Tetrahedron Letters,Vol.23,No.19,pp 2031-2032,1982 0040-4039/82/192031-02$03.00/0
Printed in Great Britain

TWO NEW ANGULAR METHYL DIOXYGENATED D:A-FRIEDO-OLEANANES

Gamini Weeratunga, Vijaya Kumar* and M. Uvais S. Sultanbawa
Department of Chemistry, University of Peradeniya, Peradeniya, Sri Lanka

Abstract: Two new trioxygenated D:A-friedo-oleananes from Elaeodendron glaucum have been shown to be the angular methyl dioxygenated 25,28-dihydroxy-D:A-friedo-oleanan-3-one(1) and 3,28-dioxo-D·A-friedo-oleanan-25-ol(2) by interconversion and deoxygenation of the alcohol(2) using Lithium-ethylene diamine reduction coupled with spectroscopic methods.

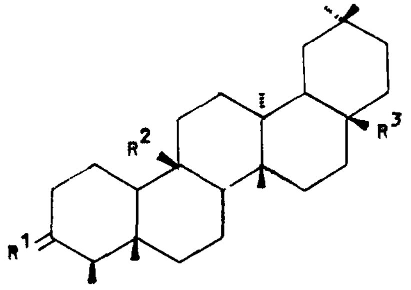
$Li\text{-}(CH_2NH_2)_2$ deoxygenation[1] of sterically hindered primary alcohol derivatives have deen used in the structural determination of angular methyl oxygenated friedelanes.[2] We now report the structural elucidation of two new angular methyl dioxygenated friedelanes from Elaeodendron glaucum[3] bark by deoxygenation of a 25-acetoxy group. The friedelane ring system is believed to assume a chair-chair-chair-twist boat-boat conformation[4] in most friedelane derivatives and not the all-chair conformation previously proposed.[5] In either conformation, the 25-angular methyl group with its 1,3-diaxial relationship with the 24 and 26 methyl groups is sterically hindered. It has been reported[6] that this steric hindrance prevents the oxidation of a hydroxymethylene or aldehyde group at this position into an acid but we have found that 25-hydroxy-D:A-friedo-oleanan-3-one(3) can be oxidised slowly to 3-oxo-D:A-friedo-oleanan-25-oic acid(4) with Jones' reagent[7] in 60% yield. $Li\text{-}(CH_2NH_2)_2$ deoxygenation of 3-oxo-D:A-friedo-oleanan-25-yl acetate(5) gave D:A-friedo-oleanan-3α-ol(6) in 65% yield confirming that the 25-acetoxy group is sufficiently hindered to be deoxygenated by this method.

Spectroscopic evidence suggests that the diol(1) is a D:A-friedo-oleanane containing an oxo and two hydroxymethylene groups[ν 3600-3100 and 1700 $cm.^{-1}$; δ 3.66(2H, s), 3.92(2H, m, W½ 2Hz); m/z 427 (100%, $M^+\text{-}CH_2OH$)] ; and the aldehyde(2) is a D:A-friedo-oleanane containing a keto, an aldehyde and a hydroxymethylene group[ν 3500-3240, 2660, 1710 and 1700 $cm.^{-1}$; δ 3.92(2H, m, W½ 2Hz, 9.5(1H, s) m/z 427(76%, M^+-CHO) and 425(58%, $M^+\text{-}CH_2OH$)] . The two compounds were shown to be interrelated as $NaBH_4$ reduction(See Scheme) gave the same triol(7)[ν 3600-3150 $cm.^{-1}$; δ 3.63(2H, s), 3.73(1H, m, W½ 3Hz), 3.91(2H, m, W½ 2Hz)] suggesting that the aldehyde group in the aldehyde(2) was in the same position as the additional hydroxymethylene group in the diol(1). The primary alcohol group in the aldehyde(2) was shown to be at the 25-position by the Huang Minlon reduction of the aldehyde(2) which gave D:A-friedo-oleanan-25-ol(8).[8]

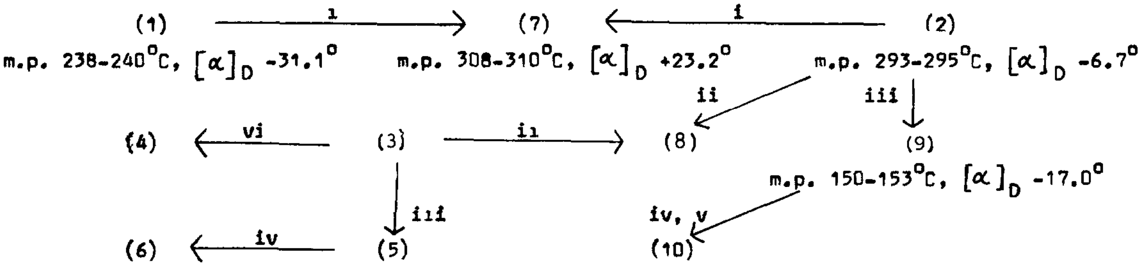
The aldehyde(2) gave an acetate(9) [ν 2700, 1740, 1710, 1700 and 1240 $cm.^{-1}$; δ 2.03(3H, s), 4.33 (2H, AB dd, J 13Hz), 9.5(1H, s)] with Ac_2O-pyridine. The acetate (35 mg) was reduced by heating with lithium(70 mg) and ethylene diamine(5 ml) under reflux for 30 min. The usual work-up[1] gave a mixture of products which on oxidation(CrO_3-pyridine)gave canophyllal(3-oxo-D:A-friedo-oleanan-

28-al)(10)[3b] in 48% yield confirming that the keto group was at the 3 and the aldehyde group at the 28 position in the friedelane ring system.

^{1}H-n.m.r., i.r., m.s and high resolution m.s. were in agreement with the proposed structures.



(1) R^1=O, R^2=R^3=CH_2OH
(2) R^1=O, R^2=CH_2OH, R^3=CHO
(3) R^1=O, R^2=CH_2OH, R^3=CH_3
(4) R^1=O, R^2=COOH, R^3=CH_3
(5) R^1=O, R^2=CH_2OAc, R^3=CH_3
(6) R^1= αOH, βH, R^2=R^3=CH_3
(7) R^1= βOH, αH, R^2=R^3=CH_2OH
(8) R^1=H . R^2=CH_2OH, R^3=CH_3
(9) R^1=O, .R^2=CH_2OAc, R^3=CHO
(10) R^1=O, R^2=CH_3, R^3=CHO



SCHEME. i $NaBH_4$, MeOH, 27°, 20 min. ii. N_2H_4, digol, KOH, 150°(3h) and 210°(3h) iii. Ac_2O, C_5H_5N iv. Li-$(CH_2NH_2)_2$, reflux, 30 min. v. CrO_3, C_5H_5N, 27° vi. 8N. CrO_3, H_2SO_4, acetone, 27°, 18 h.

We thank CIBA-GEIGY Ltd. for financial support and Drs. Hp. Fischer and J. P. Pachlatko for spectral data and Prof. S. Balasubramaniam for collection and identification of plant material.

REFERENCES AND FOOTNOTES

1. R. B. Boar, L. Joukhadar, J. F. McGhie, S. C. Misra, A. G. M. Barrett, D. H. R. Barton and P. A. Prokopiou, J. C. S. Chem Comm., 1978, 68.
2. A. A. L. Gunatilake, N. P. D. Nanayakkara and M. U. S. Sultanbawa, Tet. Letters, 1972, 1425.
3. Previous work on Elaeodendron glaucum: a. S. M. Kupchan, I. Uchida, K. Shimada, B. Yu Fei, D. M. Stevens, A. T. Sneden, R. W. Miller and R. F. Bryan, J. C. S. Chem. Comm., 1977, 255; b. A. S. R. Anjaneyulu and M. N. Rao, Phytochemistry, 1980, 19, 1163; c. A. S. R. Anjaneyulu and M. N. Rao, Indian J. Chem., 1980, 19B, 944.
4. M. Laing, M. E. Burke-Laing, R. Bartho and C. M. Weeks, Tet. Letters, 1977, 3839.
5. E. J. Corey and J. J. Ursprung, J. Amer. Chem. Soc., 1956, 5041.
6. J. S. Shannon, C. G. MacDonald and J. L. Courtney, Tet. Letters, 1963, 173.
7. K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, J. C. S., 1946, 39.
8. J. L. Courtney and W. Stern, Tet. Letters, 1965, 1607.

(Received in UK 20 January 1982)