

## Structure and Conformation of the Sesquiterpenoids Furanodienone and Isofuranodienone

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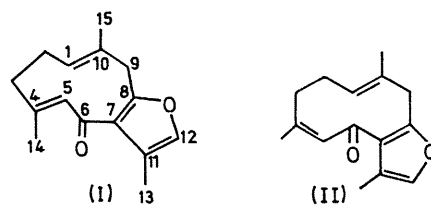
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FROM the rhizome of zedoary, *Curcuma zedoaria* Roscoe (Zingiberaceae), a number of sesquiterpenoids has been isolated.<sup>1</sup> Further studies on the constituents has resulted in the isolation of two novel furan-containing sesquiterpenoids for 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°,  $\lambda_{\max}$  241 and 269 nm. ( $\log \epsilon$  3.98 and 3.86 in EtOH),  $\nu_{\max}$  (KBr) 1645  $\text{cm}^{-1}$ , and isofuranodienone (II), m.p. 70–71°,  $\lambda_{\max}$  223 and 248 nm. ( $\log \epsilon$  4.17 and 3.95 in EtOH),  $\nu_{\max}$  (KBr) 1667  $\text{cm}^{-1}$ , possess the same molecular formula  $\text{C}_{15}\text{H}_{18}\text{O}_2$ . For elucidation of the structures, analysis of  $^1\text{H}$  n.m.r. data with the aid of double resonance experiments (see the Table)<sup>†</sup> was particularly useful. Each molecule has a

furan ring with the following substituents:  $\alpha$ -H,  $\beta$ -Me,  $\beta'$ -carbonyl, and  $\alpha'$ -methylene, and two  $\cdot\text{CH}:\text{CMe}\cdot$  groupings. One olefinic proton is long-range-coupled to the  $\alpha'$ -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



<sup>†</sup> The recording conditions of  $^1\text{H}$  n.m.r. spectra are similar to those previously reported.<sup>3</sup> Accuracies are about  $\delta \pm 0.02$  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

between  $9\beta$ -H and 15-Me, determine its conformation as illustrated in the Figure (B).

The chemical shifts ( $\delta$ ) and nuclear Overhauser effects (%) in  $\text{CDCl}_3$  and  $\text{C}_6\text{D}_6$  (in parentheses)

Observed signal	Increase in the integrated intensity of the signal observed during complete saturation of the signal irradiated in furanodienone							
	1-H	5-H	$9\alpha$ -H	$9\beta$ -H	12-H	13-H	14-H	15-H
	5.16 br dd (4.72 br dd)	5.80 br s (5.55 br s)	3.69 s (3.42 d)	3.55 d (3.55 d)	7.05 q (6.82 q)	2.13 d (2.24 d)	1.99 d (1.89 d)	1.30 d (1.07 d)
1-H	—	6(7)	(7)	17	a(a)	a(0)	7(0)	0(0)
5-H	6(7)	—	(0)	0	a(0)	a(0)	22(0)	0(0)
$9\alpha$ -H	(7)	(0)	—	b(b)	(0)	(a)	(0)	(0)
	16	0			0	0	a	4
$9\beta$ -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							
	1-H	5-H	$9\alpha$ -H	$9\beta$ -H	12-H	13-H	14-H	15-H
	5.20 br dd (5.11 br dd)	6.10 br s (5.90 br s)	3.13 d (3.03 d)	3.49 (3.35 d)	7.00 q (6.79 q)	1.91 d (1.79 d)	1.89 d (1.49 d)	1.55 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)
$9\alpha$ -H	9(9)	a(0)	—	b(b)	0(0)	a(0)	a(a)	0(0)
$9\beta$ -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)

<sup>a</sup> Not measured. <sup>b</sup> Undeterminable.

have the same constitution, 8,12-oxido-germacra-1(10),4,7,11-tetraen-6-one, and hence to be geometric isomers.

The configurations of the *cis-trans*-isomers in regard to the double bonds were determined by measurements of intramolecular nuclear Overhauser effects (NOE).<sup>2,†</sup> 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*.<sup>‡</sup> 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  $9\alpha$ -H, and between  $9\beta$ -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  $9\alpha$ -H, and

In the spectra of these two sesquiterpenoids, the spacings of doublets of doublets due to the 1-H signals and the

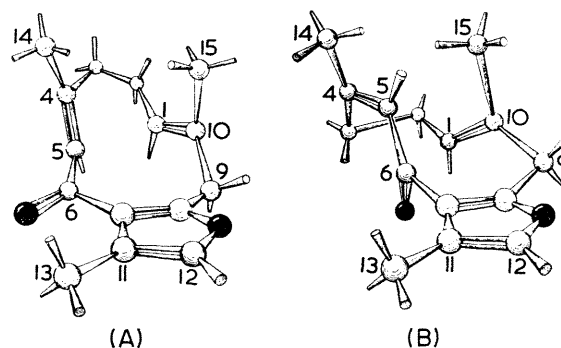


FIGURE. The molecular conformations of furanodienone (A) and isofuranodienone (B).

solvent-induced shifts of the signals on passing from  $\text{CDCl}_3$  to  $\text{C}_6\text{D}_6$  solutions are also consistent with the conformations assigned.

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<sup>‡</sup> The apparent increases in the areas of the 1- and 5-H signals on double irradiation at about 2 p.p.m. in  $\text{CDCl}_3$  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.

<sup>1</sup> Cj., H. Hikino, Y. Sakurai, and T. Takemoto, *Chem. and Pharm. Bull. (Japan)*, 1968, **16**, 1605.

<sup>2</sup> F. A. L. Anet and A. J. R. Bourne, *J. Amer. Chem. Soc.*, 1965, **87**, 5250.

<sup>3</sup> K. Tori, M. Ohtsuru, I. Horibe, and T. Takeda, *Chem. Comm.*, 1968, 943.