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FURANODIENE,
A PRECURSOR OF FURAN-CONTAINING SESQUITERPENOIDS

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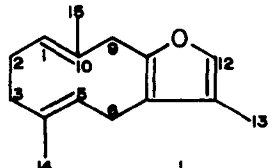
In continuation of our study on the constituents of the rhizome of zedoary, Curcuma zedoaria Roscoe (Zingiberaceae), we have recently isolated a novel sesquiterpenoid, for which the name furanodiene is proposed. We now wish to report that furanodiene possesses the structure I and is consequently the possible common precursor of sesquiterpenoids containing furan rings.

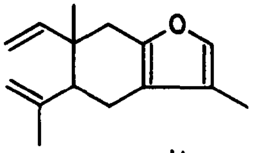


I

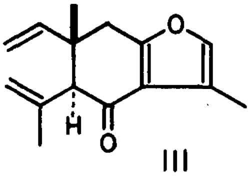
Furanodiene, m.p. 44-45°, $[\alpha]_D$ ± 0°, has the molecular formula $C_{15}H_{20}O$. In order to elucidate the structure, analysis of the NMR spectrum with the aid of double resonance experiments was particularly instructive.[*1] The spectrum exhibits three vinyl methyl signals at 1.28, 1.59, and 1.91 p.p.m. as well as three vinyl hydrogen signals at 4.96, 4.76, and 7.05 p.p.m. These hydrogens can be classified into the sebsequent three functions. The methyl doublet at 1.91 p.p.m. and the slightly multiplying quadruplet at 7.05 p.p.m., spin-coupled each other (J=1.3 c.p.s.), indicate the presence of a furan nucleus bearing a β-methyl ($C_{(13)}H_3$) and an α-hydrogen ($C_{(12)}H$). Mutual couplings are also observed between the methyl signals at 1.28 and 1.59 p.p.m. ($C_{(15)}H_3$ and $C_{(14)}H_3$) and the hydrogen signals at 4.96 and 4.76 p.p.m. ($C_{(1)}H$ and $C_{(5)}H$), respectively, a fact which demonstrates the presence of two trisubstituted double bonds. Furthermore, both vinyl hydrogen signals ($C_{(1)}H$ and $C_{(5)}H$) occurring as broad triplets (J=7 and 8 c.p.s.) show the couplings with the adjacent methylene groupings ($C_{(2)}H_2$ and $C_{(6)}H_2$), respectively. Two additional signals arising from two methylene groups ($C_{(9)}H_2$ and $C_{(6)}H_2$) appear as a broad quadruplet in an AB type at 3.44 and 3.52 p.p.m. (J=17 c.p.s.) and as a broad doublet at 3.08 p.p.m. The signal for the former methylene ($C_{(9)}H_2$) is long-range coupled with the α-hydrogen ($C_{(12)}H$) of the furan, the vinylic methyl ($C_{(15)}H_3$), and the latter methylene ($C_{(6)}H_2$). This finding reveals that the methylene ($C_{(9)}H_2$) is oriented at the α'-position of the furan ring and also attached to the carbon (C-10) bearing the vinyl methyl. The latter methylene signal ($C_{(6)}H_2$) has the appearance of a broadened doublet, the large splitting (J=8 c.p.s.) resulting from the coupling to the vinyl hydrogen ($C_{(5)}H$) and the small splittings from the couplings to the vinyl methyl ($C_{(14)}H_3$) and the allylic methylene ($C_{(9)}H_2$). The above NMR evidence leads to the formulation I for furanodiene.

The structure (I) of furanodiene thus deduced was confirmed chemically by the following observation. Pyrolysis of furanodiene resulted in a Cope rearrangement giving curzerene (II), another constituent of the zedoary rhizome.1)

8,12-Oxido-germacra-1,4,7,11-tetraene (I), which is presently designated as furanodiene, has been one of the missing links in the sesquiterpenoid biosynthesis, and now must be recognized as the common precursor of monocarbocyclic and bicarbocyclic sesquiterpenoids possessing furan rings.[*2] In reality, the zedoary rhizome, for instance, contains a number of its descendants; _i.e._, curzerene (II), curzerenone (III), epicurzerenone (IV),1) zederone (V),2) and curcolone (VI).3)



II



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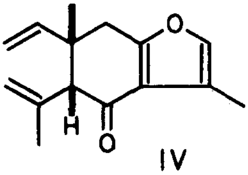

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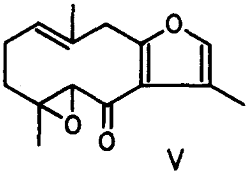
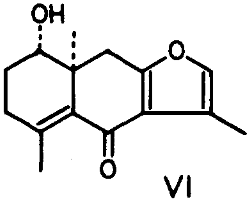


V



VI

We thank Dr. M. C. Woods, Varian Associates, for the NMDR experiments.

FOOTNOTES AND REFERENCES

[*1] The NMR spectrum was recorded at 100 Mc.p.s. in $CDCl_3$ solution _vs_. TMS as internal standard.

[*2] The furopelargones are the known exceptions, apparently following the different biogenetic pathway.4)

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