

Isolation of Two Phenylbutadiene Dimers and One Monomeric 4-Phenylbut-3-ene from *Zingiber cassumunar* (roxb.)

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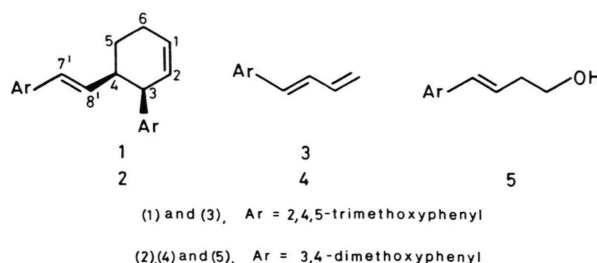
Two arylbutadiene dimers of the 3-aryl-4-styrylcyclohexene series together with a novel C₆–C₄ monomer (2-(3,4-dimethoxystyryl)ethanol) have been isolated from *Zingiber cassumunar*. Due to their co-occurrence and the chemical similarity of one portion of the molecules, a possible biosynthetic relationship between the cyclohexene dimers and the phenylbutadiene monomer of *Z. cassumunar*, based on Diels-Alder reactions, is suggested.

Continuing an earlier investigation [1] of a crude toluene-extract from wild ginger (rhizome of *Zingiber cassumunar* (roxb.)) two vanillin-H₂SO₄-positive spots were located on tlc. Monitoring by tlc, we isolated these two cassumunar-substances 1 and 2 (CS 1 and CS 2) [2] by extensive column chromatography on silica gel in low yields (1 kg crude drug gave 40 mg of CS 1 and 20 mg of CS 2 respectively).

CS 1 crystallises as colourless needles, m. p. 130 to 131 °C from methanol. It has the molecular formula ¹²C₂₆H₃₂O₆ (M⁺, 440.2200), λ_{max} (CDCl₃), 261 (4.29), 298 (3.96), 315 nm (3.94), ν_{max} (KBr), 1610, 970 and 691 cm⁻¹. Under electron bombardment the molecule undergoes a reverse Diels-Alder reaction to give the base peak at m/e 220.

CS 2 crystallises as white needles m. p. 98–101 °C from methanol. It has the molecular formula ¹²C₂₄H₂₈O₄ (380.1987). λ_{max} (CDCl₃), 240 (4.13), 267 (4.23), 273 (4.25), 289 (4.02), 303 (3.83), 3.16 (3.53), ν_{max} (KBr), 1600, 960, 685 cm⁻¹. As with CS 1, a reverse Diels-Alder reaction occurs in the mass spectrometer to give the base peak at m/e 190.

The ¹H NMR of both substances were highly informative and enabled us to define them as *cis*-3-aryl-4-styrylcyclohexenes (see 1 and 2).



Extensive decoupling of the aliphatic protons allowed the assignments shown in Table I to be made. In particular decoupling between H-2 and H-3 allowed *J*_{3,4} to be determined as 5 Hz for CS 2, and so the substituents at C-3 and C-4 must be *cis*. By analogy the same assignment was made for CS 1.

In CS 1 it was clear that the aromatic protons on each ring were *para* to each other, but this does not serve to completely define the substitution pattern of the ring. No information regarding the substitution pattern of the two methoxyl groups in each ring of CS 2 could be obtained from the ¹H NMR spectrum, but the ¹³C NMR spectra served to settle both points and to characterise CS 1 as 1 and CS 2 as 2.

The calculated values are those based on incremental shifts for simple aromatic rings [3], which are models of limited utility. Nevertheless, only the 2,4,5-trimethoxyphenyl substitution pattern is satisfactory for CS 1 and only 3,4-dimethoxyphenyl ring satisfies the requirements of CS 2 which are therefore defined as 1 and 2 respectively. The similarity of the aromatic carbons in the ¹³C NMR spectra of CS 2 and the unambiguously assigned monomer [5] (Table III) serves also to define clearly the substitution pattern of CS 2 and underline the somewhat limited use of models for this series. It is interesting to note that the 2'(2'')-OMe groups cause a significant change in the chemical shifts of C-3 and C-4 in CS 1 as compared with CS 2. CS 1 is identical with alflabene, recently isolated from *Alpinia flabellata* [4] and we call CS 2, cassumunene*.

* Following completion of this ms it came to our attention that, very recently, both CS 1 and CS 2 had been isolated from *Z. cassumunar* and characterised by X-ray analysis [5]. Our proposed structures agree completely with those found by X-ray crystallography.

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Table I. ^1H NMR of CS1 and CS2 ^a.

Proton	CS1			CS2	
	Undecoupled	Decoupled at proton	Simplified signal	Undecoupled	Simplified signal
H-1 (1H) H-2 (1H)	{ 5.6 – 5.98 m	H-6	5.91, d, $J_{12} = 10$ Hz 5.72, dd, $J_{21} = 10$ Hz $J_{23} = 4$ Hz	{ 5.72 – 6.1 m	5.95, d, $J_{12} = 11$ Hz 5.78, dd, $J_{21} = 11$ Hz $J_{23} = 7$ Hz
H-3 (1H)	4.08, m	H-2	4.08, simplif. m	3.46, m	3.46, d, $J_{34} = 5$ Hz
H-4 (1H)	2.76, m	H-4	4.08, simplif. m		3.46, simplif. m
H-5 (2H)	1.76, m	H-5	2.76, simplif. m	2.66, m	2.66, simplif. m
H-6 (2H)	2.18, m	H-4	1.76, simplif. m	1.62, m	1.62, simplif. m
H-8' (1H)	2.18, m	H-5	2.18, simplif. m	2.19, m	2.19, simplif. m
	5.74, dd $J_{8'7'} = 16$ Hz $J_{8'4} = 8$ Hz	H-4	5.74, simplif. m	5.53, dd $J_{8'7'} = 16$ Hz $J_{8'4} = 8$ Hz	5.53, d, $J_{8'7'} = 16$ Hz
H-7' (1H)	6.40, d $J_{7'8'} = 16$ Hz			6.20, d $J_{7'8'} = 16$ Hz	
Aromatic protons	6.38, s, (1H) 6.4, s, (1H) 6.66, s, (1H) 6.71, s, (1H)			6.62 – 6.72 m, (6H)	
OMe	3.62, s, (3H) 3.66, s, (3H) 3.72, s, (6H) 3.78, s, (6H)			3.69, s, (3H) 3.76, s, (3H) 3.78, s, (6H)	

^a All spectra run in CDCl_3 , chemical shifts measured in δ .

Neither substance shows any Cotton effects in the CD and they must therefore be racemic. Theoretically a dimerisation of **3** by a Diels-Alder reaction could lead to **1**, and similar dimerisation of **4** could yield **2**. It was therefore of the greatest interest that the monomer **5**, closely related to **4** could be isolated in considerably greater quantity than either **1** or **2** i. e. **1**, 40 mg, **2** 20 mg and **5** 1000 mg.

Compound **5** at room temperature is a colourless oil with molecular formula $^{12}\text{C}_{12}\text{H}_{16}\text{O}_3$ (M^+ , 208.1099), base peak 177; λ_{max} (CHCl_3), 260 (4.15), 264 (4.14), 290 (3.66), 300 nm (3.62), ν_{max} 3450, 1600, 965 cm^{-1} .

Oxidation of compound **5** with the appropriate reagents gave veratric acid and veratraldehyde. This taken together with the ^{13}C and ^1H NMR spectra, assigned as in Table III and **6** serve to unambiguously define structure **5**. As noted previously the correspondence in the ^{13}C NMR spectra between CS2 and **5** serve to confirm the structure of CS2.

In view of our isolation of cassumunaquinones **2** and **1** **8** together with allflabene **1** and cassumunene **2** it is possible to imagine a hypothetical biosynthetic scheme (Fig. 1) which serves to unify the biosyn-

Table II. ^{13}C NMR of cassumunar substances **1** and **2** ^{a, b, c, d}

Carbon atom	CS1	Calcd. value	CS2	Calcd. value
1	128.1 ⁺		128.0 ⁺	
2	131.9		132.4	
3	41.6		45.8	
4	37.3		42.6	
5	24.1		24.4	
6	25.5		24.8	
8'	129.6 ⁺		129.2 ⁺	
7'	122.7		122.0	
1'	122.6	116.9	131.2	131.3
2'	151.8	151.2	108.8	113.1
3'	98.4	100.9	149.0 [*]	145.7
4'	148.8 [*]	146.0	148.2 [*]	145.0
5'	143.4	138.0	113.8	115.3
6'	110.1	114.1	118.8	119.8
1''	119.7		133.9	
2''	150.9		110.5	
3''	97.4		148.3 [*]	
4''	148.0 [*]		147.6 [*]	
5''	142.5		111.3	
6''	115.2		128.6 ⁺	

^a All spectra in CDCl_3 , chemical shifts measured in p.p.m. downfield from TMS. ^b All assignments supported by the multiplicity of the signal in the off-resonance spectrum.

^c Identical signs indicate interchangeable assignments.

^d 1' – 6' refer to the styryl aromatic ring, 1'' – 6'' refer to the aromatic ring attached to C-3.

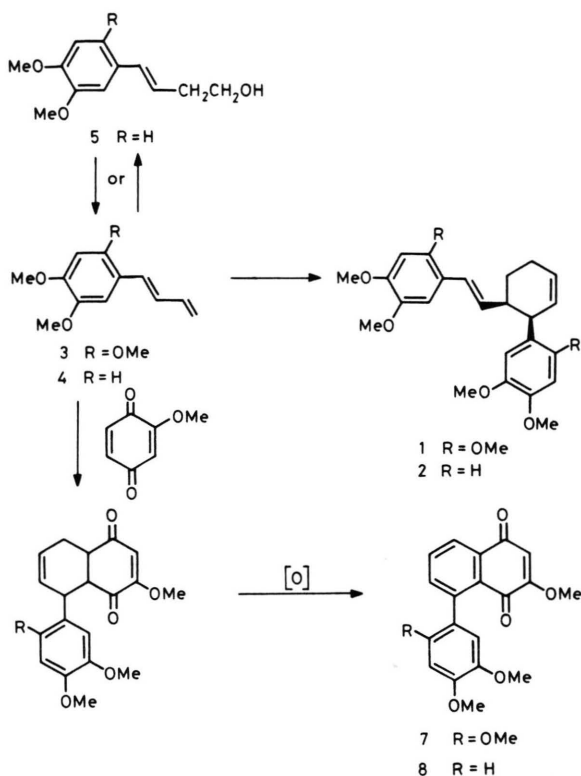


Fig. 1. Hypothetical biosynthetic scheme.

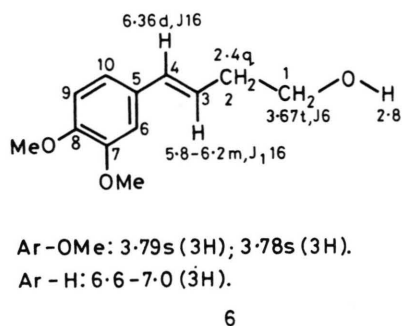
thesis of those compounds we have isolated. Clearly a monomer corresponding to **5** but with R = OMe, (Fig. 1) is missing and we are currently searching for this compound.

The question as to whether or not the dimers and the quinones are "natural products" cannot be satis-

Table III. ^{13}C NMR spectra of monomer **5** and CS2.

	Monomer 5		CS2
C-1	61.9		—
C-2	36.3		—
C-3	131.9	C-8'	129.2
C-4	124.7	C-7'	122.0
C-5	130.7	C-1'	131.2
C-6	108.9	C-2'	108.8
C-7	149.1	C-3'	149.0
C-8	148.5	C-4'	148.2
C-9	111.4	C-5'	113.8
C-10	119.1	C-6'	118.8

Signal at δ 3.67 moves to δ 4.11 on acetylation.



Scheme. Signal at δ 3.67 moves to δ 4.11 on acetylation.

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