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MEXICANOL.

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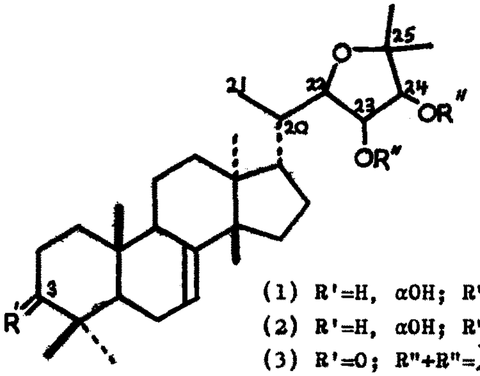
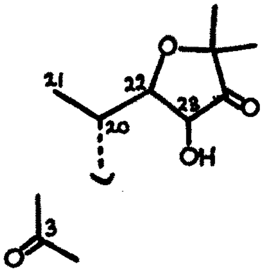
We have isolated from the heartwoods of Cedrela glaziovii [Forest Research Institute, Kepong, Selangor,] and C. mexicana [Forest Herbarium, Forestry Division, Khumasi, Ghana] a new triterpenoid, mexicanol (1), $C_{30}H_{50}O_4$, m.p. 235-37°, $[\alpha]_D - 50°$.



(1) R'=H, αOH; R"=H.
(2) R'=H, αOH; R"+R"=$>C(CH_3)_2$
(3) R'=O; R"+R"=$>C(CH_3)_2$
(4) R'=O; R"=H.
(7) R'=O; R"=Ac



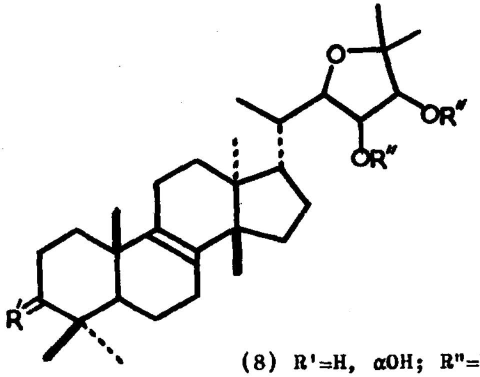
(5)
(6) $\Delta^{22(23)}$

The n.m.r. spectra of mexicanol and its derivatives indicate the presence of one secondary and seven tertiary methyl groups, suggesting a euphane or lanostane skeleton.

Three secondary hydroxyls attached at C-3, C-23 and C-24 can be chemically differentiated in two ways. Either (a) reaction of mexicanol with acetone and anhydrous copper sulphate leads to the acetonide (2), $C_{33}H_{54}O_4$, m.p. 210–12°, convertible by Jones oxidation to the 3-ketone (3), $C_{33}H_{52}O_4$, m.p. 208–10° or (b) brief Jones oxidation of mexicanol at 0° affords the ketone (4), $C_{30}H_{48}O_4$, m.p. 230–32°, the dione (5), $C_{30}H_{46}O_4$, m.p. 200–02°, and the diosphenol (6) [see below]. Acetylation of the ketone (4) leads to the diacetate (7), $C_{34}H_{52}O_6$, m.p. 219–21°, whose n.m.r. spectrum defines the functional sequence in the side chain of mexicanol: Thus the signals from H-22 (τ 6·09; d, J = 6 Hz), H-23 (τ 5·01; t, J = 6 Hz) and H-24 (τ 5·21; d, J = 6 Hz), each collapse upon double irradiation in accordance with expectation based on simple first-order treatment. Furthermore, double irradiation at H-20 (τ 8·43) simultaneously collapses the C-21 methyl doublet (τ 9·09) to a singlet and sharpens the slightly diffuse doublet (τ 6·09) arising from H-22. This situation is seen even more clearly in the n.m.r. spectrum of the previously mentioned dione (5). H-22 (τ 6·20) and H-23 (τ 5·87) now form essentially an AB quartet (J = 10 Hz) whose higher field doublet is sharpened when H-20 (τ 8·04) is irradiated; the C-21 methyl (τ 9·03, d), simultaneously collapses to a singlet.

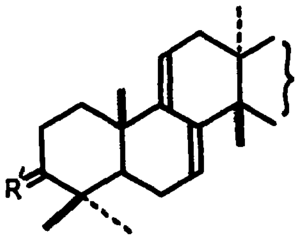
The diosphenol (6), $C_{30}H_{44}O_4$, m.p. 232–34°, also obtained from Jones oxidation of mexicanol, had $\lambda_{max.}$ 292 nm (ε, 8680 in EtOH) and 342 nm (ε, 8830 in EtOH/NaOH).

The isolated, trisubstituted, double bond [diffuse 1H singlet in (2) ($W^{\frac{1}{2}}$ 10 Hz) at τ 4·80] is placed at position 7(8) on the basis of its facile isomerisation to the $\Delta^{8(9)}$-position and its ready transformation into the 7, 9(11)-diene.



(8) R'=H, αOH; R"=H.

(10) R'=O; R"=R"=$>C(CH_3)_2$



(9) R'=H, αOH; R"=H.

Thus mexicanol is converted in almost quantitative yield (a) into iso-mexicanol (8), $C_{30}H_{50}O_4$, m.p. 211-14°, $[\alpha]_D$ -31°, when shaken in acetic acid solution with hydrogen and Adams' catalyst[1] and (b) into the diene (9), $C_{30}H_{48}O_4$, H_2O, m.p. 255-60°, $[\alpha]_D$ -174°, $\lambda_{max.}$ 232; 239; 248 nm (ε, 14,700; 16,150; 10,600), when exposed to mercuric acetate in acetic acid solution at 20°.

Comparison of the positions of the triple maxima in the U.V. with published values[2] in the lanostane and euphane series, quite clearly places mexicanol in the latter and this is supported by the ease of double bond isomerisation (*v. supra*).[3] Furthermore, the large negative $\Delta[\phi]_D$ value (-674°) for the change iso-mexicanol (8) to the $\Delta^{7,9(11)}$-diene (9) accords with previous observations[4] which distinguish between the lanostane and euphane series.

The O.R.D. curves (to be published in the full paper) of the 3-oxo-acetonides (3), $C_{33}H_{52}O_4$, m.p. 208-10°, and (10), $C_{33}H_{52}O_4$, m.p. 169-70°, $[\alpha]_D$ +7°, help to place the isolated secondary hydroxyl group in mexicanol at C-3. In the n.m.r. spectrum of (2) H-3 appears at τ 6·57 as a broad singlet ($W^{\frac{1}{2}}$ 8 Hz) indicating the axial (α) nature of the hydroxyl group.

The Cedrela glaziovii extract also yielded 3-dehydromexicanol (4), 6-hydroxycarapin[5] and a second triol, m.p. 251-53°, $[\alpha]_D$ -54° (EtOH), epimeric with mexicanol at C-23 or, more probably, C-24 (comparison of n.m.r. signals for H-22, H-23, H-24 with corresponding signals in mexicanol). This triol does not form an acetonide but with the Jones reagent affords the diosphenol (6) also obtained from mexicanol. In addition the previously reported compounds mexicanolide,[6] 7-deacetoxy-7-oxo-gedunin,[7] gedunin,[8] methyl angolensate[9] and carapin[10] were isolated.

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