Tetrahedron Letters No.49, pp. 3761-3765, 1964. Pergamon Press Ltd.
Printed in Great Britain.

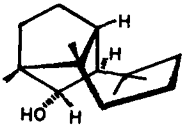
ALLOHIMACHALOL, A NEW TYPE IN SESQUITERPENOIDS+

S.C. Bisarya and Sukh Dev

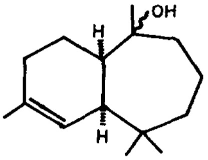
National Chemical Laboratory, Poona (India)

(Received 23 October 1964)

In continuation of our previous work[1], we have examined the alcohol part (~ 15%) of the essential oil from Himalayan deodar (Cedrus deodara, Loud.). This has been found to contain (+)-longiborneol (I, 29%) and two new sesquiterpene alcohols, now named, himachalol[6] (m.p. 67-8°, $[\alpha]_D$ +72.9° *, 41%) and allohimachalol (m.p. 85-86°, $[\alpha]_D$ +87.4°, 30%). Himachalol has been shown to possess the absolute stereostructure II, but further details of this work will not be discussed in this paper as a fuller communication is under preparation. In this paper we would like to report on the structure of allohimachalol, which is



I



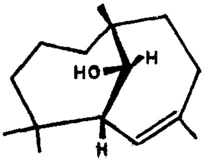
II

---

*All rotations were measured in $CHCl_3$.

+Communication No.734, National Chem. Laboratory, Poona.

now shown to possess the unique structure III, which also depicts its absolute stereochemistry.



III

Allohimachalol is an unsaturated sesquiterpene alcohol ($C_{15}H_{26}O$. TNM* test +ve. IR spectrum: C=C 1660, 853 cm^{-1}; OH 3400, 1020 cm^{-1}). On quantitative hydrogenation it yielded a dihydroderivative, $C_{15}H_{28}O$ (m.p. 102-103°, $[\alpha]_D$ +14.3°) which was fully saturated (TNM test). Thus, allohimachalol is mono-olefinic and being $C_{15}H_{26}O$, should be bicyclic.

On pyridine-chromic acid[2] oxidation, allohimachalol yielded an unsaturated ketone, $C_{15}H_{24}O$ (m.p. 68-68.5°, $[\alpha]_D$ -108.6°), in which the olefinic linkage and the carbonyl group are not conjugated (+ve TNM test. UV spectrum: no $\pi - \pi^*$ absorption, λ_{max} 290 mμ, ϵ 27. IR spectrum: C=O 1699 cm^{-1}; C=C 1660, 853 cm^{-1}). This on $NaBH_4$ reduction gave allohimachalol (~45%) and its epimer (~55%; b.p. 155-160°/3.5 mm, $[\alpha]_D$ +37.8°. IR spectrum: C=C 1665, 840, 860 cm^{-1}; OH 3450, 1025, 1070 cm^{-1}). Chromic acid oxidation[3] of dihydroallohimachalol furnished a saturated

---

* TNM = tetranitromethane.

ketone, $C_{15}H_{26}O$ (IV; b.p. 148-152°/2.5 mm, $[\alpha]_D$ -62.0°) which displayed its $\nu^{C=O}$ at 1712 cm^{-1} and did not exhibit any IR absorption in the 1400-1435 cm^{-1} region[4], where the scissoring frequency of a CH_2 flanking a carbonyl occurs.

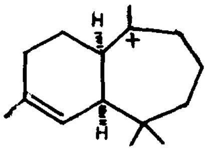
The NMR* spectrum of allohimachalol clearly showed the presence of three quaternary methyls (three 3H sharp signals at 45, 49.5 and 60 cps), one methyl on an olefinic bond (3H, somewhat broadened singlet at 106 cps), one proton attached to C linked to O (1H, essentially a quartet centred at 185 cps) and an olefinic proton (1H, broad doublet centred at 313 cps, J = 5 cps); the last two signals together with a broad doublet centred at 127 cps (1H, J = 10 cps, assignable to an allylic CH) constitute an AMX pattern with J_{AM} = 10 cps, J_{MX} = 5 cps, J_{AX} = 0.5 cps.

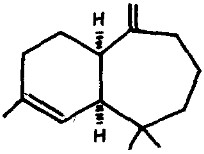
The above data in conjunction with biogenetic considerations, indicated that allohimachalol is, in all probability, a new type in sesquiterpenoids. Keeping in view the chemistry of other constituents of this oil, it was assumed, as a working hypothesis, that allohimachalol might have originated from the species V, the biogenetic progenitor of himachalenes, longiborneol and related compounds. This was confirmed in a rather simple and straightforward manner. Allohimachalol tosylate (m.p. 56-57°) on

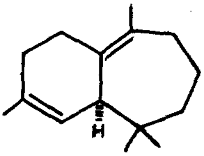
---

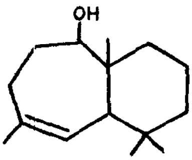
*All NMR spectra were taken on 10-20% solutions in CCl_4 on a Varian A-60 spectrometer; the signals are recorded in cps from tetramethylsilane as zero.

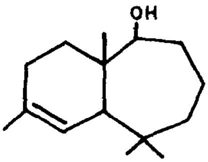
solvolysis in aq. dioxane in the presence of Li_2CO_3

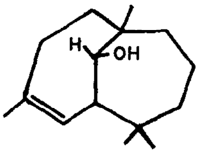

V


VI


VII


VIII


IX


X

furnished approximately 3% α-himachalene (VI), 15% β-himachalene (VII), 24% himachalol (II) and 34% allohimachalol. This reaction limits the possible structures for allohimachalol to VIII, IX and X. Since the ketone IV, derived from dihydroallohimachalol, did not display any absorption for a CH_2 α to the carbonyl, structure X is preferred; this is also in accord with the AMX- type coupling observed in the NMR spectra of allohimachalol and its epimer. Decisive chemical evidence in favour of X was obtained by the attempted bromination of the dihydroketone IV, when no bromination occurred under conditions suitable for exhaustive bromination[5]. Furthermore, the solvolysis experiment permits the unequivocal assignment of the configuration of the hydroxyl group in X, which must be antiparallel to the migrating bond. A fuller discussion of this reaction which also has a bearing on the configuration of hydroxyl function in himachalol is reserved for the detailed communication.

Since the absolute configurations of the himachalenes and the himachalol have been established[6], allohimachalol must have the absolute stereostructure III.

REFERENCES

1 T.C.Joseph and Sukh Dev, Tetrahedron Letters 216 (1961).

2 R.H.Cornforth, J.W.Cornforth and G.Popjak, Tetrahedron **18**, 1351 (1962).

3 R.G.Curtis, I. Heilbron, E.R.H.Jones and G.F.Woods, J. Chem. Soc. 457 (1953).

4 L.J.Bellamy, The Infrared Spectra of Complex Molecules pp.22-25. Methuen and Co., London (1958).

5 C.S. Barnes, D.H.R. Barton, A.R.H. Cole, J.S.Fawcett and B.R.Thomas, J. Chem. Soc. 571 (1953).

6 Sukh Dev, T.C. Joseph, R.C.Pandey and S.C.Bisarya, I.U.P.A.C. Symposium on Natural Products (Prague), 51 (1962). Fuller communications are under preparation.