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THE DITERPENES OF DACRYDIUM COLENSOI. PART IV (1)

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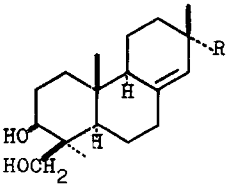
In our earlier investigations of the heartwood extractives of Dacrydium colensoi we reported (2) the presence of a diterpene diol, Compound B, $C_{20}H_{32}O_2$, m.p. 170-172°, which we now formulate as (I).

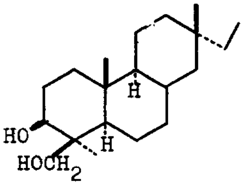
Compound B was readily hydrogenated to a dihydro derivative (II), $C_{20}H_{34}O_2$, m.p. 176-178°, which under more forcing conditions gave a saturated tetrahydro derivative (III), m.p. 145-148°, thereby establishing the tricyclic nature of Compound B. This was confirmed by the isolation of pimanthrene as the major product of the selenium dehydrogenation of Compound B.

The n.m.r. spectrum of Compound B established that one of the double bonds was vinylic (ABX system: H_A 5.13, H_B 5.12, H_X 4.20τ; J_{AX} 9.5, J_{BX} 17.6, J_{AB} 1.8 c/s), and the other trisubstituted (1H, ½ band width 3.8 c/s; 4.75τ). As the olefinic proton was unsplit it could only be placed at C-14 in association with a C-8 - C-14 double bond in a normal pimarane type skeleton. The spectrum showed only

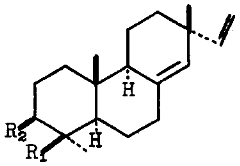


(I) R = $CH{:}CH_2$

(II) R = CH_2CH_3



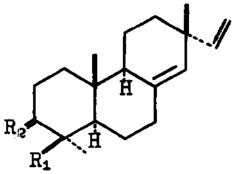
(III)



(IV) $R_1 = CH_3$; $R_2 = OH$

(V) $R_1 = CH_2OH$; $R_2 = H$

(XI) $R_1 = CH_2OAc$; $R_2 = OH$

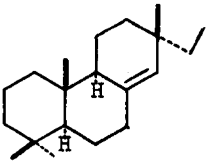


(VI) $R_1 = CH_3$; $R_2 = O$

(VII) $R_1 = CHO$; $R_2 = H_2$

(IX) $R_1 = CHO$; $R_2 = O$

(X) $R_1 = H$; $R_2 = O$



(VIII)

three of the four quaternary methyl singlets of the pimaradiene type skeleton, together with an AB system (centered at 6.19τ, J_{AB} 10.8 c/s) that can be assigned to a hydroxymethyl group attached to an asymmetric centre. A multiplet at 6.53τ established that the other hydroxyl group was secondary.

Tosylation of Compound B gave a mixture of the tosylates which on reduction with lithium aluminium hydride/tetrahydrofuran gave a mixture of the mono-ols (IV and V) which could not be separated. Following oxidation of the mixture of mono-ols with Jones' reagent, a ketone (VI), m.p. 53-56°, and an aldehyde (VII) were isolated.

Wolff-Kishner reduction of the aldehyde (VII) gave a hydrocarbon, $C_{20}H_{34}$, identical (t.l.c. and i.r.) with a sample of dihydrosandaracopimaradiene (VIII), and so established the skeleton of Compound B.

Lithium aluminium hydride reduction of the ketone (VI) gave a single product (IV), $C_{20}H_{32}O$, m.p. 125-127°, which was identical (i.r. and mixed m.p.) with a sample of sandaracopimaradien-3β-ol, thus fixing the position of the secondary hydroxyl group.

The hydroxymethyl group which has replaced a methyl group can be at C-4, C-10, or C-13. A comparison of the n.m.r. spectra of Compound B and dihydroCompound B showed that one methyl signal in the latter had moved upfield, which is characteristic of a C-13 methyl after reduction of a 15,16 vinyl double bond. Alkaline treatment of either the keto-hydroxy compound (not isolated), or the keto-aldehyde (IX).

$C_{20}H_{28}O_2$, m.p. 93-95°, gave in each case the same 3-keto nor compound (X), $C_{19}H_{28}O$, m.p. 46-48°, as the result of a reverse aldol cleavage. This established the relationship of the 3β-hydroxyl group and the hydroxymethyl group which must therefore be placed at C-4.

The chemical shifts of the hydroxymethyl (I), acetoxymethyl (XI), and formyl (IX) groups in Compound B and its derivatives (6.19, 5.65, 0.25τ respectively) all lie in the range reported for axial substituents (3,4). As sandaracopimaradien-3β,18-diol had already been isolated (5) there could be no doubt that the configuration of the hydroxymethyl group was axial. Therefore Compound B is sandaracopimaradien-3β,19-diol (I).

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