*J. Natn. Sci. Coun. Sri Lanka* 1979 7(1) : 1—3

12/50

# The Chemical Constituents of *Symplocus racemosa* Roxb.

L. B. DE SILVA AND U. L. L. DE SILVA
*Medical Research Institute, Colombo 8, Sri Lanka*

AND

M. MAHENDRAN
*Department of Chemistry, University of Colombo, Colombo 3, Sri Lanka.*

(*Paper accepted : 16 November* 1978)

**Abstract :** From *Symplocus racemosa* Roxb. oleanolic acid, acetylolesnolic acid, betulinic acid and ellagic acid have been isolated.

## 1. Introduction

*Symplocus racemosa* Roxb. is a small tree or shrub belonging to the natural order Styraceae. The leaves are 5 × 1¾ ins in dimension, obtuse, coriaceous. It is found at elevations of 4,500 ft in N.E. India, Burma and China. The sample under investigation was purchased in the local market. This is also called Srimata and Tilaka because of its use in India for making the Tilaka mark on the forehead. Extracts of the bark of *S. racemosa* have been used in Ayurvedic medicine for phlegmatic diseases, leprosy, gum diseases especially bleeding gums.[1]

Earlier work on the species have indicated the presence of glycosides,[5,6] saponins,[7] and alkaloids.[8] Petroleum ether and ether extracts of *S. racemosa* afforded a high yield of betulinic acid with smaller amounts of acetyloleanolic acid and oleanolic acid. The cold methanolic extract yielded ellagic acid. The structures were arrived at from analytical data, IR, NMR and mass spectral data together with the fragmentation pattern.[2] Final confirmation was obtained by direct comparison with authentic samples.

## 2. Experimental

*Acetyloleanolic acid.* The dried shavings of the bark of *S. racemosa* (600 g) were extracted with petroleum ether (60° — 80°C) in a soxhlet apparatus during 18 hours. Evaporation of the solvent gave a solid (20 g) which was dissolved in chloroform and clarified by passing through a half inch layer of neutral alumina in a wide tube. The eluate which showed several spots in TLC was evaporated and the residue crystallised from methanol.

Recrystallisation from chloroform/petroleum ether gave colourless needles. (10g ; 1.6% of dry weight of bark) m.p. 276—78° (lit. 268°)[3] $[\alpha]^{20}_D$ ± 70 (lit. ± 70 ± 1.5)[4] ; IR 1690, 1740 $cm^{-1}$. The mass spectrum showed a peak at m/e 452 which is M—46 (most likely M—HCOOH) (Found : C, 76.87 ; H, 9.91% Calc. for $C_{32}H_{50}O_4$ : C, 77.10 ; H, 10.04%). The NMR spectrum gave the following signals δ 5.3 (m, 1H) vinyl proton at $C_{12}$, 4.5 (t, 1H) $C_3$ proton, 2.0 (s, 3H) methyl of the acetate, 0.8 (s, 3H), 0.86 (s, 9H), 0.96 (s, 6H), 1.0 (s, 3H) 7 methyl groups. The product on hydrolysis gave oleanolic acid m.p. 308—9° (lit. 306—8°)[3] identical in all respects with an authentic specimen of oleanolic acid.

*The methyl ester* of the above compound was prepared by treating the compound with excess diazomethane and had a m.p. 221—23° (lit. 223).[3] The NMR spectrum gave the following signals : δ 5.3 (m, 1H) vinyl proton at. $C_{12}$, 3.6 (s, 3H) ester methyl ; 2.02 (s, 3H) methyl of acetate. The mass spectrum showed the molecular ion m/e 514 and the fragmentation pattern was identical to that shown by $\Delta^{12}$ unsaturated oleanenes.[2]

*Oleanolic acid.* The mother liquor after the separation of acetyloleanolic acid and evaporation gave 3 spots on TLC corresponding to the $R_F$ values of acetyloleanolic, oleanolic acid, betulinic acid. These were chromatographed on silica gel and progressively eluted with benzene, benzene/chloroform and chloroform. Fractions 30—33 from chloroform on evaporation gave oleanolic acid m.p. 308°—309° (lit. 306—8°)[3] undepressed on admixture with authentic oleanolic acid.

*Betulinic acid :* After extraction with petroleum ether, the bark was exhaustively extracted with ether during 18 hrs. The residue (18 g) which had separated on the sides of the flasks was collected, dissolved in chloroform and filtered through a thin layer of alumina (½ in). The eluate was evaporated and the residue crystallised from ether/methanol and finally from ethanol as needles m.p. 307—8° (lit. 304—21°)[3] (10g. 1.6% of dry weight of bark). The NMR spectrum contained the following signals : δ 4.6 (d, 2H) J = 3Hz vinyl protons, 1.62 (e, 3H) methyl group attached to $CH_3$—C=$CH_2$ 0.68 (s, 3H), 0.78 (s, 3H), 0.88 (s, 6H), 0.92 (s, 3H) 5 methyl groups; IR 1690, 1640, 3440 $cm^{-1}$ (Found : C, 78.40; H, 10.84 ; $C_{30}H_{48}O_3$ requires C, 78.97 ; H, 10.52%). The mass spectrum showed the molecular ion m/e 456. The identity of this compound was confirmed by the direct comparison with an authentic specimen of betulinic acid, (m. p. ; mixed m. p. TLC).

*Acetate of betulinic acid :* The betulinic acid on acetylation with acetic anhydride pyridine at room temperature gave needles m.p. 278° (lit. 287—91)[3] $[\alpha]^{20}_D$ ∓ 23° ($CHCl_3$) (lit. $[\alpha]^{20}_D$ + 22 ± 2°).[4] The NMR spectrum contained the following signals : δ 4.66 (d, 2H) J = 3Hz, 2 vinyl protons ; 4.45 (s, 1H) $C_3$ proton ; 2.0 (s, 3H) methyl of acetate, 1.7 (s, 3H) methyl group of $CH_3$—C=$CH_2$; IR, 1690, 1735, 1640 $cm^{-1}$. The mass spectrum showed the molecular ion of m/e 498 and the rest of the fragmentation pattern is identical to the pattern shown by Lupenes.[2]

*Methyl ester of betulinic acid :* The betulinic acid on methylation with excess diazomethane gave the methyl ester m.p. 218° from petroleum ether (lit 223°).[3]

*Ellagic acid :* From the cold methanolic extract of *S. racemosa*, ellagic acid was obtained, which after crystallisation from pyridine gave needles (m.p. 360°) identical with authentic ellagic acid (TLC).

## References


1. ATTYGALLE, J. ed., (1952) *Sinhalese Materia Medica*, M. D. Gunasena & Co. Ltd., Colombo.
2. BUDZIKIEWICZ, H., WILSON, J. M. DJERASSI, C. (1963) *J. Amer. Chem. Soc.* **85** : 3688
3. EYRE & SPOTTISWOODE (1953) *Dictionary of Organic Compounds*, London.
4. MATHIEU, J. P. & OURISSON, G. (1958) *Selected constants*, Optical Rotary Power, Pergamon Press.
5. NISHIDA, K., SOMINOTO, M. & KONDO, T. (1951) *J. Jap. For. Soc.*, **33** : 269.
6. NISHIDA, K., FUNSOKA, K. KONDO, T. (1951) *J. Jap. For Soc.*, **33** : 312.
7. RAO, S.B. & HORHAMURAI, L., (1954) *Arch. Pharm.*, **287** : 76.
8. TECHESCHE, R., WELZEL, P., MOLL, R. LEGLER, G. (1964) *Tetrahedron*, **20** b: 1453.