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TRITERPENOIDS OF *GARDENIA LATIFOLIA*

G. C. S. REDDY, K. N. N. AYENGAR and S. RANGASWAMI

Department of Chemistry, University of Delhi, Delhi 110 007, India

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Key Word Index—*Gardenia latifolia*; Rubiaceae; D-mannitol; sitosterol; oleanolic acid; hederagenin; siaresinolic acid; spinosic acid.

Plant. Gardenia latifolia Ait. *Previous work*: nil; On other Gardenia species; *G. turgida* [1, 2], *G. jasminoides* [3].

Results of the present work on the stem bark. The petrol extract yielded sitosterol and the alcohol extract yielded a rich crop of D-mannitol. The crude mixture of sapogenins obtained by acid hydrolysis of the mother liquor was treated with CH_2N_2 and individual methylated components were obtained by chromatography. *Methyl oleanolate*, $C_{31}H_{50}O_3$, m.p. 201–3°, $[\alpha]_D$ +92·6°; acetate m.p. 226°, $[\alpha]_D$ +68·4°; (m.m.p., TLC and IR). *Hederagenin, methyl ester*, $C_{31}H_{50}O_4$, m.p. 241–3°, $[\alpha]_D$ +99·5°; diacetate, m.p. 197–8°, $[\alpha]_D$ +93·6° (m.m.p., TLC and IR). *Siaresinolic acid, methyl ester* [4], $C_{31}H_{50}O_4$, m.p. 182–3°, $[\alpha]_D$ +68·7°; diketo ester, m.p. 212–14°, $[\alpha]_D$ +122°; dihydroxy acid (siaresinolic acid), m.p. 275–8°, $[\alpha]_D$ +92·8°; 3-*O*-acetate ester, m.p. 130–3°, $[\alpha]_D$ +82·1°; 3-*O*-acetyl-19-keto ester, m.p. 246–8°, $[\alpha]_D$ +144·3° and its rearrangement product viz methyl 3-acetyl-19-oxo-olean-13(18)-en-28-oate, m.p. 213–15°, $[\alpha]_D$ −189·2° λ_{max}^{MeOH} 255 nm (log ϵ 3·89).

Spinosic acid, methyl ester [5], $C_{31}H_{50}O_4$, m.p. 198–200°, $[\alpha]_D$ +44·8°; monoacetate, $C_{33}H_{52}O_5$; diacetate, $C_{35}H_{54}O_6$ m.p. 248–50°, $[\alpha]_D$ +67·7°; free (dihydroxy) acid, m.p. 301–2°, $[\alpha]_D$ +24·8°. The NMR and MS of the ester monoacetate suggested that it should have a hydroxyl in ring E, an acetoxyl in ring A and COOMe at C-17; its dehydro derivative was identical with 3-*O*-acetyl-19-keto-siaresinolic acid methyl ester. These suggest that spinosic acid is the 19-epimer of siaresinolic acid in which the 19-OH is axial. Confirmation for the equatorial conformation of the 19-OH in spinosic acid came from the observation that the 3-*O*-acetyl-19-keto ester gave back the parent ester diol on reduction with Na–EtOH [6]. This is the second record of isolation from a natural source [5]. The 3-*O*-acetate of the methyl ester (Ac_2O/Py, 25°, 12 hr), has not been described so far. Its properties are as below: m.p. 258–60°, $[\alpha]_D$ +44·3°: NMR ($CDCl_3$), δ 0·76, 0·85, 0·87, 0·97, 1·05, 1·16 (21H, *s*, 7 × Me), 2·03 (3H, *s*, Ac), 3·43 (1H, *d*, *J*, 12 Hz, 19α-*H*), 3·66 (3H, *s*, OMe), 4·56 (1H, *t*, *J*, 7·5 Hz, 3α-*H*), 5·5 (1H, 12-*H*); MS, *m/e* 510 (M–H_2O, 86%), 468 (25), 450 (21), 278 (28), 260 (44), 249 (14), 219 (36), 218 (18), 205 (20), 201 (100), 189 (55), 133 (42).

A new triterpenoid acid methyl ester was also isolated.

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