development of the colour intensity. The thorium (IV)-SATC complex is stable for 30 min in the buffer medium. The order of addition of reagents is not critical. The absorbance values are not affected in the temperature range 7–70 C. At higher temperature the absorbance gradually decreases.

The reddish pink thorium (IV)-SATC complex exhibits maximum absorption at 530–540 nm where thorium (IV) and the reagent blank solutions show very little absorption. All the present studies were made at 535 nm. The thorium (IV)-SATC complex obeys Beer's law over the concentration range 0.06–5.7 ppm. The optimum concentration range as evaluated by Ringbom's curve[8,9] is 0.16–5.1 ppm. The sensitivity of the reaction is 7.3 $\mu g\ cm^{-2}$ with a molar absorptivity of $3.2 \times 10^4\ l\ mol^{-1}\ cm^{-1}$ at 535 nm. The accuracy of the method is ±2%.

Job's method of continuous variation[10,11] and molar ratio[12] methods indicated the formation of 1 : 1 complex and the apparent stability constant (log K) as calculated from molar ratio and Asmus[13] methods is found to be 6.3 ± 0.1. The complex is cationic in nature.

In order to assess the possible analytical applications of the method, the effects of some ions which often accompany thorium were studied with 3 ppm of thorium(IV) and their tolerance limits in ppm are given in brackets: nitrate (6000); Mg (II), Mn (II), chloride (2400); Sr (II), Cd (II), bromide (1200), iodide (850), Yb (II), Ca (II), Zn (II), sulphate (500); Al (III), phosphate (250); Sn (II), EDTA (100); W (VI), fluoride (50); Cr (III), Ru (III), Ir (III), Mo (VI), Rh (III), Ti (IV), Ce (IV), La (III), Er (III), Gd (III), Sm (III), Pr (III), Ho (III), Y (III), oxalate, citrate, tartarate (20); Zr (IV), Fe (III), Pt (IV), Os (VIII), Nd (III) (15); Ni (II), Pd (II), V (V), Au (III), Dy (III) (10), Co (II), U (VI) (5).

A comparison of the present reagent with the literature reagents for the estimation of thorium reveals the following advantages: water solubility, simplicity, good sensitivity, stability, elimination of extraction, insensitivity to temperature in the range 7–70° C. Further the order of addition of reactants is not critical.

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A NEW DITERPENE, DIPOLOIC ACID FROM THE STEM OF *DILLENIA PENTAGYNA*

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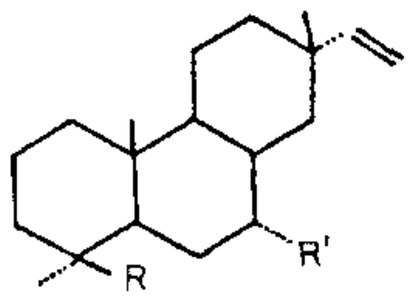
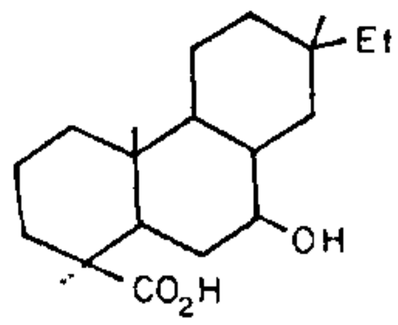
THE earlier work on the stem of the plant *Dillenia pentagyna* (N. O. Dilleniaceae) was reported by Tiwari *et al*[1,2]. In this paper the authors report the isolation and characterization of a new diterpene, dipoloic acid [7-hydroxy-pimara-(15:16)-ene-19-oic acid] (I) by physico-chemical techniques.

Dipoloic acid (I), crystallized from MeOH as white needles, m.p. 150–52° (d), analysed for $C_{20}H_{32}O_3$ (M^+ 320) and had no UV absorption above 218 nm. IR (KBr, cm^{-1}) showed the presence of hydroxyl (3400 br), carboxyl (1690), tert methyl (1380, 1360, 1210 and 1200) and vinylic group (1635, 1410, 980 and 940). Its ^1H NMR spectrum (δ, TMS) exhibited signals for tert methyl (0.94, 1.05 and 1.35) assignable to 20, 17 and 18 groups respectively. The hydroxyl proton appeared as a broad signal at 4.40 ($W^{1/2}$ 5 Hz) which disappeared on D_2O shaking. The methylene protons showed as a pair doublets at 2.45 and 3.20 (J = 17 Hz) and ABC pattern for the signal of vinylic protons at 5.45, 5.40 and 4.80 ($J_{AB} \approx 10.00$; $J_{AC} = 17.00$; $J_{BC} = 15$ Hz) which suggested that dipoloic acid possessed



(I) ; R = COOH; R' = OH
(II) , R = COOH, R' = OAc
(III) ; R = COOMe, R' = OH



(IV)

the pimarane type skeleton[3,4]. (I) formed a monoacetate (II), m.p. 102–4°, $C_{22}H_{34}O_4$ (Found; C, 73.00; H, 10.02; $C_{22}H_{34}O_4$ required; C, 72.92; H, 9.39%, M^+ at m/z 362); ν_{max}^{KBr} cm^{-1} 1725; ^1H NMR (δ, TMS) 4.90 (CH–O–$COCH_3$) indicating the secondary nature of the hydroxyl group. The equatorial orientation of the sec. OH group was inferred by coupling shape of the carbinyl protons signal. (I) on treatment with CH_2N_2 yielded (III), m.p. 110° (dec.), $C_{21}H_{34}O_3$ (Found; C, 75.38; H, 10.00; $C_{21}H_{34}O_3$ required; C, 75.44; H, 10.18%; M^+ 344); ν_{max}^{KBr} cm^{-1} 1710 ester group; ^1H NMR (δ, TMS), 3.00 (3H, 1 × $COOCH_3$) which was unaffected by boiling with grignard reagent in PhMe. This is a clear indication that carboxyl group is highly hindered position as in case of pimaric acid and its methyl ether[3,5]. The carboxylic group at C-4 was supported by the comparative studies of the pimaric acid[3–4], with that of dipoloic acid. The dihydrodipoloic acid (IV) was obtained on hydrogenation of (I) with Pd–C which had similar ^1H NMR spectrum as in (I) except that signal of $-C_2H_5$ group at δ0.92 (t, J = 9 Hz) in addition to the methyl signals indicating that vinylic group in (I) has reduced in (IV). Oxidation of (III) with MnO_2 in C_6H_6 afforded a ketone, m.p. 69–72°, $(\alpha)_D^{28}$ −62° ($CHCl_3$), $C_{20}H_{30}O_3$ (Found; C, 75.50; H, 9.40; $C_{20}H_{30}O_3$ required; C, 75.46; H, 9.43%, M^+ 318); UV λ_{max}^{MeOH} 249 nm; IR ν_{max}^{KBr} cm^{-1} principal peaks at 1722 and 1695. The ^1H NMR spectrum of this ketone exhibited a pair of ABX type quartets at δ3.12 ppm (1H, J_{AX} = 19.00 Hz, J_{AB} = 19.00 Hz), 2.80 ppm (1H, J_{BX} = 5.5 Hz; J_{AB} = 19.00 Hz, H–C–CH_2–CO), a broad singlet at δ6.65 ppm (1H, OC–CH) and a singlet at δ2.75 (3H, 1 × $COOCH_3$). The physical data of this ketone is very much similar to the ketone obtained from primaric acid as reported in the literature[3,5]. Hence the dipoloic acid has the structure 7-hydroxy-pimara-(15:16) ene-19-oic acid (I).

All the m p.s. are uncorrected.

Isolation and purification: The air dried and powdered stem of *D. pentagyna* (2 kg) was extracted with EtOH under reflux for 180 hr. The total EtOH extract was concentrated to a small volume (150 ml) and poured into H_2O (500 ml). The water insoluble fraction was extracted with C_6H_6. The C_6H_6 extract deposited a brownish solid (2.2 g). This deposit was extracted with hexane. The hexane extract yielded (I) which was purified over Al_2O_3 column (C_6H_6: $CHCl_3$, 6:4 V/V) into a colourless solid mass (900 mg). Recrystallization with MeOH (BDH) afforded colourless needles (800 mg), m.p. 150–52° (dec.). (Found; C, 74.98; H, 10.01; $C_{20}H_{30}O_3$ required; C, 75.00; H, 10.00%).

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INDIRECT POTENTIOMETRIC DETERMINATION OF REDUCING SUGARS

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SEVERAL immobilized enzyme electrodes have been reported for the determination of carbohydrate[1–3]. Recently, periodate selective electrode has been used to determine reducing sugars in blood serum[4]. However, these electrodes are difficult to fabricate and not commercially available. This paper describes the fabrication of a simple Cu-selective electrode and its application to determine reducing sugars in natural products, employing standard addition technique.

Fabrication of Graphite [Ag_2S-CuS] Electrode

A 2.5 cm long graphite rod taken from a D-type dry cell was inserted into a tightly fitting polythene tube by which 2 cm of the rod was protruding out. An 'araldite'