

The authors are thankful to Prof. Baqridi, Head of the Department of Chemistry and Dr. S. C. Gupta, Principal of the College, for providing the research facilities.

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ISOLATION OF 6-HYDROXY-2', 7-DIMETHOXY-4', 5'-METHYLENEDIOXYISOFLAVONE FROM THE PODS OF *DALBERGIA ASSAMICA*

Dalbergia assamica (family Leguminosae) is a climber having glabrous flexible pods. Seeds of this species are similar to the seeds of *D. latifolia* except that they are more smooth and smaller than the latter. It has been found to contain a rare compound, 6-hydroxy-2',7-dimethoxy-4', 5'-methylenedioxyisoflavone, the occurrence of which from *Dalbergia* species is being reported for the first time. This compound has previously been isolated from the heartwood of *Cordyla africana*¹ and *Mildbraedeodendron excelsa*². Air-dried and coarsely powdered pods (1 kg), from which seeds (255 gm) had been removed, were successively extracted with petroleum ether (60–80°), benzene and ethyl acetate. Benzene and ethyl acetate extracts were found to be similar (TLC) and combined while pet. ether extract was worked up separately.

Pet. ether extract on column chromatography over silica gel gave a compound A, while combined benzene and ethyl acetate extracts after column chromatography, preparative TLC and further purification

yielded substances A, B, C and D in workable quantities.

Compound A, a white crystalline solid (55 mg) m.p. 140°, $[\alpha]_D -28.9^\circ$ (c, 0.850 in CHCl_3); $\nu_{\text{max}}^{\text{KBr}}$: 3520 (hydroxyl) and 1649 (double bond) cm^{-1} ; showed bluish-violet colouration with Liebermann-Burchard reagent (test for sterols); acetate m.p. 127°. It was identified as β -sitosterol and confirmed by comparison (co-TLC, m.m.p.) with an authentic sample. Compound B crystallised from methanol as white needles (80 mg) m.p. 252–53° (lit² m.p. 251–52°); $\nu_{\text{max}}^{\text{KBr}}$: 3430 (hydroxy), 1640 (carbonyl), 1040 (methoxyl), 940 (methylenedioxy)³, 1618 and 1512 (aryl) cm^{-1} . $\lambda_{\text{max}}^{\text{MeOH}}$: 255, 312 nm, with NaOAc, 255, 312 nm. It gave a positive test for isoflavones and a deep green blue colour on heating with conc. sulphuric acid and gallic acid, indicating the presence of methylenedioxy group⁴. Acetylation ($\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$) afforded a monoacetate as needles from methanol m.p. 215–17°. NMR (CDCl_3 , δ): 8.0 (1H, s, C-2), 7.93 (1H, s, C-5), 7.43 (1H, s, C-6'), 7.01 (1H, s, C-3'), 6.75 (1H, s, C-8), 6.0 (2H, s, O-CH₂-O), 4.0, 3.8 (6H, s, 2 OMe), 2.41 (3H, s, OCOCH₃). This data indicated the compound to be 6-hydroxy-2', 7-dimethoxy-4', 5'-methylenedioxyisoflavone; confirmed by preparation of methyl ether (using K_2CO_3 and dimethyl sulphate in acetone). m.p.⁵ 233–34°. MS: m/e 342 (M^+), 311, 167 and 175. Mass spectra of the compound B is also similar to that reported in literature¹.

Compound C crystallised from glacial acetic acid as colourless crystals (20 mg), m.p. 295–96°, $\nu_{\text{max}}^{\text{KBr}}$ 3650 (hydroxyl), 1640 (carbonyl), 955 (methylenedioxy), 1618 and 1508 (aryl) cm^{-1} . $\lambda_{\text{max}}^{\text{MeOH}}$: 249, 295 nm, with NaOAc 257, 296 (inflection). It gave positive tests both for isoflavones and methylenedioxy grouping and characterised as ψ -baptigenin. Its identity was confirmed by comparison^{6, 7} (co-TLC, m.m.p. and IR) with an authentic sample.

Compound D, a white crystalline solid (100 mg) m.p. 288–90° $[\alpha]_D -30.9^\circ$ (c, 0.934 in CHCl_3); $\nu_{\text{max}}^{\text{KBr}}$: 3470 (hydroxyl) 1660 (double bond) cm^{-1} , showed positive tests for steroids and glycosides. Acid hydrolysis of this compound yielded β -sitosterol and glucose. It was identified as β -sitosterol- β -D-glucoside by comparing IR spectra, co-TLC and m.m.p. determination with an authentic sample.

Thanks are due to Dr. M. R. Parthasarathy, Delhi University, for a sample of ψ -baptigenin, and CSIR, India, for the award of Junior Research Fellowship to R. P. S.

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OCCURRENCE OF TRITERPENOIDS IN *AZIMA TETRACANTHA*

Azima tetracantha belongs to the little family, Salvadoraceae. The leaves and root of this plant are used in indigenous medicine¹.

From the leaves of this plant, presumably of African origin, Rall *et al.*² reported dimeric piperidine alkaloids azimine, azecarpine (minor) and carpine (minute amounts). From the leaves and roots collected in Andhra Pradesh we report here the isolation and identification of friedelin, glutinol, lupeol and β -sitosterol.

The dried material was powdered and extracted with petroleum ether, chloroform and methanol.

Petroleum ether extracts when chromatographed on silica gel afforded friedelin, m.p. 258–60°, (α)_D –22.5° (chf), C₃₀H₅₀O, identified by IR, NMR, Mass, reduction with LAH in THF to *epifriedelinol* and direct comparison with authentic samples. This was followed by glutinol, m.p. 208–10°, (α)_D + 56.9° (chf), C₃₀H₅₀O, identified by NMR, Mass, Jones oxidation to glutinone and direct comparison with authentic samples. Lupeol which came after glutinol from the column, m.p. 208–209°, (α)_D + 38° (chf), C₃₀H₅₀O was identified through its acetate, oxidation to lupeone and direct comparison with authentic samples. Finally β -sitosterol was eluted from the column.

The yields of terpenoids from roots were much lower than in leaves. The extracts of both leaves and roots did not contain any alkaloids or phenolic compounds.

This is the first report of occurrence of triterpenoids in Salvadoraceae.

The spectra were obtained from NCL, Poona and IIT, Madras. Thanks are due to Dr. P. Narasimha

Rao of Nagarjuna University, Guntur, for identifying the plant material.

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LOW TEMPERATURE PMR EVIDENCE ON THE SELF-ASSOCIATION IN THIOACIDS

THE time of spin orientation in the magnetic field (approx. 10⁻² to 10⁻³ sec.) is long as compared to the lifetime of H-bonded species (approx. 10⁻¹² to 10⁻¹³ sec.) because of the very rapid formation of H-bonds in solution. Thus only one signal is observed for the protons involved in hydrogen bonding. This signal is the weighted average of all the protons in their environments, in the free as well as in the associated forms. Hence in the case of self-associated systems, the above-mentioned fact decreases the usefulness of PMR as a method of investigating the nature of H-bonded dimers, *n*-mers and their equilibria.

We report here a low temperature PMR study on C₂H₅COSH. Of particular interest is the result that the two self associated species can be distinguished. For C₂H₅ COSH, the temperature regions due to open chain, cyclic and open chain-cyclic H-bonded dimer transition are clearly resolved. We believe this to be the first demonstration that PMR could be used to determine the self-associated species at low temperatures.

The results of our low temperature PMR spectra are tabulated in Table I and the plot of half band width (*b*_{1/2} in Hz) versus temperature is presented in Fig. 1. The variation of *b*_{1/2} values with temperature can be explained if it is assumed that (i) C₂H₅COSH contains both open chain and cyclic H-bonded dimers and (ii) that with the lowering of temperature, transition takes place from open chain to cyclic dimer. Such an assumption gets further support from low temperature infrared studies on thioacids¹ which suggest the presence of open chain and cyclic H-bonded dimers in these acids. The AB portion of the curve may then be due to the presence of open chain H-bonded dimers. Since the lowering of temperature would favour the transition from open chain to cyclic dimers, the BC portion of the curve may be taken to suggest the presence of both open and cyclic dimers.