Acetonide Formation from Olean-12-ene-16α,28- and -16β,28-diols

By JAN ST. PYREK

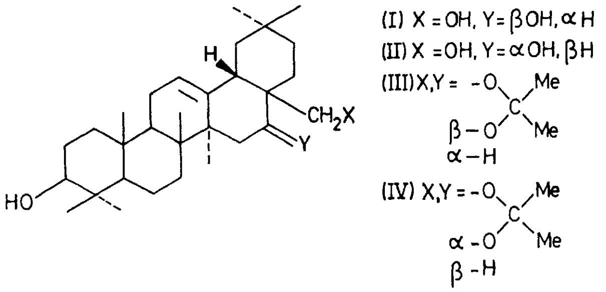
(*Instytut Chemii Organicznej PAN, Warszawa, Kasprzaka* 44, *Polska*)

Summary Olean-12-ene-16α,28- and -16β,28-diols form acetonides under *trans*-acetalization conditions.

RECENTLY Segel and Taube have described the formation of a diacetonide from olean-12-ene-3β,16α,23,28-tetraol,[1] the $LiAlH_4$ reduction product of quillaic acid.[2] Assuming that the 28-CH_2OH and 16-OH groups are in a *trans*-diaxial relation in the 16α,28-diol (*i.e.* unsuitable for acetonide formation), and in view of the failure to prepare longispinogenin (I) acetonide,[3] they concluded that all 16-hydroxyolean-12-enes have configurations opposite to the accepted ones. Evidence for the configuration of the 16-hydroxy-group, very common in oleane triterpenes,[4] is based on its reactivity and ^1H n.m.r. spectra, and appears to be unquestionable, so the only possible explanation of the above acetonide formation is a change of the ring D conformation to a flexible form, suitable for 'acetonidation', similar to that reported for bicyclic compounds.[5] To confirm this, longispinogenin (I) and primulagenin A (II) were tested under conditions similar to those used by Segel and Taube.[1]

Treatment with excess of 2,2-diethoxypropane in acetone (25°; toluene-*p*-sulphonic acid catalysis) transformed (I) and (II) into their respective acetonides (III) (46%, m.p. 190°, M^+ 498) and (IV) (80%, m.p. 223°, M^+ 498). Equilibrium was reached in 1—2 min, and mixed acetals were also formed. If no 2,2-diethoxypropane was added, only traces of the acetonide (IV) were detected after reaction for 24 h. Both acetonides regenerated the parent triols on hydrolysis with AcOH.

The ^1H n.m.r. spectrum[6] of (III) shows: δ 1·38 and 1·44 (each s, acetonide- Me), 3·18 and 3·81 (ABq, J 11·5 Hz,



28-CH$_2$), and 4·12 (dd, $J_{15\beta,16\alpha}$ 12, $J_{15\alpha,16\alpha}$ 6 Hz, 16α-H). The last signal, typical for an axial proton, is of similar shape to that in the spectra of compound (I) or its triacetate.[7] The spectrum of (IV)[6] shows: δ 1·38 and 1·39 (s, acetonide-Me), 3·34 and 3·93 (ABq, J 11·6 Hz, 28-CH$_2$), and 3·67 (dd, $J_{15\alpha,16\beta}$ 4·3, $J_{15\beta,16\beta}$ 13·5 Hz, 16β-H). The coupling constant values indicate that 16β-H and 15β-H are eclipsed, ring D being in the boat conformation. 16-H in primulagenin A triacetate gives a broad singlet, $w_{\frac{1}{2}}$ 7 Hz.

The change in conformation of ring D from the chair (which results in a 1,3-diaxial interaction of 16α-OH with 14α-Me and 21α-H) to the boat form, provides the driving force of the comparatively easy acetonide formation from primulagenin A (II). The possibility of a boat form for ring D has been considered as an explanation of the acetyl group migration between positions 16 and 28 in primulagenin A,[8] and, further, in the case of olean-11,13(18)-dienes, acetonides were obtained from both 16α,28- and 16β,28-diols under standard conditions.[9]

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[4] 'Rodd's Chemistry of Carbon Compounds,' 1969, vol. II **C**, 438.

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[6] 100 MHz ^{1}H n.m.r. spectra in CDCl$_3$, expected analytical and spectral data were obtained.

[7] Longispinogenin was obtained from sunflower flowers along with new triterpene triols, J. St. Pyrek in preparation.

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