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Chemical Constituents of *Garuga pinnata* Roxb.

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Hydrocarbons, n-alkanols, esters, ketone, fatty acids, sterols and a new branched secondary alcohol, 6-propyltetradecan-7-ol, have been isolated from the petrol extracts of *G. pinnata* leaves and stem bark.

GARUGA pinnata Roxb. belongs to the family Burseraceae. The juice of the leaves mixed with honey is given in asthama. The juice of the stem is used as remedy for the opacity of conjuctiva. The decoction of the roots is used for pulmonary infections[1]. The aqueous extract and the ethanolic extract have been found to possess antiinflammatory and antiallergic activities[2].

Burseraceae family consists of about 20 genera having about 600 species of plants. Hardly, less than 5% of the plants have been chemically investigated. The major work done, is on the chemical examination of the gum exudates of these plants. Number of terpenes particularly di- and tri-terpenes from the genera *Canarium*[3,4], *Commiphora*[5,6] and *Boswellia*[7-9] and lignans from the genus *Bursera*[10] have been isolated. Amentoflavone, a biflavonoid, has been isolated from *G. pinnata* by Rahaman *et al*[11]. No systematic chemical investigations of these plants have been reported, hence the detailed chemical investigation of *G. pinnata* was undertaken.

The hot petrol extracts, cold acetone and methanol extracts of the leaves and stem bark have been investigated. In the present paper we report the isolation and characterisation of some of the known aliphatic compounds and a new branched secondary aliphatic alcohol from the petrol extracts of the leaves and the stem bark. All these compounds except for sitosterol, are being reported for the first time from the family *Burseraceae*.

Experimental

Petroleum ether extract of leaves : The powdered dry leaves (4 kg) were extracted successively with hot petroleum ether (b.p. 60-80°) in Soxhlet extractors. The petrol extract of the leaves (25 g) was chromatographed over silica gel, using petrol-ethyl acetate-methanol solvent system. The column was monitored by tlc, and sixteen different fractions were collected. These on further resolution by column chromatography and preparative layer chromatography yielded fractions A to F, which showed single spots on tlc. However, except for fraction D, all the remaining fractions were found to be mixtures of the homologous compounds on further detailed glc and mass spectral analysis, indicating that a single spot on tlc may not necessarily be due to a single compound, particularly so in the case of waxes.

Results and Discussion

Fraction A : Fraction A was least polar compound obtained from the column chromatography of the petroleum ether extract. It was semi-solid. The ir spectrum showed peaks for saturated hydrocarbon. Glc analysis on Dexil 300 showed it to be a mixture. The mass spectrum showed it to be a mixture of straight chain and branched chain saturated hydrocarbons. The highest peak was observed at *m/e* 240, indicating that heptadecane may be present as one of the components.

Fraction B : Fraction B on repeated crystallisation from ethyl acetate gave compound (B1) as white granules, m.p. 82-83° ; ν_{max} (nujol) 3300 (OH), 1120 and 720 cm^{-1} ; δ ($CDCl_3$) 0.86 (t, *J* 6 Hz, terminal Me), 1.25 (br, s), 3.85 (t, *J* 6 Hz CH_2O) ; *m/e* 410 (M^+), 392 ($M^+ - 18$) and successive loss of 14 mass units. On the basis of the above spectral data and by comparing it with the available literature data[12], it was identified as n-octacosanol.

The mother liquor of the above fraction on concentration deposited white granules, m.p. 83-84° ; ν_{max} (nujol) 3300 (OH), 1065 and 710 cm^{-1}. The mass spectrum showed it to be a mixture of n-alkanols. It showed weak peaks at *m/e* 522, 494, 480, 466, 452 and 438 corresponding to the M^+ peaks of C_{36}, C_{34}, C_{32}, C_{30}, C_{28} and C_{26} alkanols. The intense peaks due to loss of water ($M^+ - 18$) from the above corresponding M^+ peaks were observed at *m/e* 504, 476, 462, 448, 434 and 420.

Fraction C : Fraction C was recrystallised from ethyl acetate, m.p. 85-86° ; ν_{max} (nujol) 1735 (ester C=O), 1180 and 720 cm^{-1} ; δ ($CDCl_3$) 0.80 (t, not well defined), 1.22 (br, s), 2.25 (t, *J* 6 Hz, $(CO-CH_2)$ and 4.08 (t, *J* 6.5 Hz, CH_2-O-CO). The EI-MS spectrum was characteristic of the mixture of long chain esters. It showed M^+ peaks at *m/e* 928, 900, 862, 844, 816, 788, 760 and 732 corresponding to the esters of the chain lengths C_{62}, C_{60}, C_{58}, C_{56}, C_{54}, C_{52} and C_{50} carbon atoms. The mass spectrum also showed two more groups of intense peaks. The major peaks at *m/e* 569, 481, 453, 425, 397, 369, 341, 373, 285 and 257

were due to acid moieties ($R-COO^+H_2$) of esters which correspond to the acids having C_{24} to C_{16} even number of carbon atoms. The other intense group of peaks were observed at *m/e* 476, 448, 420, 392 and 364, were due to the C_{34}, C_{32}, C_{30}, C_{28} and C_{26} alcohols, which may be due to the β-cleavage of the esters.

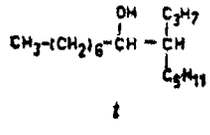
Fraction D : Fraction D was obtained by preparative layer chromatography, m.p. 81-82 ; ν_{max} (nujol) 1705 (ketone) and 720 cm^{-1} ; δ ($CDCl_3$) 0.84 (t, *J* 5 Hz), 1.28 (br, s), 2.31 (t, *J* 7.5 Hz) ; EI-MS : *m/e* 422 (M^+), 407 (M^+-15), 225 (peak), 240 (M^+, $C_{16}H_{32}O$) and 197. On the basis of the above spectral data and by comparison with the literature data[18], it was identified as 15-nonacosanone.

Fraction E : Fraction E was crystallised as white flakes from methanol, m.p. 76-78° ; ν_{max} (nujol) 3500-2900 (OH), 1700 (acid C=O), 1360, a number of bands 1350-1180 (*trans*-$(CH_2)_n$-chain), 930 and 715 cm^{-1}. δ ($CDCl_3$) 0.86 (t, *J* 5.5 Hz), 1.25 (br, s), 2.35 (t, *J* 5H, CH_2-CO). The ir spectrum was similar to that of the authentic sample of palmitic acid. The above spectral data indicate it to be a fatty acid. The methyl ester of the acid was prepared in the usual method by the addition of CH_2N_2. The product obtained (semi-solid) was purified by passing through a small silica gel filtration column, ν_{max} (nujol) 1735 (ester C=O), 1180, 1105 and 710 cm^{-1}, EI-MS *m/e* 298, 270, 242, 185, 157, 143, 129, 115, 111, 101, 97, 88 and 74. The glc analysis of the methyl ester was carried out on SE-30 (10%) at 245° and the retention times were compared with those of the authentic samples. On the basis of the glc analysis it was found to be a mixture of capric acid (11.8%), myristic acid (4.19%), palmitic acid (54.8%) and stearic acid (18.22%) along with the small amount of unsaturated acids (11.3%).

Fraction F : Fraction F was recrystallised from methanol as fine needles giving positive Liebermann-Buchard test for steroids, m.p. 133-34° ; ν_{max} (nujol) 3450 (OH), 1630 (unsaturation), 1250, 1050, 950 and 925 cm^{-1} ; δ ($CDCl_3$) 0.67 (t, 3H), 0.80 (d, 3H), 0.82 (t, 3H), 0.92 (d, 3H), 1.59 (br, s, D_2O-exchangeable), 3.50 (m, 1H), 5.06 (t, 1H) and 5.36 (br, d, 2H) ; EI-MS : *m/e* 414, 412, 400, 273, 255, 231, 299, 213, 399, 381, 329, 303, 392, 379, 327, 301, 385, 367, 315 and 219. On the basis of the above spectral data it was found to be a mixture of phytosterols. The mass spectral fragmentations showed the presence of sitosterol, stigmasterol and campesterol[14] of which sitosterol was a major component.

Petroleum ether extract of stem bark : The stem bark was also subjected to the similar treatment as it was done for the leaves. Hydrocarbon mixture, sitosterol and fatty acid mixture containing myristic acid (23%), palmitic acid (46%) and stearic acid (28%) as major acids were isolated and characterised on the basis of spectral and chemical studies. Besides these a new branched secondary alcohol, compound (G) was isolated and characterised on the basis of the spectral data.

Characterisation of compound G : Compound G was purified by preparative layer chromatography as white crystalline compound, m.p. 74-76° ; ν_{max} (nujol) 3300-3500 (OH), 1250, 1100 and 720 cm^{-1} ; δ ($CDCl_3$) 0.88 (t, 9H), 1.25 (br, s, 26H), 3.85 (m, 1H) ; EI-MS : *m/e* 256, 213, 185, 171, 157 and 129 (base peak). The above spectral data indicated it to be a saturated secondary alcohol. The mass spectrum showed M^+ peak at 256 indicating it to have a probable molecular formula $C_{17}H_{36}O$. The peak at *m/e* 213 (M-43) indicated the presence of C_3H_7 unit. The intense peak at *m/e* 129 ($C_8H_{17}O$) might be due to α-splitting of a secondary alcohol in which hydroxy group is retained. The fragmentation pattern below *m/e* 129 was similar to that of a straight chain compound, *i.e.* successive loss of 14 mass units, indicating that this fragment was a straight chain fragment. On the basis of mass spectral and pmr spectral data a tentative structure I has been assigned to this alcohol and Scheme 1 shows the formation of the important fragment ions.



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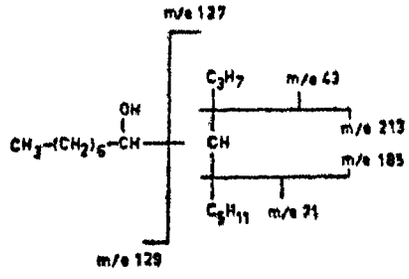

Scheme 1

References

1. R. N. Chopra, S. L. Nayar and I. C. Chopra, Glossary of Indian Medicinal Plants, C.S.I.R., New Delhi, 1956.
2. S. R. Amladi, Personal communication.
3. C. W. M. Bandaranayke, *Phytochemistry*, 1980, **19**, 255.
4. V. K. Hinge, S. K. Paknikar, K. G. Das, A. K. Bose and S. C. Bhattacharyya, *Tetrahedron*, 1966, **22**, 2161.
5. Maradiju, *Phytochemistry*, 1982, **21**, 677.
6. V. D. Patil, U. R. Nayak and Sukh Dev, *Tetrahedron*, 1973, **29**, 341.
7. R. Nicoletti, G. Santarelli and N. L. Forcellese, *Tetrahedron Lett.*, 1966, 6783.

8. G. P. COTTRELL and T. G. HALSALL, *J. Chem. Soc.*, 1960, 2762.
9. B. PARDHY and S. C. BHATTACHARYYA, *Indian J. Chem., Sect. B*, 1978, 16, 170.
10. C. B. S. RAO, "Chemistry of Lignans", Andhra University Press, Waltair, 1978, p. 89, and references therein.
11. F. Q. ANSARI, W. H. ANSARI and W. RAHAMAN, *Indian J. Chem., Sect B*, 1978 16, 846.
12. A. POLLARD, A. C. CHIBNAL and S. H. PIPER, *Biochem. J.*, 1939, 27, 1889.
13. SHRIDHY and COLLISON, *Biochem. J.*, 1971, 25, 600.
14. S. S. FRIEDLAND, G. H. LANE, R. T. LOGMAN, K. E. TRAIN and M. J. O'NEALM, *Anal. Chem.*, 1959, 31 162.