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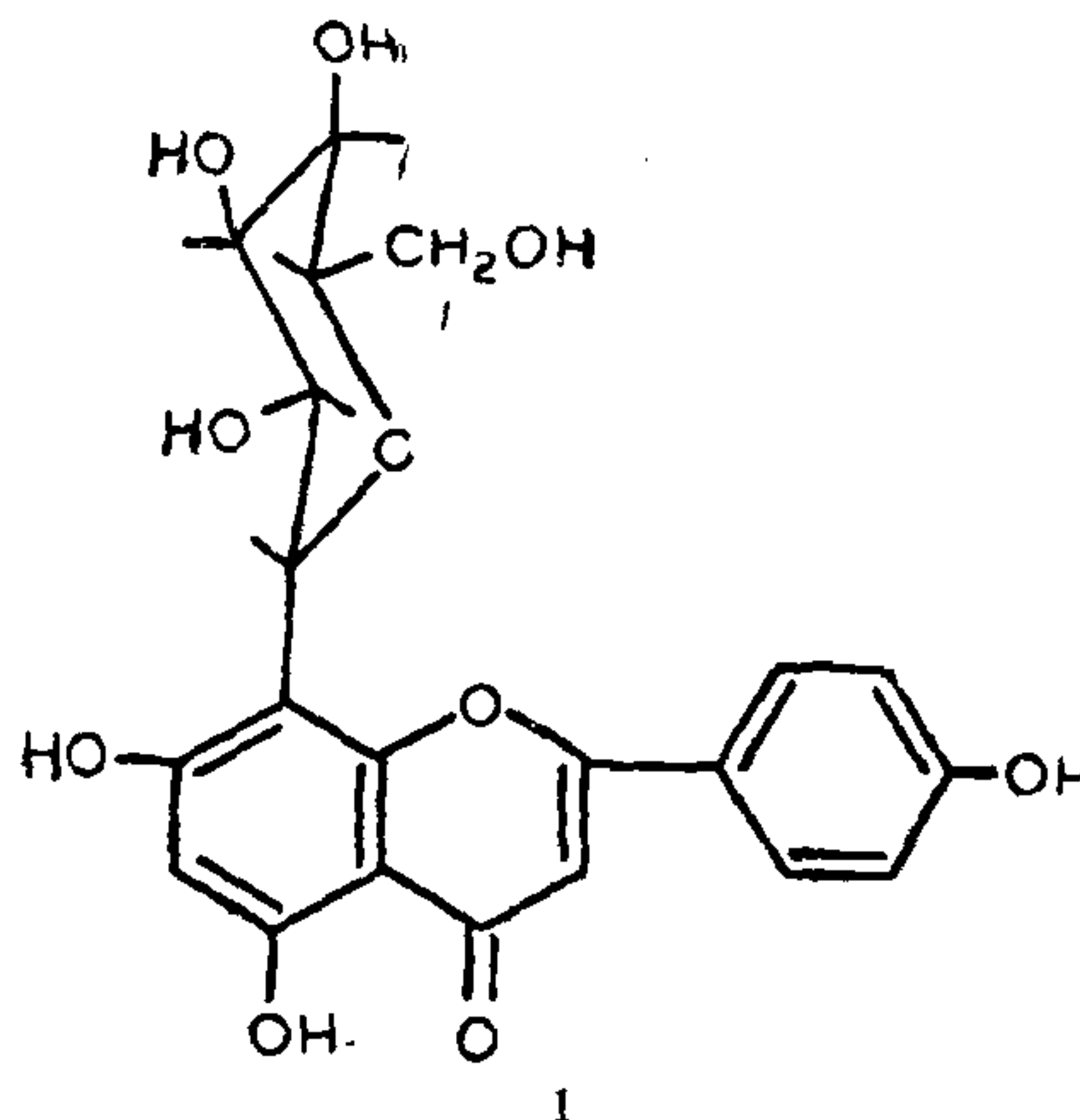
CHEMICAL INVESTIGATION OF INDIAN MEDICINAL PLANTS USED FOR LEPROSY

I. Constituents of the Flowers of *Ochrocarpus longifolius* Benth. and Hook. f. (Guttiferae)

Ochrocarpus longifolius is commonly known as Nagkesar. Its flowers are used in the indigenous system of treatment as stimulant, carminative and aphrodisiac. These are also used for the treatment of haemorrhoids, blood diseases, leprosy and dyspepsia^{1,2}. A pharmacognostical study of the flower buds had been reported earlier³. Of particular interest is the report by Khan *et al.*⁴ that the petrol extract of the flowers possesses a good antibacterial activity. We began a systematic investigation of the chemical constituents of the flowers in order to locate the active principles responsible for this activity.

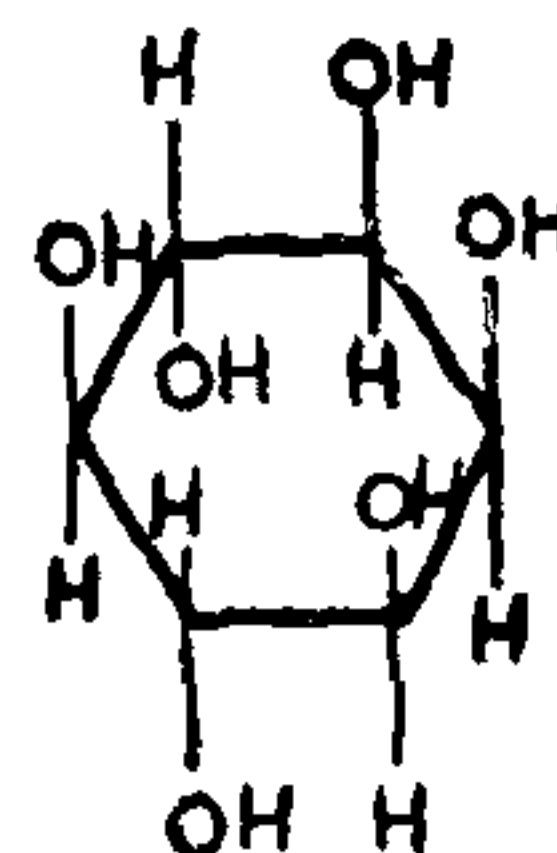
The phenolic extractives from the alcoholic extract of the flowers on repeated crystallisation gave a yellow compound (I), m.p. 256°, which gave the usual colour reactions of flavonoids. On acetylation it yielded a heptaacetate, m.p. 257°. The results of its NMR spectral studies were comparable with those of vitexin heptaacetate.

On action with hydroiodic acid, (I) gave an aglycone which was acetylated to give a compound, m.p. 180°, identical with apigenin triacetate.



Compound (I) was resistant to ordinary hydrolysis, but ferric chloride oxidation⁵ followed by treatment with resins IRC-120(H)⁺ and IRA-400(OH)⁻ to remove Fe³⁺ and Cl⁻ ions, gave arabinose (Paper chromatography, *n*-butanol-acetic acid-water 20:5:10 by volume). The compound (I) was therefore characterised as vitexin. Further confirmation was provided by super-imposable I.R. spectra of the acetate with an authentic sample of vitexin acetate.

During the course of our investigation, another compound (II), m.p. 220–21°, was also isolated from the alcoholic extract of the flowers. It did not show any depression in m.p. on mixed melting with meso-inositol. I.R. spectra of this compound and meso-inositol were superimposable which confirmed its identity as meso-inositol.



II

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ASCORBATE-M(II) SYSTEMS—EQUILIBRIUM STUDIES

L-ASCORBIC ACID (Vitamin C) solution in water readily undergoes aerial oxidation in presence of traces of some transitional metal ions¹ especially under alkaline conditions. The reversible oxidation-reduction of L-ascorbic acid in biological systems is probably influenced by the thermodynamic and kinetic stabilities of ascorbic acid-transitional metal complexes. The stabilities of a number of metal ions determined by physico-chemical techniques are reported in literature²⁻⁴. These studies are scanty specially with the biologically active metal ions and they do not throw any light on the role of metal ions on ascorbic acid oxidation. We have now determined the step stability constants of ascorbic acid complexes with bivalent metal ions namely, Fe(II), Mn(II), Co(II), Ni(II), Be(II) and Pb(II) using Bjerrum-Calvin pH titration technique⁵⁻⁶ in aqueous solutions of ionic strength 0.05 M (KNO₃) at 25°C. During the pH titration reaction mixtures were kept saturated with N₂ gas to avoid aerial oxidation of L-ascorbic acid.

Materials and Methods

Solutions of Analar grade reagents of BDII (India) were prepared in redistilled water. The metal ion solutions were standardized by conventional techniques. L-ascorbic acid (BDII) was used as such. Potassium nitrate solution was employed to maintain

constant ionic strength. Philips pH meter (PR 9405) was used to record the changes in pH during titration.

Following sets of reaction mixtures were prepared for studying each of the complexes:

Total volume	KNO ₃ (1 M)	HNO ₃ (0.10 M)	Water	Metal ions (0.01 M)
100.0 ml				
Solu- tion A	5.0 ml	10.0 ml	85.0	..
95.0 ml*				
Solu- tion B	do.	do.	80.0	..
95.0 ml*				
Solu- tion C	do.	do.	75.0	5.0 ml

* 0.0440 g of ascorbic acid was transferred with 5 ml of water (TCL₀ = 2.5 × 10⁻³ M).

The solutions were titrated by standard KOH solution in an air-tight bottle in which N₂ was constantly bubbled and change in pH measured. After the titration the analysis⁸ of ascorbic acid showed that it remained unoxidised during titration. In the titration of metal-ligand systems turbidity was observed at pH 9.0 for Mn(II), Fe(II), Ni(II) and Co(II) as pH 7.0 for Pb(II). For Be(II) no turbidity appeared.

On the basis of above data, the titration curves were prepared from which \bar{n} , nH and pL were calculated by Irving and Rossotti method⁹ and finally pK_n and $\log k_n$ were evaluated from formation curves by Bjerrum half \bar{n} method. The nature of formation curves indicates that only Be(II) forms stable 1:2 complexes whereas others form only 1:1 complex which probably hydrolyse at higher pH. The relevant stability constants are given in Table I.

TABLE I
Stability constants of ascorbic acid-metal complexes at ionic strength of 0.06 M (KNO₃ 0.05M + HNO₃ 0.01M) T 25°C

Cation	log K ₁	log K ₂
Be ²⁺	9.0 (8.84)	7.9 (8.08)
Pb ²⁺	8.2	..
Mn ²⁺	5.2	..
Fe ²⁺	6.9	..
Co ²⁺	5.6	..
Ni ²⁺	5.6	..