Structure and Conformation of the Sesquiterpenoids Furanodienone and Isofuranodienone

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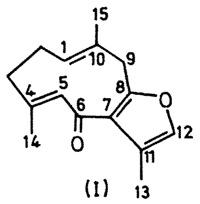
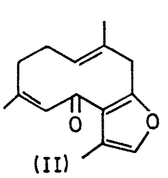
FROM the rhizome of zedoary, *Curcuma zedoaria* Roscoe (Zingiberaceae), a number of sesquiterpenoids has been isolated.[1] Further studies on the constituents has resulted in the isolation of two novel furan-containing sesquiterpenoids for which the names furanodienone and isofuranodienone are suggested. We describe evidence for the structures and the conformations of the two isoprenoids.

Both furanodienone (I), m.p. 89·5—90·5°, λ_{max} 241 and 269 nm. (log ϵ 3·98 and 3·86 in EtOH), ν_{max} (KBr) 1645 cm.$^{-1}$, and isofuranodienone (II), m.p. 70—71°, λ_{max} 223 and 248 nm. (log ϵ 4·17 and 3·95 in EtOH), ν_{max} (KBr) 1667 cm.$^{-1}$, possess the same molecular formula $C_{15}H_{18}O_2$. For elucidation of the structures, analysis of ^1H n.m.r. data with the aid of double resonance experiments (see the Table)† was particularly useful. Each molecule has a furan ring with the following substituents: α-H, β-Me, β′-carbonyl, and α′-methylene, and two ·CH:CMe· groupings. One olefinic proton is long-range-coupled to the α′-methylene and also coupled to the other methylene protons, and the other olefinic proton signal appears as a broad singlet at a somewhat lower field, showing that the



(I)



(II)

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† The recording conditions of ^1H n.m.r. spectra are similar to those previously reported.[3] Accuracies are about $\delta \pm 0{\cdot}02$ p.p.m. for chemical shifts and about $\pm 2\%$ for NOE's. Signals are expressed without fine splittings.

carbon bearing this olefinic proton is adjacent to the carbonyl. As a result, both compounds are considered to have the same constitution, 8,12-oxido-germacra-1(10),4,-7,11-tetraen-6-one, and hence to be geometric isomers.

The chemical shifts (δ) *and nuclear Overhauser effects* (%) *in* $CDCl_3$ *and* C_6D_6 (*in parentheses*)

Increase in the integrated intensity of the signal observed during complete saturation of the signal irradiated

in furanodienone

Observed signal	1-H	5-H	9α-H		9β-H	12-H	13-H	14-H	15-H
	5·16 br dd	5·80 br s		3·69 s		7·05 q	2·13 d	1·99 d	1·30d
	(4·72 br dd)	(5·55 br s)	(3·42 d)		(3·55 d)	(6·82 q)	(2·24 d)	(1·89 d)	(1·07 d)
1-H	—	6(10)	(7)	17	(0)	a(a)	a(0)	7‡(0)	0(0)
5-H	6(7)	—	(0)	0	(0)	a(0)	a(0)	22‡(0)	0(0)
9α-H	(7)	(0)	—		b(b)	(0)	(a)	(0)	(0)
	16	0				0	0	a	4
9β-H	(0)	(0)	b(b)		—	(0)	(a)	(0)	(4)
12-H	a(a)	a(a)	(0)	a	(0)	—	25(28)	a(0)	a(0)

in isofuranodienone

Observed signal	1-H	5-H	9α-H	9β-H	12-H	13-H	14-H	15-H
	5·20 br dd	6·10 br s	3·13 d	3·49	7·00 q	1·91 d	1·89 d	1·55 d
	(5·11 br dd)	(5·90 br s)	(3·03 d)	(3·35 d)	(6·79 q)	(1·79 d)	(1·49 d)	(1·34 d)
1-H	—	0(0)	b(b)	b(b)	a(a)	b(a)	b(0)	0(0)
5-H	b(0)	—	a(0)	a(0)	0(0)	a(0)	33(30)	14(16)
9α-H	9(9)	a(0)	—	b(b)	0(0)	a(0)	a(a)	0(0)
9β-H	0(0)	a(0)	b(b)	—	0(0)	a(0)	a(a)	12(10)
12-H	a(a)	a(a)	a(0)	a(0)	—	22(23)	a(0)	0(0)

[a] Not measured. [b] Undeterminable.

The configurations of the *cis–trans*-isomers in regard to the double bonds were determined by measurements of intramolecular nuclear Overhauser effects (NOE).[2,†] As summarized in the Table, saturation of the 14- or 15-Me signal in (I) had no effect on the 5- or 1-H signal, respectively; this indicates that both trisubstituted double bonds are *trans*.‡ On the other hand, no interaction between the 15-Me and the 1-H in (II) was observed, showing that the C-1 : C-10 double bond is *trans*, while saturation of the 14-Me signal gave rise to a considerable increase in the area of the 5-H signal, demonstrating the C-4 : C-5 bond to be *cis*. These facts enable us to deduce the structures of (I) and (II).

The conformations of the ten-membered rings in these two terpenoids were elucidated by the more extensive determination of NOE values. In (I), an increase in the integrated intensity of the 1-H signal caused by saturation of the 5-H signal, or *vice versa*, indicates that the ten-membered ring adopts the conformation in which 14-Me and 15-Me are *syn*. Further, observations of the NOE's between 1-H and 9α-H, and between 9β-H and 15-Me clearly define the actual conformation of (I) as depicted in the Figure (A). On the other hand, in (II), the NOE's observed between 5-H and 15-Me, between 1-H and 9α-H, and between 9β-H and 15-Me, determine its conformation as illustrated in the Figure (B).

In the spectra of these two sesquiterpenoids, the spacings of doublets of doublets due to the 1-H signals and the solvent-induced shifts of the signals on passing from $CDCl_3$ to C_6D_6 solutions are also consistent with the conformations assigned.

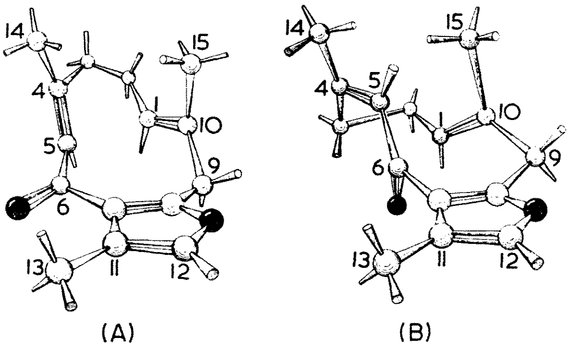

FIGURE. *The molecular conformations of furanodienone* (A) *and isofuranodienone* (B).

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‡ The apparent increases in the areas of the 1- and 5-H signals on double irradiation at about 2 p.p.m. in $CDCl_3$ must be due to overlapping of the signals arising from some other protons situated close to these protons. Therefore, caution should be exercised for NOE measurements in such cases.

[1] *Cf.*, H. Hikino, Y. Sakurai, and T. Takemoto, *Chem. and Pharm. Bull.* (*Japan*), 1968, **16**, 1605.
[2] F. A. L. Anet and A. J. R. Bourne, *J. Amer. Chem. Soc.*, 1965, **87**, 5250.
[3] K. Tori, M. Ohtsuru, I. Horibe, and T. Takeda, *Chem. Comm.*, 1968, 943.