

1. Campbell, Rodwill V. M. and Tannock, James, *J. Chem. Soc.*, 1973, Perkin, I, 2222.
2. Meegan, Mary J. and Donnelly, Derilla M. X., *Phytochemistry*, 1975, 14, 2283.
3. Briggs, L. H., Colebrook, L. D., Fales, H. M. and Wildman, W. C., *Analyt. Chem.*, 1957, 29, 904.
4. Harper, S. H., Kemp, A. D., Underwood, W. G. E. and (in part) Campbell, R. V. M., *J. Chem. Soc.*, 1969 (C), p. 1109.
5. Ollis, W. D., Rhodes, C. A. and Sutherland, I. O., *Tetrahedron*, 1967, 23, 4741.
6. Parthasarathy, M. R., Seshadri, T. R. and Varma, R. S., *Phytochemistry*, 1976, 15, 226.
7. Rameshwar Dayal and Parthasarathy, M. R., *Planta Medica*, 1977, 31, 246.

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.

Dept. of Pharmaceutical Sciences,
Andhra University,
Waltair 530 003,
May 6, 1978.

E. VENKATA RAO.
P. R. S. PRASADA RAO.

1. Chopra, R. N., Nayar, S. L. and Chopra, I. C., *Glossary of Indian Medicinal Plants*, C.S.I.R., New Delhi, 1956, p. 32.
2. Rall, G. J. H., Smalberger, T. M., DeWaal, H. L. and Arndt, R. R., *Tetrahedron Letters*, 1967, p. 3465.

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.

TABLE I
Low temperature PMR spectra of $C_2H_5CO_2H$ in
 $CDCl_3 + 50 \text{ Vol}\% CS_2$

$t, ^\circ C$	CH_3 group, δ ppm (J-values, Hz), t	$-CH_2$ group, δ ppm (J-values, Hz), q	$-SH$ group, δ ppm ($b_{1/2}$, Hz)
+ 5	1.134 (7.50)	2.634 (7.33)	4.576 (1.5)
- 10	1.130 (7.45)	2.640 (7.34)	4.578 (1.7)
- 30	1.096 (7.25)	2.642 (7.50)	4.693 (2.0)
- 40	1.092 (7.20)	2.652 (7.50)	4.700 (2.0)
- 56	1.084 (7.00)	2.672 (7.50)	4.800 (2.0)
- 70	1.086 (7.00)	2.705 (7.48)	4.850 (2.5)
- 84	1.088 (7.00)	2.755 (7.00)	4.951 (4.0)
- 90	1.086 (7.00)	2.756 (7.01)	4.981 (5.2)
- 97	1.088 (7.01)	2.755 (7.00)	5.008 (7.1)
- 101	1.088 (7.00)	2.755 (7.00)	5.010 (8.4)
- 108	1.088 (7.00)	2.755 (7.00)	5.010 (10.0)
- 111	1.080 (7.25)	2.775 (7.166)	5.010 (10.0)
- 113	1.080 (7.25)	2.775 (7.166)	5.011 (10.0)

t —triplet; q —quartet; $b_{1/2}$ —half band width.

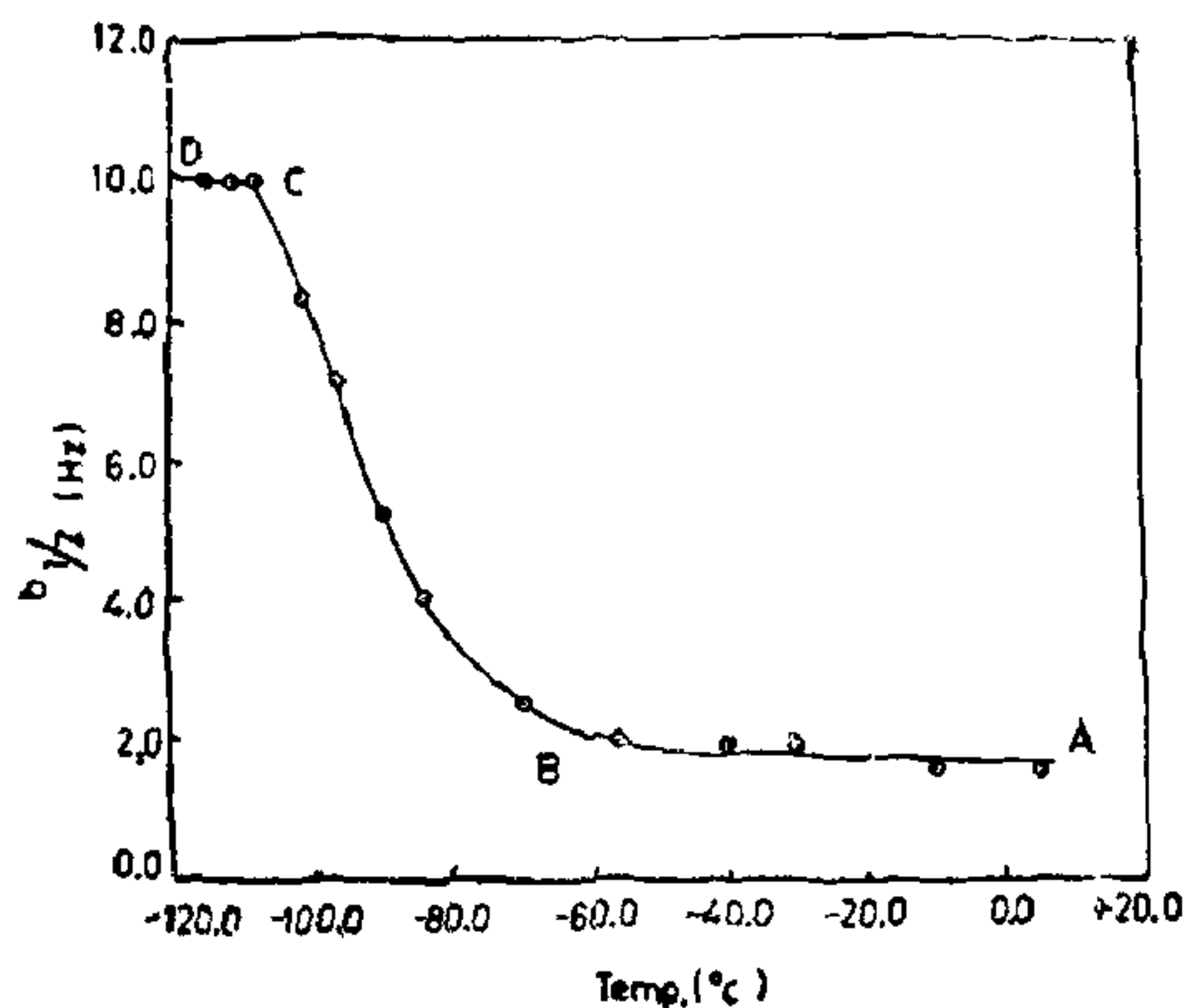


FIG. 1. Half band width variation of $-SH$ proton with temperature on 60 MHz varian NV-14 spectrometer.

The CD portion of the curve may then be attributed to be mainly due to cyclic H-bonded dimer.

The author is indebted to CSIR (India) and Alexander Von Humboldt Stiftung, West Germany, for the financial assistance. Thanks are also due to D^r. C. O. Meese for recording the PMR spectra.

Department of Chemistry,
Punjab Agricultural University,
Ludhiana 141 004, India,
May 11, 1978.

H. S. RANDHAWA.

- Alencastro, R. B. D. and Sandorfy, C., *Can. J. Chem.*, 1973, 51, 1443.

OCCURRENCE OF TRACE FOSSIL *PALAEODICTYON CARPATHICUM* IN THE UPPER FLYSCH SUCCESSION (UPPER CRETACEOUS), MALLA JOHAR AREA, PITHORAGARH DISTRICT, UTTAR PRADESH

THE trace fossils are bioturbation structures having a well defined shape. The study of trace fossils is quite useful in the reconstruction of environment of deposition as the type of burrows (trace fossils) generally reflect the ecological conditions and thus characterise an environment (Seilacher)⁵.

The present note records the occurrence of *Palaeodictyon carpathicum* Matyasovzky for the first time from Indian subcontinent and perhaps from Asia. It has been seen as a net in the grayish black calcareous shale of the Upper Flysch succession of Malla Johar area, Pithoragarh district, U.P. It is recorded from the exposures north of Sancha Malla on the Sancha Malla—Balcha Dhura mule track.

The Upper Flysch sequence is the youngest formation of the Tethyan succession of Kumaon Himalaya, U.P. It overlies the Giumal Sandstone of Lower Cretaceous age and underlies the Exotic Blocks (Heim and Gansser)¹. It, however, shows a tectonic contact with the Exotic Blocks. The Upper Flysch sediments are characterised by good development of *Globotruncana* and radiolarian oozes and are considered as deep sea deposits (Heim and Gansser¹, Mungain and Sastry³).

Systematic Description

The scheme proposed by Nowak⁴ for the classification of *Palaeodictyon* into different species has not been found useful and thus the old scheme of classification is followed in the present work (Ksiazkiewicz)².

Palaeodictyon carpathicum Matyasovzky (Fig. 1)

Meshes about 5 to 9 mm wide consisting of pentagons and hexagons, often irregular. Smaller the size of the meshes, more regular the network. Ridges are less than 1 mm to 2 mm in thickness,