Tetrahedron Letters No.11, pp. 855–857, 1970. Pergamon Press. Printed in Great Britain.

PREISOCALAMENDIOL, A PLAUSIBLE PRECURSOR OF ISOCALAMENDIOL

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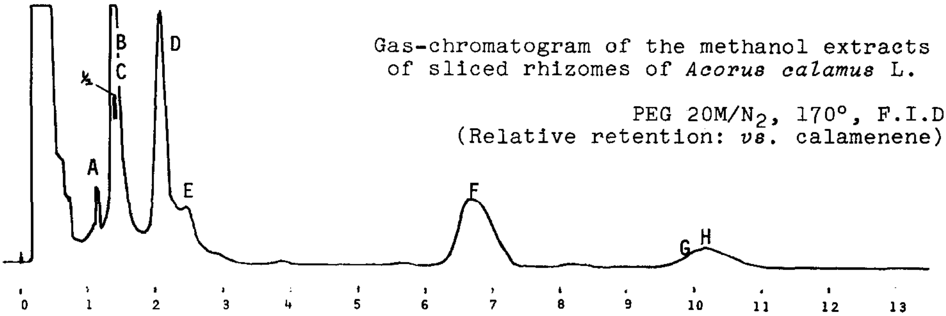
(Received in Japan 7 January 1970; received in UK for publication 2 February 1970)

In the previous papers,[1,2] we reported isolation and structures of three elemene-type sesquiterpenes (I, II and III) as well as a cadinene-type one, isocalamendiol(IV). We further examined sesquiterpenic components of *Acorus calamus* L.* for the purpose of finding such a germacrone-type precursor as 3,7-dimethyl-10-isopropylcyclodecan-2,6-dien-1-one(V).[1] We here describe the isolation of another new germacrone-type compound, preisocalamendiol(VI) from the above plant.

Sliced rhizomes of the plant were immersed in methanol for a month at room temperature, and then the methanolic solution was concentrated under reduced pressure below 25°. The gas-chromatogram of the methanol extracts thus obtained is shown below, and each of the remarkable peaks is also assigned.



Gas-chromatogram of the methanol extracts of sliced rhizomes of *Acorus calamus* L.

PEG 20M/N_2, 170°, F.I.D.
(Relative retention: *vs.* calamenene)

A: Epishyobunone(II), B: Isoshyobunone(III), C: Shyobunone(I),
D: Preisocalamendiol(VI), E: Dehydroxyisocalamendiol(VII),
F: Asarone and its isomers, G: Calamendiol, H: Isocalamendiol(IV)

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* Collected in Aichi Prefecture, Japan (in July).

A colorless liquid corresponding to the peak D was obtained by the preparative G.L.C.(PEG 20M/nitrogen, 115°), and its physical data are as follows.

VI: $C_{15}H_{24}O$ (Obs. 220.1813, Calc. 220.1827); relative retention: 2.08 *vs.* calamenene(PEG 20M/N_2, 115°); ν_{max}^{film}: 3080, 1705, 1642, 897 cm^{-1}; $\delta_{ppm}^{TMS}(CCl_4)$: 0.86(*3*H, d, J=*6.7*Hz), 0.91(*3*H, d, J=*6.7*Hz), 1.37(*1*H, near s), 2.83(*1*H, d, J=*15*Hz), 3.24(*1*H, d, J=*15*Hz), 4.84(*1*H, br.s), 4.95(*1*H, br.s) and 4.9∿5.3(*1*H, br.).

All of the physical data were in complete agreement with those of the thermal isomerization product(VI) of shyobunone(I) already reported.[3]

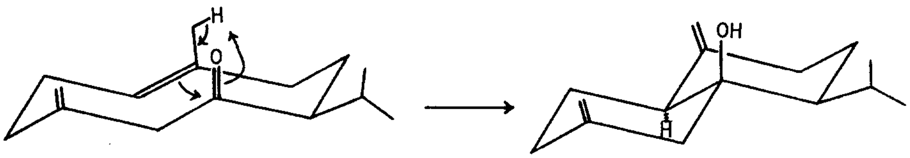
We could also isolate, in the next trap, a small amount of dehydroxyisocalamendiol(VII) corresponding to the peak E, which was identical with the dehydration product obtained by treatment of isocalamendiol(IV) with $POCl_3$-pyridine.[3] However, this compound seems to be an artifact: when heated in a sealed tube at 180° (see the Table), VI afforded the same compound VII, in high yield.

Table. Thermal Isomerization of Preisocalamendiol(VI)

Time(min.)	VI (%)	VII (%)	Other products(%)
0	100	0	0
7.5	99	1	0
22	83	17	0
42	48	46	6
90	3	86	11

Peak-height of gas-chromatogram(PEG 20M/N_2, 115°, flame-ionizer detector) was served as an approximate value of content(%).

It is indicated, in the above experiment, that dehydroxyisocalamendiol(VII) can be formed directly from preisocalamendiol(VI), as shown below.

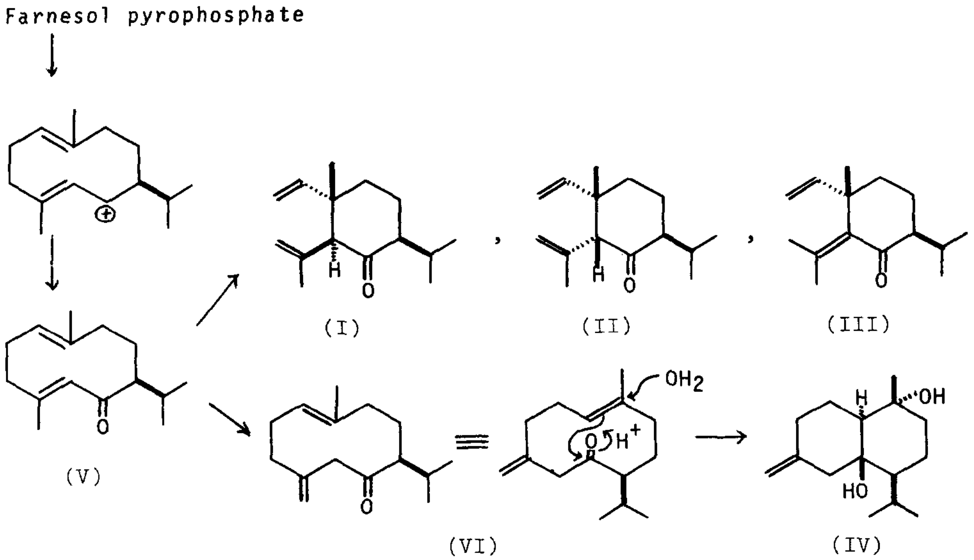


(VI) (VII)

Furthermore, treatment of preisocalamendiol(VI) with silicic acid-benzene led to the formation of calamenene, indicating that the carbon skeleton of preisocalamendiol(VI) is readily converted into a cadinene-type one.

On the biogenetic point of view, preisocalamendiol(VI) is regarded as a key intermediate for isocalamendiol(IV).

Biogenesis of Sesquiterpenes of *Acorus calamus* L.



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