oxlate ($1 \times 10^{-4}M$ in $0{\cdot}01M$ HNO_3) in which the proportion of the two was continuously varied, the absorbances were measured at 645 nm

The maximum change in absorbance is observed when $Fe(5MeOATS)^{+2}$ and EDTA or oxalate are present in equimolar proportion. It may be concluded, therefore, that iron(III) forms 1 : 1 complexes with $EDTA^{-4}$ and $C_2O_4^{-2}$.

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Chemical Investigation of the Barks of Tecomella undulata, Heterophragma adenophylum and Millingtonia hortensis (Bignoniaceae)

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We have recently reported the isolation and identification of lapachol, dehydrotectol, veratric acid and β-sitosterol from the bark of *T. undulata* and β-sitosterol, lapachol and β-sitosterol from the heartwoods of *H. adenophylum* and *M. hortensis* respectively[1]. No work has been done on the barks of *H. adenophylum* and *M. hortensis*. In this communication we report the isolation of *n*-hentriacontanol and ϵ-sitosterol from the bark of *T. undulata* and *n*-hentriacontanol and β-sitosterol from the barks of *H. adenophylum* and *M. hortensis*.

The ether-soluble fraction of the benzene extract of bark of *T. undulata* was further fractionated into acidic and neutral fractions. The neutral fraction was chromatographed over Brockmannalumina (deactivated with 10% acetic acid). The fraction from petrol : benzene (1 : 1) gave a colourless compound, m.p. 83°–84° and fraction from benzene (100%) gave colourless needles, m.p 143°–144

The coarsely powdered bark of *Heterophragma adenophylum* (2 kg) was extracted with boiling benzene for 3×12 hr. Complete removal of the solvent at reduced pressure gave an orange-yellow waxy material (3·00 g.). It was chromatographed over deactivated alumina (125 g) yielding a colourless compound (0·05 g), m.p. 81°–82° from petrol : benzene (1 : 1) fraction and another colourless compound (1·50 g), m p. 134°–135°. from petrol : benzene (1 : 4) fraction

Similarly, coarsely powdered bark of *Millingtonia hortensis* (2 kg) was extracted with benzene for 3×12 hr. Removal of the solvent at reduced pressure gave a reddish brown mass (3 g). It was chromatographed over deactivated alumina (125 g) and gave a colourless compound (0·05 g), m.p. 82°–83°, from petrol : benzene (1 : 1) fraction and another colourless compound (1·25 g), m p. 134°–135°, from the benzene (100%) fraction

All the three compounds, m.p. 81°–84°, isolated from different barks, were recrystallised from acetone : ether (5 : 1) as colourless granules; m.p. 84°–85°. These were all homogeneous on T.L.C., using silicagel G adsorbent, C_6H_6-EtOAc solvent and 1% acidic ceric sulphate developer

The I.R. spectrum showed adsorption at 3300 (–OH stretching due to polymeric association), 2900, 2818 (C–H stretching), 1472 ($-CH_2$ bending), 1379 (C–CH_3 bending), 1060 (C–O stretching of a primary alcohol) and doublet at 730 and 720 [$-(CH_2)_n$-bending ($n > 4$) vibration due to straight chain methylene groups]

The mass spectrum of all showed molecular ion peak at m/e 452. Besides the peak at m/e 31 due to $CH_2 = OH$, significant peaks, at low masses, found were m/e 45, 59, 73, etc. resulting from cleavage at C–C bonds successively removed from oxygen atom. The ions at high mass end of spectrum occurred at the intervals of fourteen as expected[2] for a higher primary alcohol. A M-18 peak at m/e 434 caused by the loss of mater and common to mass spectrum of alcohols could be detected[3]. A close study of

IR[4] and mass[3] spectra of alcohols led confirmation of the compounds as hentriacontanol-1 which was confirmed by direct comparison m.m.p. with authentic sample 84°–85°.

The colourless needles, m.p. 144°–145°, from the bark of *T. undulata* gave positive Liebermann. Burchard test for sterol. Its IR spectra showed absorption at 3400 cm^{-1} (–OH stretching). The identity of sterol as e-sitosterol was confirmed by preparation of its acetate[5] (Acetic anhydride/pyridine). m.p. 128°.

The colourless compounds, m.p. 134°–135°, from the barks of *H. adenophylum* and *M. hortensis* gave positive Liebermann Burchard test for sterol. The identity of sterol as β-sitosterol was confirmed by its mixed melting points, I.R. spectrum and its acetate[6]. m.p. 128°.

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Spectrophotometric studies of the Chelates of Iron(III) with 2-Hydroxy-5-methyl Acetophenone Semicarbazone Systems

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THE chelating tendencies of 2-hydroxy phenone semicarbazones have not been investigated fully. Our laboratory has been interested in studying the chelating properties of 2-hydroxy phenones and their derivatives. As a part of this program it was considered worth while to explore the analytical potentiality of 2-hydroxy phenone semicarbazones. The present note describes the results of spectrophotometric studies of the green (λ_{max} = 600 nm) coloured solution formed when iron(III) react with alcoholic solution of 2-hydroxy-5-methylacetophenone semicarbazone and the colourless complexes formed by iron(III) with oxalate and diamino-ethane tetra-acetate ions at low *p*H using 2-hydroxy-5-methyl-acetophenone semicarbazone as an auxiliary ligand

Experimental

2-Hydroxy-5-methyl a etophenone (m.p. 49°) was prepared by Fries migration of the corresponding phenyl acetate using anhydrous aluminium chloride in the absence of solvent. The 2-hydroxy-5-methyl acetophenone semicarbazone (5MeOAS; m.p. 212°) was obtained as pale yellow crystals by refluxing 1 : 1 mole of 2-hydroxy-5-methyl acetophenone and semicarbazide hydrochloride in methanol for 1·5 hr. The product was purified by recrystallization from hot acetic acid. Standard solutions were prepared by dissolving weighed amounts of the reagent in pure methanol

All other chemicals used were of A.R. quality. The stock solutions of iron(III), ammonium oxalate, and Na_2EDTA were prepared by dissolving a calculated amount of each in 0·01M nitric acid. The concentrations of iron (III) and oxalate in solution were determined by standard gravimetric and volumetric methods. Dilute solutions of desired concentrations were obtained, as and when needed, using these stock solutions. All aqueous solutions were prepared in water twice distilled over alkaline permanganate in all glass pyrex unit.

Spectrophotometric measurements were made on Beckman DU spectrophotometer, using 1 cm glass cells. All measurements were carried out at 30° ±0·5° in a 50% methanol–50% water (v/v) medium adjusted to 0·005M with respect to nitric acid.

Results and Discussion

The nature of complexes was determined by the method of Vosburgh and Cooper[1]. The observations showed that only one complex with λ_{max} of 600 nm is formed in the system. The composition of the complex was determined by Job's method[2] using equimolar and non-equimolar solutions, slope-ratio method[3] and molar-ratio method[4]. It was found to be 1 : 1 in all the cases. The apparent stability constant log K = 5·3±0·1 of the complex was calculated from absorbance data by the method of Mukherji and Dey[5].

Colourless complexes of iron(III) :

The method used here have been described earlier by Babko *et al.*[6,7]. In this method a solution containing $Fe(5MeOAS)^{+2}$ ($1\times10^{-4}M$) was prepared by mixing equal volumes of iron(III) ($2\times10^{-4}M$) and 5MeOAS ($1\times10^{-3}M$). The continuous variation[2]