Tetrahedron Letters No.19, pp. 1181-1185, 1964. Pergamon Press Ltd.
Printed in Great Britain.

THE DITERPENOIDS OF <u>ERYTHROXYLON MONOGYNUM</u> -II. DEVADAROOL, A NEW TYPE IN TETRACYCLIC DITERPENOIDS

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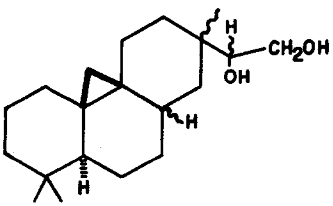
(Received 24 March 1964)

DEVADAROOL (1), $C_{20}H_{34}O_2$, m.p. 124-125°, $[\alpha]_D^{28}$ +11.9° ($CHCl_3$; C, 1.31%) is shown to possess the structure I, and thus, represents a new type in diterpenoids*.



I

Infrared spectrum (ν^{OH} 3450, 1025, 1055, 1080 cm^{-1} transparent between 1500 - 2500 cm^{-1}) and active hydrogen measurements fixed the function of the oxygen atoms in

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*However, several triterpenes having a cyclopropane ring cis-fused to C_9 - C_{10} position are known, e.g. see McCrindle and Djerassi (2).

devadarool as two hydroxyls. The PMR spectrum* was devoid of any absorption in the olefinic hydrogen region; this together with the low UV end absorption (ϵ_{215} 179, ϵ_{220} 52, ϵ_{225} 15) serves to show the absence of any ethylenic linkage in devadarool, which being $C_{20}H_{34}O_2$** must be tetracyclic.

The PMR spectrum, further, showed the presence of three methyl groups (46, 57, 63 cps) which should be quaternary; signals centred at 161 (1H) and 214 (2H) cps and assignable to protons attached to a carbon carrying the hydroxyl, make it possible to characterise the two hydroxyls in devadarool as secondary and primary. An important feature of the PMR spectrum was the presence of a pair of doublets (each equal to one H) centred at 6 and 32 cps (J = 4 cps) and ascribable to two non-equivalent hydrogens of a methylene group in a cyclopropane ring; this resonance has been suggested (2) as diagnostic for a cyclopropane ring of the type encountered in cycloartenol. In conformity with the presence of such a cyclopropane ring, devadarool showed a peak at 1.643 μ (ϵ = 0.432) in

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*The spectra were taken on 5-15% solutions in CCl_4 or $CDCl_3$ on a Varian A-60 spectrometer; the signals are recorded in cps from tetramethylsilane as zero.

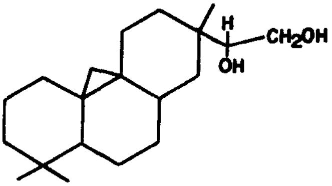
**The molecular formula was confirmed by the mass spectrum taken by the courtesy of Dr.C.Enzell. The fragmentation pattern will be discussed in the full publication.

the near IR (3); as expected (4), it also gave a distinct pale yellow colour with tetranitromethane.

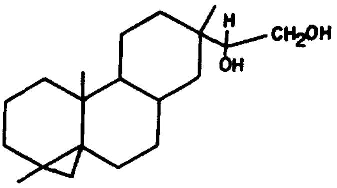
On selenium dehydrogenation, devadarool furnished 1,7-dimethylphenanthrene which serves to characterise the basic carbon-framework in the molecule.

On oxidation with chromic acid devadarool yielded a nor-acid, $C_{19}H_{30}O_2$, m.p. 196-198°, $[\alpha]_D^{29}$ +21.3° ($CHCl_3$); the same product was obtained when devadarool was first oxidised with $NaIO_4$ and the resulting crude product (aldehyde) further oxidised with silver oxide. Thus, the two hydroxyls in devadarool must occur as an α-glycol side-chain. The PMR spectrum of the nor-acid and its methyl ester showed the methyl signals at 49, 62, 75 cps, and 48, 62, 72 cps respectively; the deshielding of one of the methyls would indicate (1) that the glycol side-chain must be attached to a carbon carrying a methyl group.

The above findings, when considered along with the isoprene rule (5), lead to the formulation of devadarool as (II); the only alternative (III), possible on the basis of the above data, being considered less likely on biogenetic grounds.

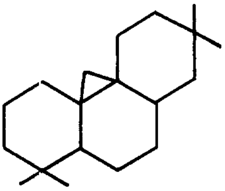


II

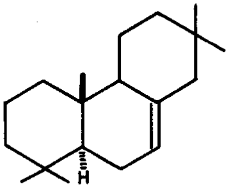


III

Decisive evidence in favour of II was obtained as follows. The crude aldehyde, obtainable by periodate cleavage of devadarool, on Wolff-Kishner reduction yielded a hydrocarbon, $C_{19}H_{32}$, m.p. 54 - 55°, $[\alpha]_D$ + 18.22°($CHCl_3$) [PMR : methyl signals at 43, 53 (6H), and 60 cps, cyclopropane methylene protons (2H) as a pair of doublets centred at 5 and 30 cps (J = 4 cps); pale yellow colour with tetranitromethane], which showed a well-resolved doublet (1362, 1382 cm^{-1}), having an intensity ratio of 1:1.1 in the IR; since the band at lower frequency is considered highly diagnostic of the gem-dimethyl group and its intensity has been used (6) to calculate the number of such systems, the nor-hydrocarbon must contain two gem-dimethyl groups, as depicted in IV. This rules out the alternative III for devadarool.



IV



V

Further support for II, which also helps in establishing the nature of A/B ring-junction, was obtained by the acid-catalysed equilibration of IV and V*. Both hydrocarbons (IV and V) after being treated with perchloric acid

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*We are grateful to Dr.C.Enzell for kindly supplying this material.

in acetic acid-ethyl acetate at ~ 80° for 2 hr, gave materials showing exactly identical thin-layer-chromatograms (six spots; $AgNO_3$-Silica gel) (7), which we consider as a proof for the generation of the same carbonium-ions.

The results presented so far, suffice to define the gross structure and partial stereo-chemistry of devadarool as depicted in I.

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