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THE ABSOLUTE CONFIGURATION OF A VETIVER ACORADIENE. THE CONVERSION OF CAROTOL TO ACORADIENES.

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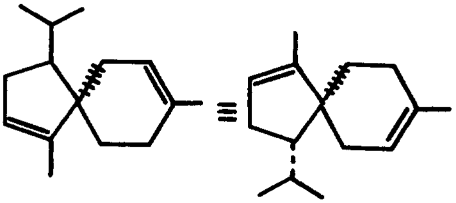
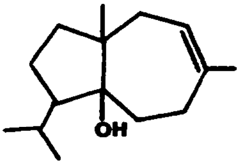
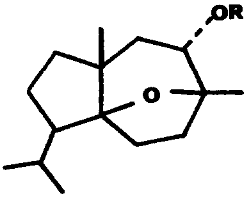
Recently, Kaiser and Naegeli reported the isolation[1] of two new acoradienes from the essential oil of <u>Vetiveria zizanoides</u> (Stapf) and proceeded to synthesize[2] one of these in racemic form by an ingenious and unequivocal method. These same authors assigned the absolute configuration indicated in I to this naturally occurring sesquiterpenoid "on grounds of co-occurrences with (+)-α-cedrene, (+)-prezizaene and (+)-zizaene in vetiver oil".[1,2]



I

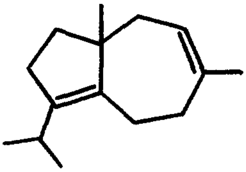


II

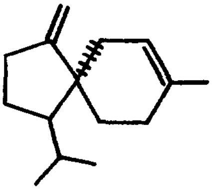


III

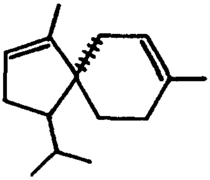
We now show that, in fact, this acoradiene has the enantiomeric configuration to that indicated in I by its formation by a stereochemically unambiguous means from the sesquiterpenoid carotol (II) of known absolute configuration.[3-7] The relative configuration of carotol is known both from various chemical transformations[3] and from an X-ray analysis[7] of daucyl (±)-alaninate hydrobromide (III, R = $\mathrm{COCH(CH_3)NH_3^{\oplus}Br^{\theta}}$). Daucol (III, R = H) is obtained easily from carotol on treatment of the latter with a peracid[8,3]. The absolute configuration of carotol is known from the circular dichroism curves of α-bromodaucone and daucone[3]. The latter is simply the oxidation product of daucol while the former is obtained on bromination of the latter. In addition, carotol has been correlated with (-) dihydrocarvone[4,5] and finally the latter was converted into (+)-daucene (IV) which, in turn,



IV



V



VI

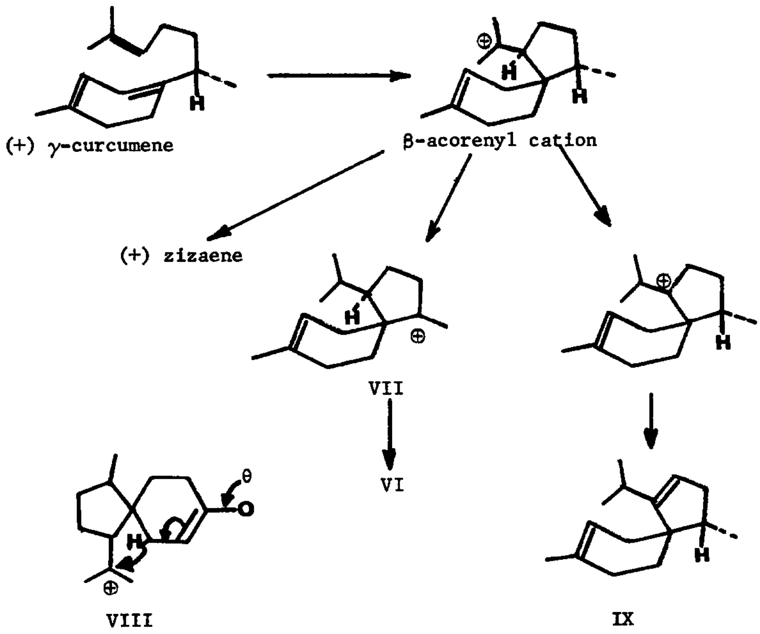
was converted into carotol, albeit, in very low yield[6]. However, carotol is converted into daucene in good yield by treatment with thionyl chloride in pyridine[3]. In fact, it was a reinvestigation of the latter reaction which led us to the isolation of an acoradiene identical to the one reported by Kaiser and Naegeli[1]. The recent synthesis of (-)daucene from (R)-(+)-limonene offers further substantiation to the assigned absolute configuration of carotol[9].

Gas chromatographic analysis (10% XE-60 column) of the product obtained from treatment of carotol with thionyl chloride in pyridine at 0° (essentially the conditions previously reported[3]) revealed, in addition to daucene (65%), three other products A(3%), B(11%), and C(21%) listed in order of increasing retention time[10]. Chromatography of this material on silica gel impregnated with silver nitrate (25%) gave first compound B shown to be identical with an authentic sample of the acoradiene of Kaiser and Naegeli[1] by glc on three different columns and by NMR and IR spectral comparisons[11]. In addition, the mass spectrum of B and that reported for I[1] were identical. Finally, both B and the authentic sample of acoradiene gave essentially identical plain negative optical rotatory dispersion curves (C,1.51,$[\Phi]_{589}$-33.8, authentic sample[11] C 1.20,$[\Phi]_{589}$-30.6). Next, daucene (plain positive ORD curve) was eluted from the column followed by compound C mixed with daucene. A pure sample of C (plain positive

ORD curve) was obtained by preparative glc (12 ft, 5% carbowax column) and on the basis of its IR (ν^{CCl_4} 1635,885cm^{-1}), nmr (δ^{CDCl_3} 4.79, 2H, δ5.41, 1H) and mass spectra (Calc. for $C_{15}H_{24}$ m/e 204.188. Found m/e 204.186±0.004) C has been assigned structure V.

From the known absolute configuration of carotol (II) and the method of preparation[12], acoradienes B and C were assigned the absolute configurations indicated in VI and V respectively. Thus, the absolute configuration of B is seen to be enantiomeric to the previously assigned configuration shown in I[1]. However, the configuration VI is consistent with the co-occurrence of this compound with (+) zizaene as seen in Scheme I via the previously postulated β-acorenyl cation indicated. Thus, we are suggesting that VI arises biogenetically from the β-acorenyl cation precursor of (+) zizaene by a 1,4-hydride shift to give cyclopentyl cation VII which yields VI on deprotonation. Recently, Corey and Balanson[13] suggested a 1,4-hydride shift in a related system as indicated in VIII. Finally, the second acoradiene isolated by Kaiser and Naegeli[1] from vetiver oil, if it arises from the same β-acorenyl cation precursor, would have structure IX[14].

SCHEME 1



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10. On a single occasion 25% of acoradiene VI (B) was obtained from the thionyl chloride reaction. Mesyl chloride in pyridine gave similar results to those obtained with thionyl chloride but the rate was considerably less. On the other hand 90% formic acid at room temperature rapidly transformed carotol into daucene (85%) and acoradiene **B** (VI) (15%) apparently giving none of acoradiene **C** (V).

11. We are indebted to Dr. R. Kaiser, Givaudan-Esrolko AG, Zurich, for an authentic sample of acoradiene I.

12. A mechanistically related conversion of carotol oxide to an acoratriene has been described. E. Demole, P. Enggist and C. Borer, *Helv. Chim. Acta*, **54**, 1845 (1971).

13. E. J. Corey and R. D. Balanson, *Tetrahedron Letters*, 3153 (1973).

14. Kaiser and Naegeli[1] were indecisive about the position of the double bond in the six-membered ring and we simply point out that both acoradienes may arise from the same β-acorenyl cation. If the other acoradiene arises from an α-acorenyl cation precursor, the double bond in the six-membered ring will be on the other side.