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SHORT COMMUNICATION

BIOGENETICALLY RELATED TRITERPENES FROM *ELATERIOSPERMUM TAPOS* BARK

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Abstract—The acetates and palmitates of β-amyrin and germanicol and the acetates of ψ-taraxasterol and lupeol were isolated from *Elateriospermum tapos* bark.

Elateriospermum tapos (Euphorbiaceae)* exudes copious amounts of light petroleum-soluble latex from the bark. Although evaporation of the solvent gave a crystalline solid, such a solid was a complex mixture, as shown by $AgNO_3$-impregnated silicic acid TLC analysis. The acetone-soluble part of the resin yielded acylated triterpene and triterpene alcohol fractions on chromatography. By repeated chromatography of the former fraction on an $AgNO_3$-impregnated column, six compounds were isolated in pure state and were identified as β-amyrin palmitate[1] (I), germanicol palmitate (III), β-amyrin acetate[2,3] (II), germanicol acetate[1] (IV), ψ-taraxasterol acetate (V) and lupeol acetate (VI);[1,4] one of these, III, is a new compound. The triterpenes are arranged in the order of elution from the column and, therefore, represent the increasing order of binding strength with silver ion. These triterpenes were conveniently characterized by their i.r., NMR and mass spectroscopic data. The acetates II, V and VI were further unambiguously established by direct comparison with authentic samples.‡ Hydrolysis of I gave β-amyrin and palmitic acid. Respective hydrolysis of III and IV afforded germanicol. In addition, palmitic acid derived from I and III was ascertained, as the methyl ester, by direct comparisons with a mixture of methyl palmitate and stearate in a VPC column. It was noted that ψ-taraxasterol acetate[5] (V) and lupenyl-I acetate[5] exhibit indistinguishable i.r. and mass spectra[6] and no mutual depression of the m.n.s. These two acetates, however, showed an unambiguous difference in the retention time on a SE 30 column. Incidentally, this is the first instance acetate V has been isolated from

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natural source. The triterpene alcohol fraction was acetylated, wherefrom the presence of the acetate II, IV, V and VI were detected by TLC analysis.

Acid-catalysed rearrangements of lupeol to germanicol, ψ-taraxasterol and lupenyl-I and some interconversions among these triterpenes[5,7,8] have been clearly established and discussed with the well-understood behaviours of carbonium ions by Jones, Halsall and co-workers.[5] This further suggests the possible biogenetic relations among these triterpenes.[9-11] It is, therefore, significant that these triterpenes, with the exception of lupenol-I, are found in the same bark latex.

EXPERIMENTAL

Bark* of *Elateriospermum tapos* (4 kg) was chopped to small pieces and soaked with light petroleum overnight. The combined extracts were evaporated to afford resin (221 g). The resin was separated to the acetone-soluble (190 g) and powdery precipitate (37 g). The acetone-soluble residue (13 g) was chromatographed on a silicic acid column to yield a forerun (139 mg) and fraction A (4·74 g) and fraction B (1·14 g). On an $AgNO_3$-impregnated (10%) silicic acid plate, both fractions A and B showed six predominant spots. The fraction A was repeatedly chromatographed on an $AgNO_3$-impregnated (10%) column using light petroleum and benzene as eluents to give the following compounds.

Lupeol acetate. M.p. 214–216° from EtOH (lit.[1] 215–216°); i.r. 1715, 1250, 1020 and 975 cm^{-1}; τ 8·26 (t, J = 0·5 Hz, 3H), 5·50 (d of d, 1H) and 5·32 (AB quartet, J = 2 Hz, 2H); *m/e* (rel. %), 468 (100), 218 (45), 204 (38), 189 (63). A mixed m.p. with the authentic lupenyl acetate[6] (m.p. 217–217·5°) is 214–215°. *Dihydrolupeol acetate*: m.p. 246–248° from hydrogenation (lit.[2] 245–246°); i.r. 1720, 1255 cm^{-1}; NMR τ 5·60 (d of d, J = 5·5 and 8 Hz, 1H); *m/e* (rel. %), 470 (8·7), 189 (100), 175 (43) and 163 (70). *Lupeol:* m.p. 210–211° from hydrolysis (lit.[1] 210–211°); i.r. 3615 and 1060; NMR τ 6·80 (d of d, J = 5 and 10 Hz, 1H) and 5·38 (AB quartet, J = 2·5 Hz, 2H).

Germanicol acetate. M.p. 281–282° from EtOH (lit.[1] 283–284°); i.r. 1735, 1245 and 1030 cm^{-1}; NMR τ 5·60 (d of d, J = 5 and 9 Hz, 1H) and 5·20 (broad d, J = 1·5 Hz, 1H); *m/e* (rel. %) 468 (25), 205 (45), 204 (100), 189 (77), 177 (78).

ψ-Taraxasterol acetate. M.p. 243–244° from EtOH (lit.[1] 240–241°); i.r. 1735, 1650, 1250 and 1040 cm^{-1}; NMR τ 5·56 (d of d, J = 6 and 9 Hz, 1H) and 4·77 (m, 1H); *m/e* (rel. %) 468 (9·9), and 189 (100). The retention time of ψ-taraxasterol acetate on a VPC column (3% SE 30 on Aeropak 30, 5 ft × ¼ in., 230°) was 7 min 24 sec and that of lupenyl-I acetate was 8 min.

β-Amyrin acetate. M.p. 235–242° from EtOH (lit.[1] 236°); i.r. 1735, 1245 and 1030 cm^{-1}; NMR τ 5·58 (d of d, J = 6 and 9 Hz, 1H) and 4·87 (d of d, J = 3 and 4 Hz, 1H); *m/e* (rel. %) 468 (14), 218 (100), 203 (39) and 189 (20). Mixed m.p. with authentic β-amyrin acetate‡ (m.p. 236–244°) is 234–244°.

β-Amyrin palmitate. M.p. 76–77° from EtOH (lit.[1] 77°); i.r. 1730 and 1250 cm^{-1}; NMR τ 5·60 (d of d, J = 6 and 9 Hz, 1H) and 4·88 (m, 1H); *m/e* (rel. %) 664 (0·27), 218 (100), 219 (19), 203 (24) and 189 (16). The compound was hydrolysed to β-amyrin, m.p. 195–196°, (lit.[1] 199–200°) and methyl palmitate (esterification with CH_2N_2). A VPC comparison of this ester with methyl stearate (R_f 3 min) and methyl palmitate (R_f 1 min 44 sec) on 3% SE 30 on Aeropak 30 (5 ft × ¼ in., 190°) showed that this ester is methyl palmitate.

Germanicol palmitate. M.p. 109–111°; i.r. 1730, 1250 and 980 cm^{-1}; NMR τ 5·60 (d of d, J = 5 and 9 Hz, 1H) and 5·20 (broad, J = 1·5 Hz, 1H); (rel. %) 664 (0·38), 205 (100), 189 (48) and 177 (66).

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