Tetrahedron Letters No.3, pp.100-104, 1961. Pergamon Press Ltd.,
Printed in the United States of America.

TRITERPENOID COMPOUNDS. 7β-HYDROXY-A_1-BARRIGENOL[1]

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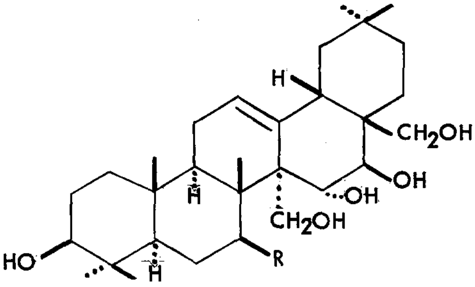
(Received 1 February 1961)

THE hexahydroxy-triterpene compound, $C_{30}H_{50}O_6$, m.p. 308-310°, $[\alpha]_D$ + 37° (dioxan) isolated from *Pittosporum undulatum* Vent.[2] and *P. phillyraeoides* DC.[3] is now identified as 7β-hydroxy-A_1-barrigenol or 3β,7β,15α,16β,27,28-hexahydroxyolean-12-ene (I; R = OH) on the basis of the structure (I; R = H) proposed for A_1-barrigenol[2].



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[1] Part IV: H.R. Arthur, A.R.H. Cole, Miss K.J.L. Thieberg and D.E. White, *Chem. and Ind.* 926 (1956).

[2] A.R.H. Cole, D.T. Downing, J.C. Watkins and D.E. White, *Chem. and Ind.* 254 (1955).

[3] A.L. Beckwith, A.R.H. Cole, J.C. Watkins and D.E. White, *Austral. J. Chem.* **9**, 428 (1956).

We have not been able to obtain an acetate resembling that described by Cornforth and Earl[4] so that we cannot confirm the previous suggestion[2] that our compound is pittosapogenin[4]. However, by comparison of our compound and its acetate with R_1-barrigenol and its acetate[5] (NMR, IR and mixed m.p.) we have shown that our compound is identical with R_1-barrigenol.

7β-Hydroxy-A_1-barrigenol gives a yellow colour with tetranitromethane, resists hydrogenation over Adams catalyst and shows the characteristic absorption at 1654, 836 and 810 cm $^{-1}$ (Nujol) of a tri-substituted double bond. Biogenetic considerations and preparation of a hexa-acetate, m.p. 186-187.5°, $[\alpha]_D$ - 28°, a tetrabenzoate, m.p. 333.5-334°, $[\alpha]_D$ + 24°, a diethylidene, m.p. 236-237°, $[\alpha]_D$ + 47.5°, and a di-isopropylidene derivative, m.p. 218-219°, $[\alpha]_D$ + 39°, suggested that it might be a hydroxy-A_1-barrigenol. The tetrabenzoate was oxidised to a bright yellow, non-enolisable α-diketone, m.p. 307.5-308.5°, $[\alpha]_D$ + 46°, [ϵ_{max} 40 at 443 mμ and 241 at 333 mμ (dioxan)] and the hexa-acetate to a conjugated ketone, m.p. 233.5-234°, $[\alpha]_D$ - 13.5° [ϵ_{max} 12,960 at 242 mμ; 1752 (acetates) and 1672 cm $^{-1}$], products strongly reminiscent of A_1-barrigenyl tribenzoate diketone and 11-oxo-A_1-barrigenyl penta-acetate[2].

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[4] J.W. Cornforth and J.C. Earl, J. Proc. Roy. Soc. N.S. Wales **72**, 249 (1938).

[5] Yau-Tang Lin, Tung-Bin Lo and Su-Chan Su, J. Chinese Chem. Soc. (Taiwan) Ser. II, **4**, 77 (1957).

The diethylidene derivative, characterised as the *x*, *y*-diacetate, m.p. 313-313.5°, $[\alpha]_D$ + 35°, formed an *x*-oxo-*y*-acetate, m.p. 319-321°, $[\alpha]_D$ + 56°, by selective oxidation and acetylation. The oxo-acetate gave a positive Zimmermann reaction and afforded the *x*,*y*-diacetate on reduction with lithium aluminium hydride and reacetylation. These reactions indicate that the *x*-hydroxyl is 3β.

More vigorous oxidation of the 3β,*y*-diol formed a 3,*y*-dioxo compound, m.p. 280-282.5°, $[\alpha]_D$ + 9°. This is stable to potassium permanganate, and hence cannot be an aldehyde.

Partial hydrolysis of the diethylidene-3β,*y*-diacetate gave the *y*-hydroxy-3β-acetate, m.p. 304.5-306°, $[\alpha]_D$ + 42°, and a trace of the isomeric 3β-hydroxy-*y*-acetate, m.p. 282.5-284°, $[\alpha]_D$ + 41° (mixed m.p. 261-286°). The 3-monoacetate was oxidised to the *y*-oxo-3β-acetate, m.p. 295-299°, $[\alpha]_D$ - 27°, which failed to form a semicarbazone and did not give a Zimmermann test. Lithium aluminium hydride reduction of the *y*-oxo-3β-acetate or the 3,*y*-diketone yielded the 3β,epi-*y*-diol, m.p. 298-300°, $[\alpha]_D$ + 37°. Mild acetylation afforded the epi-*y*-hydroxy-3β-acetate, m.p. 322.5-323°, $[\alpha]_D$ + 46°, dehydrated by phosphoryl chloride in pyridine to the anhydro-3β-acetate, m.p. 248-248.5°, $[\alpha]_D$ + 104.5°, which has the *cis*-disubstituted double bond of a cyclo-olefin (absorption at 1682 (in CCl_4) and 752 and 738 cm^{-1} (in CS_2)). Hydrogenation over Adams catalyst in acetic acid formed a diethylidene-3β-acetate, m.p. 284.5-285°, shown by mixed m.p. and infrared comparison to be identical with diethylidene-A_1-barrigenyl acetate (15α, 27:16β, 28-di-*O*-ethylidene-olean-12-en-3β-yl acetate), m.p. 285-285.5°, $[\alpha]_D$ + 53°.

Hydrolysis of the anhydro-acetate followed by oxidation of the intermediate alcohol, m.p. 217-219°, $[\alpha]_D$ + 103°, yielded the anhydro-3-ketone, m.p. 275-278°, which contained an isolated keto group (band at 1705 cm $^{-1}$) hence proving that the y-function cannot be in ring A.

Substituents at $C_{(y)}$ absorb at 3613 (hydroxyl), 1747 (acetate), 1737 (ketone) and 3433 cm $^{-1}$ (epi-hydroxyl). We consider these displaced values are due to the close proximity of these groups to one pair of ethylidene oxygen atoms. This could occur if $C_{(y)}$ were $C_{(7)}$ or $C_{(22)}$ but the oxidation of the y-hydroxyl to a hindered ketone which, with lithium aluminium hydride, affords the readily dehydrated epi-y-hydroxyl is at variance with the known behaviour at $C_{(22)}$[6]. Hence the equatorial 7β-position is indicated.

This was confirmed by autoxidation of the diethylidene y-keto-3β-acetate in the presence of potassium t-butoxide[7]. This

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[6] C. Djerassi, E. Farkas, A.J. Lemin, J.C. Collins and F. Walls, J. Amer. Chem. Soc. 76, 2969 (1954); A. Sandoval, A. Manjarrez, P.R. Leeming, G.H. Thomas and C. Djerassi, J. Amer. Chem. Soc. 79, 4468 (1957); G. Cainelli, A. Melera, D. Arigoni and O. Jeger, Helv. Chim. Acta 40, 2390 (1957).

[7] D. Arigoni, D.H.R. Barton, E.J. Corey, O. Jeger et al., Experientia 16, 41 (1960).

afforded a diosphenol identified by its ultraviolet absorption (ϵ_{max} 3000 at 279 mμ changing to 1500 at 328 mμ in alkaline solution) and thus demonstrated the presence of the group $>CH-CH_2-CO-\overset{|}{\underset{|}{C}}-$. This confirms the suggestion that our hexahydroxy compound is 7β-hydroxy-A_1-barrigenol.

Satisfactory analyses have been obtained for all compounds mentioned, except the diosphenol which was not isolated. Infrared measurements are on carbon tetrachloride solutions and ultraviolet on ethanol solutions unless otherwise indicated.

We are greatly indebted to Dr. A.R.H. Cole and his collaborators for the infrared measurements and their interpretation, to Professor Y-T. Lin for the samples of R_1-barrigenol and its acetate, to Professor M. Shamma and Mr. Ralph Mumma for NMR spectra and to Professor D.H.R. Barton and Mr. John Templeton who carried out the autoxidation.