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FUNCTIONALISATION OF 25-METHYL GROUP OF D:A-FRIEDOOLEANANES

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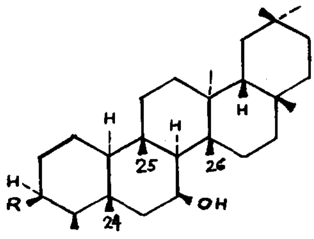
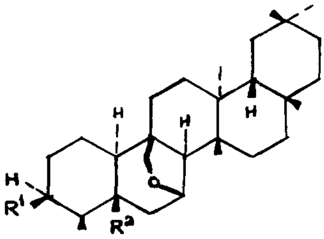
Although a number of triterpenoids of D:A-friedooleanane group with oxygen function at C-25 have been isolated and their structures suggested[1-5], direct correlation with a triterpene of known structure and configuration has not been possible yet for the lack of a suitable method for introducing an oxygen function at C-25 methyl group. The present communication describes the first successful method for the functionalisation of the C-25 methyl group from known precursors friedoolean-7β-ol (Ia)[6-8] and 3β-acetoxy friedoolean-7β-ol (Ib)[6-8].

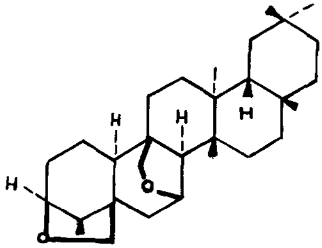
The axial 7β-hydroxyl group in both Ia and Ib suffers from severe 1,3-diaxial interaction by three methyl groups at C-24, C-25 and C-26, and hence it was suspected that hypohalite oxidation[9] might effect functionalisation of any or all of the three methyl groups. Irradiation of a mixture of Ib, lead tetraacetate, iodine and calcium carbonate in cyclohexane for 3.5 hrs with a 500 watt tungsten lamp furnished a gummy mixture which could be resolved into three components on chromatography over alumina. The least polar fraction (5%), m.p. 274-276° was identified as _epi_-friedelanol acetate (I.R., TLC and mixed mp), presumably formed by



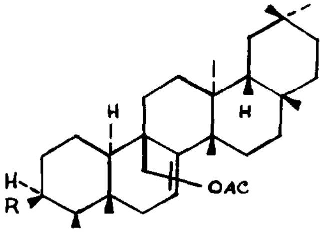
I a, R = H
b, R = OAC



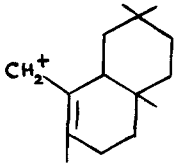
II a, R^1 = H, R^2 = CH_3
b, R^1 = OAC, R^2 = CH_3
c, R^1 = OAC, R^2 = CH_2I



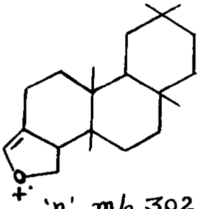
III



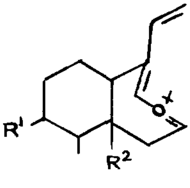
IV a, R = H
b, R = OAC



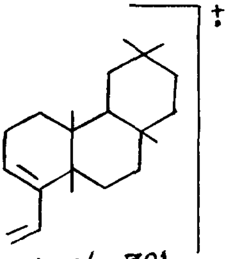
'm' m/e 205



'n' m/e 302



'O' R^1 = H, R^2 = CH_3; m/e 205
R^1 = OAC, R^2 = CH_3; m/e 263
R^1 = OAC, R^2 = CH_2I; m/e 389



'p' m/e 301

hydrogen radical exchange with cyclohexane.

The second component $C_{32}H_{52}O_3$ to come out of the column, m.p. 215-218°, $(\alpha)_D$ + 44.7° (50%), M^+ 484, IR 1740, 1250 (acetate) and 842 and 850 cm^{-1} (ether); NMR : 0.85 (3H, d, J=4 Hz), 0.99 (3H, s), 1.05 (3H, s), 1.09 (3H, s), 1.12 (3H, s), 1.30 (3H, s) and 1.39 (3H, s) for one secondary and six tertiary methyl groups; 2.02 (3H, s, $-CO.CH_3$); AB quartet at 3.49 and 3.78 (2H, J=4 Hz, $-CH_2-O-$ at C-25); 4.29 (1H, m, H at C-7) and 4.92 (1H, m, H at C-3) was attributed structure (IIb) on the basis of these data coupled with mass spectrometric fragmentation pattern described below.

The most polar component, $C_{32}H_{51}O_3I$, m.p. 123-125° contained iodine and was attributed structure (IIc), IR 1725, 1230 (acetate) and 842 (ether); NMR six methyl signals in the region 0.88 to 1.2, 2.18 (3H, s, $-CO.CH_3$), 2.64 and 2.84 (2H, AB quartet, J=4 Hz, shielded $O-CH_2-$), 3.62 (2H, s, $-CH_2.I$), 4.25 (2H, broad m, overlapped C-7 and C-3 H). On treatment with $LiAlH_4$ IIc afforded the diether (III), $C_{30}H_{48}O_2$, m.p. 221-225°, M^+ 440, IR no acetate peak, peak at 850 cm^{-1} (ether), NMR six methyl signals in the region 0.82 to 1.28; 3.42 and 3.61 (2H, AB quartet, J=2 Hz, $-O-CH_2-$ at C-25), 3.84 (2H, broad, $-O-CH_2-$ at C-24), 4.09 - 4.52 (2H, m, overlapped C-7 and C-3 H).

Similar irradiation of Ia in presence of lead tetracetate and iodine furnished after chromatography only two products. The less polar component (10%) was friedelane, m.p. 245-246°. The more polar component (60%), $C_{30}H_{50}O$, m.p. 204-206°, M^+ 426, IR 840 and 850 cm^{-1} (ether) was attributed structure (IIa) on the basis of mass spectral data.

The mass spectra[10] of each of IIa, IIb and IIc showed a peak at m/e 205 corresponding to the ion 'm', thus demonstrating that the C-26 methyl group had not been affected, A peak at m/e 302 from each of IIa, IIb and IIc corresponded to ion 'n'[11] and definitely established that functionalisation had taken place at C-25. This conclusion was further supported by the appearance of a peak at m/e 205 from IIa, at m/e 263 from IIb and at m/e 389 from IIc corresponding to the ion 'O'.

IIb on mild treatment with BF_3-etherate in acetic anhydride gave the en-acetate (IVb), $C_{34}H_{54}O_4$, m.p. 160-162°, M^+ 526, NMR 2.0 (6H, s, -CO.$C\underline{H}_3$ at C-3 and C-25), 4.84 (1H, broad, -C=C-$\underline{H}$ at C-7). Similar treatment of IIa furnished IVa, m.p. 122-126°, M^+ 468. The mass spectra of each of IVa and IVb gave a prominent peak at m/e 301 corresponding to the ion 'p' formed by RDA cleavage followed by elimination of $-CH_2$.OAc.

All the compounds gave fairly good C,H-analytical data.

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REFERENCES

1. J.L. Courtney and R.M. Gascoigne, J. Chem. Soc. 2115 (1956).
2. J.L. Courtney, R.M. Gascoigne and A.Z. Szumer J. Chem. Soc. 2119 (1956).
3. J.S. Shannon, C.M. Macdonald and J.L. Courtney, Tetrahedron Letters 173 (1963).
4. J.L. Courtney and W. Stern, Tetrahedron Letters 1607 (1965).
5. H.S. Garg and C.R. Mitra, Phytochem. 10, 865 (1971).
6. P. Sengupta, A.K. Chakraborty, A.M. Duffield, L.J. Durham and C. Djerassi, Tetrahedron 24, 1205 (1968).
7. P. Sengupta and J. Mukherjee, Tetrahedron 24, 6259 (1968).
8. P. Sengupta, J. Indian Chem. Soc. 51, 131 (1974).
9. K. Heusler and J. Kalvoda in 'Organic Reaction in Steroid Chemistry' Vol.II, Ed. J. Fried and J.A. Edwards, Van Nostrand, p. 237 (1972).
10. For the mass spectra of friedelanes see ref. 3 and 6 above and J.L. Courtney and J.S. Shannon, Tetrahedron Letters 13 (1963).
11. See E. Fujita, T. Fujita and Y. Nagao, Tetrahedron 28, 555 (1972).