

GERMACRENE D, A KEY INTERMEDIATE OF CADINENE GROUP COMPOUNDS
AND BOURBONENES

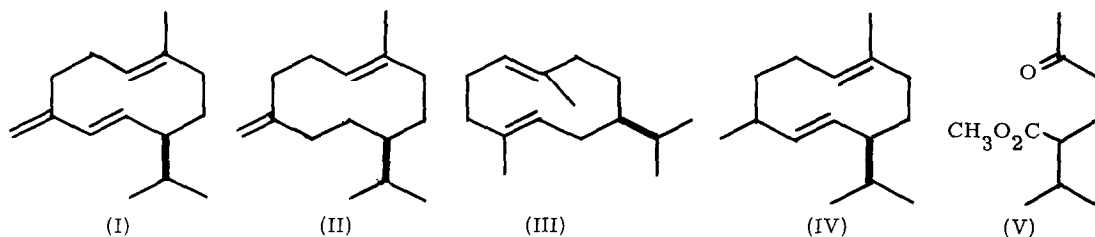
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In the course of examination of the essential oil obtained from Pseudotsuga japonica, a most conspicuous peak in its gas chromatogram was observed to disappear during column chromatography on silica gel. Meanwhile, this labile compound was also noticed to be present in other oils from different sources, such as Pittosporum Tobira, Kadsura japonica¹⁾ and Piper Kadsura. The isolation of it was attained by column chromatography on alumina impregnated with silver nitrate and preparative gas chromatography operated at 140°C.

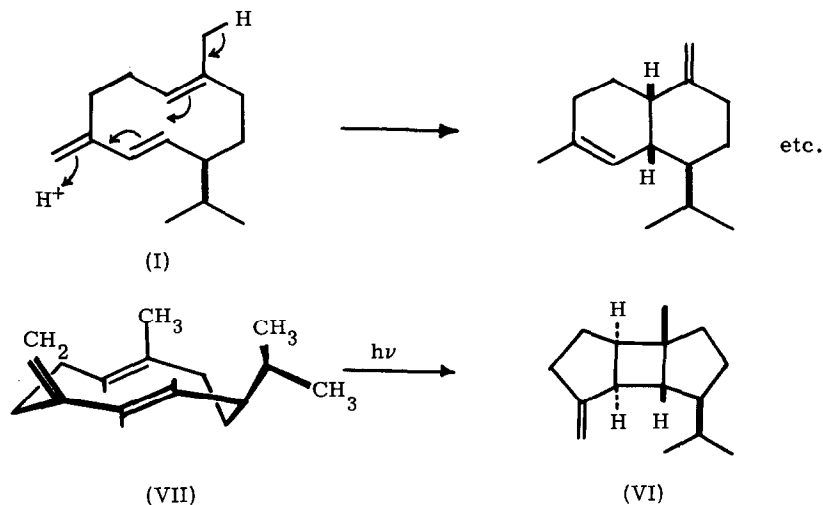
Germacrene D (I), $C_{15}H_{24}$ [α]_D²³ -240°, was shown to have the following partial constitutions by IR and NMR spectra. An isopropyl group: ν 1360 and 1375 cm^{-1} ; two doublet signals at 0.91 and 0.86 ppm ($J = 6$ cps). A terminal methylene group: ν 880 and 1620 cm^{-1} ; δ 4.78 ppm. A methyl group on double bond: δ 1.52 ppm. A trans-disubstituted double bond: ν 980 cm^{-1} ; AB part of ABX type signals at 5.23 (A) and 5.83 ppm (B) ($J_{AB} = 16$ cps, $J_{AX} = 6$ cps). A trisubstituted double bond: δ 5.0 ~ 5.5 ppm (broad).

Hexahydro derivative of (I) was identified as germacrane by comparing its IR spectrum with the one reported by Sorm et al.²⁾ Partial hydrogenation of (I) with Pd-BaSO₄ in ethanol gave three dihydro derivatives, (II), (III), and (IV). (III) was identical with dihydrogermacrene obtained from costunolide by Bhattacharyya et al.³⁾ Thermal isomerization of (III) gave readily dihydro-elemene. Ozonolysis of (I) followed by esterification with diazomethane yielded a compound (V) which showed the identical IR, NMR, and MS spectra with those of the authentic sample obtained from piperitone. From these physical and chemical properties, the constitution of the new labile hydrocarbon was deduced to be expressed by the formula (I) and was named germacrene D.¹⁾ Chemical and photochemical isomerization of (I) afforded final and decisive information



By treatment with silica gel, (I) was entirely isomerized and afforded a mixture of hydrocarbons from which (+)- γ -muurolene, (-)- α -amorphene, α -muurolene, (+)- δ -cadinene, and (+)- γ -cadinene were isolated as the main products. Thermal isomerization of (I) showed principally the same result as silica gel promoted conversion or acid catalyzed isomerization did. Photoisomerization of (I) using low pressure Hg-lamp resulted mainly in (-)- β -bourbonene (VI). α -Bourbonene and β -copaene were also found as the minor products. These facts, together with the noted transannular interaction between two double bonds in the cyclodecane ring ($\lambda_{\text{max}}^{\text{n-hexane}} = 259 \text{ m}\mu$, $\epsilon = 4500$), show that (I) prefers the conformation shown by (VII) in which these two double bonds in the ring are situated parallel and face to face with each other, and three substituents, isopropyl, methyl, and exocyclic methylene groups are oriented in the same direction, β to the plane of the ring.

Nomenclatural basis and genetic importance of this compound, in connection with the another isomer germacrene C, have been stated elsewhere.¹⁾ Nevertheless, the authors wish to stress here again the meaning of this compound as a key intermediate in the genetic course for cadinene group compounds. At least, γ -isomers of cadinene, muurolene, and amorphene, as well as α - and β -bourbonenes, originated solely from germacrene D in the plant materials in very high possibility.



References

- 1) K. Morikawa and Y. Hirose, *Tetrahedron Letters*, in press
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- 3) G. H. Kulkarni, G. R. Kelkar and S. C. Bhattacharyya, *Tetrahedron* 20, 1301 (1964).