadyl(IV) ions and excess of o-diphenol showed no distinct inflection at $\bar{z} = 2$, as illustrated in Fig. 1, indicating overlap of the successive complex formation. The inflection observed (Fig. 1) at $\bar{z} = 4$ corresponds to the complete form- of the VOL_2 species. Due to the overlapping nature of the complexation, the least squares method was used to obtain the stability constants, K_1 and K_2, for the o-diphenol complexes. Examples of the calculations are given in Table 11.

In the potentiometric titrations of vanadyl(IV) ions with the less acidic phenolic ligands, inflections at slightly less than $\bar{z} = 2$ were obtained. This suggests additional formation of the hydroxo species,[64] $VOL(OH)^-$, at the higher pH values required for complete complex formation. In previous investigations,[65] the interference from the formation of the hydroxo species was overcome by depressing the pH of complexation with a large excess of ligand. However, the limited solubility of some of the phenolic ligands used in the present investigation only permitted the use of a moderate excess of ligand. If, however, $\bar{n}$ values of less than 1.5 were used in the calculation (least squares method) then correlation coefficients of close to unity were obtained, as shown in Table 11.

Table 7 lists the stability constants, K_1 and K_2, for the vanadyl(IV) complexes. Equilibrium constants, k_1 and k_2, for reactions (8) and (9) were also determined using equation (22) Section B. Values of k_1 and k_2 determined in the present investigation compare favourably with published[65] values for a number of o-diphenol complexes, as shown in Table 7.

TABLE 7.

Stability constants, K_1 and K_2, and equilibrium constants, k_1 and k_2, for vanadyl(IV) complexes of o-diphenols.

Ligand	log K_1	log K_2	pk_1	pk_2
4-methylcatechol	17.95	15.80	5.65	7.80
4-tert.-butylcatechol	17.86	15.70	5.74	7.90
4-hydroxycatechol	17.78	15.70	5.62	7.70
pyrocatechol	17.52	15.57	5.48(5.43)[a]	7.43(7.30)
3-methoxycatechol	17.37	15.30	5.53	7.60
pyrogallol	17.35	16.21	5.30(5.21)	6.44(6.51)
brazilin	17.41	15.44	5.19	7.16
catechin	17.09	15.10	5.16	7.15
robinetinidol	17.10	15.78	4.95	6.27
dihydrorobinetin	17.07	15.68	4.98	6.37
2,3-dihydroxynaphthalene	16.31	14.29	4.64	6.66
3,4-dihydroxybenzenesulfonate	16.19	14.02	4.61(4.56)	6.78(6.81)
DHNS	16.07	13.91	4.28	6.44
propyl gallate	15.76	14.32	4.24	5.68
Tiron	16.80	14.44	3.45(3.49)	5.81(5.91)
4-chloroacetylcatechol	15.29	13.55	4.11	5.85
protocatechuic aldehyde	14.97	13.24	4.03	5.76
4-nitrocatechol	13.98	12.38	3.67	5.27

[a]Values in parentheses are published[65] equilibrium constants.
$T = 20^{\circ}$, $I = 0.1$.

A comparison of the stability constants, K_1, in Tables 1, 6 and 7 shows that the stabilities of the ML_1 species increases in the order, Ca, Mg, Co, Ni, Zn, Pb, Cu, VO. This stability order also holds for the wattle tannin complexes, as shown by the pH values at incipient

precipitation, given in Table 2.

Ratios of K_1 and K_2 (Table 7) for the vanadyl(IV) complexes are generally much lower than for any of the other o-diphenol complexes studied. This is attributed to the presence of the V = O bond in the vanadyl(IV) complexes being able to relieve the high electron density on the metal in the VOL_2^{2-} species resulting in a more stable complex. A similar electronic effect has been shown to take place in vanadyl complexes with trans (i.e. trans to the V = O bond) electron donors.[261]

Correlation between the ligand association constants and the stability constants, K_1, for the vanadyl(IV) complexes gave the normal linear relationship (except for Tiron) as shown in Fig. 12. However, in a similar correlation of the stability constants, K_2, (Fig. 12) the points for all the 1,2,3-trihydroxybenzene derivatives deviate from the straight line drawn for the o-dihydroxybenzene derivatives. The direction of deviation indicates that the vanadyl(IV) complex species, VOL_2, are more stable for the 1,2,3-trihydroxybenzene complexes relative to those of the o-dihydroxybenzene complexes. However, the general relationship between ligand acidity and complex stability still holds for the former complexes as shown by the separate linear relationship in Fig. 12.

TABLE 8.

Determination of stability constants for the Cu(II) and Zn(II) complexes of catechin.

Metal ion : (1)copper(II)						(2) zinc(II)					
pH	v'''	v''	$\bar{n}_a$	$\bar{n}$	pL	pH	v'''	v''	$\bar{n}_a$	$\bar{n}$	pL
5.0	0.48	0.00	2.000	0.240	14.521	7.0	0.60	0.08	1.990	0.261	10.521
5.2	0.85	0.00	2.000	0.425	14.146	7.2	1.02	0.11	1.985	0.458	10.159
5.4	1.27	0.01	2.000	0.630	13.786	7.4	1.49	0.165	1.975	0.671	9.805
5.6	1.61	0.015	2.000	0.798	13.420	7.6	1.99	0.75	1.960	0.888	9.458
5.8	1.84	0.02	2.000	0.910	13.045	8.0	2.80	0.55	1.910	1.178	8.753
6.2	2.16	0.03	2.000	1.065	12.281	8.2	3.27	0.80	1.863	1.326	8.417
6.4	2.42	0.04	1.998	1.191	11.913	8.4	3.81	1.12	1.800	1.494	8.100
6.6	2.77	0.05	1.996	1.363	11.560	8.6	4.40	1.55	1.715	1.662	7.805
6.8	3.17	0.06	1.994	1.560	11.220	8.8	5.01	2.12	1.613	1.792	7.521
7.0	3.53	0.08	1.990	1.734	10.880	9.0	5.53	2.71	1.500	1.880	7.246
7.2	3.81	0.11	1.985	1.864	10.532						

Application of the least squares method to values in columns 5 and 6 for system (1) and columns 11 and 12 for system (2), using equation (13) Section C gave : (1)correlation coefficient=0.99, log K_1=13.99 and log K_2=11.30 and (2)correlation coefficient=0.98, log K_1=10.12 and log K_2=8.13.

Experimental data used in equation (17) Section B, and equation (11) Section C :

$T_M^o = 2 \times 10^{-3}$ M, $T_L^o = 8 \times 10^{-3}$ M, $V^o = 50$ ml, N = 0.1 N KOH, $E^o = 0$, pKaKb = 22.25, pKb = 13.25.

TABLE 9.

Determination of stability constants for the Ni(II) and Co(II) complexes of 4-chloroacetylcatechol and 2,3-dihydroxynaphthalene.

System:

(1)Ni(II)-4-chloroacetylcatechol						(2)Co(II)-2,3-dihydroxynaphthalene					
pH	v'''	v''	$\bar{n}_a$	$\bar{n}$	pL	pH	v'''	v''	$\bar{n}_a$	$\bar{n}$	pL
6.4	4.00	3.35	1.912	0.340	8.834	7.0	2.52	2.10	1.975	0.213	9.120
6.6	4.55	3.54	1.865	0.541	8.485	7.2	2.93	2.17	1.958	0.388	8.751
6.8	5.12	3.80	1.800	0.733	8.148	7.4	3.41	2.26	1.935	0.594	8.391
7.0	5.64	4.14	1.715	0.875	7.819	7.6	3.89	2.39	1.903	0.788	8.037
7.6	6.96	5.46	1.385	1.083	6.925	7.8	4.31	2.58	1.855	0.933	7.685
7.8	7.33	5.86	1.285	1.144	6.670	8.4	5.60	3.66	1.585	1.224	6.700
8.0	7.67	6.21	1.197	1.220	6.436	8.6	6.10	4.10	1.475	1.356	6.419
8.2	7.96	6.47	1.132	1.316	6.220	8.8	6.60	4.54	1.365	1.509	6.165
8.4	8.20	6.66	1.086	1.418	6.016	9.0	7.04	4.96	1.263	1.647	5.931
8.6	8.40	6.80	1.052	1.521	5.821	9.2	7.36	5.26	1.190	1.764	5.712
8.8	8.56	6.89	1.031	1.619	5.630	9.4	7.61	5.54	1.123	1.842	5.499

Least squares method (as for Table 8) gave :

(1)correlation coefficient = 0.98, $\log K_1 = 8.57$, $\log K_2 = 5.90$,

(2)correlation coefficient = 0.99, $\log K_1 = 8.59$, $\log K_2 = 6.20$.

Experimental data used in equation (14) Section B, and equation (11) Section C :

(1) $T_M^o = 1.887 \times 10^{-3}$ M, $T_L^o = 7.547 \times 10^{-3}$ M, $V^o = 53$ ml, $E^o = 5.66 \times 10^{-3}$

pKaKb = 19.4, pKb = 12.0

(2) $T_M^o = 1.923 \times 10^{-3}$ M, $T_L^o = 7.692 \times 10^{-3}$ M, $V^o = 52$ ml,

$E^o = 3.846 \times 10^{-3}$ M, pKaKb = 20.95, pKb = 12.4;

N = 0.1 N KOH

TABLE 10.

Determination of stability constants for the Mg(II) complex of 4-nitrocatechol and determination of $\bar{n}$ and pL values for the Ca(II) complex of 4-chloroacetylcatechol.

System : (1) Mg(II)-4-nitrocatechol						(2) Ca(II)-4-chloroacetylcatechol					
pH	v'''	v''	$\bar{n}_a$	$\bar{n}$	pL	pH	v'''	v''	$\bar{n}_a$	$\bar{n}$	pL
7.6	5.88	5.51	1.122	0.321	5.554	9.0	5.98	5.91	1.023	0.068	5.180
7.8	6.16	5.68	1.080	0.444	5.351	9.2	6.06	5.95	1.013	0.109	4.981
8.0	6.40	5.80	1.050	0.571	5.156	9.4	6.14	5.98	1.008	0.159	4.785
8.2	6.60	5.88	1.030	0.699	4.965	9.6	6.23	6.01	1.003	0.219	4.592
8.4	6.75	5.94	1.015	0.798	4.775	9.8	6.36	6.05	0.998	0.310	4.404
8.6	6.88	5.98	1.005	0.896	4.560	10.0	6.51	6.10	0.991	0.413	4.218
9.2	7.20	6.095	0.982	1.125	4.029	10.2	6.68	6.16	0.979	0.510	4.033
9.4	7.34	6.15	0.971	1.225	3.845	10.4	6.87	6.28	0.968	0.608	3.851
9.6	7.50	6.24	0.956	1.317	3.668						
9.8	7.68	6.355	0.927	1.428	3.499						
10.0	7.90	6.54	0.889	1.527	3.336						

Least squares method (as for Table 8) gave : (1) correlation coefficient = 0.99, $\log K_1 = 5.26$ and $\log K_2 = 3.38$.

Data used in equation (14) Section B and equation (11) Section C.

(1) and (2), $T_M^o = 1.923 \times 10^{-3}$ M, $T_L^o = 7.692 \times 10^{-3}$ M,

$E^o = 3.846 \times 10^{-3}$ M, $V^o = 52$ ml, N = 0.1 N, I = 0.1; pKaKb =

(1) 17.65 and (2) 19.4, pKb = (1) 10.9 and (2) 12.0.

TABLE 11.

Determination of stability constants, K_1 and K_2, for the vanadyl(IV) complexes of catechin and robinetinidol.

Ligand : (1) catechin					(2) robinetinidol				
pH	v'''	v''	$\bar{n}$	pL	pH	v'''	v''	$\bar{n}$	pL
3.6	2.25	1.89	0.361	17.318	3.4	2.10	1.82	0.281	17.511
3.7	2.38	1.91	0.471	17.128	3.5	2.24	1.86	0.381	17.319
3.8	2.51	1.92	0.591	16.938	3.6	2.38	1.89	0.491	17.129
3.9	2.63	1.93	0.701	16.748	3.7	2.55	1.91	0.641	16.943
4.0	2.75	1.95	0.801	16.557	3.8	2.71	1.92	0.791	16.756
4.1	2.86	1.96	0.901	16.367	3.9	2.83	1.93	0.901	16.566
4.4	3.10	1.98	1.120	15.788	4.0	3.00	1.95	1.051	16.381
4.5	3.20	1.985	1.215	15.597	4.1	3.13	1.955	1.176	16.193
4.6	3.30	1.99	1.310	15.407	4.2	3.24	1.96	1.281	16.003
4.7	3.40	1.995	1.405	15.216	4.3	3.34	1.97	1.371	15.813

Least squares method (as for Table 8) gave :

(1)correlation coefficient =0.99, log K_1 = 17.09, log K_2 = 15.10;

(2)correlation coefficient = 0.99, log K_1 = 17.10, log K_2 = 15.78.

Experimental data used in equations as for Table 10 :

$T_M^o = 1 \times 10^{-3}$ M, $T_L^o = 6 \times 10^{-3}$ M, $E^o = 4 \times 10^{-3}$ M, V^o = 50 ml,

N = 0.1 N, I = 0.1, $\bar{n}_a = 2$;

(1)pKaKb = 22.25, pKb = 13.25; (2)pKaKb = 22.05, pKb = 13.25.

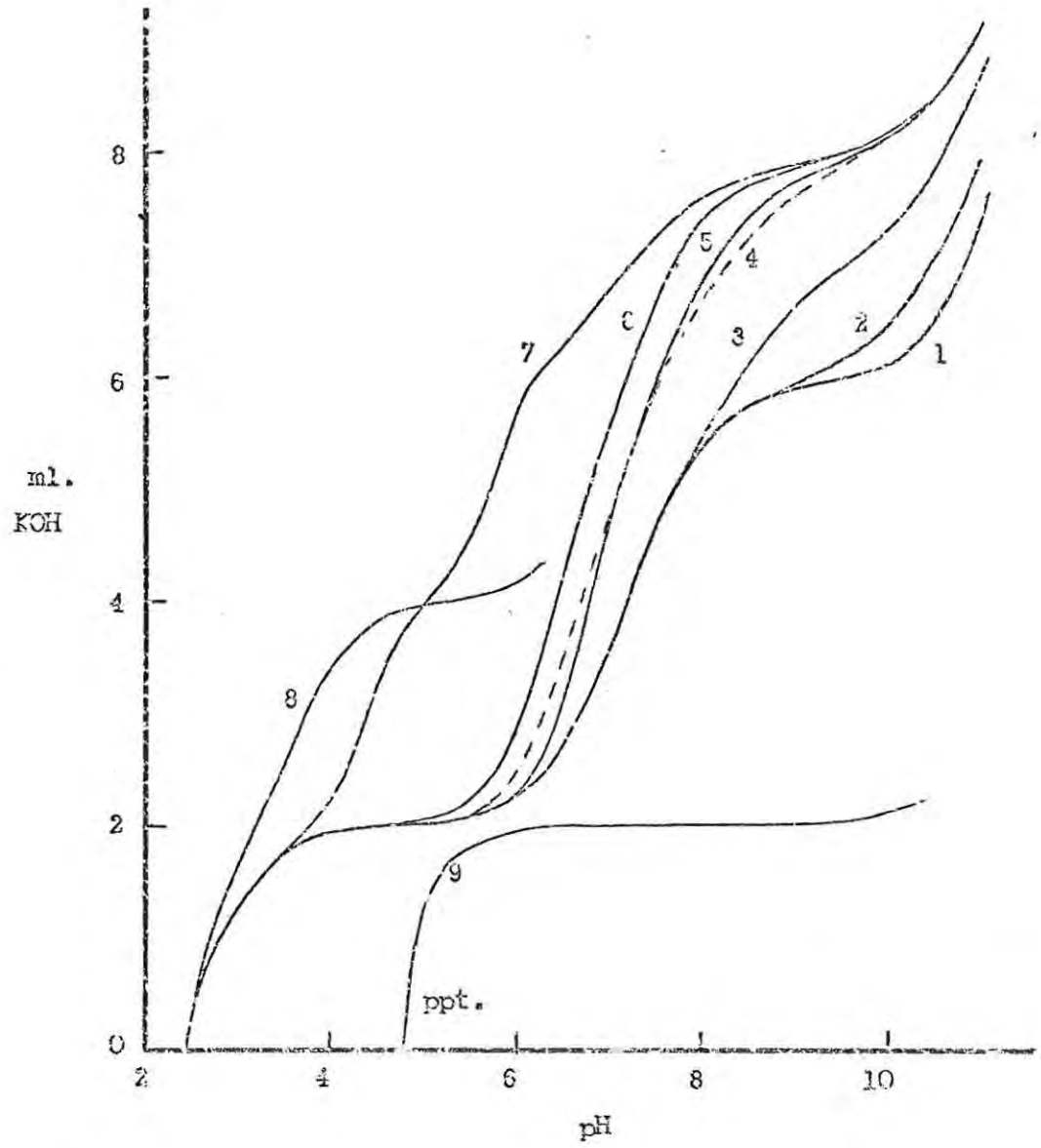


FIG. 1 . Potentiometric titration curves for (1) - (8) 0.008 M protocatechuic aldehyde + 0.004 N HCl with T_M^o = 0.002 M of (2) Ca(II), (3) Mg(II), (4) Ni(II), (5) Co(II), (6) Zn(II), (7) Cu(II) and T_M^o = 0.001 M of (8) vanadyl(IV); (9) 0.002 M of Pb(II) and pyrocatechol; V^o = 50 ml., N = 0.1 N KOH and I = 0.1 N KCl.

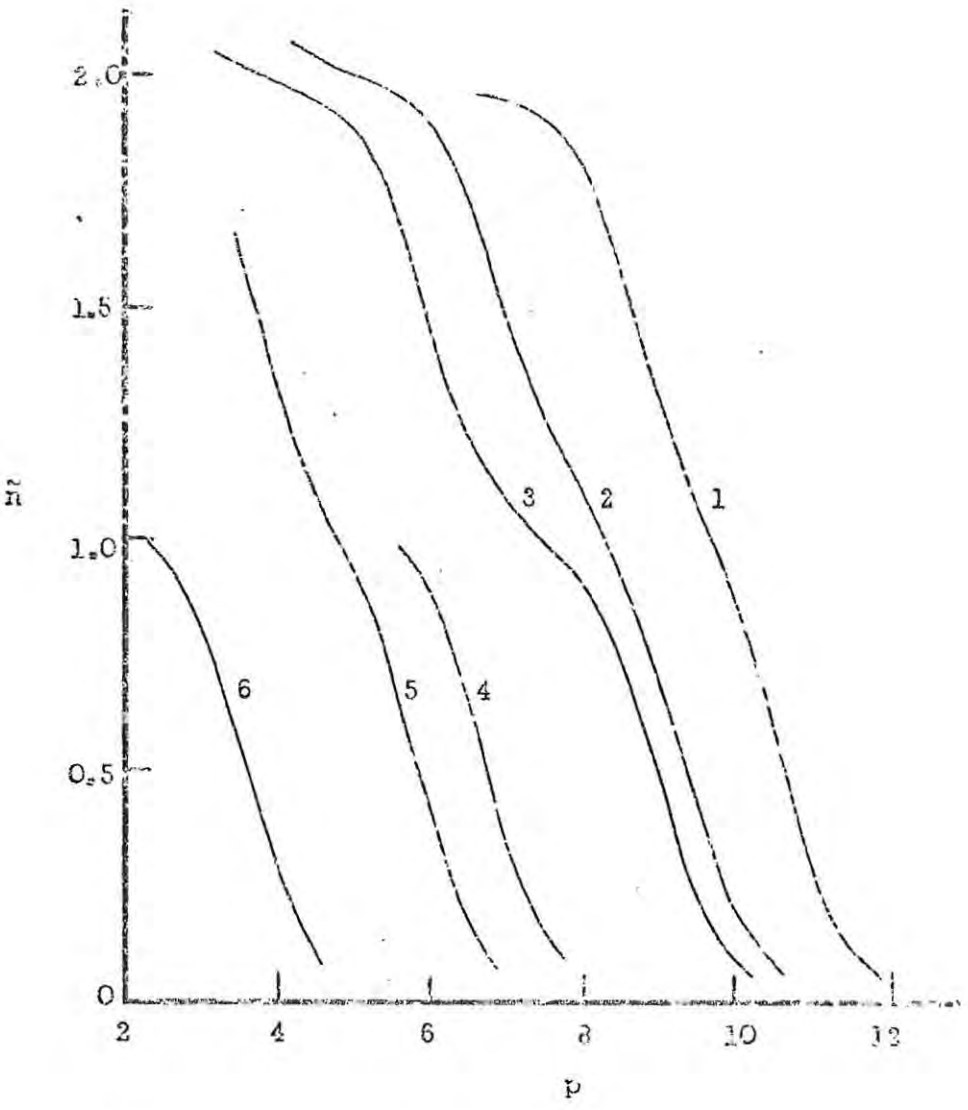


FIG. 2 . Formation curves for (1) Zn(II)-4-methylcatechol (2) Co(II)-pyrocatechol, (3) Ni(II)-protocatechuic acid, (4) Mn(II)-pyrogallol, (5) Mn(II)-4-chloroacetylcatechol, (6) Ca(II)-4-nitrocatechol.

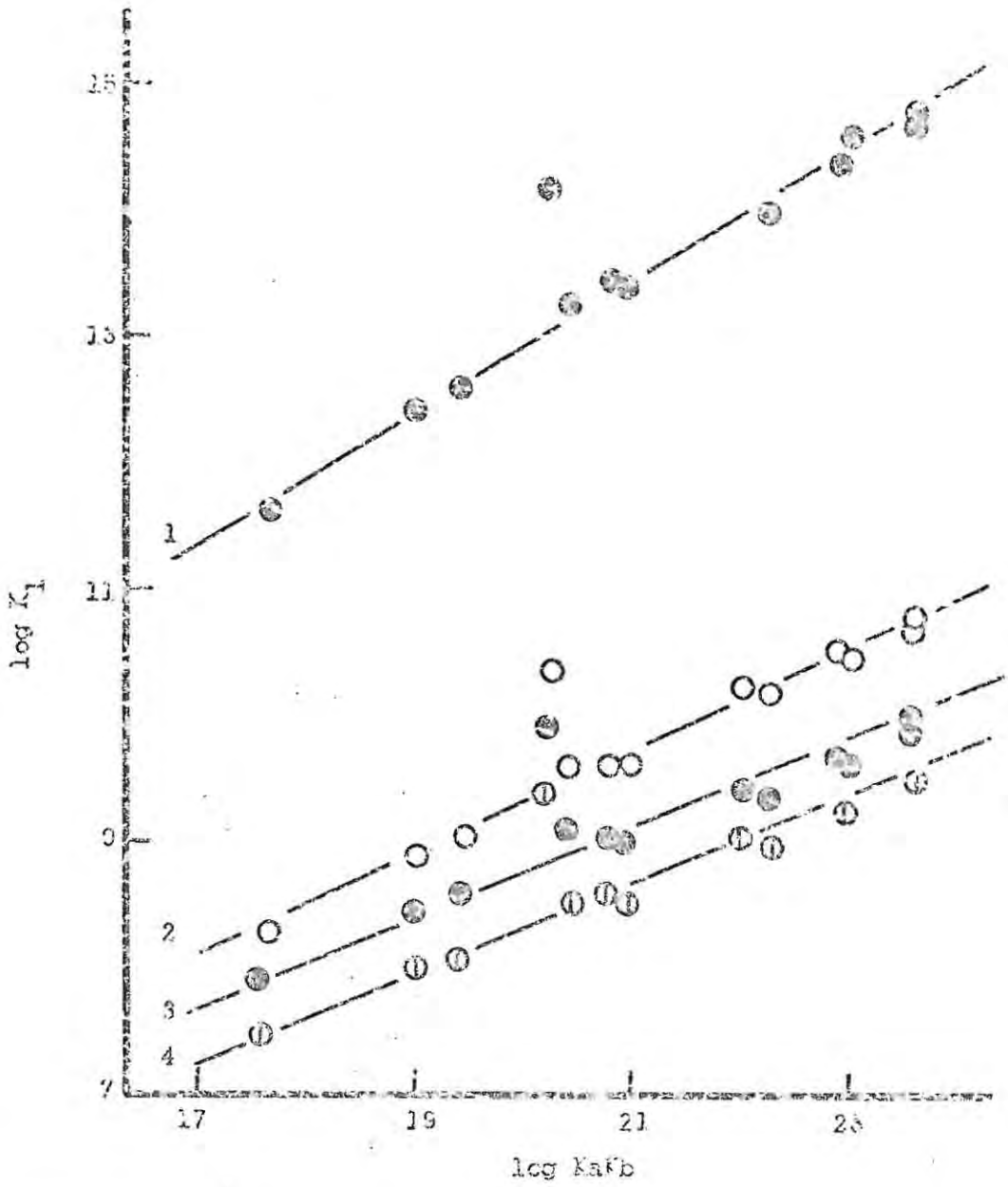


FIG. 3. Relation between the ligand association constants, $K_a K_b$, and the stability constants, K_1, for the (1) Cu(II), (2) Zn(II), (3) Ni(II) and (4) Co(II) complexes of o-dipherols.

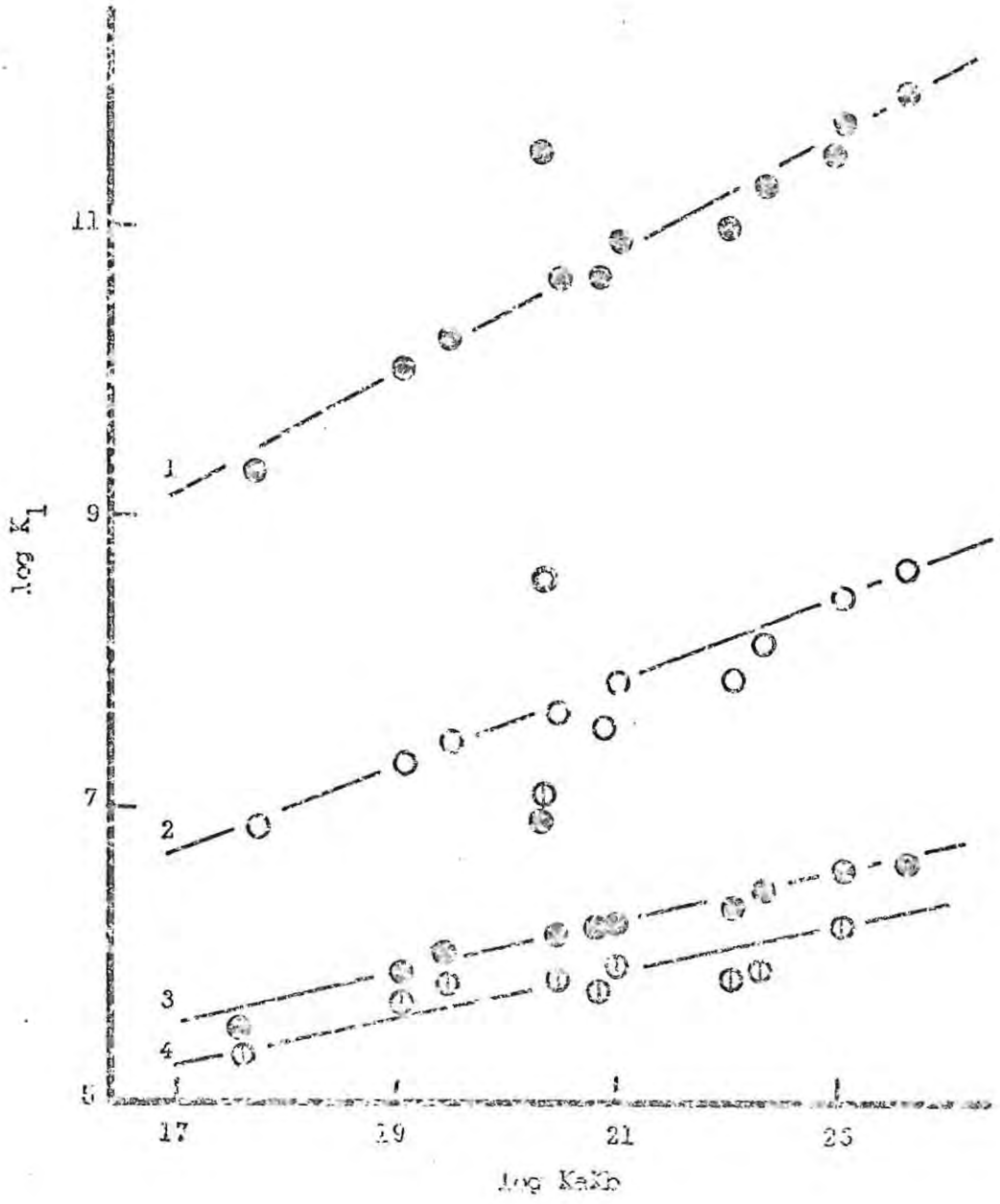


FIG. 4. Relation between the ligand association constants, KaKb, and the stability constants, K_2, for the (1) Cu(II), (2) Zn(II), (3) Co(II) and (4) Ni(II) complexes of o-diphenols.

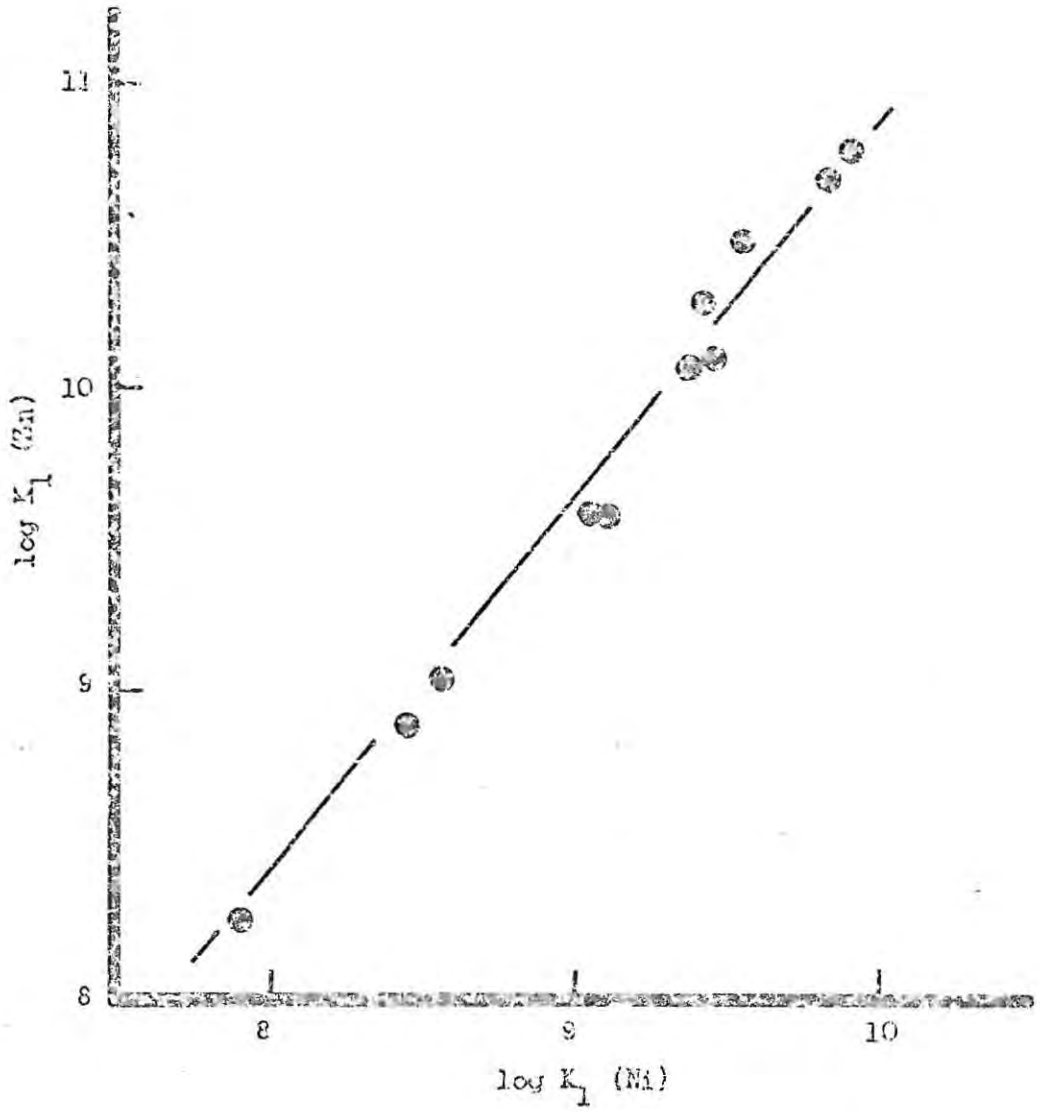


FIG. 5. Relation between the stability constants, K_1, for the Zn(II) and Ni(II) complexes of *o*-diphenols.

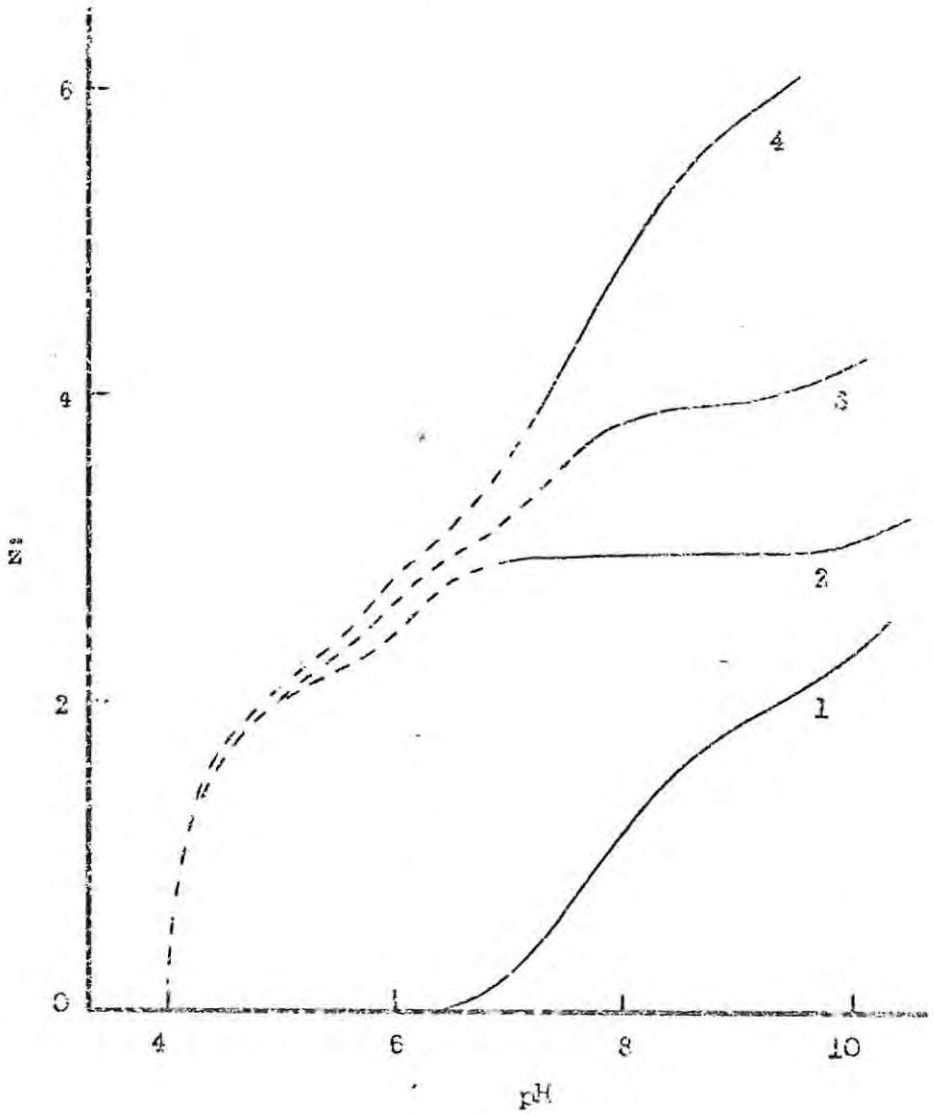


FIG. 6. Potentiometric titration curves for the Cu(II)-propyl gallate system; (1) T_L^o = 0.004 M, (2) $T_M^o = T_L^o$ = 0.002 M; (3) T_M^o = 0.002 M, T_L^o = 0.004 M; (4) T_M^o = 0.003 M, T_L^o = 0.008 M. N = 0.1 N KOH, I = 0.1. Dashed lines indicate presence of precipitate.

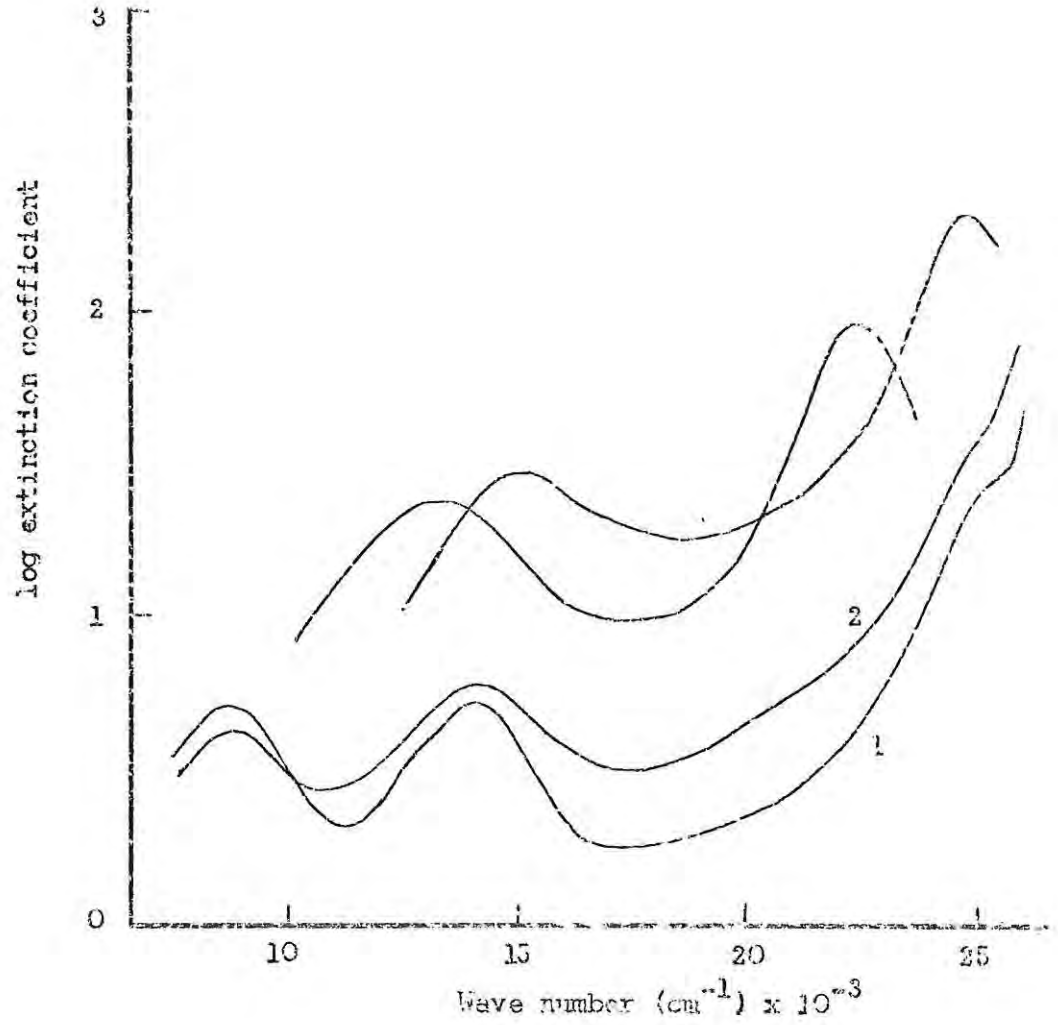


FIG. 7. Absorption spectra of (1) NiL complex species of DHNS, (2) NiL_2 complex species of 4-methylcatechol, (3) CuL_1 complex species of Tiron and (4) CuL_2 complex species of catechin.

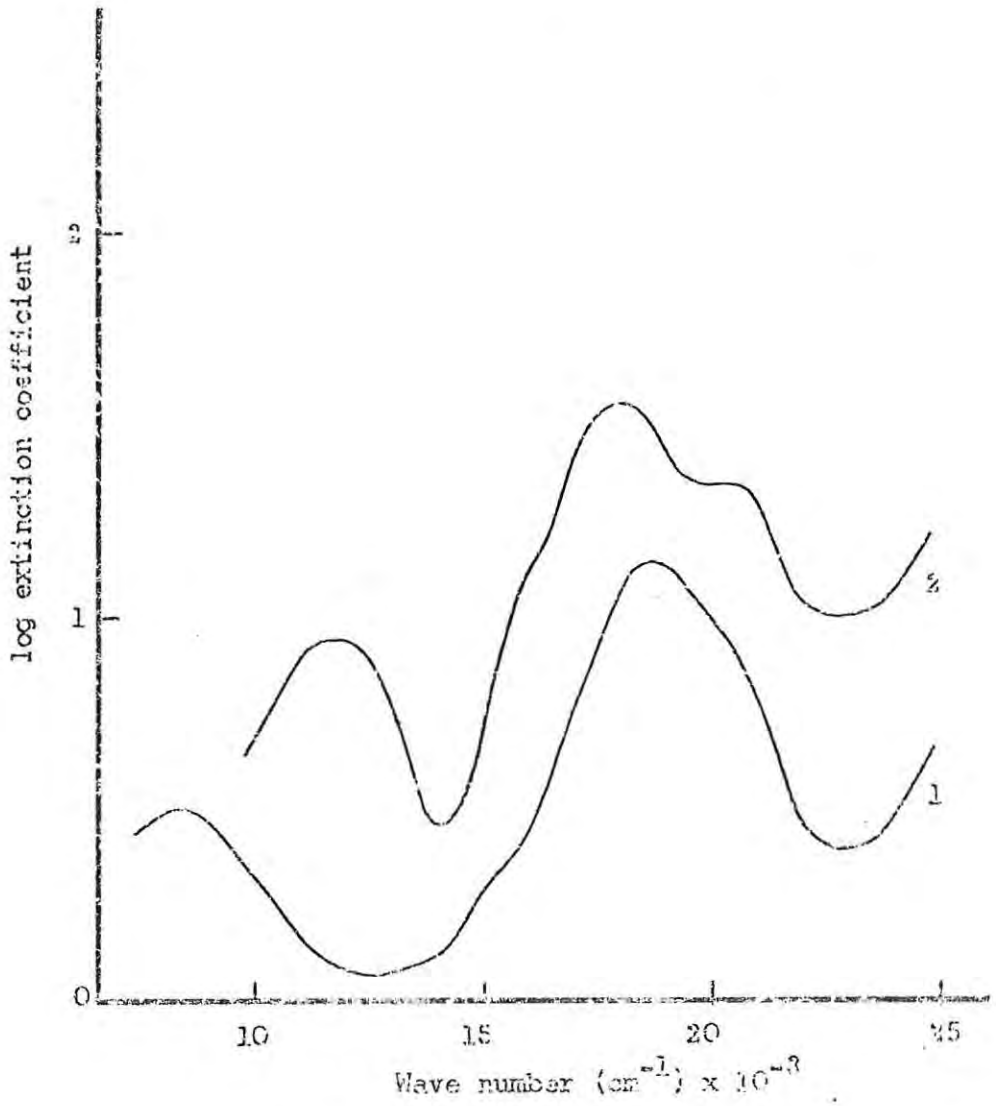


FIG. 8. Absorption spectra of (1) CoL_1 complex species of Tiron and (2) CoL_3 complex species of pyrocatechol.

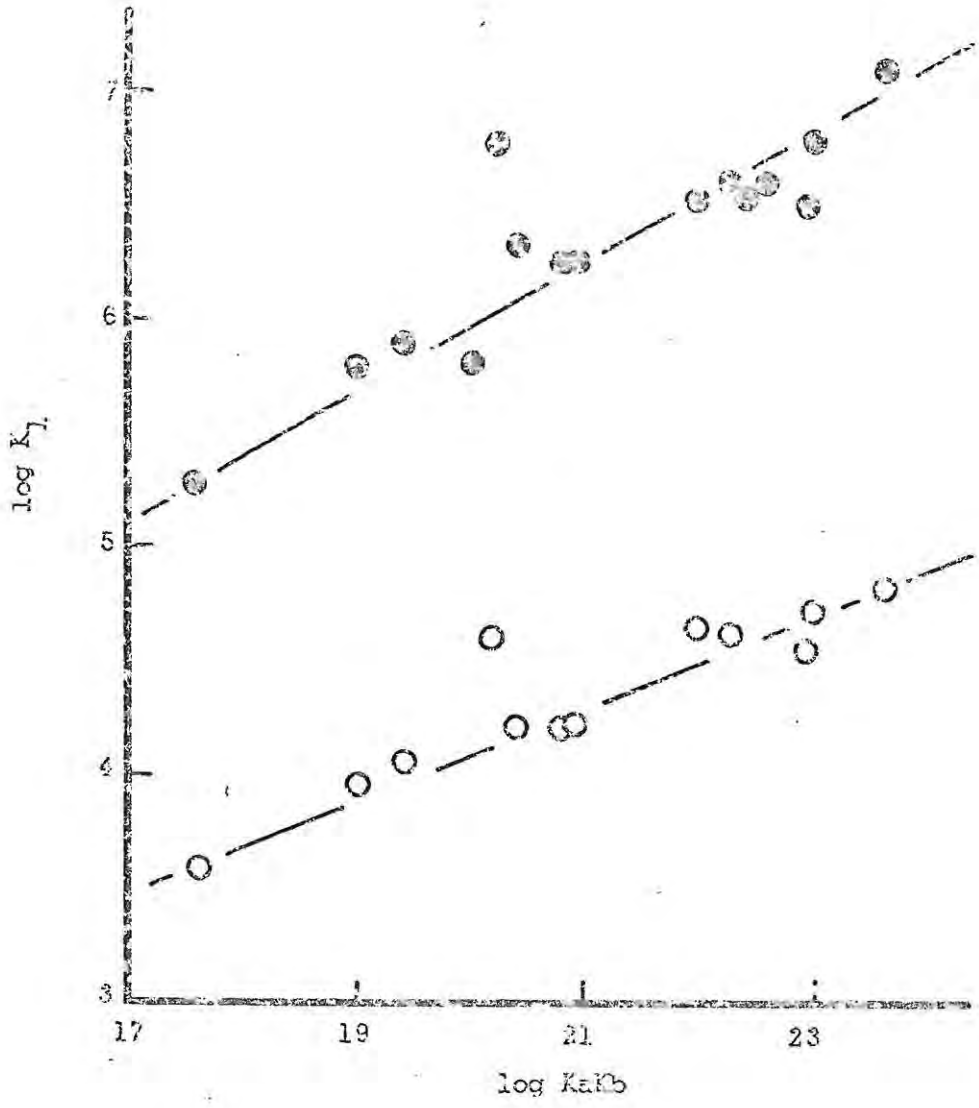


FIG. 11. Relation between the stability constants, K_1, for the Mg(II) ● and Ca(II) ○ complexes of o-diphenols and the ligand association constants, KaKb.

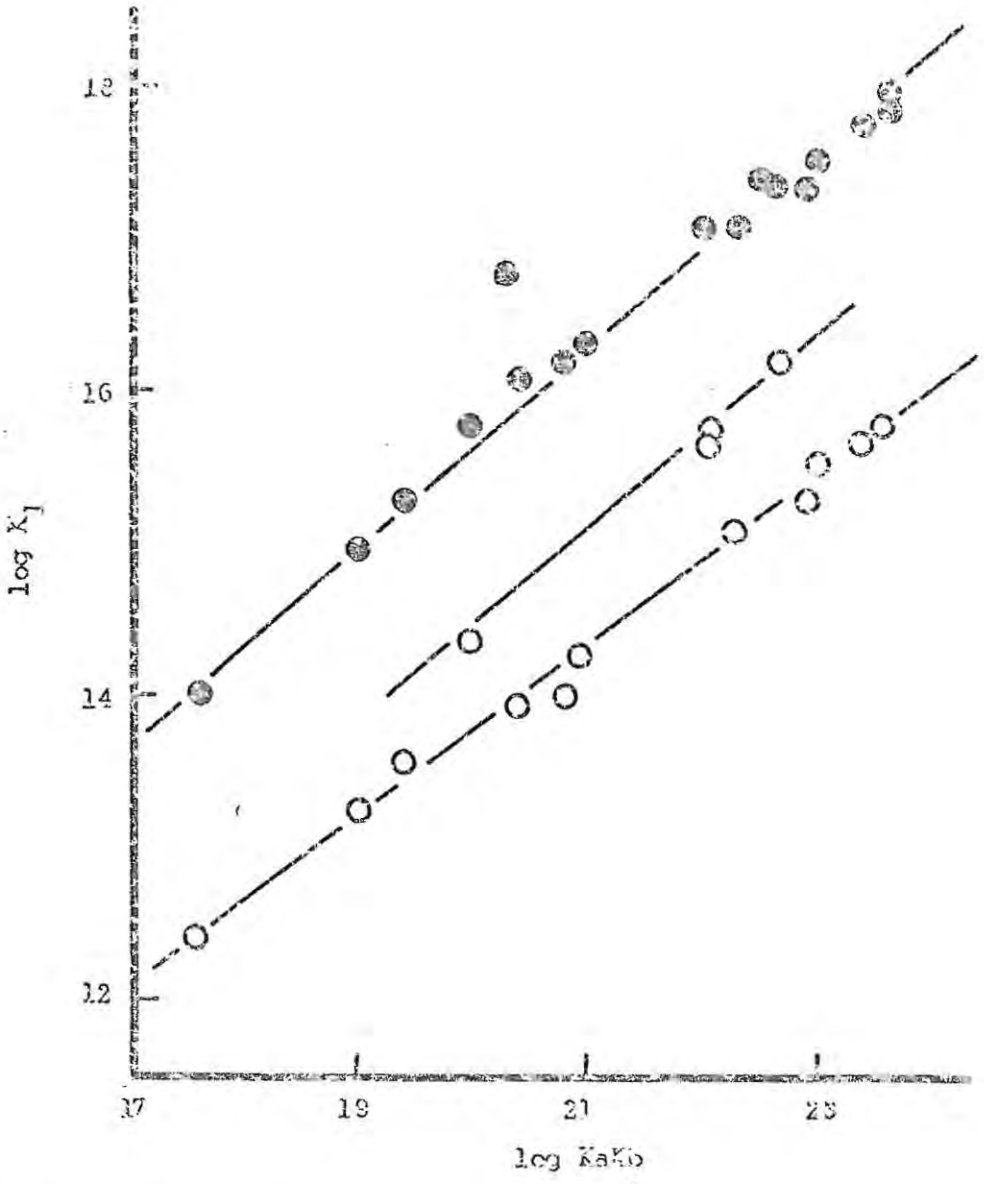


FIG.12. Relation between the stability constants, K_1 ● and K_2 ○ , for vanadyl(IV) complexes of o-diphenols and the ligand association constants, KaKb.

E. CHARGE TRANSFER COMPLEXES OF o-DIPHENOLS.

The oxidisable nature of phenolic ligands results in the formation of intensely coloured charge transfer complexes with a number of reducible metal ions.[25]

1. Titanium(IV) complexes.

Due to the high charge to radius ratio of Ti(IV) ions, no simple octahedral hexa-aquo species are present in aqueous media.[131] One of the main hydrolysis products in acid solution has been shown to be $Ti(OH)_2^{2+}$, which exists as an hydrated octahedral species.[131] The aqueous stock solution of Ti(IV) was made highly acidic to prevent the formation of insoluble titanium dioxide, which forms at pH greater than two.

The intense yellow colours of the o-diphenol complexes of Ti(IV) enabled the equilibria to be studied by spectrophotometric methods. The intensity of the colours was found to be dependent on the pH indicating that protons are liberated on complexation. Absorption spectra of solutions containing Ti(IV) ions and excess of ligand were recorded at various pH values as illustrated in Fig. 1. The yellow colour of the complexes is due to the strong absorption band in the blue region of the spectrum. The final yellow species of both o-dihydroxybenzene and 1,2,3-trihydroxybenzene derivatives has been shown to be the tris-chelate, TiL_3.[25,86,129,130] Spectral data of the o-diphenol complexes are given in Table 1. Absorbance values at 430 nm for the pyrocatechol, protocatechuic acid, DHNS and Tiron complexes are in agreement with published values.[25,86]

TABLE 1.

Spectral data and equilibrium constants, k_1', for o-diphenol complexes of Ti(IV).

Ligand	Absorption maxima kK	Extinction coefficient x 10^{-3}	Extinction coefficient x 10^{-3} at 430 nm	pk'
4-methylcatechol	25.8	10.8	8.3	6.63
pyrocatechol	26.0	11.3	8.2	6.16
catechin	26.0	12.5	9.5	5.42
pyrogallol	26.3	12.0	8.3	5.50
robinetinidol	26.3	12.7	9.2	4.95
3,4-dihydroxybenzenesulfonate	26.3	14.4	9.8	4.30
Tiron	26.3	15.5	10.0	3.03
protocatechuic acid ($-COO^-$)	26.1	14.3	9.9	-
protocatechuic acid (-COOH)	26.3	16.0	10.3	3.80
gallic acid ($-COO^-$)	26.5	16.4	11.2	-
gallic acid (-COOH)	26.7	18.4	11.7	3.45
propyl gallate	26.7	19.5	12.6	3.33
4-chloroacetylcatechol	(26.7)[a]		15.7	3.27
protocatechuic aldehyde	(26.7)[a]		15.0	2.82
2,3-dihydroxynaphthalene	27.3	32.0	13.3	4.19
DHNS	27.6	39.0	15.0	3.69

[a]Values in parentheses refer to shoulders.

The intermediate complex species have been shown to be dependent on the ligand concentration.[86,129] In solutions containing a very large excess of the o-diphenol ligand (T_L/T_M = 400 - 4000), the following equilibria occur[86,130] :

$$TiO^{2+}(Ti(OH)_2^{2+}) + 2H_2L \rightleftharpoons TiO(LH)_2 + 2\,H^+ \quad (1)$$

$$TiO(LH)_2 + H_2L \rightleftharpoons TiL_3^{2-} + 2H^+ \quad (2)$$

The species, $TiO(LH)^+$, have also been detected at low pH.[86,129] However, a very large excess of ligand was not possible for some of the o-diphenols due to their limited solubility in aqueous media. In order to

ensure similar experimental conditions, the spectrophotometric investigation was carried out with molar ratios of Ti(IV) to ligand in the range 1 : 30 - 40. Under these conditions the formation of the $TiO(LH)_2$ species, with wavelength maxima in the region of 435 nm,[130] were not observed as shown by the absorption spectra (Fig. 1). The only maxima are in the region of 380 nm, corresponding to the direct formation of the species, TiL_3.

The equilibrium involved in the formation of the species, TiL_3, under the experimental conditions used, was solved by logarithmic analyses of the extinction curves (absorbance vs. pH plots), shown in Fig. 2. For the reaction :

$$Ti^{4+} + x\,H_2L \rightleftharpoons TiL_3^{2-} + h\,H^+ \qquad (3)$$

the number of protons liberated on complexation and the number of ligand molecules involved were determined with the aid of the equation[86] :

$$\log \frac{A}{A_1^o - A} = h\,pH + x \log \left[H_2L\right] + \log k' \qquad (4)$$

where k' is the equilibrium constant for reaction (3), A is the absorbance at a fixed wavelength and A_1^o is the maximum absorbance at complete formation of the TiL_3 species. Slopes of $\log \frac{A}{A_1^o - A}$ vs. pH plots give the number of protons liberated, if the concentration of the ligand is not appreciably ltered by complexation. Slopes of $\log \frac{A}{A_1^o - A}$ vs. $\log \left[H_2\ddot{L}\right]$ plots at fixed pH give the number of ligand molecules involved in the equilibrium. The application of these treatments is illustrated in Fig. 3. Slopes of the straight lines gave h = 3 and x = 2. The following equilibrium, for the formation of the TiL_3 species, would satisfy

these results :

$$TiO(LH)^{+} + 2\ H_2L \rightleftharpoons TiL_3^{2-} + 3\ H^{+} \qquad (5)$$

It was evident from the absorption spectra (Fig. 1) that the extinction coefficients of the initial species, $TiO(LH)^{+}$, are negligable relative to the very large extinction coefficients (Table 1) of the final species, TiL_3. The metal ion reactant (reaction 5) cannot be an uncomplexed species because complexation occurs at pH > 2 (Figs. 1 and 2). Hence insoluble TiO_2 would be expected[129] to form, whereas no such precipitates were observed. The equilibrium constants, k', for reaction (5) were determined from the extinction curves using the following equation :

$$k' = \frac{A\left[H\right]^3}{(A_1^{\circ} - A)\left[(T_L - T_M) - 2T_M\, A/A_1^{\circ}\right]^2} \qquad (6)$$

where T_M and T_L are the respective metal ion and ligand concentrations. Values of k_1' for the o-diphenol complexes of Ti(IV) are listed in Table 1. Examples of the calculation are given in Table 4.

Values of k' (Table 1) for the protocatechuic acid and gallic acid complexes are related to the carboxyl substituent in the undissociated form, since complexation is complete at pH values lower than the region in which carboxyl ions form. Absorption spectra of these complexes at higher pH values did not remain unchanged as for the other o-diphenol complexes. This is shown in Fig. 2. The decrease in absorbance between pH 4 - 6 for the protocatechuic acid complex has been interpreted as being due to the formation of the TiL_3 species from the TiL_2 species.[122] The author is of the opinion, however, that this interpretation is incorrect. The decrease in extinction coefficient and the shift in the

absorbance maxima for the protocatechuic acid and the gallic acid complexes, in the region from pH 4 - 6 (Table 1) is ascribed to the ionisation of the carboxyl groups of those ligands co-ordinated to the metal ion. The electronic influences of the carboxyl substituent in the dissociated and undissociated state are different,[116] hence these will affect the charge transfer process as will be shown later (p. 242). Approximate values of the dissociation constants for the carboxyl groups in the TiL_3 complexes of protocatechuic acid and gallic acid were determined from the extinction curves (Fig. 2), at the half-neutralisation point ($\bar{n}_a = 0.5$, Section A). Values of pK = 5 for both the above complexes were obtained. These values compare with pK = 5.10 and 5.01 for a similar dissociation process in the Ge(IV)-protocatechuic acid and -gallic acid complexes, respectively. Both the Ti(IV) and Ge(IV) complexes have the same overall charge *viz.* ML_3^{2-}. Therefore the electronic influences of the *o*-dihydroxo complexed group (*cf.* p. 155) would be expected to be the same. This is reflected in the close agreement of the above dissociation constants for the two sets of complexes.

An immediate orange precipitate formed in solutions containing Ti(IV) ions and wattle tannin. Although the sulfited derivative of wattle tannin formed a soluble, yellow complex with Ti(IV), the equilibrium constants, k', could not be determined. The large excess of wattle tannin which was necessary to meet the requirement, $T_L/T_M = 40$ as for the other *o*-diphenol complexes and also to allow for the polymeric nature of wattle tannin, resulted in gross optical interference from the tannin solution. However, the absorption spectrum of Ti(IV) ions and a much lower concentration of wattle tannin ($T_L/T_M = 15$) at pH = 6, compared with a blank

of the same tannin concentration, gave an absorption maximum at 26,300 cm^{-1} (extinction coefficient = 13,000). A comparison of these values with those for the wattle tannin monomers (Table 1) indicates that the same TiL_3 species is formed.

The equilibrium constants, k', for the o-diphenol complexes of Ti(IV) were correlated with the dissociation constants of the ligand and the result shown in Fig. 4. The linear relationship (except for Tiron) again shows the generally found dependence of complexation (reaction 5) on the acidity of the ligand. Similar relationships have also been obtained for the equilibrium constants of reactions (1) and (2).[129]

The constants, k', for the Ti(IV) complexes were also correlated with the equilibrium constants, k'_3, for the Ge(IV) complexes (Section C). Although the requirement[216] of similar valencies is satisfied, the nature of the equilibria are not similar. However, the linear relationship shown in Fig. 4 includes the point for Tiron, indicating that the latter requirement is not an important factor in this correlation. The points for the two wattle tannin monomers, catechin and robinetinidol, may both be superimposed on the straight lines in Fig. 4

The strong absorption bands of the o- diphenol complexes of Ti(IV) have been assigned to a charge transfer process from ligand to metal.[25] From Table 1 the wave numbers of maximum absorption move to higher energies, with increasing electron-withdrawing character of the substituent relative to the unsubstituted phenol and vice versa. Hence, according to the electrostatic interpretation of charge transfer (p. 107), the process is from ligand to metal as found previously.[25] Because Ti(IV)

has a d^0 configuration, the charge transfer bands in Table 1 may be assigned to the transition $\pi \longrightarrow t_{2g}$ on a molecular orbital model (p. 111). The close proximity of the strong phenolic absorption bands prevented the detection to any higher energy bands ($\pi \longrightarrow e_g$).

Correlation between the wave numbers of maximum absorption and the corresponding extinction coefficients (Table 1) yielded separate linear relationships for the o-dihydroxybenzene and 1,2,3-trihydroxybenzene complexes as illustrated in Fig. 5. Similar relationships were found for the Fe(III) complexes (Section B). This figure may be used to illustrate the correctness of the previous assumptions, concerning the protocatechuic acid and gallic acid complexes. From Table 1 the effect of carboxyl ionisation is to lower the extinction coefficient and the energy required for charge transfer. Fig. 5 shows that the decrease in extinction coefficient should result in a decrease in transition energy, as observed for both protocatechuic acid and gallic acid. In addition the electron-withdrawing character of the carboxyl group is greatest in the undissociated state.[116] Hence, on ionisation of the carboxyl group the electron-withdrawing character decreases, therefore the charge transfer process (ligand to metal) will be less hindered. This results in the observed shift to lower energies.

Correlation of the wave numbers of maximum absorption for the o-diphenol complexes of Ti(IV) with those for the Fe(III) complexes, gave a linear relationship as shown in Fig. 6. This illustrates that the electronic influences of the different phenolic substituents have a similar effect on the charge transfer processes in the two sets of

o-diphenol complexes.

Optical electronegativities (χ_{opt}) have been determined from the spectrophotometric data of many charge transfer complexes.[133] For ligand (L) to metal (M) charge transfer, Jorgensen[134] derived the equation :

$$\nu^{*}_{CT} = 30{,}000\ (\chi_{opt}(L) - \chi_{opt}(M)) \qquad (7)$$

where ν^{*}_{CT} is the energy of the charge transfer band, corrected for changes in spin-pairing energy during the transition (see below), and $\chi_{opt}(M)$ and $\chi_{opt}(L)$ are the optical electronegativities of the accepter and donor orbitals on the metal and ligand, respectively. Jorgensen, in considering the optical electronegativity of a particular metal ion in an octahedral complex, refers to the approximately nonbonding t_{2g} level (ligand field approach). The spin-pairing energy (SPE) of a given configuation is given by[133,134] :

$$SPE = \left[\langle S(S+1) \rangle - S(S+1) \right] D \qquad (8)$$

where $\langle S(S+1) \rangle$ is the average value of $S(S+1)$ for a given configuration l^q and is given by :

$$S(S+1) = \frac{q(q+2)}{4} - \frac{(2l+2)q(q-1)}{2(4l+1)} \qquad (9)$$

(l is the orbital quantum number, S is the total spin quantum number, and q is the number of electrons in the d-subshell). D is the spin-pairing energy parameter and, for d electrons, is approximately equal to 7 B (B is the Racah parameter of interelectronic repulsion). ν^{*}_{CT} is then given by :

$$\nu^{*}_{CT} = \nu_{CT}(\text{observed}) - \Delta SPE \qquad (10)$$

where Δ SPE is the difference between the spin-pairing energy in the excited and ground state.

For the o-diphenol complexes of Ti(IV) the charge transfer may be represented by $L^{n}t_{2g}^{o}e_{g}^{o} \longrightarrow L^{n-1}t_{2g}^{1}e_{g}^{o}$. The ground state has $l = 2$, $S = 0$, $q = 0$, hence SPE = 0. The excited state has $l = 2$, $S = \frac{1}{2}$, $q = 1$, hence SPE = 0. Thus no correction of the transition energy is necessary. For the Fe(III) complexes the charge transfer ($\pi \longrightarrow t_{2g}$) may be represented by $L^{n}t_{2g}^{3}e_{g}^{2} \longrightarrow L^{n-1}t_{2g}^{4}e_{g}^{2}$. The ground state has $l = 2$, $S = \frac{5}{2}$, $q = 5$ hence SPE = $-\frac{20}{3}D$. The excited state has $l = 2$, $S = 2$, $q = 6$ hence SPE = $-4D$. Thus the change in spin-pairing energy is Δ SPE = $+\frac{8}{3}D$.

In order to determine the optical electronegativities of the o-diphenolato ligands, the optical electronegativities of the metal ion are required. Unfortunately, values of $\chi_{opt}(M)$ for octahedral Ti(IV) and high-spin, octahedral Fe(III) have not been determined. However, $\chi_{opt}(M)$ values are known for tetrahedral Ti(IV) and high-spin tetrahedral Fe(III) viz. 1.8 and 2.4 - 2.5, respectively.[133] It has also been shown that for V(III), the difference between octahedral and tetrahedral values of $\chi_{opt}(M)$ is -0.2.[133] Octahedral values of $\chi_{opt}(M)$ are lower than those in a tetrahedral environment because, in crystal-field theory, the spherical perturbation of the metal ion orbitals is linearly dependent upon the co-ordination number. Therefore, on this basis approximate values of $\chi_{opt}(M)$ for octahedral Ti(IV) and high-spin octahedral Fe(III) of 1.6 and 2.3, respectively, were determined. Using the above value for octahedral Ti(IV), the values of ν_{CT}(observed) for the TiL_3 complexes

(Table 1), and equation (7), then values of $\chi_{opt}(L)$ for the o-diphenolato ligands in the region of 2.5 were obtained. Optical electronegativities are only approximate and are therefore quoted to one decimal point.[133] Using the value of $\chi_{opt}(Fe(III),O_h) = 2.3$, the values of ν_{CT}(observed) for the FeL_3 complexes (Table 7, Section B), the value of B = 740 cm^{-1} for the related tris(oxalato)iron(III) ion,[135] and equations (7) and (10), then values of $\chi_{opt}(L)$ for the o-diphenolato ligands, also in the region of 2.5, were obtained. The close agreement of the values of $\chi_{opt}(L)$ for the two sets of o-diphenol complexes, provides some justification for the assumptions which have been made.

2. Molybdenum(VI) complexes.

Sodium molybdate was used as the source of molybdenum(VI) ions. In aqueous solution, molybdate, MoO_4^{2-}, ions exist as discrete tetrahedra.[264] Aqueous solutions of MoO_4^{2-} ions and o-dihydroxybenzene and 1,2,3-trihydroxybenzene derivatives at pH 7 have been shown to form bis-chelates according to the equilibrium [81,85,265] :

$$MoO_4^{2-} + H_2L \rightleftharpoons MoO_2L_2^{2-} \qquad (11)$$

The complexes are orange in colour, due to a strong absorption band in the blue region of the spectrum. The absorption band has been assigned to a charge transfer process from ligand to metal.[25]

The absorption spectra of solutions containing MoO_4^{2-} ions and excess of the o-diphenol ligand ($T_L/T_M = 40$) were recorded at pH 7. The Mo(VI) complexes with the less acidic phenols gave broad absorption maxima in the region of 400 nm. Due to the close proximity of the strong phenolic

absorption bands, absorption maxima were not observed for all the o-diphenol complexes. Spectral data for the Mo(VI) complexes are given in Table 2. The effect of the phenolic substituents on the charge transfer process is in accordance with a transition from ligand to metal, since an electron-releasing substituent results in a shift of the absorption band to lower energy, relative to pyrocatechol and vice versa (Table 2).

TABLE 2.

Spectral data for Mo(VI) complexes, $MoO_2L_2^{2-}$, of o-diphenols.

Ligand	Absorption max. kK	Extinction coefficient x 10^{-3}
4-methylcatechol	24.7	4.4
4-tert.-butylcatechol	24.7	3.8
pyrocatechol	25.0	4.3
catechin	25.0	4.5
3,4-dihydroxybenzenesulfonate	25.6	5.5
pyrogallol	25.3	4.5

Solutions of MoO_4^{2-} ions and wattle tannin also form an intensely coloured (orange) charge transfer complex. The complex is completely soluble in aqueous media, even at high ionic strengths. Use was made of the intense colour formation between MoO_4^{2-} ions and wattle tannin to develop a novel method of tannin analysis. Absorbance values of solutions, containing an excess of sodium molybdate and varying amounts of wattle tannin of known tannin content, obeyed Bear's Law as shown in Fig. 7. Absorbance measurements were determined at 400 nm, corresponding to the broad absorption band of the Mo(VI)-wattle tannin complex in this region of the spectrum. Colour formation is immediate, but not permanent.

After a period of 30 min. absorbance values decrease slowly with time. Any optical interference from the tannin solution was eliminated by using a blank of the same tannin concentration, without sodium molybdate. Solutions of MoO_4^{2-} ions are completely transparent at 400 nm. The optical measurements were determined at 20°C but a change of ± 5° had no effect on the absorbance values.

The analytical method given in Fig. 7 was checked with different wattle tannin extracts. The tannin content of these extracts was determined by standard methods.[15] Table 3 shows that there is good agreement between the standard methods and the spectrophotometric method utilising the Mo(VI)-wattle tannin complex. The Official (Hide Powder) Method allows a maximum difference of three percent in total tannin content between results obtained by different analysts, using the same sample.[266]

TABLE 3.

Comparisons of standard methods for determining tannin content with that using the Mo(VI)-wattle tannin complex.

Extract	Molybdate method		Hide Powder method*	Ultraviolet method[15]
	A	% tannin	% tannin	% tannin
Acetone extract	0.480	76.5	-	75.8
Cold water extract	0.304	49.	-	49.3
Commercial extracts:				
Vryheid stick bark	0.408	66	65.5	66.0
Vryheid fresh bark	0.455	73	73.4	72.5
Comec	0.422	68	69.0	68.5

*Analysed by a commercial firm.

An attempt was made to develop a similar spectrophotometric method using the yellow-coloured W(VI)-wattle tannin complex. However, solutions

of sodium tungstate and wattle tannin gave no absorption maximum, due to the overlap of the phenolic absorption band with that of the W(VI) complex. Hence, at wavelengths, 380 - 450 nm, corresponding to the tail of the charge transfer band, small errors in setting the wavelength scale resulted in large variations of the absorbance values. Due to the non-reproducibility of the results, the W(VI)-wattle tannin complex could not be used for the analytical determination of wattle tannin.

TABLE 4.

Determination of equilibrium constants, k', for Ti(IV) complexes of catechin and 4-chloroacetylcatechol.

Ligand : catechin			4-chloroacetylcatechol		
pH	A	pk'	pH	A	pk'
3.61	0.374	5.42	3.10	0.355	3.26
3.70	0.476	5.44	3.16	0.425	3.26
3.73	0.515	5.42	3.23	0.495	3.27
3.82	0.600	5.43	3.30	0.550	3.29
3.88	0.650	5.40	3.38	0.610	3.26

Experimental data used in equation (6) :

Wavelength = 380 nm, $A_1^o = 0.755$, $T_M = 6 \times 10^{-5}$ M, $T_L = 2 \times 10^{-3}$ M, I = 0.1, l = 1 cm.

Wavelength = 400 nm, $A_1^o = 0.70$, $T_M = 3 \times 10^{-5}$ M, $T_L = 1 \times 10^{-3}$ M I = 0.1, l = 1 cm.

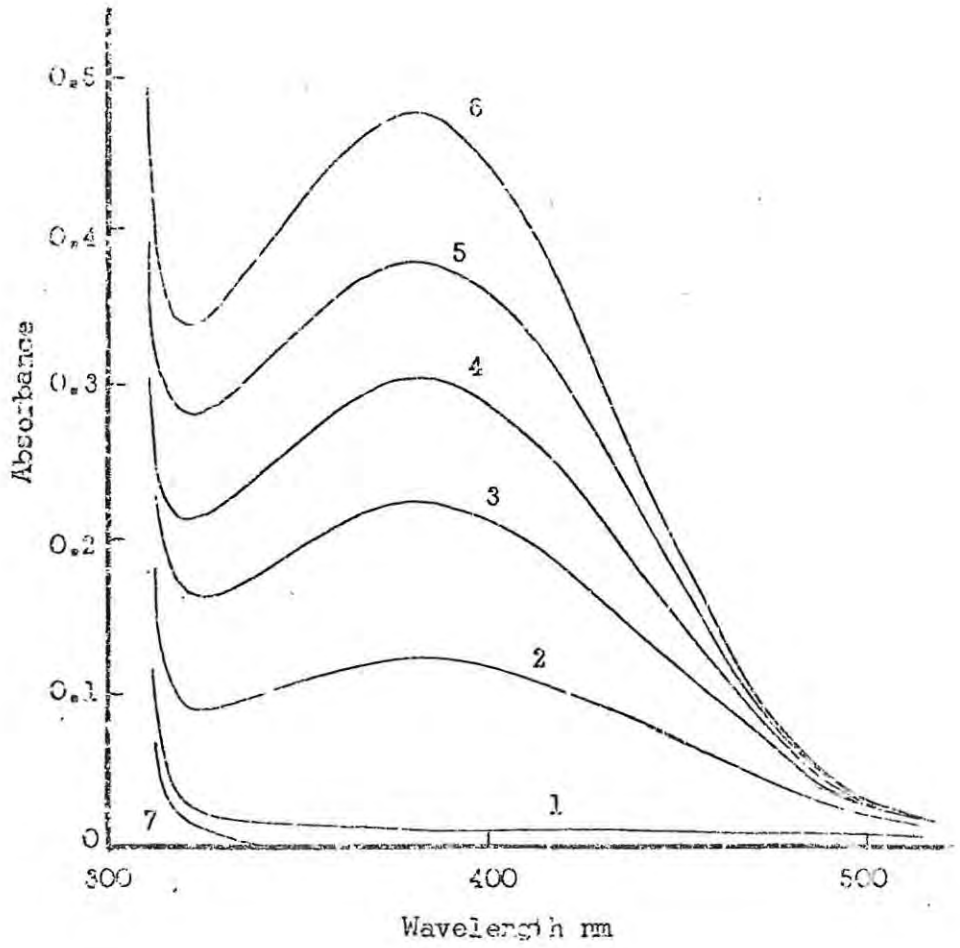


FIG. 1. Absorption spectra of the Ti(IV)-Tiron system at pH values : (1)2.50, (2)2.62, (3)2.98, (4)3.10, (5)3.25 and (6)3.8-6.0; (7)ligand, $I = 0.1$, $T_M = 3.2 \times 10^{-5}$ M, $T_L = 1 \times 10^{-3}$ M, $l = 1$ cm.

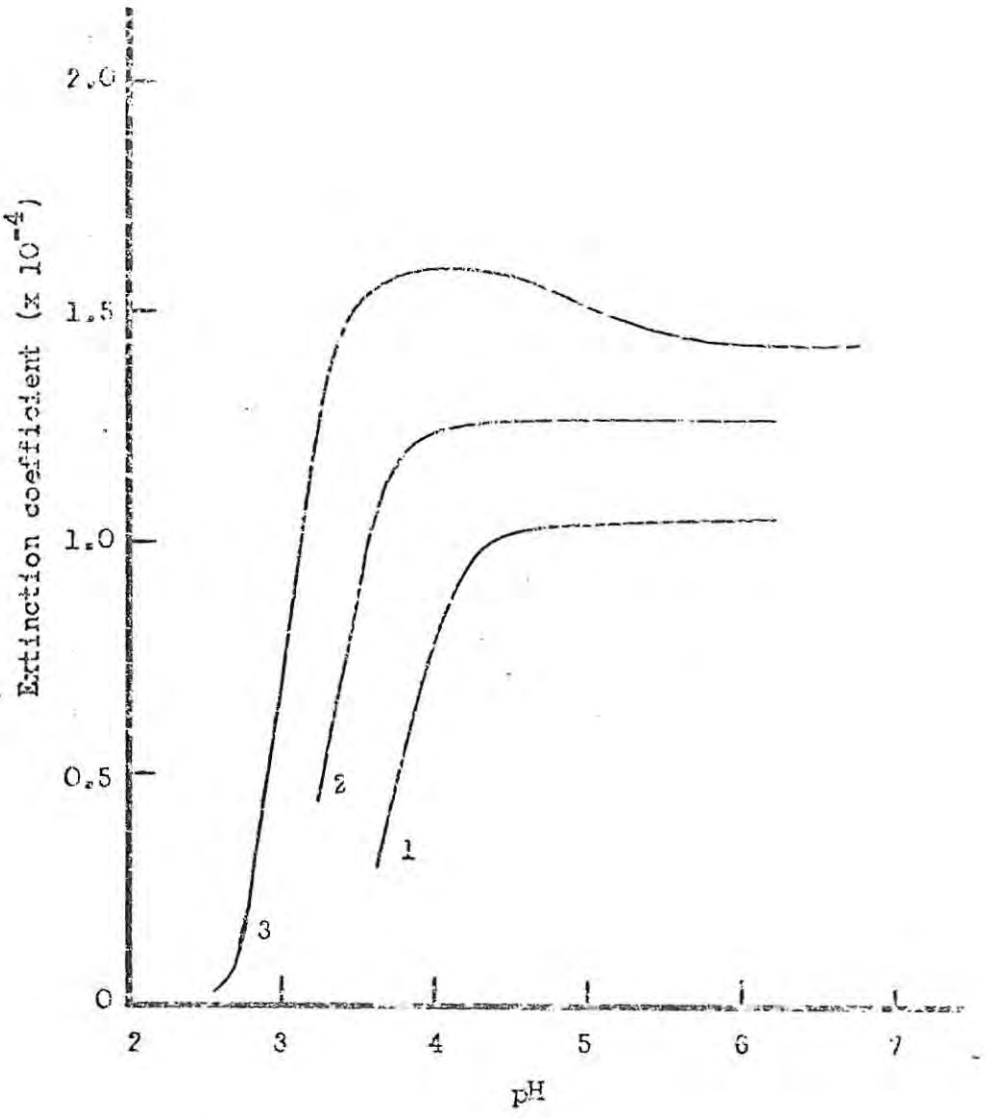


FIG. 2. Extinction curves for Ti(IV) complexes of (1)4-methylcatechol, $T_L/T_M = 40$, $T_M = 1 \times 10^{-4}$M; (2)robinetidudol and (3) protocatechuic acid, $T_L/T_M = 33$, $T_M = 6 \times 10^{-5}$M. Analytical wavelength = 390 mμ, l = 0.1.

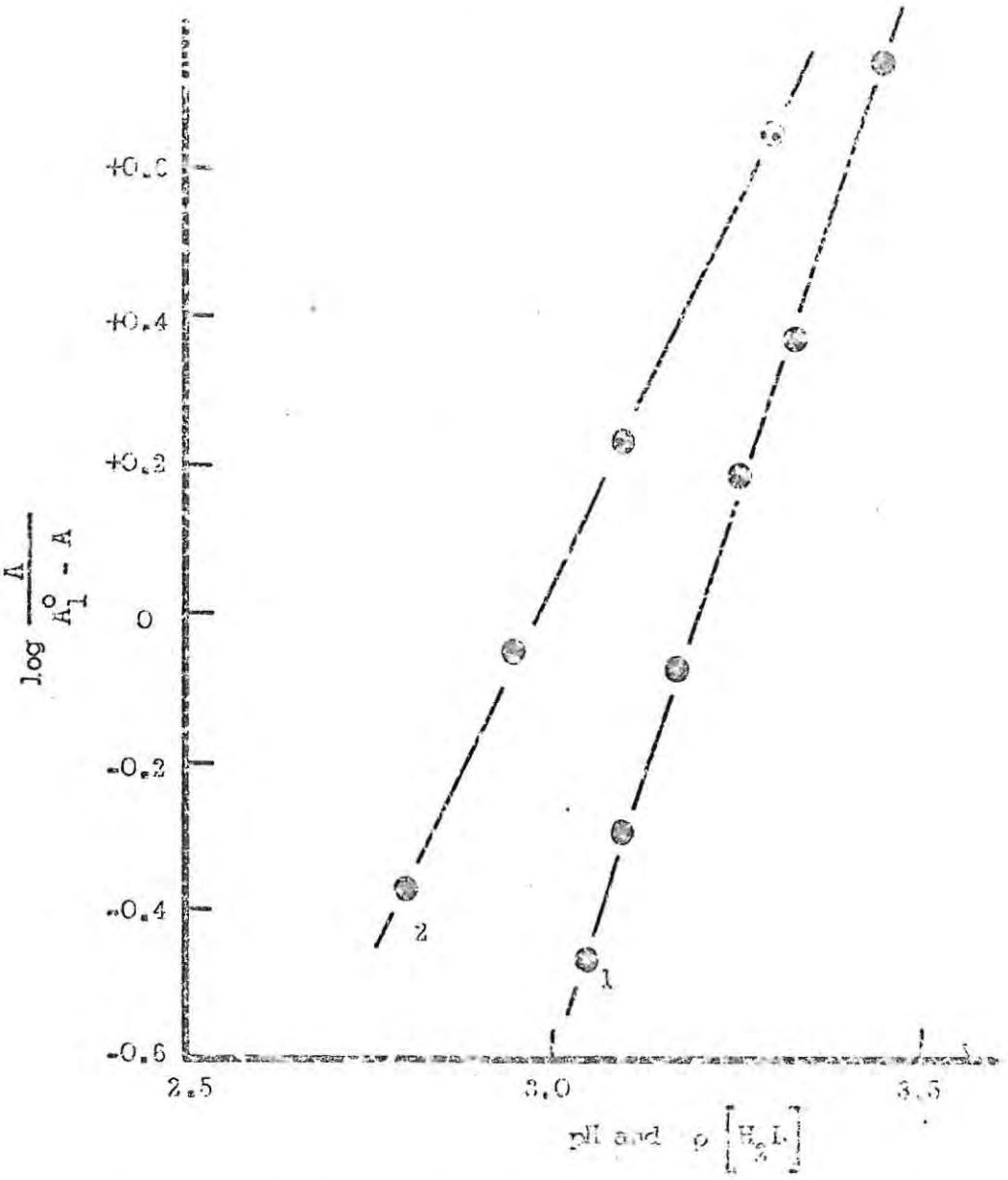


FIG. 3. Logarithmic analyses of extinction curves for Ti(IV) complexes of (1) 2,3-dihydroxynaphthalene, $C_L/C_M = 50$, $C_M = 2 \times 10^{-5}$ M, wavelength = 370 nm ($\log \frac{A}{A_1^o - A}$ vs. pH); (2) Tiron, at pH 2.7, $C_M = 6 \times 10^{-5}$ M, wavelength = 380 nm, ($\log \frac{A}{A_1^o - A}$ vs. $p\left[H_2L\right]$); I = 0.1, l = 1 cm.

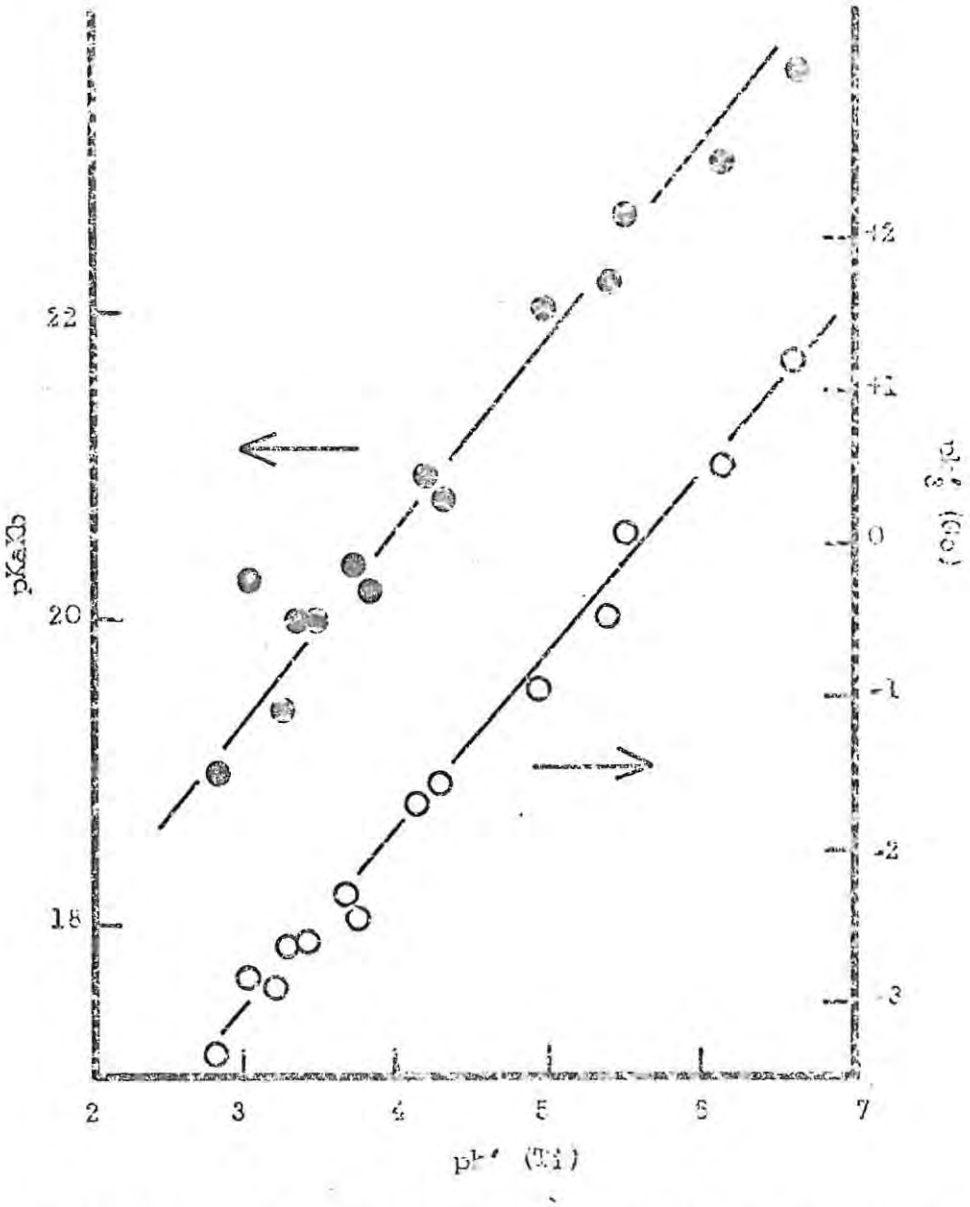


FIG. 4. Relation between equilibrium constants, k', for o-diphenol complexes of Ti(IV) and ligand dissociation constants, $K_a K_b$, (left scale ●), and equilibrium constants, k'_g, for o-diphenol complexes of Ge(IV) (right scale ○).

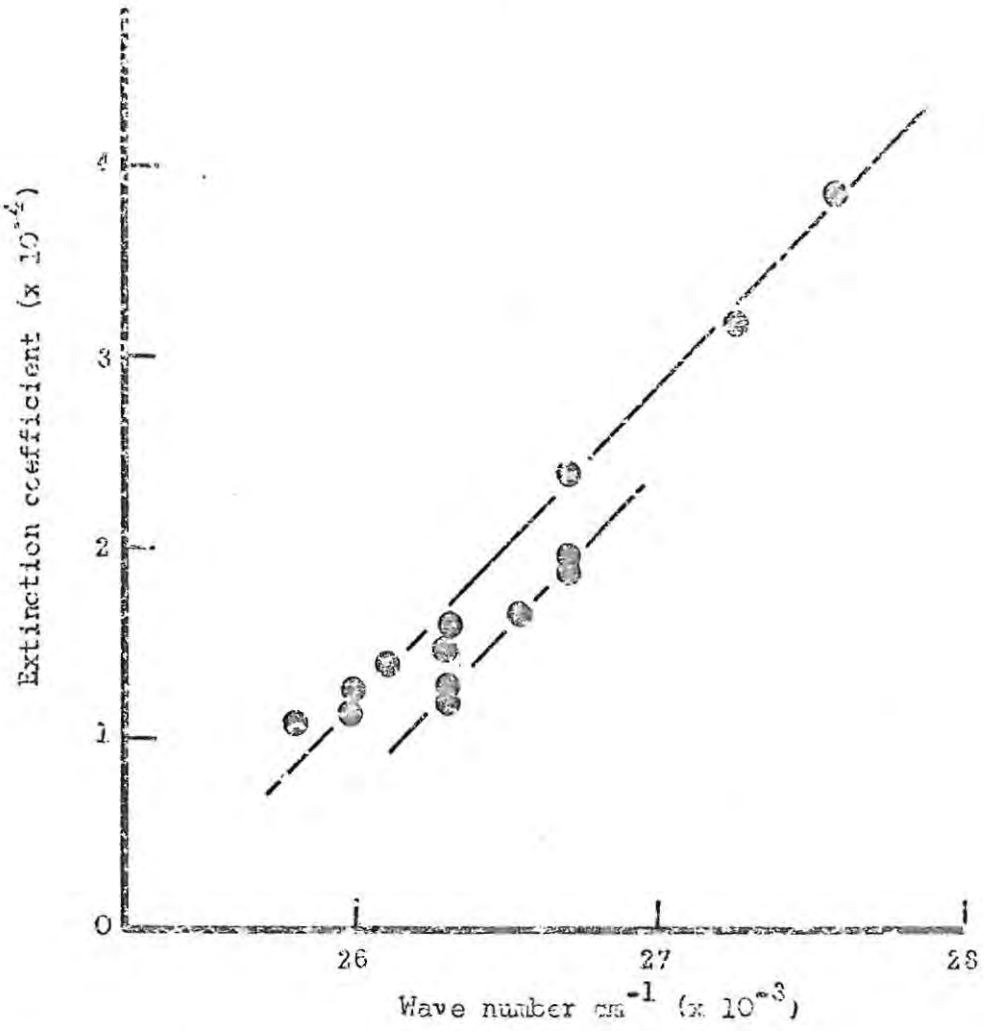


FIG. 5. Relation between extinction coefficients and wave numbers of the energe transfer absorption bands of Ti(IV) complexes of o-diphenols.

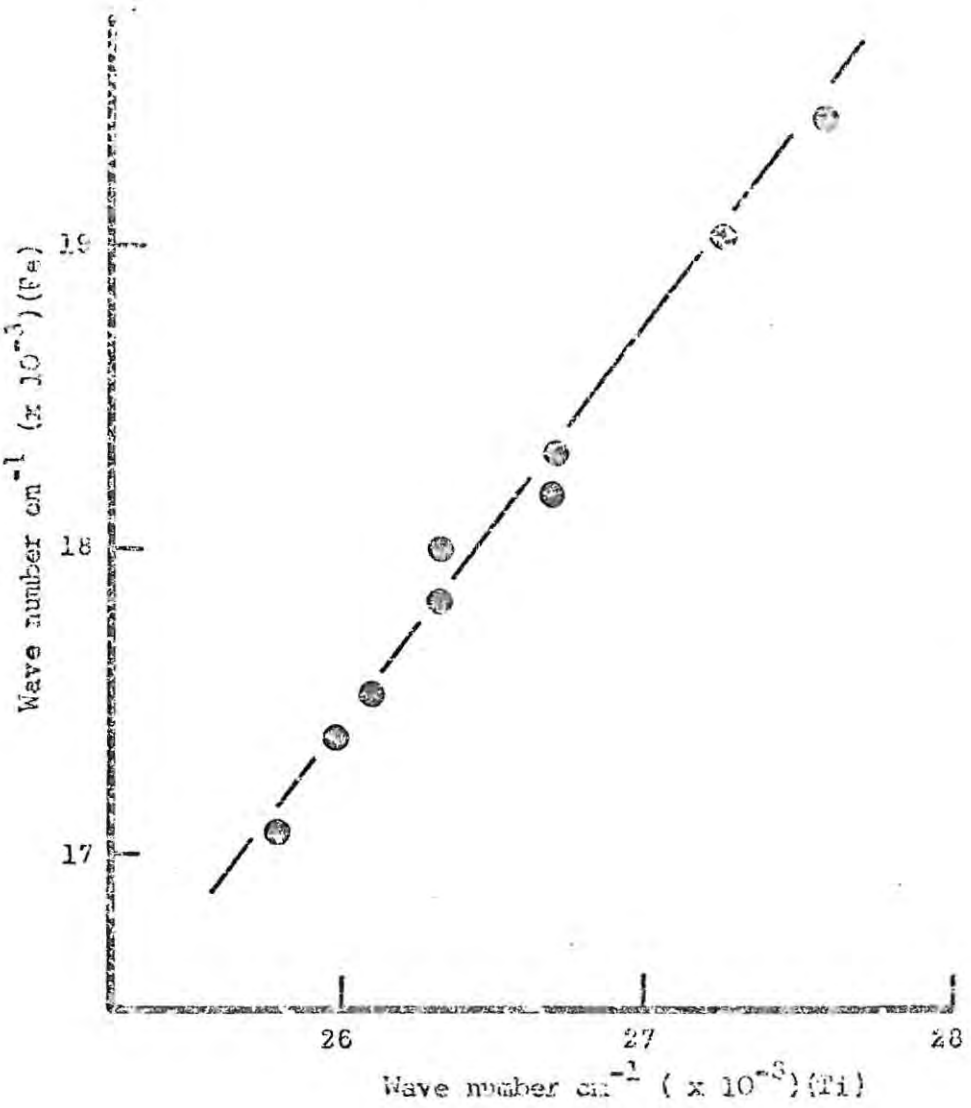


FIG. 6. Relation between the wave numbers of charge transfer bands of TiL_3 and FeL_2 o-diphenol complexes.

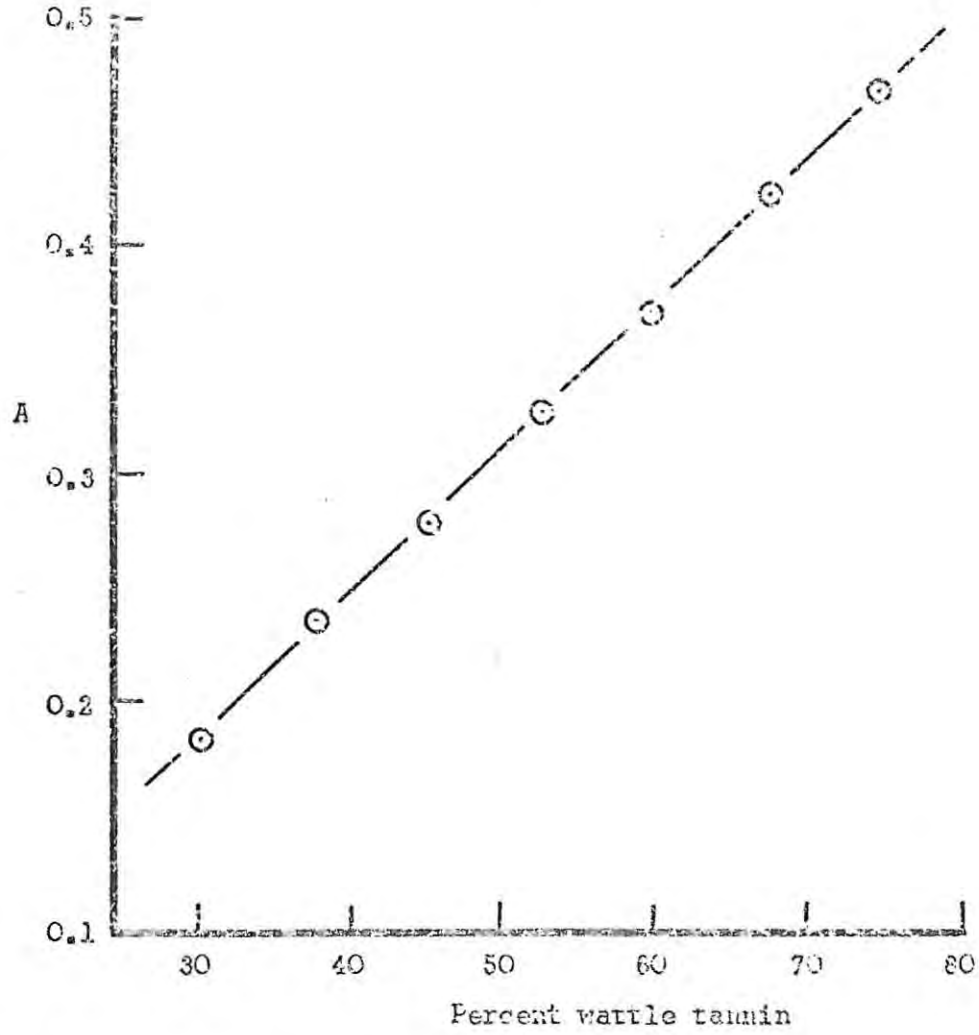


FIG. 7. Spectrophotometric determination of wattle tannin. Analytical procedure : 10 ml. of an aqueous solution containing 1 g./l (accurately weighed) wattle tannin is added to 20 ml. 0.5 M-sodium acetate and 10 ml. 0.01 M -sodium molybdate and made up to 100 ml. After 5 min. the absorbance is measured at 400 nm (1 cm cells) against a blank of the above solution without sodium molybdate and sodium acetate.

SUMMARY

The complex equilibria of the metal ions, Fe(III), Ge(IV), Al(III), B(III), Co(II), Ni(II), Cu(II), Zn(II), Mg(II), Ca(II), Pb(II), V(IV) and Mo(VI) with a series of related o-diphenol ligands have been investigated by potentiometric and spectrophotometric methods. Results obtained for the model o-diphenol complexes are related to those of the wattle tannin complexes. Generally, the reaction between metal ions and o-dihydroxybenzene compounds results in the liberation of both phenolic protons of the o-dihydroxyl groups, with the formation of a 5-membered chelate ring. Successive complex formation is dependent on the metal ion. For the Fe(III), Al(III), Ge(IV) and Ti(IV) systems a final, octahedral tris-chelate is formed. B(III), on the other hand only forms a mono-chelate with o-diphenols in dilute solution.

Dissociation constants of the phenolic ligands have been determined and have been correlated with the substituent constants, σ^-. The relationships obtained are used to estimate the values of unknown dissociation constants and to check proposed values. From the ultraviolet absorption spectra of the phenolic compounds, a set of extinction coefficients have been derived which have been used to calculate the extinction coefficients of flavanoid compounds.

Stability constants for all the o-diphenol complexes studied, with one exception, are shown to be directly related to the acidity of the ligand. Complexes with the ligand Tiron are anomalous, because the points for Tiron deviate from the linear relationships which have been established between the stabilities of the other o-diphenol complexes and

the ligand acidities. However, in the correlations of complex stability between pairs of metal ions the anomalous behaviour of Tiron did not occur. Approximate stability constants for the wattle tannin complexes of Ge(IV), Al(III) and B(III) have been determined. In view of the fact that the points for these complexes correspond to the linear relationships established for the model o- diphenol complexes, it indicates that wattle tannin conforms to the normal behaviour of phenolic ligands. The equilibria of the Fe(III)-4-chloroacetylcatechol system have been proposed to be influenced by intramolecular hydrogen bonding between the chlorine atom on the substituent and bound water molecules. This influence has not been detected in any other metal complexes formed with this ligand.

1,2,3-Trihydroxybenzene derivatives form different Fe(III) and Cu(II) complex species to those of the o-dihydroxybenzene derivatives. In the 1,2,3-trihydroxybenzene complexes, the third adjacent hydroxyl group (i.e. adjacent to the o-dihydroxo chelate) has been found to be responsible for the observed differences. Fe(III) and Cu(II) complexes of the flavanoid monomers form similar complex species to their o-dihydroxybenzene and 1,2,3-trihydroxybenzene analogues. The results obtained for the Fe(III)-wattle tannin system indicate that wattle tannin reacts with Fe(III) ions as a derivative of 1,2,3-trihydroxybenzene.

The stability constants, K_1, for the o-diphenol complexes follow the order Co(II) $<$ Ni(II) $<$ Cu(II) $>$ Zn(II) which is in agreement with the order found by Irvine and Williams. This stability order has been established also for the wattle tannin complexes. However, the stability order for the constants, K_2, is Ni $<$ Co $<$ Cu $>$ Zn. On the basis of the

spectrophotometric results the anomalous order, Ni < Co is ascribed to stabilisation of the Co(II) complexes by trigonal distortion. Absorption spectra of the Cu(II) complexes indicate that the o-diphenol complexes are more tetragonally distorted than the hexa-aquo complex. From the position of the lowest energy absorption band of the Ni(II) complexes, it has been established that the position of the o-diphenolato ligands in the spectrochemical series is close to that of water.

The stability order for the divalent alkaline-earth metal complexes is shown to be Mg > Ca. This order parallels the reciprocal of the ionic radii of the metal ions. Pb(II) ions and the o-diphenols without ionic substituents, including wattle tannin, form insoluble 1 : 1 complexes in aqueous media. The stability constants, K_1, for the divalent metal complexes of o-diphenols follow the order VO > Cu > Pb > Zn > Ni > Co > Mg > Ca.

The strong visible absorption bands of the o-diphenol complexes of Fe(III) are attributed to charge transfer and are interpreted on the basis of electrostatic and molecular orbital models. The electronic effects of the phenolic substituents show that the charge transfer in the Fe(III), Ti(IV) and Mo(VI) complexes is from ligand to metal. Optical electronegativities have been determined for the o-diphenolato ligands from the spectrophotometric results of the octahedral Ti(IV) and Fe(III) complexes. Use has been made of the intense coloration between molybdate ions and wattle tannin to develop a spectrophotometric method for analysis of tannins.

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