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α-PSEUDOWIDDRENE, A NEW SESQUITERPENE HYDROCARBON FROM THUJOPSIS DOLABRATA SIEB. ET ZUCC.

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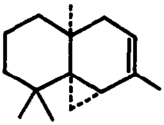
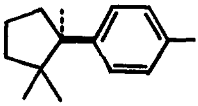
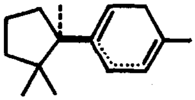
Although extensive chemical analyses have been performed on the Hiba wood oil (Thujopsis dolabrata Sieb. et Zucc. var. hondai Makino), thujopsen (I) (1), cuparene (II) (1) and isomeric cuprenenes (III) (2) are the sesquiterpene hydrocarbons isolated so far. This is rather surprising in view of wide variation of carbon skeletons (not less than 6 types, i.e. thujopsane, cuparane, widdrane, cedrane, elemane and selinane) found for the oxygenated sesquiterpenic congeners (1). With interest in the biogenetic relationship of these constituents, a search of minor hydrocarbon constituents in the oil was undertaken. The study culminated in the isolation of six new hydrocarbons of various carbon skeletons including the long-sought β-chamigrene (IV) (3) and α-pseudowiddrene (V), a new natural product of unique carbon skeleton.

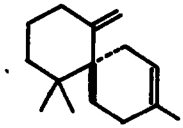

I


II

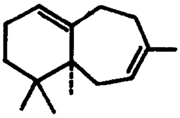

III

Careful fractionations of the neutral wood oil (4) using the combination of silver nitrate-impregnated silica gel column chromatography and preparative gas chromatography resulted in the isolation of α-cedrene (trace), β-cedrene (1% of the sesquiterpene hydrocarbon), β-elemene (trace), ε-selinene (trace), β-chamigrene (IV) (1%) and α-pseudowiddrene (V) (1%), in addition to I (89%), II (2%) and III (5%).

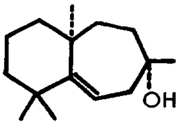
Structure of V, colorless oil, $C_{15}H_{24}$, m/e 204 (M^+), 189 (base peak), 133, $[\alpha]_D^{26}$ +67.7° ($CHCl_3$), was deduced in the following way. Spectral data disclosed the presence of two trisubstituted double bonds



IV



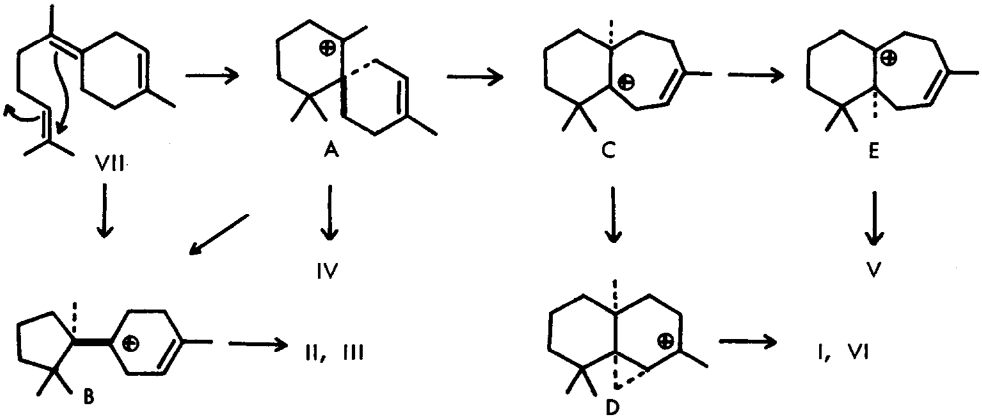
V



VI

(ν 1660, 837, 818 cm^{-1} , δ 5.25, 2H, m) (hence bicyclic), one vinylic methyl group (δ 1.58, 3H, br.s), and three tertiary methyl groups (δ 0.85, 6H, s, 0.92, 3H, s). UV end-absorption (ϵ_{220} 1290) and the absence of nmr signals around 2.6 ppm due to doubly allylic hydrogens suggested the separation of the double bonds at least by two carbon units. This is consistent with the number of allylic hydrogens (δ 1.80-2.40, 8H). These structural features coinside with those of the hydrocarbon, obtained by either acid-catalyzed isomerization of thujopsene (I) or dehydration of widdrol (VI) (5). Subsequent direct comparison of natural V with the isomerization product proved their identity.

The isolation of V as well as IV in Thujopsis dolabrata has some biogenetic significance: Biogenetic precursor leading to thujopsane – widdrane type of sesquiterpenes as well as to cedrane and cuparane is considered to be bisabolene VII, although its presence in the wood oil is still unknown. The cyclization of VII as indicated below would give the ion A, which may loose a proton to yield IV. The isolation of IV gives the direct support to the presence of A in the plant. The ion A may rearrange to the ion B which is the direct precursor of II and III (6) or alternatively to the ion C, a precursor of I and VI.



The formation of I and VI from this ion through the ion D has been discussed previously (7). The present identification of V establishes the presence of the ion E in the plant and gives a support to the presence of the directly-connected ion C (7) as has been demonstrated experimentally (5,7). Thus, the result described in this paper unambiguously indicates the involvement of the ions A, C and E in the biosyntheses of these constituents.

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References and Footnotes

1) S. Itô, K. Endo, H. Honma and K. Ota, Tetrahedron Letters, 3777 (1965) and references therein.

2) T. Nozoe and H. Takeshita, Ibid., 14 (1960). W. G. Dauben and P. Oberhänsli, J. Org. Chem., **31**, 315 (1966).

3) S. Itô, K. Endo, T. Yoshida, M. Yatagai and M. Kodama, Chem. Comm., 186 (1967).

4) Two samples (oil A and B) were analysed and found to contain both IV and V through in a different ratio. Oil A: Collected in Shimokita Penninsula, Aomori Prefecture. The sew dust was steam distilled. I (83%), IV (1.3%), V (1%). Oil B: Collected in Sakunami, Miyagi Prefecture. The shavings were extracted with n-hexane. I (89%), IV (1%), V (0.5%).

5) The isomerization product: $C_{15}H_{24}$; m/e 204; $[\alpha]_D^{23}$ +65.3°($CHCl_3$); λmax 192 nm (ε 13900); ν_{max} 1660, 840-820 cm^{-1} ; δ 0.85, 0.85, 0.93 (3H, each s), 1.57 (3H, d, J=2), 5.27 (2H, m). S. Itô, M. Yatagai and K. Endo, Tetrahedron Letters, 1149 (1971). W. G. Dauben, L. E. Friedrich, P. Oberhänsli and E. I. Aoyagi, J. Org. Chem., **37**, 9 (1972).

6) The pathway VII ⟶ B by the direct cyclization is also plausible (8).

7) S. Itô, M. Yatagai, K. Endo and M. Kodama, Tetrahedron Letters, 1153 (1971) and references therein.

8) T. Yoshida, K. Endo, S. Itô and T. Nozoe, Yakugaku Zasshi, **87**, 434 (1967) and references therein.