CHEMISTRY LETTERS, pp. 1059-1060, 1977. Published by the Chemical Society of Japan

OXIDATION OF D:B-FRIEDO-OLEAN-5(10)-ENE. A COMMENT ON THE STRUCTURE OF "ALNUS-5(10)-EN-1-ONE" FROM *EUPHORBIA NERIFOLIA*

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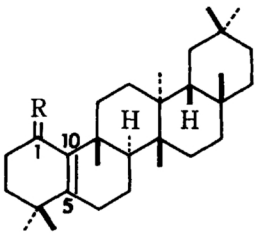
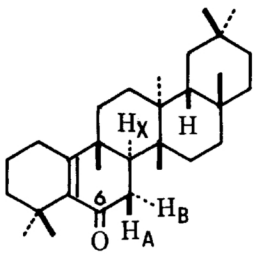
The Ratcliffe oxidation of D:B-friedo-olean-5(10)-ene (2) gave D:B-friedo-olean-5(10)-en-1-one (1), D:B-friedo-olean-5(10)-en-6-one (3), and D:B-friedo-olean-5(10)-ene-1,6-dione (4). The spectral data of the enone (1) are not identical with the corresponding values reported for a triterpene ketone "alnus-5(10)-en-1-one" isolated from *Euphorbia nerifolia*, indicating that the structure of this natural triterpene must be revised.

It has been reported that a triterpene ketone, $C_{30}H_{48}O$, mp 312-314 °C, $[\alpha]_D$ + 50° ($CHCl_3$), isolated from *Euphorbia nerifolia*, can be formulated as alnus-5(10)-en-1-one[1] (1; D:B-friedo-olean-5(10)-en-1-one), based on the spectral data and chemical evidence including its conversion into known alnus-5(10)-ene (2; D:B-friedo-olean-5(10)-ene).[1] However, the UV absorption (λ_{max} 218 nm, log ε 3.87)[1] described for this triterpene seems to be incompatible with the formula (1) having an α,β-unsaturated ketone moiety. The present paper deals with a preparation of D:B-friedo-olean-5(10)-en-1-one (1).

D:B-Friedo-olean-5(10)-ene (2)[2] was treated with chromium trioxide in a mixture of pyridine and dichloromethane[3] at room temperature for 20 h to give D:B-friedo-olean-5(10)-en-1-one (1; yield 8 %), mp 257.5-259 °C, $[\alpha]_D$ - 53° ($CHCl_3$); IR (Nujol) 1660 cm^{-1}; UV (EtOH) λ_{max} 249 nm (ε 19100); PMR ($CDCl_3$) absence of olefinic proton; mass spectrum m/e 424.3756 (M^+; m/e 424.3703 calcd for $C_{30}H_{48}O$),[4] D:B-friedo-olean-5(10)-en-6-one (3; y: 18 %), mp 243-245 °C, $[\alpha]_D$ - 11° ($CHCl_3$); IR (Nujol) 1655 cm^{-1}; UV (EtOH) λ_{max} 250 nm (ε 10800); PMR ($CDCl_3$) absence of olefinic



1 R = O
2 R = H_2



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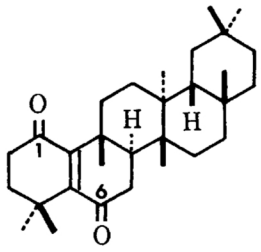

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proton; mass spectrum m/e 424.3788 (M^+; 424.3703 calcd for $C_{30}H_{48}O$),[4] and D:B-friedo-olean-5(10)-ene-1,6-dione (4; y: 9 %), mp 236-237 °C, $[\alpha]_D$ - 8° ($CHCl_3$); IR (Nujol) 1680 cm^{-1}; UV (EtOH) λ_{max} 264 nm (ε 9800); PMR ($CDCl_3$) absence of olefinic proton; mass spectrum m/e 438.3626 (M^+; m/e 438.3496 calcd for $C_{30}H_{46}O_2$).[4,5]

On oxidation with the Ratcliffe reagent,[3] each of the enone (1 and 3) yielded the enedione (4). The Huang-Minlon reduction of both 1 and 3 gave the olefin (2). The presence of a grouping $-CO-CH_AH_B-\dot{C}H_X-$ (J_{AB} = 18, J_{AX} = 12, and J_{BX} = 6 Hz) in the enone (3) was revealed by the PMR measurement using $Eu(fod)_3$-d_{27} as a shift reagent coupled with PMDR experiments.[6] A 5(10)-en-6-one moiety was thus given for this enone (3); this led to a 5(10)-en-1-one structure for the other enone (1).

The spectral data and physical constants of 1 thus prerared were found to be not identical with those reported[1] for "alnus-5(10)-en-1-one". It is therefore suggested that the structure of this natural triterpene requires revision.[7]

REFERENCES

1) A. S. R. Anjeneyulu, L. R. Row, C. Subrahmanyam, and K. S. Murty, Tetrahedron, 29, 3909 (1973).
2) J. M. Beaton, F. S. Spring, R. Stevenson, and J. L. Stewart, Tetrahedron, 2, 246 (1958); S. Chapon, Bull. Soc. Chim. Fr., 1955, 1076 and 1630.
3) R. Ratcliffe and R. Rodehorst, J. Org. Chem., 35, 4000 (1970).
4) A satisfactory result was obtained for this formula by elemental analysis.
5) The starting material (y: 6 %) was recovered.
6) When $Eu(fod)_3$-d_{27} was added to a 7 % (w/v) solution of 3 in $CDCl_3$ in a molar ratio of 3 and the shift reagent (1:1), the signals due to H_A, H_B, and H_X were observed at δ 12.40, δ 11.92, and δ 6.42, respectively.
7) As we have in hand neither the natural triterpene "alnus-5(10)-en-1-one" nor the plant, no further information on the structure of this ketone was obtained. However, the reported IR absorption at 880 cm^{-1} might suggest the presence of $C=CH_2$ in this natural product.

(Received July 7, 1977)