

Terpenoids and Related Compounds. Part 25.¹ Structures of the 25-Nortriterpenoids Putrol and Putrone

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The suggested structures of putrol (1a) and putrone (1b) have been supported by the conversion of putrone into *D*: *A*-friedo-oleana-7,9(11)-diene (2). The latter has also been synthesised from 25-acetoxy-*D*: *A*-friedo-olean-7-ene (3a).

SESHADRI and his co-workers² isolated an alcohol (putrol) and its corresponding ketone (putrone) from the leaves of *Putranjiva roxburghii*. From physical data, especially mass spectrometric fragmentation patterns, putrol and putrone were suggested² to be the 25-nortriterpenoids (1a and b), respectively. However these structures were

putrone (1b) but settles their stereochemistry at all asymmetric centres except C-3 in putrol (1a).

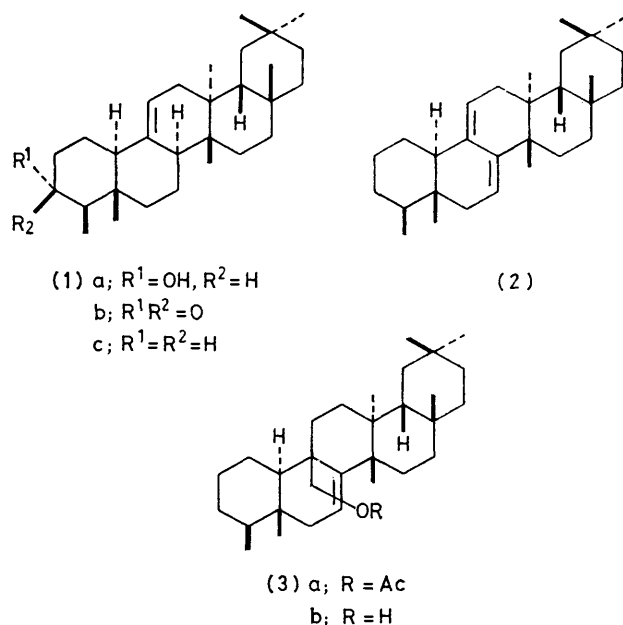
EXPERIMENTAL

N.m.r. spectra were recorded in deuteriochloroform at 100 MHz using tetramethylsilane as internal standard. Optical rotations were measured in chloroform. Light petroleum used had b.p. 60–80° unless otherwise stated.

25-Nor-D: *A*-friedo-olean-9(11)-ene (1c).—A mixture of putrone (1b) (0.4 g) (isolated from the leaves of *P. roxburghii* following the method of Seshadri and his co-workers²) and 99% hydrazine hydrate (5 ml) in diethylene glycol (40 ml) was refluxed for 1 h. Potassium hydroxide (0.4 g) was added and the mixture was refluxed for a further 1 h. The condenser was then removed and the mixture heated until the inner temperature reached 190 °C. The condenser was replaced and the mixture was refluxed for a further 12 h. Usual work-up furnished a solid (0.4 g) which was chromatographed over silica gel (20 g). Elution with light petroleum yielded a solid (0.36 g) which was crystallised from chloroform–methanol to give the pure *alkene* (1c), m.p. 170–174°, $[\alpha]_D^{25}$ 2.2° (Found: C, 87.2; H, 12.0. $C_{29}H_{48}$ requires C, 87.4; H, 12.2%), ν_{max} 850 cm^{-1} (trisubstituted double bond), δ 0.62–1.52 (4-, 5-, 13-, 14-, and 17-Me and 20-Me₂) and 5.23br (1 H, H-11), *m/e* 396 (M^+), 381, 257, 243, 229, 205, 191, and 123.

Oxidation of (1c) with Selenium Dioxide. **25-Nor-D**: *A*-friedo-oleana-7,9(11)-diene (2).—The hydrocarbon (1c) (0.2 g) and selenium dioxide (0.2 g) in glacial acetic acid (60 ml) were heated on a steam-bath for 1 h. The mixture was filtered and the filtrate on usual work-up furnished a semi-solid mass (0.2 g) which was chromatographed over silica gel. Elution with light petroleum (b.p. 40–60°) gave a solid (0.12 g) which on crystallisation from chloroform–methanol yielded the pure *diene* (2), m.p. 165–168°, $[\alpha]_D^{25}$ –20.93° (Found: C, 88.3; H, 11.65. $C_{29}H_{46}$ requires C, 88.25; H, 11.7%), ν_{max} 872 cm^{-1} (trisubstituted double bond), λ_{max} (cyclohexane) 249 (ϵ 9 100) and 255 nm (11 000), δ 0.75 (3 H, d, *J* 6 Hz, 4-Me), 0.8–1.28 (18 H, 6 × s, 5-, 13-, 14-, and 17-Me and 20-Me₂), and *ca.* 5.5 (2 H, m, H-7 and -11), *m/e* 394 (M^+), 379, 255, 242, 241, 215, and 205.

25-Hydroxy-D: *A*-friedo-olean-7-ene (3b).—25-Acetoxy-*D*: *A*-friedo-olean-7-ene (3a) (0.23 g) and lithium aluminium hydride (0.4 g) in tetrahydrofuran (40 ml) were refluxed for 6 h. Usual work-up furnished a solid (0.24 g) which was chromatographed over silica gel (20 g). Elution with light petroleum–benzene (7 : 3, v/v) furnished a solid (0.2 g) which on crystallisation from chloroform–methanol yielded pure *alkene* (3b), m.p. 192–194°, $[\alpha]_D^{25}$ –55.35° (Found: C, 83.65; H, 11.85. $C_{30}H_{50}O$ requires C, 83.45; H, 11.8%), ν_{max} 3 480 (OH) and 860 cm^{-1} (trisubstituted double bond),



not correlated with any known derivative of *D*: *A*-friedo-oleanane. In this paper we confirm these structures by correlating them with that of a known *D*: *A*-friedo-oleanane derivative.

Putrone (1b), isolated from the leaves of *P. roxburghii*, was subjected to Huang Minlon reduction to yield 25-nor-*D*: *A*-friedo-olean-9(11)-ene (1c), which on oxidation with selenium dioxide furnished 25-nor-*D*: *A*-friedo-oleana-7,9(11)-diene (2).

The diene (2) was also prepared from 25-acetoxy-*D*: *A*-friedo-olean-7-ene (3a), the synthesis of which we have previously described.³ The acetate (3a), on treatment with lithium aluminium hydride, gave the corresponding unsaturated alcohol (3b), which on refluxing with lead tetra-acetate and copper(II) diacetate in benzene under nitrogen furnished the diene (2), identical with the sample obtained from putrone (1b).

This not only confirms the structures of putrol (1a) and

δ 0.76 (3 H, d, J 4 Hz, 4-Me), 0.83—1.22 (18 H, $6 \times s$, 5-, 13-, 14-, and 17-Me and 20-Me₂), 3.78 (2 H, q, J 12 Hz, H₂-25), and 5.72 (1 H, $2 \times d$, J 4 and 7 Hz, H-7), m/e 426 (M^+), 411, 408, 395, 302, 271, 243, 220, 205, and 189.

25-Nor-D : A-friedo-oleana-7,9(11)-diene (2) from (3b).—A mixture of the alcohol (3b) (0.2 g), lead tetra-acetate (1 g) and copper diacetate (0.1 g) in benzene was refluxed in an atmosphere of N₂ for 3 h. The mixture was filtered and worked up as usual to yield a gummy mass (0.2 g) which was chromatographed over silica gel (20 g). Elution with light petroleum furnished a solid (0.11 g) which on crystallisation from chloroform–methanol yielded the pure diene (2), m.p. 165—168°, identical (mixed m.p., t.l.c., rotation, and n.m.r., mass and i.r. spectra) with the diene obtained from putrone.

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