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THE DITERPENOIDS OF ERYTHROXYLON MONOGYNUM - IV
ALLODEVADAROOL, DEVADAROOL AND HYDROXYDEVADAROOL*

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In continuation of our previous work[1,2,3] we wish to report the complete structure elucidation of allodevadarool, devadarool and hydroxydevadarool.

Allodevadarool

Allodevadarool (compound C_2[1]), $C_{20}H_{34}O_2$ (m.p. 147-148°; $[\alpha]_D^{28}$ +79.12, $CHCl_3$) has the following structural features: three methyl groups, all quaternary (NMR spectrum+: 3H sharp singlets at 46, 55 and 64 cps, cf. devadarool[2]); $\begin{matrix} C - C \\ C - C \end{matrix} >= CH_2$ (IR spectrum: 895, 1640, 3100 cm^{-1}; NMR spectrum: 2H singlet at 271 cps); $-CHOH.CH_2OH$ ($NaIO_4$ cleavage; IR spectrum: 3400, 1087, 1055, 1035 and 1015 cm^{-1}, cf. devadarool[2]; NMR spectrum: 1H and 2H signals centred at 152 and 210 cps respectively, cf. devadarool[2]). From its end absorption (ϵ_{210} 330, ϵ_{215} 70)

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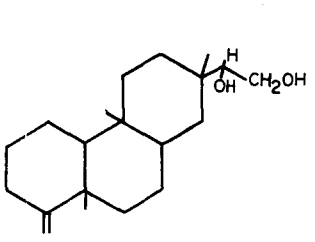
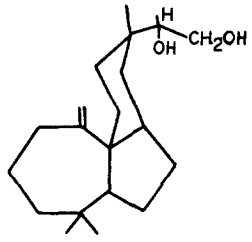
+All NMR spectra were measured in 10-20% solutions in CCl_4 or $CDCl_3$ on a Varian A-60 spectrometer; the signals are recorded in cps from tetramethylsilane as zero.

and the above NMR data, it is clear that allodevadarool possesses only one ethylenic linkage and consequently should be tricyclic. Dehydrogenation with selenium yielded 1,7-dimethylphenanthrene. The above structural features cannot be incorporated in a 'normal' diterpenoid tricyclic framework and consequently allodevadarool must possess a rearranged diterpene skeleton. Two structures (I, II) appeared attractive from biogenetic considerations:



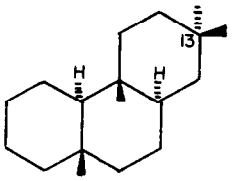
I



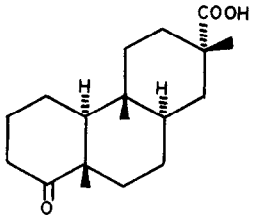
II

$NaIO_4$ oxidation of allodevadarool yielded an aldehyde (NMR signal for the aldehyde proton: 1H singlet at 560 cps) which on Wolff-Kishner reduction yielded a mixture of saturated[4] (III; ε_{215} 421. NMR spectrum: No vinyl protons, quaternary methyl signals at 42, 47, 53 and 53 cps) and unsaturated hydrocarbon (IV; IR spectrum: $>C=CH_2$ 1635, 898 cm^{-1}. NMR spectrum: $>C=CH_2$, 2H singlet at 264 cps; quaternary methyl signals at 44, 54, 54 and 63 cps). Since, the NMR signal of a quaternary methyl in IV had shifted upfield in the saturated compound III[5], structure I was preferred for allodevadarool. This was confirmed as follows: ozonolysis of allodevadarool followed by $NaIO_4$

cleavage and Wolff-Kishner reduction yielded a bis-nor hydrocarbon, $C_{18}H_{32}$, ($[\alpha]_D$ +26°) which had its IR spectrum superimposable on that of compound V ($[\alpha]_D$ -29°) described by Kitahara and his co-workers[6,7]; since the rotations are of opposite sign, the bis-nor-hydrocarbon from allodevadarool must be represented by the antipode of V, for which the absolute stereochemistry has been established[7]. Next, the stereochemistry of the α-glycol side-



V

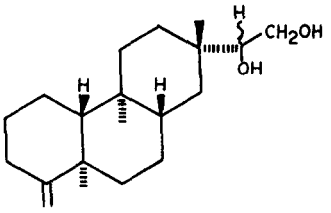


VI

chain at C_{13} was determined. $NaIO_4$ cleavage followed by oxidative ozonolysis yielded a bis-nor keto acid ($C_{18}H_{28}O_3$, m.p. 208-210°. Methyl ester, m.p. 86-87°, $[\alpha]_D$ +53°) which was found to be different (IR spectrum) from the keto-acid VI (m.p. 210-212°; Methyl ester, m.p. 98-100°, $[\alpha]_D$ -28.4°), a degradation product of dolabradiene[6,7].

The above considerations lead to the establishment of the absolute stereostructure of allodevadarool

as VII*.



VII

Devadarool

During the course of above work it was found that the nor-hydrocarbon III was, surprisingly, identical (GLC, IR and NMR) with the major hydrogenation (PtO_2-AcOH) product of the nor-hydrocarbon (m.p. 54-55°) derived from devadarool[2]. Hence the structure of the nor-hydrocarbon from devadarool must be represented by VIII+. Furthermore,

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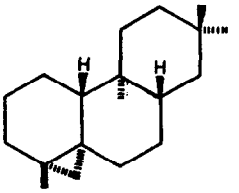
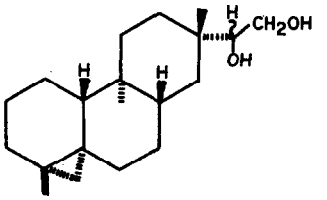
*Very recently Connolly et al.[8] have described the isolation of three diterpene glycols - erythroxydiols X, Y and Z - from the same source. The first two compounds correspond to our compounds C_1 (devadarool) and C_2 (allodevadarool)[1] respectively. These authors have arrived at the same structure for their erythroxydiol Y (allodevadarool), but following completely different procedures.

+This structure is still in accord with the behaviour of this compound on acid treatment reported earlier. However, this conflicts with the IR spectral data on the estimation of gem-dimethyl groups; since the structure of allodevadarool has been correlated in a straightforward manner with dolabradiene of well-established structure, it follows that the quantitative IR spectral measurements for the gem-dimethyl groups, even in a hydrocarbon, must be taken with reserve.

acetylation of dihydroallodevadarool yielded a product



VIII



IX

(m.p. 114-115°) which was found to be identical (mixed m.p., IR spectrum) with one of the products of the catalytic hydrogenation of devadarool acetate. These correlations establish the absolute stereostructure of devadarool as IX.

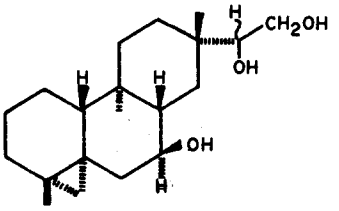
Connolly et al.[8,9] in a very recent publication studied the structure of erythroxydiol X (identical with our devadarool) and preferred the structure IX to our earlier structure[2] on the basis of identity of the mass spectra of erythroxydiol X and Y. The present work provides decisive chemical evidence in favour of IX.

Hydroxydevadarool*

Hydroxydevadarool (compound D[1], m.p. 181.5 - 182°, triacetate, m.p. 123-124°) is shown to possess the absolute stereostructure X. The relevant evidence is as follows. Chromic acid oxidation of compound D gave a nor-ketoacid

*With R. Misra and R.C.Pandey.

$C_{19}H_{28}O_3$ (XI, m.p. 168-170°. Methyl ester, XII, m.p.68-70°), which on Wolff-Kishner reduction furnished an acid $C_{19}H_{30}O_2$,



X

m.p. 196-198°, identified (IR, mixed m.p., TLC) as the nor-acid from devadarool[2]. Thus, compound D is devadarool with another secondary hydroxyl function. The position of this hydroxyl group was evident from the NMR spectrum of the keto ester (XII), which displayed a doublet (1H) centred at 185 cps (J = 12 cps) assignable to a C<u>H</u> proton ∝ to the carbonyl; this limits the position of the carbonyl function to C_7 and C_{14}. However, since the keto acid XI does not decarboxylate at ~200°, position 14, which is β to the carboxyl is ruled out. Thus, the new hydroxyl function must be located at C_7. Moreover since, in the triacetate none of the quaternary methyl signals (54, 61, 68 cps) has suffered a diamagnetic shift[10] relative to the signals for devadarool diacetate (45, 61, 61 cps), the new hydroxyl group at C_7 should be equatorial.

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9 Connolly et al.[8] attribute an absolute configuration to our earlier structure, which was never implied in our publication; as a matter of fact the word absolute does not occur in the paper.

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