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GERMACRENE-C, PRECURSOR OF δ-ELEMENE

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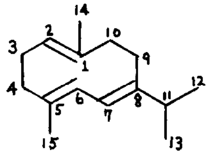
The precursor of δ-elemene, which was predicted by M. D. Sutherland et al. to be 1,5-dimethyl-8-isopropyl-cycrodeca-1,5,7-triene (I),$^{1)}$ has been obtained from the dry fruits of Kadsura japonica by extraction-evaporation at the temperature below 40°.$^{*)}$

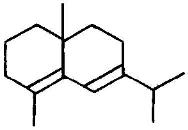
(I) shows $[\alpha]_D^{24}$ = 0.00° (C, 5.55 in $CHCl_3$) and M^+ : m/e 204.

The product from a Cope rearrangement of the pure hydrocarbon (I) was solely δ-elemene and the conversion rate at 100° for 5 hr (half-life condition for pregeijerene$^{2)}$) was 40 %.

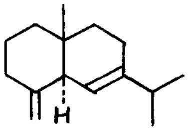
On the other hand, (I) was completely changed into a few hydrocarbons when allowed to stand in n-hexane with silica gel powder for several hours. The main products were identified as (II) and (III) on the basis of spectral data and a hydrogenation product.



(I)



(II)



(III)

In addition to above facts, UV and NMR spectral data of germacrene-C show a close similarity with those of pregeijerene$^{2)}$: UV ($_{max}^{n\text{-Hexane}}$ 254.5_{mu}, = 11000) and NMR $\delta_{ppm}^{CCl_4}$: 1.10 (6H, d, J = 6.8_{cps} : C-12 and C-13 methyls),

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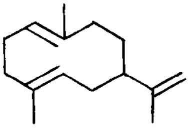
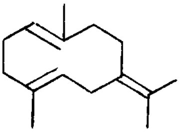
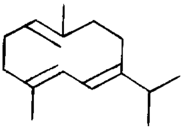
*) The acetone extract was first freed from waxy components by alumina chromatography and then purified by the method of silver nitrate adduct.$^{2)}$ The successful isolation of germacrene-C owed a great deal to the Dr. M. D. Sutherland's suggestion.

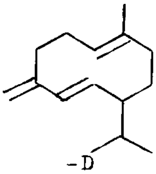
1.15 (3H : C-1 methyl, this methyl signal overraps with one of doublet signals of isopropyl methyls), 1.56 (3H, S : C-5 methyl), 4.92 (1H, broad : C-2 proton) and 5.18, 6.20 (1H, 1H, AB system q. $J_{AB} = 9.3_{cps}$: C-6 and C-7 protons). The C-1 methyl signal separates in benzene solution, $\delta^{benzene}_{ppm}$: 1.04 (6H, d, $J = 6.8_{cps}$: C-12 and C-13 methyls) and 1.16 (3H, d, $J = 1.6_{cps}$: C-1 methyl).

Thus, germacrene-C is expressed by the structure (I) having trans, trans, cis-cyclodecatriene nucleus like pregeijerene. The name, germacrene-C, is proposed according to be distribution of the double bonds of the isomers found or to be found.

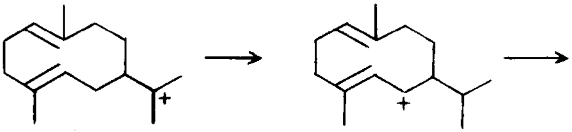

Germacrene-A


-B


-C


-D

The isomer A has not been found, B prepared from germacrone[3)], and D has recently been isolated from natural sources[4)]. At present, we have an opinion that both germacrene-C and D could be derived from a germacrenium ion (IV) through 1,3-hydride shift.



(IV)

Kadsura japonica shows a beautiful contrast of biogenetic development into two directions toward C and D in different parts, namely, in the fruits toward C[5)] and in the stems and leaves toward D.[6)]

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