

(+)-2,5-DIEPI- β -CEDRENE, A NEW SESQUITERPENE FROM *SCIADOPITYS VERTICILLATA* SIEB. ET ZUCC.

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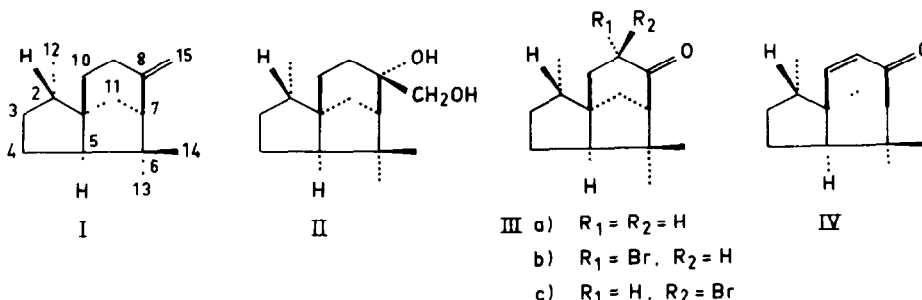
The wood extractives of *Sciadopitys verticillata* Sieb. et Zucc. (Cupressaceae) have previously been studied in some detail.¹⁻⁴ The low boiling neutral constituents have now been further investigated and we wish to report the isolation and structure determination of a new sesquiterpene hydrocarbon, (+)-2,5-diepi- β -cedrene (I).

The low-boiling neutral part of a light petroleum soluble extract of the wood was fractionally distilled at low pressure. The fraction (about 0.2 % of the dry wood), b.p. 96-97° (4 mm Hg) was found to contain a mixture of (-)- α -cedrene (traces), (+)- β -cedrene and a new sesquiterpene (GLC, 2 % Apiezon L, 0.05 % Igepal and 0.05 % stearic acid on 80/100 Chromosorb G at 175°, rel. retention times 1.00, 1.05 and 0.96, respectively; TLC, 10 % AgNO₃ on Silica gel, 2 % ether in light petroleum, R_F 0.75, 0.35 and 0.45, respectively).

The three compounds were separated by argentation column chromatography and the (-)- α - and (+)- β -cedrenes identified by comparison with authentic samples. The new sesquiterpene C₁₅H₂₄ exhibits the following properties: $[\alpha]_D^{25} + 15.4^\circ$ (0.72 in CHCl₃); IR, characteristic bands at 1650 and 875 cm⁻¹ (exocyclic = CH₂); NMR*, 5.54 m (2H, =CH₂), 8.91 s and 9.14 s (each 3H, geminal dimethyl group), 9.17 d (3H, J 6.5 cps, CH - CH₃).

* NMR spectra are recorded from CDCl₃ solutions (ca 5 %) on a Perkin Elmer R12 instrument (60 MHz). Chemical shifts are given in τ units (TMS, internal standard). The following abbreviations are used: m = multiplet, s = singlet, d = doublet.

The spectral properties of the new sesquiterpene (I) indicated a close structural relationship with (+)- β -cedrene (MS spectra almost identical). On oxidation with osmium tetroxide, the sesquiterpene (I) gave a diol (II), $C_{15}H_{26}O_2$, m.p. 129-130°, $(\alpha)_D^{25} + 2.8^\circ$ (c 0.72 in $CHCl_3$), which on periodate oxidation yielded a norketone (IIIa), $C_{14}H_{22}O$, m.p. 61.5 - 63.5°, $(\alpha)_D^{25} - 2.2^\circ$ (c 1.31 in $CHCl_3$), IR 1710 cm^{-1} (6-membered ring ketone). Bromination of this norketone (IIIa) gave a mixture of two monobromo derivatives (TLC, silica gel, 30 % ether in light petroleum, R_F 0.67 and 0.59) which were separated by column chromatography. The compound with R_F 0.67 was found to be an "axial" α -bromonorketone (IIIb), $C_{14}H_{21}OBr$, m.p. 87-89° $(\alpha)_D^{25} - 68.8^\circ$ (c 0.65 in $CHCl_3$), IR 1710 cm^{-1} (axial α -bromoketone in 6-membered ring). The other α -bromonorketone (R_F 0.59) was found to be the "equatorial" isomer (IIIc), $C_{14}H_{21}OBr$, m.p. 99-101°, $(\alpha)_D^{25} - 2.1^\circ$ (c 0.61 in $CHCl_3$), IR 1720 cm^{-1} (equatorial α -bromoketone in 6-membered ring). The two α -bromonorketones could both be dehydrobrominated (Li_2CO_3/DMF) to the α,β -unsaturated norketone (IV) $C_{14}H_{20}O$, m.p. 48.5-49°, $(\alpha)_D^{25} - 497^\circ$ (c 0.45 in $CHCl_3$), λ_{max}^{EtOH} 240 nm (ϵ 8530).



Detailed spectroscopic studies (NMR and MS) and further chemical degradation indicated that the sesquiterpene (I) must be of a new tricyclic type but closely related to (+)- β -cedrene. The structure of the sesquiterpene was determined by X-ray phase structure determination on the "equatorial" α -bromonorketone (IIIc). The compound (IIIc) crystallizes in space group $P2_12_12_1$ with four molecules per unit cell. The cell dimensions are $a = 12.740$ (3), $b = 7.465$ (1), $c = 14.335$ (3) Å. The X-ray intensity data were collected on a Siemens automatic diffractometer.

The crystal structure was solved by the heavy atom method. The position of the bromine atom was determined from a three-dimensional Patterson map. Successive use of Fourier and difference Fourier syntheses revealed all the non-hydrogen atoms and anisotropic refinement resulted in an R index of 0.072. At this stage a difference Fourier synthesis was calculated

and the hydrogen atoms were located and introduced into the least-squares analysis with isotropic temperature factors. The residual was reduced to 0.054 and the average estimated standard deviations in bond distances involving non-hydrogen atoms are 0.01 Å.

Fig. 1 shows a perspective view of the molecule. The two five-membered rings are in a trans-configuration resulting in a considerable internal strain, cf. also bond lengths C(1)-C(2) and C(6)-C(7).

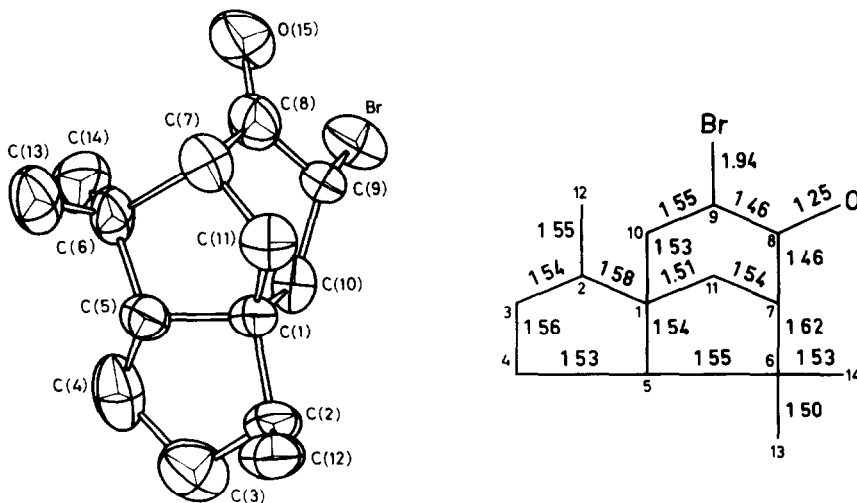
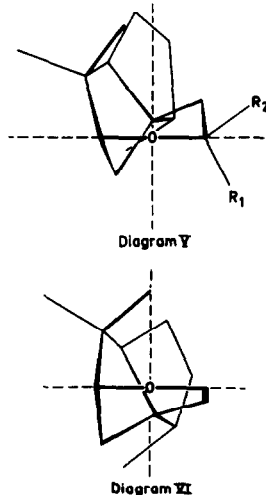


Fig. 1 A perspective view and the bond lengths of the α -bromonorketone (IIIc)

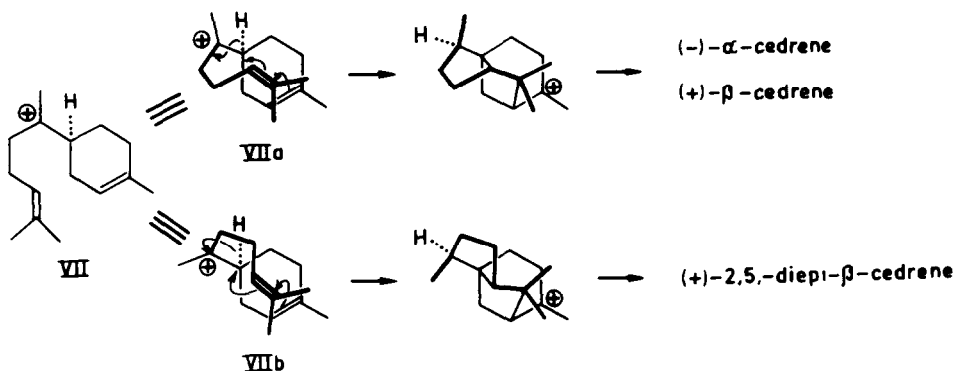
The absolute configuration of the sesquiterpene (I) follows from CD data of the norketone (IIIa) which exhibits a negative CD due to the $n \rightarrow \pi^*$ transition ($[\theta]_{295} - 2267$) and of the "axial" α -bromonorketone (IIIb) exhibiting a weak negative CD ($[\theta]_{324} - 1979$). According to the α -haloketo rule (cf. ref. 5) the axial bromo-substituent of compound (IIIb) will make a positive contribution to the CD thus cancelling some of the negative overall effect of the ring system. The strong negative CD ($[\theta]_{295} - 5019$) of the "equatorial" α -bromonorketone (IIIc) may be explained by the contributions from the ring system and from the bromosubstituent



which is in a negative octant (cf. octant diagram V).

The α,β -unsaturated norketone (IV) exhibits strong negative CD minima due to the $n \rightarrow \pi^*$ ($(\theta)_{374} - 512$, $(\theta)_{357} - 1255$, $(\theta)_{343} - 1439$, $(\theta)_{329} - 976$) and $\pi \rightarrow \pi^*$ ($(\theta)_{236} - 3793$, $(\theta)_{206} - 4694$) transitions. These data are in agreement with those predicted^{6,7} from the octant diagram (VI).

It is of interest to note that the biogenesis of (-)- α -cedrene and of the new sesquiterpene, I, (+)-2,5-diepi- β -cedrene, may proceed via a common precursor (VII) which in the two conformations (VIIa and b) will cyclise to the cedrane and 2,5-diepicedrane skeletons, respectively.



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