
S K Ghosh, S K Dutta, M Roy, Kakoli Majumdar & Saktipada Das*
Department of Chemistry, University of Kalyani, Kalyani 741 235, West Bengal

Received 10 November 2000; accepted (revised) 20 November 2001

Structure of the natural product 25-formyl D:A-friedoolean-3-one 1 has been established by its synthesis from putranjivadione 2. Compound 2 is converted into 7β, 25-oxido-D:A-friedoolean-3β-ol 4 which on treatment with lithium in ethylenediamine yields D:A-friedoolean-3β, 25-diol 5 as one of the products. 5 on oxidation with CrO3 in pyridine affords 1.

Although a number of naturally occurring 25-oxygenated D: A-friedooleananes have been isolated and their structures suggested1-7, but none of them was synthesised or correlated with any known compound. 25-Formyl-D: A-friedoolean-3-one 1 was isolated by Courtney et al.8, 2 from Siphonodon australae and subsequently by Anjaneyulu et al.9 and Sultanbawa et al.10 from Elaeodendron glaucum but its structure was only proposed on the basis of physicochemical evidences. In continuation to our work on the synthesis of 25-oxygenated D: A-friedooleananes10-11, we establish herein the proposed structure of 1 by its synthesis from putranjivadione 2, a compound of known11 structure and stereochemistry.

Putranjivadione 2 isolated from the bark of Putranjiva roxburghii Wall was converted to 3β-acetoxy-7β, 25-oxido-D: A-friedooleanane 3 by reported13 procedure. 3 on hydrolysis with 5% methanolic KOH furnished the corresponding 3β-hydroxy derivative 4. The IR spectra of 4 (3350 cm⁻¹ and no band for acetoxyl group) confirmed complete hydrolysis of 3. The substituted tetrahydrofuran ring in 4 was then opened14 by treatment of 4 with lithium in boiling ethylenediamine under N2 atmosphere for 6 hr to afford D: A-friedoolean-3β, 25-diol 5 (ca 15%) and D: A-friedoolean-3β, 7β-diol 6 (ca 10%). The unreacted 4 was however recovered in ca 70% yield. D: A-friedoolean-3β, 25-diol 5, on acetylation afforded D: A-friedoolean-3β, 25-diacetate 7. Both 5 and 7 were characterized by elemental analyses and spectral data (see Experimental). 5 on oxidation with chromium trioxide in pyridine furnished 25-formyl-D: A-friedoolean-3-one 1, identified by comparing its physical and spectral data with those reported in the literature.

Experimental Section

General. All melting points reported are uncorrected. Petrol used had b. p. 60-80°. Homogeneity of compounds was checked by TLC on dried silica gel (BDH) plates and spots were visualized with iodine vapours. IR spectra were recorded on a Perkin-Elmer 1330 spectrophotometer (νmax in cm⁻¹) and 1H NMR spectra on a Varian XL-200 (200 MHz) instrument using TMS as internal standard (chemical shifts in δ, ppm). All solvents were purified, distilled and dried before use. Analytical samples were routinely dried in vacuo over P2O5 for 24 hr at room temperature.

Isolation of putranjivadione 2 and its subsequent conversion to 3, m.p. 216-18°C (lit.13 m.p. 215-18°C), were carried out by reported procedures12,13.

Alkaline hydrolysis of 3. Compound 3 (0.8 g) was taken in 5% methanolic KOH (30 mL) and the mixture was refluxed for 4 hr after addition of 20 mL ben-
benzene. Usual work up yielded a solid (0.75 g, single spot in TLC) which crystallised from a mixture of CHCl₃ and MeOH to afford colourless crystals of 4 (0.52 g, m.p. 246–50°C. IR : 3500 cm⁻¹ (OH).

**Lithium in ethylenediamine reduction of 4.** Small pieces of metallic lithium (0.3 g) were added to a suspension of 4 (0.3 g) in dry ethylenediamine (30 mL) and the mixture was refluxed under nitrogen atmosphere for 6 hr. The reaction mixture was cooled rapidly in ice, treated with solid NH₄Cl to destroy excess unreacted lithium and acidified with 6 M HCl. The organic material thus precipitated was extracted with ether to furnish the crude reaction product (ca 0.3 g, three close spots in TLC) which was chromatographed over a column of silica gel to afford solid-A, solid-B and solid-C in benzene, benzene-ethyl acetate (19: 1) and benzene-ethyl acetate (9: 1) eluents, respectively. Solid-A (0.03g) on crystallisation from a mixture of chloroform - acetone afforded colourless crystals of 1 (0.026 g, m.p. 298-99°C, [α]D = -60.5°C (lit.¹ m.p. 305-07°C, [α]D = -62.1°C) (Found: C, 81.85; H, 10.89; M⁺ 440. C₃₀H₅₈O₂ requires C, 81.76; H, 10.98%; M⁺ 440); IR : 1705 (-CHO), 1720 (C=O-CO) cm⁻¹. ¹H-NMR : 0.69 (s, 3H), 0.90 (d, 3H, C₃-Me), 0.96 (s, 9H), 1.10 (s, 3H), 1.21 (s, 3H), 2.30 (m, 3H, C₃-H and C₇-H₂), 10.24 (s, 1H, -CHO). MS : 440 (M⁺), 455, 425, 411, 395, 376, 316, 315, 303, 259 (base peak), 205, 189.

**Acknowledgement**

We thank (Late) Prof. P Sengupta for his interest and kind donation of some authentic samples. We are thankful to M/s East India Pharmaceutical Works Limited, Calcutta for financial assistance and RSIC, CDRI, Lucknow for elemental analyses and mass spectral data.

**References**