Triterpenoids of *Artocarpus heterophyllus*

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Isolation of prenylated flavones¹ and cycloartane derivatives² was reported earlier from *A. heterophyllus* by other workers. We reported³ the isolation of two new tetracyclic triterpenoids of cycloartane series from the same source. Further studies on the plant revealed the occurrence of three triterpenoids, (24*R*)- and (24*S*)-9,19-cyclolanost-25-ene-3 β ,24-diol and 9,19-cyclolanost-23-ene-3,25-diol. The characterisation of these compounds is reported in this presentation.

Hexane-Me₂CO (95 : 5) eluates of the ether extract of the latex of *A. heterophyllus* on rechromatography over neutral alumina afforded a material (1), m.p. 140–42°, which was found not to be homogeneous on tlc. This material showed the presence of hydroxyls ($\nu_{\max}$ 3 330 cm⁻¹). It

1; R¹ = R² = H
2; R¹ = Ac, R² = H

3; R¹ = R² = H
4; R¹ = Ac, R² = H

was, therefore, purified by acetylation (Ac₂O/py) to afford a diacetate (2), C₃₄H₅₄O₄ (from DEPT), m.p. 121–23° (MeOH). It exhibited in its ir spectrum bands for cyclopropane methylene (3 030 cm⁻¹), two acetates (1 738, 1 730, 1 242 cm⁻¹) and an *exo*-methylene (1 648 cm⁻¹). The 200 MHz ¹H nmr spectrum of 2 showed besides other signals, resonances for cyclopropane methylene (δ 0.32 and 0.56, 1H, d each, *J* 4.1 Hz), two *exo*-methylene protons (δ 4.86, 4.92, 1H, m, each) and two secondary acetates (δ

2.04, 3H, s, OCOCH₃; 2.05, 3H, s, OCOCH₃; 4.55, 1H, dd, *J* 10.0, 5.0 Hz, H-3 α ; 5.11, 1H, t, *J* 6.7 Hz, H-24; δ 80.6, d, C-3 and 77.6 and 78.1, d, C-24). The 50 MHz ¹³C nmr spectrum of 2 revealed doubling of certain carbon resonance signals. Comparison of the cmr data of 2 with those of other cycloartane derivatives^{3–5} showed doubling of resonances associated with C-24 and its adjacent carbons C-17 and C-26 in 2. The doubling of the signals for these carbons is consistent with the presence of a mixture of C-24 epimers^{3,5} in 2. These data coupled with other information led to the structure 2 for the diacetate and thence to the structure 1 for the parent triterpenoid. The structure 2 was confirmed from detailed studies of its ¹H, ¹³C nmr and MS data (vide Experimental) as also by comparison of the data with those reported⁶ for 24-epimeric pairs of 9,19-cyclolanost-25-ene-3 β ,24-diol diacetate. Previously this epimeric pair (2) was isolated from *Euphorbia trigona*⁶ and *Mangifera indica*⁵. This, however, constitutes the first isolation of 2 from *A. heterophyllus*.

The latter fractions of hexane-Me₂CO (95 : 5) eluates on concentration yielded a material which was crystallised from petrol-Me₂CO mixture to afford 9,19-cyclolanost-23-ene-3,25-diol (3), m.p. 170–73° (lit.⁷ 204°), $\nu_{\max}$ 3 320 (OH), 3 030, 970 cm⁻¹. It gave reddish pink colouration with Liebermann-Burchardt reagent for triterpenes. In the 300 MHz ¹H nmr spectrum, it showed the presence of two cyclopropane methylene protons (δ 0.31, 0.54, 1H, d each, *J* 4.5 Hz), two methyl protons on a carbon bearing a hydroxyl function (δ 1.30, 26-CH₃ and 27-CH₃), a secondary hydroxyl (δ 3.27, 1H, dd, *J* 10 and 4.8 Hz, H-3 α) and two olefinic protons (δ 5.59, 2H, m, H-23 and H-24). The chemical shift and coupling constant of H-3 is typical of triterpenes bearing a β -equatorial hydroxyl at 3. Besides showing other carbon resonance signals in the 75 MHz ¹³C nmr spectrum, it exhibited signals at δ 29.8 (C-19, t), 70.7 (C-25, s), 78.9 (C-3, d) and at 125.6 (C-24, d) and 139.5 (C-23, d). The ¹³C nmr data of 3 have been completely interpreted and assigned (vide Experimental). On acetylation of 3 with Ac₂O/py at room temperature, it, however, yielded an oily product 4 (lit.⁷ m.p. 148°), $\nu_{\max}$ 3 520 (OH), 1 715 and 1 260 (acetate) cm⁻¹. Although ¹H, ¹³C nmr and MS data completely elaborated the structure 3 for the triterpenoid, yet the physical characteristics of 3 and 4 differed significantly from those reported⁷ for 9,19-cyclolanost-23-ene-3,25-diol and its corresponding acetate. This difference may be due to the different modes of isolation and purification of the compound obtained from

**Deceased.

two different plant sources by two groups of workers. ^{13}C nmr data for 3 are being reported for the first time.

Experimental

Plant material was collected locally and identified⁸. M.ps. are uncorrected. ^1H nmr (200 and 300 MHz) and ^{13}C nmr (50 and 75 MHz) spectra (CDCl_3) were recorded with reference to TMS or CHCl_3 at δ 7.26. Silica gel (B.D.H., 60–120 mesh) and silica gel (Merck) were used for cc and tlc respectively. Samples were routinely dried over P_2O_5 for 24 h.

The air-dried latex (1 kg) of *A. heterophyllus* was kept soaked in ether for 1 month. The organic layer was then filtered through cellite bed. After evaporation of the solvent the crude extract was chromatographed over neutral alumina and the column was eluted with solvents of increasing polarity. Concentrated hexane- Me_2CO (95 : 5) eluates were subjected to rechromatography over neutral alumina using the same solvent (hexane- Me_2CO , 9 : 1) elution technique; collections were 500 ml each. Fr. 4 on concentration gave a residue which was crystallised from Me_2CO to yield 1, m.p. 140–42°; ν_{max} 3 330 cm^{-1} . Acetylation of 1 with $\text{Ac}_2\text{O/py}$ at room temperature furnished 2, $\text{C}_{34}\text{H}_{54}\text{O}_4$ (from DEPT), m.p. 121–23° (MeOH); R_f 0.66 (petrol : Me_2CO , 9 : 1, Si-gel); ν_{max} 3 030, 1 738, 1 730, 1 648, 1 242 cm^{-1} ; ^1H nmr δ 0.32, 0.56 (ABq, J 4.1 Hz, $2\times\text{H-19}$), 0.33 (6H, $2\times\text{CH}_3$), 0.87 (6H, $2\times\text{CH}_3$), 0.94 (3H, CH_3), 1.70 (3H, $\text{C}_{25}\text{-CH}_3$), 2.04 (3H, s, OCOCH_3), 2.05 (3H, s, OCOCH_3), 4.55 (1H, dd, J 10 and 5 Hz, H-3 α), 4.86 (1H, m, H-26), 4.92 (1H, m, H-26), 5.11 (1H, t, J 6.7 Hz, H-24); ^{13}C nmr δ 31.5 (t, C-1), 26.8 (t, C-2), 80.6 (d, C-3), 39.4 (s, C-4), 47.1 (d, C-5), 20.9 (t, C-6), 28.0 (t, C-7), 47.8 (d, C-8), 20.1 (s, C-9), 25.9 (s, C-10), 25.8 (t, C-11), 35.4 (t, C-12), 45.2 (s, C-13), 48.8 (s, C-14), 32.8 (t, C-15), 26.4 (t, C-16), 52.05 (52.03) (d, C-17), 17.8 (q, C-18), 29.7 (t, C-19), 35.7 (d, C-20), 18.2 (q, C-21), 29.06 (t, C-22), 29.3 (t, C-23), 77.6 (78.1) (d, C-24), 143.0 (143.41) (s, C-25), 112.4 (113.2) (t, C-26), 18.0 (q, C-27), 19.3 (q, C-28), 25.4 (q, C-29), 15.1 (q, C-30), 170.4 and 171.0 (s, $2\times\text{OCOCH}_3$), 21.2 and 21.3 (q, $2\times\text{OCOCH}_3$); m/z (rel. int.) 466 [$M^+ - \text{CH}_3\text{COOH}$], 161 (6.7), 159 (6.7), 133 (9.4), 107 (17.5), 81 (21.8), 55 (19.5), 43 (100).

Frs. 9–11 yielded a solid residue which was crystallised from petrol- Me_2CO mixture to afford 3, $\text{C}_{30}\text{H}_{50}\text{O}_2$ (from DEPT), m.p. 170–73° (lit.⁷ 204°); R_f 0.21 (petrol- Me_2CO ,

9 : 1, Si-gel); ν_{max} 3 320, 3 090, 970 cm^{-1} ; ^1H nmr δ 0.31, 0.54 (ABq, J 4.5 Hz, $2\times\text{H-19}$), 0.80 (3H, CH_3), 0.84 (3H, CH_3), 0.86 (3H, CH_3), 0.87 (3H, CH_3), 0.96 (3H, CH_3), 1.30 [6H, $\text{C}_{25}\text{-(CH}_3)_2$], 3.27 (1H, dd, J 10 and 4.8 Hz, H-3 α), 5.59 (2H, m, H-23 and H-24); ^{13}C nmr δ 32.04 (t, C-1), 26.58 (t, C-2), 78.90 (d, C-3), 40.56 (s, C-4), 47.22 (s, C-5), 21.13 (t, C-6), 28.10 (t, C-7), 47.91 (d, C-8), 20.13 (s, C-9), 26.30 (s, C-10), 26.01 (t, C-11), 35.64 (t, C-12), 45.45 (s, C-13), 48.93 (s, C-14), 32.94 (t, C-15), 30.49 (t, C-16), 52.12 (d, C-17), 18.3 (q, C-18), 29.83 (t, C-19), 36.46 (d, C-20), 18.03 (q, C-21), 39.10 (t, C-22), 139.54 (d, C-23), 125.65 (d, C-24), 70.68 (s, C-25), 30.05 (q, C-26), 29.97 (q, C-27), 19.33 (q, C-28), 25.48 (q, C-29), 14.0 (q, C-30). On acetylation ($\text{Ac}_2\text{O/py}$ at room temperature), 3 yielded an oily material 4; R_f 0.39 (petrol : Me_2CO , 9 : 1, Si-gel); ν_{max} 3 520, 1 715, 1 260 cm^{-1} . Compound 4 could not be induced to crystallise.

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