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Further Characterization of the Constituents of a Thai Medicinal Plant, *Zingiber cassumunar* Roxb.[1]

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Thirteen aromatic compounds, having C_6–C_4, C_6–C_8–C_6 or C_6–C_{10} carbon skeletons, were isolated from the rhizomes of a Thai medicinal plant, *Zingiber cassumunar*. Eight compounds were new among these, and their structures were elucidated as **6**, **7**, **8**, **9**, **10**, **11**, **12**, and **13** by chemical and spectral methods. The structures were confirmed by ^{13}C-NMR spectroscopy.

Keywords——*Zingiber cassumunar*; Zingiberaceae; "plai"; 3-phenyl-4-styryl-cyclohex-1-enes; 1-(3,4-dimethoxyphenyl)butadiene; 1-phenylbut-1-enes; 2-methoxy-8-phenylnaphthoquinones; structure elucidations; ^{13}C-NMR

Zingiber cassumunar Roxb. (Zingiberaceae), commonly known as 'plai', is a traditional Thai herbal drug used as an embrocation.[3] When we started work on the constituents of the rhizomes of the plant in 1969, little was known about them. After our preliminary surveys[4] the topic was set aside for nearly ten years, but recently we took up this work again. The results thus far obtained are presented here.

The chloroform extract of the rhizomes was separated by silica gel column and preparative thin-layer chromatographies to give thirteen constituents, **1**—**13**. The results of other research on the same material were recently published, and the structures of six constituents were established by Amatayakul and her associates.[5] Five of the compounds isolated in our experiments, *i.e.* *cis*-3-(3,4-dimethoxyphenyl)-4-[(*E*)-3,4-dimethoxystyryl]cyclohex-1-ene (**1**), *cis*-3-(2,4,5-trimethoxyphenyl)-4-[(*E*)-2,4,5-trimethoxystyryl]cyclohex-1-ene (alflabene[6]) (**2**), *cis*-3-(3,4-dimethoxyphenyl)-4-[(*E*)-2,4,5-trimethoxystyryl]cyclohex-1-ene (**3**), (*E*)-4-(3,4-dimethoxyphenyl)but-3-en-1-ol (**4**), and 8-(3,4-dimethoxyphenyl)-2-methoxynaphtho-1,4-quinone (**5**), are among those characterized,[5] and their identities were established by comparison of the spectral data. The structures of the other eight compounds, **6**, **7**, **8**, **9**, **10**, **11**, **12** and **13**, were elucidated by spectral and chemical procedures as described below.

The compound **9**, mp 61—62°, $C_{28}H_{46}O_4$, has an ester group (ν_{max} 1728, 1236 cm^{-1}) and a long chain alkyl group (δ 1.27 (s, methylene), 0.89 (t, methyl)). The proton magnetic resonance

1) This paper constitutes Part VIII of Studies on Thai Medicinal Plants. Part VII: P. Chantarasomboon, K. Yoshihira, S. Natori, K. Watanabe, Y. Goto, and M. Kugo, *Shoyakugaku Zasshi*, **28**, 7 (1974).
2) Location: *a) 2-2-1, Oshika, Shizuoka 422, Japan*; *b) Kamiyoga 1-chome, Setagaya-ku, Tokyo 158, Japan*; *c) Yod-Se, Bangkok, Thailand*; *d) 11 Nanakuma, Nishi-ku, Fukuoka 814, Japan.*
3) S. Phongbunrod, "Maithet Muang Thai," Kasaem Bannakit, Bangkok, 1965, p. 373.
4) S. Natori, M. Kuroyanagi, and T. Dechatiwongse, presented at the Annual Meeting of the Japanese Society of Pharmacognosy, Abstracts of Papers, 1969, p. 52; T. Dechatiwongse and K. Yoshihira, *Bull. Dep. Med. Sci.* (Thailand), **15**, 1 (1973).
5) T. Amatayakul, J.R. Cannon, P. Dampawan, T. Dechatiwongse, R.G.F. Giles, C. Huntrakul, K. Kusamuran, M. Mokkhasamit, C.L. Raston, V. Reutrakul, and A.H. White, *Aust. J. Chem.*, **32**, 71 (1979).
6) I. Mori, Y. Nakachi, K. Ueda, D. Uemura, and Y. Hirata, *Tetrahedron Lett.*, **1978**, 2297.

(PMR) signal pattern of **9** except for the signals of the long chain fatty acid residue is superimposable on that of **4**. These data suggested that **9** is the palmitate of **4**, and the structure was confirmed by the preparation of the palmitate from **4**.

The compound **12**, an oil, $C_{12}H_{14}O_2$, has a phenyl group bearing two methoxyl groups (δ 3.81 (3H, s), 3.83(3H, s)) and a butadienyl group (δ 6.00—6.22 (3H, m), 4.95—5.39 (2H, m)). The PMR suggested that the substitution pattern of the methoxyl groups on the phenyl group is the same as that of **4**. These observation indicated the structure (*E*)-1-(3,4-dimethoxyphenyl)butadiene for **12**. The structure was confirmed by synthesis from veratrum aldehyde (**20**) through **21** by means of the Grignard reaction and dehydration (Chart 2). The geometry of **12** was considered to be *trans* from the course of the synthesis.[6]

The compound **10**, an oil, $C_{12}H_{16}O_2$, and the compound **11**, an oil, $C_{13}H_{18}O_3$, have an ethylvinyl side chain [δ 1.07 (3H, t, J=7 Hz), 2,20 (2H, m), 6.00 (1H, dt, J=16, 5 Hz), 6.32 (1H, d, J=16 Hz) in **10** and δ 1.09 (3H, t, J=7 Hz), 2.22 (2H, m), 6.05 (1H, dt, J=16, 5 Hz), 6.71 (1H, d, J=16 Hz) in **11**], in which the olefinic groups are *trans* (J=16 Hz). In the PMR spectra two singlet signals for aromatic protons and those for three methoxyl groups [δ 3.76 (3H) and 3.83 (6H)] appeared for **11**, while three aromatic protons with a signal pattern similar to that of **9** and signals of two methoxyl groups [δ 3.76 (3H) and 3.83 (3H)] appeared for **10**. These data suggested that the structures of **10** and **11** were (*E*)-1-(3,4-dimethoxyphenyl)but-1-ene and (*E*)-1-(2,4,5-trimethoxyphenyl)but-1-ene, respectively. These structures were confirmed by synthesis from veratrole (**14**) and 1,2,4-trimethoxybenzene (**15**), respectively, by means of the Friedel–Craft reaction followed by reduction and dehydration (Chart 2).

The compound **7**, mp 81—82°, $C_{24}H_{28}O_4$, has the same molecular formula as **1** and a similar infrared (IR) spectrum. The ultraviolet (UV) spectrum of **7** is superimposable on that of **1** but not on those of **2** and **3** (Fig. 1). These observations suggested that the compound has the same chromophore as **1** but not **2** and **3**. Mass spectra (MS) of **7** and **1** showed similar fragmentation patterns, *i.e.* the base peaks of both compounds, considered to be due to retro-Diels–Alder cleavage (Chart 1), were observed at *m/e* 190 and main fragments at *m/e* 175 and 159. PMR spectra of both compounds showed the presence of four methoxyl groups on aromatic rings, six aromatic protons, four olefinic protons, and methylene and methine protons, but the signal patterns showed slight differences. These data suggested that **7** is a stereoisomer

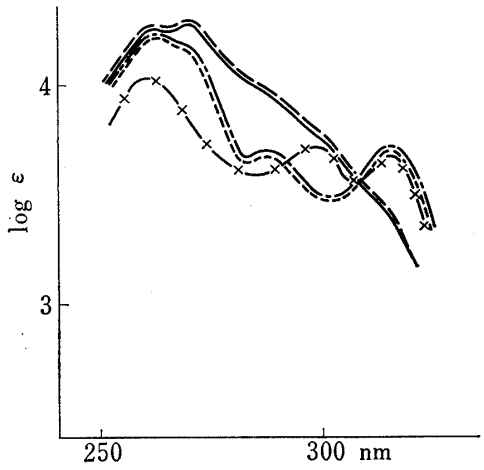
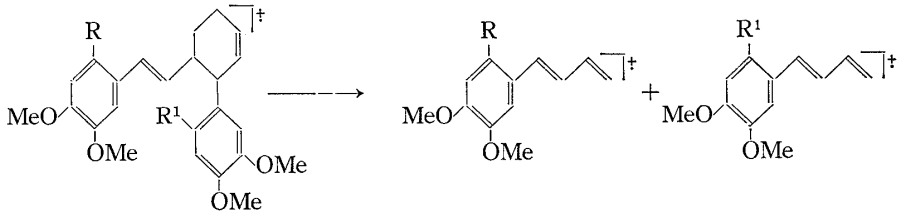


Fig. 1. UV Spectra of C_6–C_8–C_6 Type Compounds (in EtOH)

1: ———, **7**: – – – –, **3**: ————, **8**: – – – – –, **2**: – × – ×.



1, **7**: R=R¹=H	M^+ *m/e* 380	*m/e* 190	*m/e* 190
3, **8**: R=OMe, R¹=H	M^+ *m/e* 410	*m/e* 220	*m/e* 190
2: R=R¹=OMe	M^+ *m/e* 440	*m/e* 220	*m/e* 220
6: R=H, R¹=OMe	M^+ *m/e* 410	*m/e* 190	*m/e* 220

Chart 1

Table I. ^1H Chemical Shifts of the C_6–C_4 and

Compd.	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9
1	arom. H 6.71 (br. s)		OMe 3.70 or 3.82 (s)		arom. H 6.71 (br. s)	CH 6.24 (d, J=16)	CH 5.51 (dd, J=16, 9)	CH 2.69 (m)
2	OMe 3.70, 3.72, 3.80 or 3.85	arom. H 6.47 (s)	OMe 3.70, 3.72, 3.80 or 3.85		arom. H 6.68 or 6.72 (s)	CH 6.43 (d, J=15)	CH 5.75 (dd, J=15, 8)	CH 2.80 (m)
3	OMe 3.75 or 3.83 (s)	arom. H 6.43 (s)	OMe 3.75 or 3.83 (s)		arom. H 6.70 (s)	CH 6.55 (d, J=16)	CH 5.52 (dd, J=16, 8)	CH 2.77 (m)
8	OMe 3.73, 3.84 or 3.87 (s)	arom. H 6.47 (s)	OMe 3.73, 3.84 or 3.87 (s)		arom. H 6.90 (s)	CH 6.48 (d, J=16)	CH 6.16 (dd, J=16, 7.5)	CH 2.30 (m)
6	arom. H 6.73 (br. s)		OMe 3.79, 3.85 or 3.86 (s)		arom. H 6.73 (br. s)	CH 6.14 (d, J=16)	CH 5.88 (dd, J=16, 8)	CH 2.74 (m)
7	arom. H 6.74 (m)		OMe 3.81, 3.83 or 3.85 (s)		arom. H 6.74 (m)	CH 6.19 (d, J=15)	CH 5.88 (dd, J=15, 2)	CH 2.17 (m)
4	arom. H 6.87 (dd, J=8, 1.5)	arom. H 6.64 (d, J=8)	OMe 3.79 or 3.80 (s)		arom. H 6.71 (d, J=1.5)	CH 6.35 (d, J=16)	CH 5.93 (d, t, J=16, 6)	CH_2 2.42 (q, J=6)
9	arom. H 6.83 (m)		OMe 3.88—3.90 (s)		arom. H 6.83 (m)	CH 6.42 (d, J=16)	CH 5.97 (d, t, J=16, 6)	CH_2 2.54 (q, J=7)
10	arom. H 6.90 (dd, J=8, 1.5)	arom. H 6.65 (d, J=8)	OMe 3.79 or 3.82 (s)		arom. H 6.75 (d, J=1.5)	CH 6.32 (d, J=16)	CH 6.00 (d, t, J=16, 5)	CH_2 2.20 (m)
11	OMe 3.76 or 3.83 (s)	arom. H 6.60 (s)	OMe 3.76 or 3.83 (s)		arom. H 6.60 (s)	CH 6.71 (d, J=16)	CH 6.05 (d, t, J=16, 5)	CH_2 2.22 (m)
12	arom. H 6.70—6.93 (m)		OMe 3.81 or 3.83 (s)		arom. H 6.70—6.93 (m)	CH	CH 6.00—6.62 (m)	CH

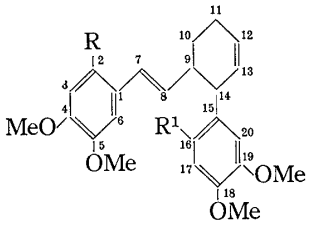
a) The following tentative numberings are used:

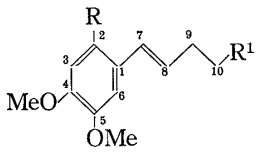
or a position isomer of **1**. Dehydrogenation of both compounds, **1** and **7**, with DDQ gave the same product (**22**), but catalytic hydrogenation of the compounds gave different products, **23** and **24**, respectively. These results indicated that **7** is *trans*-3-(3,4-dimethoxyphenyl)-4[(*E*)-3,4-dimethoxystyryl]-cyclohex-1-ene, *i.e.*, the diastereomer (*trans* isomer) of **1** which had been established to be the *cis* isomer by Amatayakul *et al.*[5]

The compound **8**, mp 108—110°, $C_{25}H_{30}O_5$, has the same molecular formula as **3** and showed an MS fragmentation pattern similar to that of **3**, *i.e.* the base peak at *m/e* 220 and a main fragment at *m/e* 190, considered to be due to retro-Diels–Alder cleavage (Chart 1). The UV spectrum of **8** is superimposable on that of **3** (Fig. 1). The PMR spectrum of **8** showed the presence of five methoxyl groups on aromatic rings, five aromatic protons, four olefinic

C_6–C_8–C_6 Type Compounds (in $CDCl_3$)

C-No.[a]									
C-10	C-11	C-12	C-13	C-14	C-16	C-17	C-18	C-19	C-20
CH_2 1.68(br. t, J=7)	CH_2 2.24 (m)	CH 5.56—6.07 (m)	CH	CH 3.51 (m)	arom. H 6.71 (br. s)		OMe 3.73 or 3.87		arom. H 6.71 (br. s)
CH_2 1.81(br. t, J=6)	CH_2 2.18 (m)	CH 5.60—5.95 (m)	CH	CH 4.15 (m)	OMe 3.70, 3.72, 3.80 or 3.85 (s)	arom. H 6.47	OMe 3.70, 3.72, 3.80 or 3.85		arom. H 6.68 or 6.72
CH_2 1.68(br. t, J=6)	CH_2 2.20 (m)	CH 5.55—6.13 (m)	CH	CH 3.52 (m)	arom. H 6.59—6.85 (m)		OMe 3.75 or 3.83		arom. H 6.59—6.85 (m)
CH_2 1.85 (m)	CH_2 2.22 (m)	CH 5.55—5.90 (m)	CH	CH 3.20 (m)	arom. H 6.70—6.80 (m)		OMe 3.73, 3.84 or 3.85		arom. H 6.70—6.80 (m)
CH_2 1.74 (br. q, J=6.5)	CH_2 2.20 (m)	CH 5.6—5.95 (m)	CH	CH 4.14 (m)	OMe 3.69 (s)	arom. H 6.46 (s)	OMe 3.79, 3.85 or 3.86		arom. H 6.77 (s)
CH_2 1.88 (m)	CH_2 2.17 (m)	CH 5.47—5.90 (m)	CH	CH 3.17 (m)	arom. H 6.74 (m)		OMe 3.81, 3.83 or 3.85		arom. H 6.74 (m)
CH_2–OH 3.68(t, J=6)	2.73 (br. s)								
CH_2—O—CO—CH_2—CH_2—$(CH_2)_{12}$—CH_3 4.17(t, J=7)	2.30(t, J=7)	1.60 (m)	1.27 (s)	0.89(t, J=6)					
CH_3 1.07(t, J=7)									
CH_3 1.09(t, J=7)									
CH_2 4.95—5.39 (m)									





protons, and methylene and methine protons as in the case of **3**. These results indicated that the compound is a stereoisomer of **3** as **7** is of **1**. The PMR signal pattern of the cyclohexene portion of **8** was similar to that of **7** (*trans* isomer) but different from that of **3** (*cis* isomer) (Table 1). The compounds **3** and **8** were dehydrogenated with DDQ to give the same product (**25**). In the case of **8**, another product (**26**) was also obtained. The molecular formulae of **25** and **26** ($C_{25}H_{24}O_5$ by MS) indicated that both compounds were formed by dehydrogenation with DDQ accompanied by intramolecular cyclodehydrogenation.[7] The presence of a phe-

7) J.M. Matheson, O.C. Musgrave, and C.J. Webster, *Chem. Commun.*, **1965**, 278; A.B. Turner, "Synthetic Reagents," Volume 3, ed. by J.S. Pizey, John Wiley and Sons, Inc., New York, 1977, p. 193.

nanthrene skeleton was confirmed by the UV[8] and PMR[9] spectra of **25** and **26**. The proton at C-8 of **25** (δ 7.54—7.75) appeared at higher field than that of **26** (δ 7.62—7.92) and the proton at C-1 of **26** (δ 6.97) appeared at higher field compared with that of **25** (δ 7.11) due to the anisotropy[10] of the trimethoxyphenyl group. Thus, the structure of **25** was assigned as 2,3-dimethoxy-9-(2,4,5-trimethoxyphenyl)phenanthrene and that of **26** as 2,3-dimethoxy-10-(2,4,5-trimethoxyphenyl)-phenanthrene. The formation of **25** could be explained in terms of a shift of the trimethoxyphenyl group to the neighboring carbon in the course of the dehydrogenation reaction. The mechanism of the migration reaction and the difference between **3** and **8** as regards dehydrogenation require further study. Catalytic hydrogenation of **3** and **8** gave the corresponding tetrahydro derivatives, **27** and **28**, respectively. These results indicated that **8** is a diastereomer (*trans* isomer), *i.e. trans*-3-(3,4-dimethoxyphenyl)-4-[(*E*)-2,4,5-trimethoxystyryl]cyclohex-1-ene, of **3**, which was shown to be the *cis* isomer.[5]

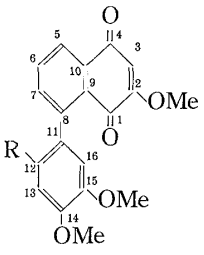
The compound **6**, a viscous oil, $C_{25}H_{30}O_5$, has the same molecular formula as **3** and showed a similar MS fragmentation pattern, *i.e.* the base peak at *m/e* 220 and the dominant fragment peak at *m/e* 190 formed by the retro-Diels–Alder cleavage (Chart 1). The PMR signal pattern of the cyclohexene portion of **6** was similar to that of **2**, which was elucidated as a *cis* analog having an additional methoxyl group by X-ray analysis.[5] The PMR signal pattern due to

Table II. ^{1}H Chemical Shifts of C_6–C_{10} Type Compounds (in $CDCl_3$)

Compd.	C-No.[a] C-2	C-3	C-5	C-6	C-7
5	OMe 3.84, 3.86 or 3.93	quinoid H 6.16(s)	arom. H 8.17(dd, J=7.8, 1.8)	arom. H 7.70(t, J=7.8)	arom. H 7.52(dd, J=7.8, 1.8)
13	OMe 3.83, 3.86 or 3.95	quinoid H 6.13(s)	arom. H 8.16(dd, J=7.8, 1.8)	arom. H 7.69(t, J=7.8)	arom. H 7.51(dd, J=7.8, 1.8)

Compd.	C-No.[a] C-12	C-13	C-14	C-15	C-16
5	arom. H 6.77(dd, J=8.5, 2)	arom. H 6.92(d, J=8.5)	OMe 3.84, 3.86 or 3.93		arom. H 6.81(d, J=2)
13	OMe 3.64(s)	arom. H 6.59(s)	OMe 3.83, 3.86 or 3.95		arom. H 6.71(s)

a) The following tentative numberings are used:



8) M.S. Newman and R.L. Childers, *J. Org. Chem.*, **32**, 62 (1967).
9) R.M.G. Bavin, K.D. Bartle, and J.A.S. Smith, *Tetrahedron*, **21**, 1087 (1965); Y. Nagai and H. Uno, *Chem. Pharm. Bull.*, **27**, 2056 (1979).
10) N.F. Chamberlain, "The Practice of NMR Spectroscopy," Plenum Press, New York and London, 1974, p. 206.

the (*E*)-olefin conjugated to the phenyl group was similar to that of **1**, having two methoxyl groups at C-3 and C-4 on the A-ring. These data suggested that the compound **6** has two methoxyl groups on the A-ring and three methoxyl groups on the C-ring, and a *cis* configuration of the phenyl and the styryl groups on the cyclohexene ring. Thus, the structure of **6** was shown to be *cis*-4-[(*E*)-3,4-dimethoxystyryl]-3-(2,4,5-trimethoxyphenyl)cyclohex-1-ene.

Although the compounds **6**, **7**, and **8** have two asymmetric centers, these compounds did not show optical rotation, as in the case of compounds **1**, **2**, and **3**,[5] indicating that they are present as racemates.

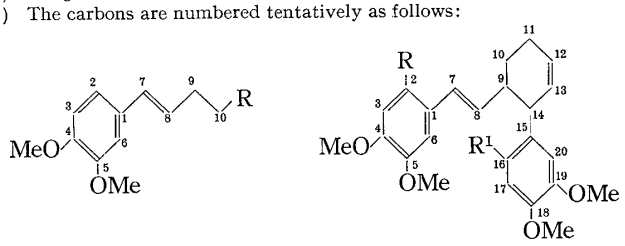
The compound **13**, mp 164—165°, $C_{20}H_{18}O_6$, showed UV and IR spectra similar to those of **5**, which was shown to be a naphthoquinone derivative.[5] The PMR spectrum of **13** showed almost the same signal pattern as that of **5** except for the aromatic protons on the phenyl ring; *i.e.*, compound **13** has two singlet aromatic protons and three methoxyl groups on the phenyl ring. These data indicated that **13** is 2-methoxy-8-(2,4,5-trimethoxyphenyl)-naphtho-1,4-quinone.

^{13}C-Nuclear magnetic resonance (^{13}C-NMR) spectroscopy gave further support to the structures, especially as regards the stereochemistry, of the compounds **1**—**3** and **6**—**8**. The

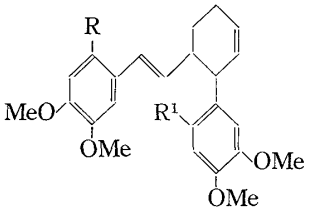
Table III. ^{13}C Chemical Shifts[a] of C_6–C_4 Type and C_6–C_8–C_6 Type Compounds (in $CDCl_3$)

C-No.	Compd.								
	1	**2**	**3**	**6**	**7**	**8**	**4**	**9**	**10**
C-1[b]	131.0	119.8	119.1	131.5	131.0	118.9	130.5	130.5	131.3
C-2	118.8	150.9	150.9	118.6	118.8	150.9	119.1	119.1	118.9
C-3	111.2	98.5	98.2	111.1*	111.3*	98.1	111.3	111.3	111.4
C-4	148.1*	148.8	148.9*	147.8	148.1**	148.5*	148.6	148.7	148.3
C-5	149.0*	143.5	143.5	148.8	149.0**	143.3	149.1	149.0	149.2
C-6	108.9	110.2	109.9	108.6*	108.9**	109.7	108.8	108.9	108.9
C-7	128.5	122.7	122.8	128.2	128.8	123.2	132.4	132.0	128.5
C-8	132.4	131.9	132.8	131.5	132.2	132.4	124.4	123.7	130.7
C-9	42.6	41.6	42.9	41.3	45.4	45.6	36.4	32.5	26.0
C-10	24.4	25.5	24.4	25.2	27.9	27.9	62.1	63.5	13.8
C-11	24.8	24.1	24.9	24.1	24.6	24.6			
C-12	128.0	128.0	128.0	128.0	127.5	127.5			
C-13	129.1	129.7	129.2	129.6	130.3	130.3			
C-14	45.8	37.3	45.9	37.2	48.0	48.1			
C-15	133.9	122.7	134.1	122.1	137.6	137.6			
C-16	121.9	151.8	122.0	151.6	120.4	120.3			
C-17	110.5	97.5	110.5	97.0	110.0	110.8			
C-18	147.6	148.0	147.6	147.8	147.4	147.2			
C-19	148.1*	142.5	148.2*	142.3	148.6**	148.9*			
C-20	113.7	115.3	113.8	115.0	111.7	111.7			
OMe	55.9	56.9	56.7	56.7	55.8	56.8	55.9	56.0	55.9
	55.8	56.7	56.5	56.3		56.6	55.8		55.8
		56.4	56.1	56.1		56.0			
		56.2	55.9	55.9		55.8			
			55.8	55.7					

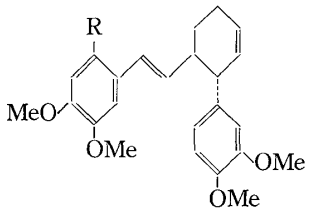
a) Assignments with asterisks in a given column may be reversed.
b) The carbons are numbered tentatively as follows:



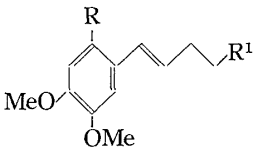
assignments of the chemical shifts of the compounds were based on the SCS value of mono-substituted benzenes,[11] the olefinic carbon shieldings of some alkyl and phenyl cyclohexenes,[12] selective decouplings, and relative correlations of the compounds (Table III). The configuration of the cyclohexene ring affects the chemical shifts of the methine carbons at C-9[13] and C-14, the methylene carbon at C-10 and the aromatic carbons at C-15, C-16 and C-20. As shown in Fig. 2, the signals of the methylene carbon at C-10, the methine carbons at C-9 and C-14, and the aromatic carbon at C-15 of the *trans* isomers (**7** and **8**) showed lower field shifts, and those of the aromatic carbons at C-16 and C-20 of the *trans* isomers showed higher field shifts, compared with the *cis* isomers (**1** and **3**). The substitution pattern of the methoxyl group on the phenyl ring affects the chemical shifts of carbons such as C-1, C-2, C-3, C-5, C-6, C-9, C-14, C-15, C-16, C-17, and C-20. The signals of methine carbons at C-9 and C-14 and



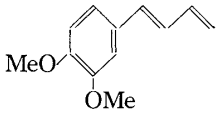
1: R=R¹=H
2: R=R¹=OMe
3: R=OMe, R¹=H
6: R=H, R¹=OMe



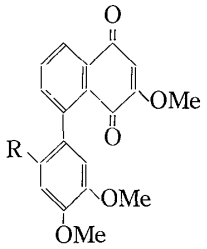
7: R=H
8: R=OMe



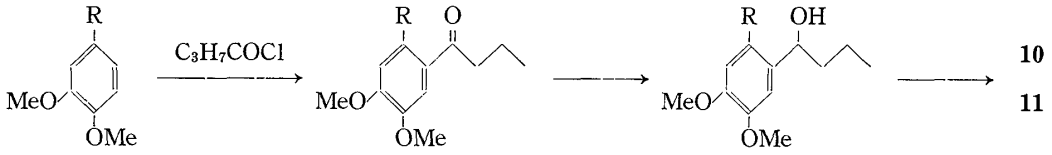
4: R=H, R¹=OH
9: R=H, R¹=O-pal
10: R=R¹=H
11: R=OMe, R¹=H



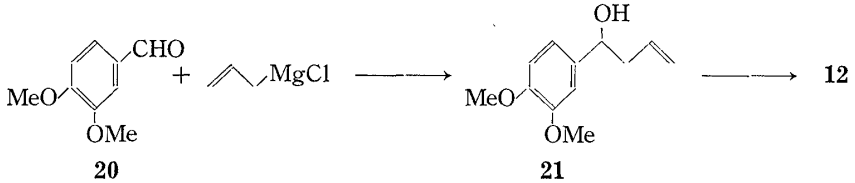
12



5: R=H
13: R=OMe



14: R=H
15: R=OMe
16: R=H
17: R=OMe
18: R=H
19: R=OMe
10
11



20
21
12

Chart 2

11) J.B. Stothers, "Carbon 13 NMR Spectroscopy," Academic Press, New York, 1972, p. 196.
12) T.K. Wu and B.P. Dailey, *J. Chem. Phys.*, **41**, 2796 (1964).
13) The numberings of carbon atoms adopted for the discussion of ^{13}C-NMR are those shown in Table III as a matter of convention.

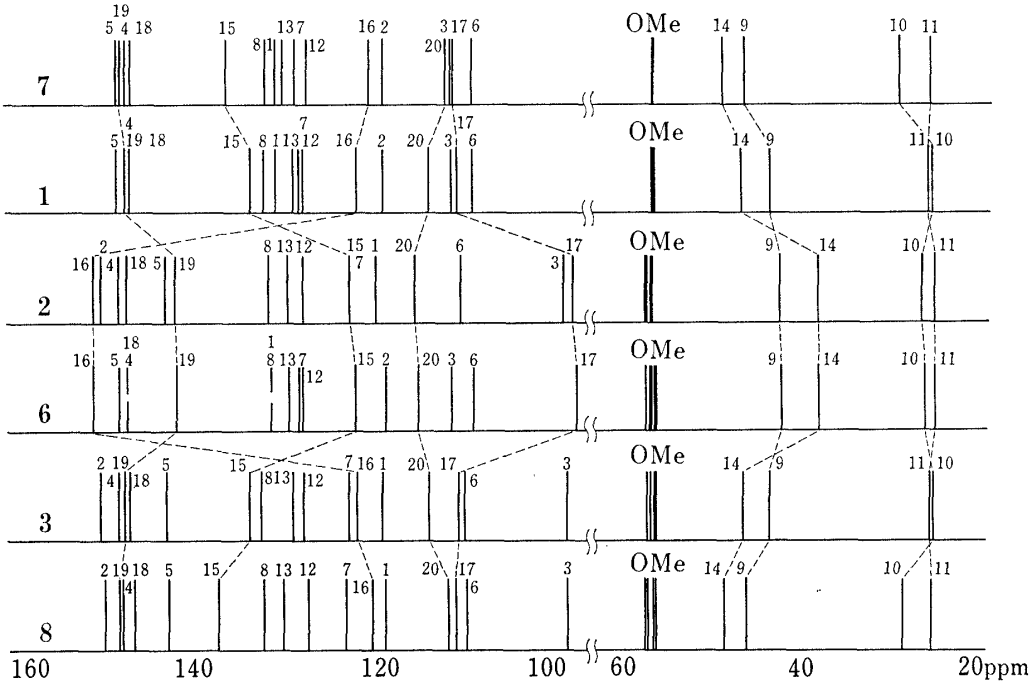
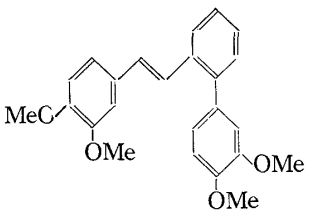
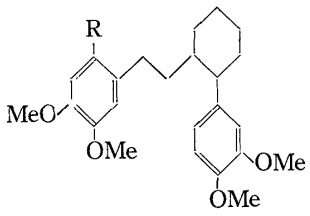


Fig. 2. Stick Diagram of the ^{13}C Chemical Shifts of C_6–C_8–C_6 Type Compounds

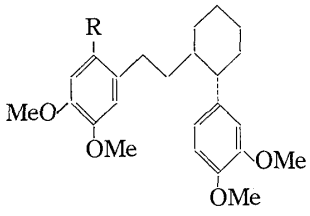
The numberings of carbon atoms are those adopted in Table III.



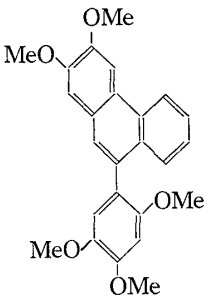
22



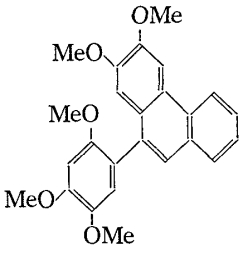
23: R=H
27: R=OMe



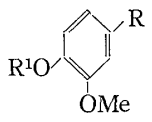
24: R=H
28: R=OMe



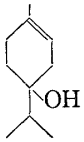
25



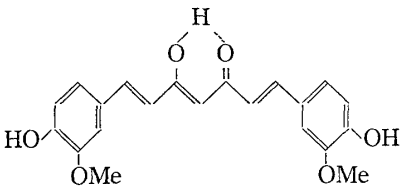
26



29: R=CHO, R^1=H
30: R=COOH, R^1=H
31: R=COOH, R^1=Me



32



33

Chart 3

aromatic carbons at C-15 and -17 of **2** and **6**, having a methoxyl group at C-16, appeared at higher field compared with the compounds having no methoxyl group at C-16, such as **1** and **3**. Thus the stereochemistries of **7** and **8** and the structure of **6** were confirmed.

Several known compounds, *i. e.*, vanillin (**29**), vanillic acid (**30**), veratric acid (**31**), terpinen-4-ol (**32**) and curcumin (**33**),[14] which is a common constituent (having a C_6–C_7–C_6 carbon skeleton) of *Curcuma longa* and other *Curcuma* spp., were also identified from the rhizomes.

Of the compounds isolated from the rhizomes, compounds **1**—**3** and **6**—**8** have a C_6–C_8–C_6 carbon skeleton, compounds **4** and **9**—**12** have a C_6–C_4 carbon skeleton, and compounds **5** and **13** have a C_6–C_{10} carbon skeleton. C_6–C_8–C_6 type compounds are rare as natural products, and C_6–C_4 type compounds are not particularly common. The C_6–C_8–C_6 type compounds may be formed by a Diels–Alder dimerization of C_6–C_4 type compounds. The isolation of the diene type compound, **12**, which may be converted to **1** or **6** by dimerization, supports this biogenetic hypothesis. The coexistence of the C_6–C_8–C_6 and C_6–C_4 type compounds with a C_6–C_7–C_6 type compound (curcumin)[15] is noteworthy from the standpoint of the biogenesis of these compounds.

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO IRA-2 machine, and UV spectra on a Hitachi model 200-10 spectrometer. Optical rotations were determined on a JASCO DIP-180 automatic polarimeter. PMR spectra were recorded on Hitachi R-24B (60 MHz) and Hitachi R-22 (90 MHz) machines with tetramethylsilane as an internal standard (δ value). ^{13}C-NMR were recorded on a JEOL FX-100 spectrometer with tetramethylsilane as an internal standard (δ value). MS were recorded on JEOL JMS 01SG-2 and Hitachi RMS-4 machines. Column chromatography was carried out on silica gel (Wakogel C-200). Preparative TLC (PLC) was carried out using Kieselgel PF_{254} (Merck $200 \times 200 \times 0.7$ mm). Analytical TLC was carried out using Kieselgel $60F_{254}$ (Merck).

Isolation of Constituents——Dried, chipped rhizomes of *Z. cassumunar* (2 kg) were extracted with chloroform at room temperature. The chloroform extract (60 g) was chromatographed on a silica gel column using a benzene–ethyl acetate gradient system as the developer to give many fractions, which were combined to give ten fractions, fractions I—X, on the basis of TLC. Fraction I was chromatographed on a silica gel column to give three fractions, fractions I-1, I-2, and I-3. Fraction I-1 was rechromatographed to give **12** (50 mg) and **10** (60 mg). Fraction I-2 was purified by PLC to give **11** (30 mg) and fraction I-3 gave a crystalline compound, which was recrystallized from ethanol to give **9** (200 mg). Fraction II gave terpinen-4-ol (**32**, 3.2 g). Fraction III gave a crystalline compound, which was recrystallized from ethanol to give **7** (1.3 g), and the mother liquor was rechromatographed to give **7** (2.0 g) and vanillin (**29**) (100 mg). Fraction IV gave a crystalline compound, which was recrystallized from ethanol to give **1** (2.0 g), and the mother liquor was purified by column chromatography to give a further crop of **1** (2.3 g). Fraction V gave a crystalline compound, which was recrystallized from ethanol to give **3** (400 mg). Fraction VI was purified by PLC (benzene–EtOAc, 5 : 1) to give **6** (300 mg). Fraction VII was chromatographed on silica gel to give **8** (250 mg), which was recrystallized from *n*-hexane–benzene. Fraction VIII gave a crystalline compound, which was recrystallized from ethanol to give **2** (500 mg). Fraction IX showed many colored spots on TLC, and was separated by repeated PLC (benzene–EtOAc, 5 : 1) to give curcumin (**33**) (150 mg), **5** (120 mg), **13** (30 mg), veratric acid (**31**) (60 mg) and vanillic acid (**30**) (50 mg). Fraction X gave an oil (**4**) (1.5 g).

***cis*-3-(3,4-Dimethoxyphenyl)-4-[(*E*)-3,4-dimethoxystyryl]cyclohex-1-ene** (**1**)——mp 99—101° (from *n*-hexane–benzene) (lit.[5] mp 99.5—100.0°), $[\alpha]_D$ ±0° (MeOH), IR ν_{max}^{KBr} cm^{-1}: 1582, 1510, 1268, 1255; UV λ_{max}^{EtOH} nm (log ε): 262 (4.28), 268 (4.27), 286 (sh, 3.99), 300 (sh, 3.79), 312 (sh, 3.49). MS *m/e*: 380.190 (M^+) (Calcd for $C_{24}H_{28}O_4$, 380.199). *Anal.* Calcd for $C_{24}H_{28}O_4$: C, 75.76; H, 7.42. Found: C, 75.84; H, 7.48.

***cis*-3-(2,4,5-Trimethoxyphenyl)-4-[(*E*)-2,4,5-trimethoxystyryl]cyclohex-1-ene** (**2**)——mp 133—135° (from EtOH) (lit.[5] mp 134—135°), $[\alpha]_D$ ±0° (MeOH), IR ν_{max}^{KBr} cm^{-1}: 1603, 1506, 1225, 1206, UV λ_{max}^{EtOH} nm (log ε): 205 (4.53), 261 (4.03), 298 (3.75), 314 (3.72). MS *m/e*: 440.217 (M^+) (Calcd for $C_{26}H_{32}O_6$, 440.220). *Anal.* Calcd for $C_{26}H_{32}O_6$: C, 70.89; H, 7.32. Found: C, 70.95; H, 7.47.

***cis*-3-(3,4-Dimethoxyphenyl)-4-[(*E*)-2,4,5-trimethoxystyryl]cyclohex-1-ene** (**3**)——mp 110—112° (from MeOH) (lit.[5] mp 120.5—121.0°), $[\alpha]_D$ ±0° (MeOH), IR ν_{max}^{KBr} cm^{-1}: 1610, 1593, 1515, 1255; UV λ_{max}^{EtOH} nm (log ε):

14) V. Lampe, J. Milobedzka, and St. V. Kostanecki, *Ber.*, **43**, 2163 (1910); K.R. Srinivasan, *J. Pharm. Pharmacol.*, **5**, 448 (1953).

15) P.J. Roughley and D.A. Whiting, *J. Chem. Soc., Perkin I*, **1973**, 2379.

262 (4.28), 270 (4.20), 287 (3.76), 314.5 (3.72). MS *m/e*: 410.219 (M^+) (Calcd for $C_{25}H_{30}O_5$, 410.209). *Anal.* Calcd for $C_{25}H_{30}O_5$: C, 73.14; H, 7.37. Found: C, 73.35; H, 7.45.

***cis*-4-[(*E*)-3,4-Dimethoxystyryl]-3-(2,4,5-trimethoxyphenyl)cyclohex-1-ene** (**6**)——Viscous oil, $[\alpha]_D$ ±0° (MeOH), IR ν_{max}^{film} cm^{-1}: 1605, 1585, 1510, 1466, 1318, 1274, 1260, 1204, 1140, 1036, 970; UV λ_{max}^{EtOH} nm (log ε): 205 (4.83), 262 (4.29), 269 (sh, 4.28), 287 (4.08), 300 (sh, 3.98), 313 (sh, 3.56). MS *m/e*: 410.207 (M^+) (Calcd for $C_{25}H_{30}O_5$, 410.209).

***trans*-3-(3,4-Dimethoxyphenyl)-4-[(*E*)-3,4-dimethoxystyryl]cyclohex-1-ene** (**7**)——mp 81—82° (from EtOH), $[\alpha]_D$ ±0° (MeOH), IR ν_{max}^{KBr} cm^{-1}: 1582, 1515, 1260, 1232, 1139; UV λ_{max}^{EtOH} nm (log ε): 262 (4.27), 268 (4.27), 286 (sh, 3.99), 299 (sh, 3.77), 312 (sh, 3.49). MS *m/e*: 380.199 (M^+) (Calcd for $C_{24}H_{28}O_4$, 380.199). *Anal.* Calcd for $C_{24}H_{28}O_4$: C, 75.76; H, 7.42. Found: C, 76.06; H, 7.63.

***trans*-3-(3,4-Dimethoxyphenyl)-4-[(*E*)-2,4,5-trimethoxystyryl]cyclohex-1-ene** (**8**)——mp 108—110° (from *n*-hexane–benzene), $[\alpha]_D$ ±0° (MeOH), IR ν_{max}^{KBr} cm^{-1}: 1606, 1594, 1512, 1262, 1220, 1210, 1159, 1144; UV λ_{max}^{EtOH} nm (log ε): 262 (4.24), 269 (sh, 4.19), 287 (3.93). MS *m/e*: 410.210 (M^+) (Calcd for $C_{25}H_{30}O_5$, 410.209). *Anal.* Calcd for $C_{25}H_{30}O_5$: C, 73.14; H, 7.37. Found: C, 72.98; H, 7.39.

(*E*)-4-(3,4-Dimethoxyphenyl)but-3-en-1-ol (**4**)——Oil, IR ν_{max}^{film} cm^{-1}: 3380, 1600, 1583, 1515, 1268, 1240, UV λ_{max}^{EtOH} nm (log ε): 214 (4.32), 260 (4.18), 266 (sh, 4.16), 298 (sh, 3.70). MS *m/e*: 208 (M^+).

(*E*)-4-(3,4-Dimethoxyphenyl)but-3-en-1-yl Palmitate (**9**)——mp 61—62° (from EtOH), IR ν_{max}^{KBr} cm^{-1}: 1728, 1595, 1580, 1510, 1260, 1236; UV λ_{max}^{EtOH} nm (log ε): 260 (4.18), 267 (sh, 4.17), 294 (3.73), 299 (sh, 3.69), 312 (sh, 3.43). MS *m/e*: 446 (M^+). *Anal.* Calcd for $C_{28}H_{46}O_4$: C, 75.29; H, 10.38. Found: C, 75.62; H, 10.38.

(*E*)-1-(3,4-Dimethoxyphenyl)but-1-ene (**10**)——Oil, IR ν_{max}^{film} cm^{-1}: 1608, 1592, 1515, 1271; UV λ_{max}^{EtOH} nm (log ε): 213 (4.34), 260 (4.17), 266 (sh, 4.15), 298 (sh, 3.67). MS *m/e*: 192 (M^+).

(*E*)-1-(2,4,5-Trimethoxyphenyl)but-1-ene (**11**)——Oil, IR ν_{max}^{film} cm^{-1}: 1615, 1518, 1216, 1042; UV λ_{max}^{EtOH} nm (log ε): 207 (4.37), 259 (4.02), 267 (sh, 3.96), 314 (3.76). MS *m/e*: 222.129 (M^+) (Calcd for $C_{13}H_{18}O_3$, 222.126).

(*E*)-1-(3,4-Dimethoxyphenyl)butadiene (**12**)——Oil, IR ν_{max}^{film} cm^{-1}: 1595, 1506, 1265; UV λ_{max}^{EtOH} nm (log ε): 203 (4.26), 222 (sh, 3.90), 260 (sh, 3.64), 298 (sh, 3.30), 310 (sh, 3.20). MS *m/e*: 190.098 (M^+) (Calcd for $C_{12}H_{14}O_2$, 190.099).

8-(3,4-Dimethoxyphenyl)-2-methoxynaphtho-1,4-quinone (**5**)——mp 182—184° (from MeOH) (lit.[5] mp 181—182°), IR ν_{max}^{KBr} cm^{-1}: 1692, 1648, 1620, 1588, 1262, 1230, 1038; UV λ_{max}^{EtOH} nm (log ε): 204 (4.75), 236 (4.39), 248 (sh, 4.32), 275 (4.31). MS *m/e*: 324.103 (M^+) (Calcd for $C_{19}H_{16}O_5$, 324.100). *Anal.* Calcd for $C_{19}H_{16}O_5$: C, 70.36; H, 4.98. Found: C, 70.07; H, 4.99.

2-Methoxy-8-(2,4,5-trimethoxyphenyl)naphtho-1,4-quinone (**13**)——mp 164—165° (from MeOH), IR ν_{max}^{KBr} cm^{-1}: 1681, 1638, 1607, 1574, 1505, 1204, 1023, UV λ_{max}^{EtOH} nm (log ε): 205 (4.56), 240 (4.33), 276 (4.19), 317 (sh, 3.67). MS *m/e*: 354.113 (M^+) (Calcd for $C_{20}H_{18}O_6$, 354.110).

Vanillin (**29**)——mp 80—81° (from MeOH), IR ν_{max}^{KBr} cm^{-1}: 3130, 1672, 1594, 1432, 1303, 1270, 1160.

Vanillic Acid (**30**)——mp 213° (from benzene), IR ν_{max}^{KBr} cm^{-1}: 3745, 2940, 1682, 1600, 1300, 1247, 1212.

Veratric Acid (**31**)——mp 181.5—182.5° (from benzene), IR ν_{max}^{KBr} cm^{-1}: 2910, 1675, 1689, 1422, 1300, 1276, 1236.

Terpinen-4-ol (**32**)——Oil, IR ν_{max}^{film} cm^{-1}: 3440, 2900, 1460, 1435, 1375, 1066, 925, 887.

Curcumin (**33**)——mp 186—188° (from MeOH), IR ν_{max}^{KBr} cm^{-1}: 3450 (br), 1628, 1602, 1510, 1432, 1285, 1205, 1156, 1030, 964.

DDQ Dehydrogenation of 1——A solution of **1** (200 mg) and DDQ (360 mg) in dry benzene (30 ml) was refluxed for 1 hr and the reaction mixture was filtered. The filtrate was concentrated and the resulting viscous product was purified by PLC. Recrystallization from MeOH–$CHCl_3$ gave **22** (110 mg), mp 147—148°, IR ν_{max}^{KBr} cm^{-1} 1597, 1506, 1462, 1265, 1249, 1143, 1024, UV λ_{max}^{EtOH} nm (log ε): 207 (4.64), 291 (4.26), 317 (4.74), PMR (δ in $CDCl_3$): 3.82, 3.85, 3.90 (each 3H, 6H, 3H, s, OMe×4), 6.65—7.05 (6H, m, arom. H), 6.90 (2H, s, olefin H), 7.20—7.45 (3H, m, arom. H), 7.66 (H, dd, J=8, 3 Hz, arom. H). MS *m/e*: 376.174 (M^+) (Calcd for $C_{24}H_{24}O_4$, 376.168). *Anal.* Calcd for $C_{24}H_{24}O_4$: C, 75.90; H, 6.46. Found: C, 75.90; H, 6.46.

DDQ Dehydrogenation of 7——Compound **22** (70 mg), mp 143—145° (from MeOH–$CHCl_3$), was obtained from **7** (200 mg) and DDQ (360 mg); it was found to be identical with **22** obtained from **1** by TLC, IR and PMR.

DDQ Dehydrogenation of 3——Similar treatment of **3** (110 mg) with DDQ (160 mg) gave **25** (40 mg), mp 198—199° (from MeOH–$CHCl_3$), IR ν_{max}^{KBr} cm^{-1}: 1610, 1503, 1269, 1210, 1160, 1032; UV λ_{max}^{EtOH} nm (log ε): 203 (4.74), 257 (4.86), 279 (4.58), 307 (sh, 4.20), 336 (3.61), 354 (3.34); PMR (δ in $CDCl_3$): 3.54 (3H, s, OMe at C-2′), 3.74, 3.89, 3.90, 4.01 (each 3H, s, OMe×4), 6.60 (H, s at C-3′), 6.78 (H, s, at C-6′), 7.11 (H, s, at C-1), 7.25—7.55 (2H, m, at C-6 and -7), 7.47 (H, s, at C-10), 7.54—7.75 (H, m, at C-8), 7.92 (H, s, at C-4), 8.48 (H, m, at C-5). MS *m/e*: 404.164 (M^+) (Calcd for $C_{25}H_{24}O_5$, 404.163).

DDQ Dehydrogenation of 8——The reaction of compound **8** (150 mg) and DDQ (220 mg) gave **25** (60 mg), mp 198—199° (from MeOH–$CHCl_3$); it was found to be identical with **25** obtained from **3** by TLC and IR. The by-product, **26** (30 mg), was separated by PLC, mp 194—195° (from MeOH–$CHCl_3$), IR ν_{max}^{KBr} cm^{-1}: 1610, 1500, 1272, 1210, 1158, 1033; UV λ_{max}^{EtOH} nm (log ε): 203 (4.80), 254.5 (4.86), 279 (4.57), 294 (sh, 4.40), 335 (3.77), 352 (3.46); PMR (δ in $CDCl_3$): 3.61 (3H, s, OMe at C-2′), 3.78, 3.81, 3.96, 4.07 (each 3H, s, OMe×4), 6.62 (H, s, at C-3′), 6.84 (H, s, at C-6′), 6.97 (H, s, at C-1), 7.27—7.60 (2H, m, at C-6 and 7), 7.51 (H, s, at

C-9), 7.62—7.92 (H, m, at C-8), 7.96 (H, s, at C-4), 8.46 (H, m, at C-5). MS *m/e*: 404.160 (M^+) (Calcd for $C_{25}H_{24}O_5$, 404.163).

Catalytic Hydrogenation of 1——A solution of **1** (100 mg) in MeOH (10 ml) was shaken with Pd-C (5%) (50 mg) in an H_2 atmosphere for 12 hr, then the reaction mixture was filtered. The filtrate was concentrated to give a crystalline product, which was recrystallized from *n*-hexane to give **23** (50 mg), mp 99—101°, IR ν_{max}^{KBr} cm^{-1}: 1590, 1511, 1255, 1240, 1148, 1031; UV λ_{max}^{EtOH} nm (log ε): 229 (4.17), 279 (3.72), 287 (sh, 3.62); PMR (δ in $CDCl_3$): 1.2—2.1 (11H, m, $-CH_2-\times5$, $-CH\langle$), 2.1—2.6 (2H, m, $-CH_2-$), 2.67—2.95 (1H, m, $-CH\langle$), 3.80, 3.84, 3.87 (each 3H, 6H, 3H, s, OMe×4), 6.48 (H, d, $J=2$ Hz, at C-6), 6.51 (H, dd, $J=2$, 8 Hz, at C-2), 6.67 (1H, dd, $J=2$, 8 Hz at C-16), 6.68 (1H, d, $J=2$ Hz, at C-20), 6.72 (1H, d, $J=8$ Hz, at C-3 or -17), 6.81 (1H, d, $J=8$, at C-17 or -3); ^{13}C-NMR (δ in $CDCl_3$): 20.6 (t), 25.7 (t), 26.6 (t), 27.3 (t), 29.6 (t), 33.6 (t), 39.3 (d), 46.0 (d), 55.6 (q), 55.7 (q), 55.8 (q), 110.7 (d), 111.0 (d), 111.2 (d), 111.5 (d), 119.2 (d), 120.0 (d), 135.2 (s), 138.4 (s), 146.8 (s), 148.4 (s), 148.5 (s). MS *m/e*: 384.230 (M^+) (Calcd for $C_{24}H_{32}O_4$, 384.230). *Anal.* Calcd for $C_{24}H_{32}O_4$: C, 74.97; H, 8.39. Found: C, 74.65; H, 8.29.

Catalytic Hydrogenation of 7——Similar treatment of **7** (100 mg) provided **24** (60 mg), which was recrystallized from *n*-hexane to give colorless crystals, mp 80—81°, IR ν_{max}^{KBr} cm^{-1}: 1596, 1518, 1265, 1246, 1160, 1145; UV λ_{max}^{EtOH} nm (log ε): 229.5 (4.22), 279 (3.77), 287 (sh, 3.66); PMR (δ in $CDCl_3$): 1.0—1.7 (8H, m, $CH_2\times4$), 1.7—1.95 (2H, m, $-CH_2-$), 2.0—2.4 (2H, m, $-CH_2-$), 2.3—2.6 (1H, m, $-CH\langle$), 3.78, 3.83, 3.86 (each 3H, 6H, 3H, s, OMe×4), 6.47 (H, d, $J=2$ Hz), 6.59 (H, dd, $J=2$, 8 Hz), 6.61 (H, d, $J=2$ Hz), 6.63 (H, dd, $J=2$, 8 Hz), 6.73 (H, d, $J=8$ Hz), 6.78 (H, d, $J=8$ Hz); ^{13}C-NMR (δ in $CDCl_3$): 2.65 (t), 26.9 (t), 32.1 (t), 35.9 (t), 36.3 (t), 41.4 (d), 50.4 (d), 55.3 (q), 55.7 (q), 55.8 (q), 110.5 (d), 111.0 (d), 111.5 (d), 119.5 (d), 120.0 (d), 135.4 (s), 139.3 (s), 146.8 (s), 146.9 (s), 148.6 (s), 148.7 (s). MS *m/e*: 384.232 (M^+) (Calcd for $C_{24}H_{32}O_4$, 384.230). *Anal.* Calcd for $C_{24}H_{32}O_4$: C, 74.97; H, 8.39. Found: C, 75.02; H, 8.31.

Catalytic Hydrogenation of 3——Similar treatment of **3** (100 mg) provided the product **27** (45 mg), which was recrystallized from *n*-hexane, mp 82—83°, IR ν_{max}^{KBr} cm^{-1}: 1608, 1595, 1517, 1235, 1215, 1151, 1036; UV λ_{max}^{EtOH} nm (log ε): 205 (4.81), 228.5 (4.29), 286 (3.86); PMR (δ in $CDCl_3$): 1.2—2.05 (11H, m, $-CH_2-\times5$, $-CH\langle$), 2.05—2.60 (2H, m, $-CH_2-$), 2.65—2.95 (H, m, $-CH\langle$), 3.70, 3.77, 3.83, 3.87 (each 3H, 3H, 3H, 6H, s, OMe×5), 6.43 (H, s), 6.47 (H, s), 6.67 (H, d, $J=2$ Hz), 6.68 (H, dd, $J=2$, 8 Hz), 6.80 (H, d, $J=8$ Hz); ^{13}C-NMR (δ in $CDCl_3$): 20.6 (t), 25.7 (t), 26.6 (t), 28.1 (t), 29.5 (t), 39.7 (d), 46.1 (d), 55.7 (q), 55.9 (q), 56.1 (q), 56.3 (q), 56.6 (q), 97.9 (d), 110.6 (d), 111.2 (d), 114.1 (d), 119.2 (d), 122.8 (s), 138.6 (s), 142.4 (s), 146.7 (s), 147.3 (s), 148.4 (s), 151.4 (s). MS *m/e*: 414.244 (M^+) (Calcd for $C_{25}H_{34}O_5$, 414.241). *Anal.* Calcd for $C_{25}H_{34}O_5$: C, 72.43; H, 8.27. Found: C, 72.66; H, 8.24.

Catalytic Hydrogenation of 8——Similar treatment of **8** (80 mg) provided the product **28** (50 mg), mp 89—90° (from *n*-hexane), IR ν_{max}^{KBr} cm^{-1}: 1610, 1590, 1520, 1470, 1265, 1225, 1208, 1159, 1043, 1038, 1025; UV λ_{max}^{EtOH} nm (log ε): 206 (4.38), 228.5 (4.04), 282 (3.64), 286 (3.65); PMR (δ in $CDCl_3$): 1.0—1.7 (8H, m, $CH_2\times4$), 1.7—1.9 (3H, $-CH_2-$, $-CH-$), 1.9—2.4 (2H, m, $-CH_2-$), 2.4—2.6 (H, m, $-CH\langle$), 3.63, 3.74, 3.81, 3.84 (each 3H, 3H, 3H, 6H, s, OMe×5), 6.42 (1H, s, at C-3 or -6), 6.45 (1H, s, at C-6 or -3), 6.58 (1H, dd, $J=2$, 8.5 Hz, at C-16), 6.59 (1H, d, $J=2$ Hz, at C-20), 6.77 (1H, d, $J=8.5$ Hz at C-17). *Anal.* Calcd for $C_{25}H_{34}O_5$: C, 72.43; H, 8.27. Found: C, 72.78; H, 8.40.

Synthesis of the Palmitate (9) from 4——A solution of **4** (200 mg) in pyridine (1.5 ml) was treated with palmitoyl chloride (200 mg) and the whole was left to stand for 12 hr at room temperature. The reaction mixture was poured into ice-water and extracted with ether. The ether layer was washed with saturated $NaHCO_3$ solution, dilute HCl, and water successively, then dried over Na_2SO_4. Ether was evaporated off to give a viscous product, which was purified by PLC and recrystallized from EtOH to give colorless needles (150 mg), mp 61—62°; this material was identical with **9** as judged by mp, TLC, IR and PMR results.

The Friedel-Crafts Reaction of Veratrole (14) with Butyroyl Chloride——$AlCl_3$ (2.8 g) was added gradually to a solution of **14** (2 g) and butyroyl chloride (1.8 g) in CS_2 (30 ml) at 0°, and the whole was stirred for 3 hr at room temperature. After standing overnight at room temperature, the reaction mixture was poured into ice-water and extracted with ether. The ether solution was washed with KOH solution and water, dried over Na_2SO_4, and concentrated to give a crystalline product, which was chromatographed on silica gel and recrystallized from *n*-hexane to give the acylated product, **16** (1.3 g), mp 53—54°, IR ν_{max}^{KBr} cm^{-1}: 1664, 1595, 1588, 1513, 1420, 1260, 1240, 1165, 1153, 1025, 810; PMR (δ in $CDCl_3$): 1.01 (3H, t, $J=7$ Hz, $-CH_3$), 1.78 (2H, m, $-CH_2-C\underline{H}_2-CH_3$), 2.93 (2H, t, $J=7$ Hz, $-CO-C\underline{H}_2-CH_2-$), 3.92 (6H, s, OMe×2), 6.84 (H, d, $J=10$ Hz, arom. H), 7.48 (H, br. s, arom. H), 7.57 (H, br. d, $J=10$ Hz, arom. H). *Anal.* Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.68; H, 7.82.

The Friedel-Crafts Reaction of 1,2,4-Trimethoxybenzene (15) with Butyroyl Chloride——1,2,4-Trimethylbenzene (2 g) was acylated with butyroyl chloride (1.7 g) and $AlCl_3$ (2.5 g) in CS_2 (30 ml) to give a crystalline product, which was recrystallized from *n*-hexane as colorless prisms, **17** (1.5 g), mp 75—77°, IR ν_{max}^{KBr} cm^{-1}: 1648, 1601, 1508, 1272, 1215, 1150, 1021; PMR (δ in $CDCl_3$): 0.96 (3H, t, $J=7$ Hz, CH_3), 1.70 (2H, m, $-CH_2-C\underline{H}_2-CH_3$), 2.92 (2H, t, $J=7$ Hz, $-CO-C\underline{H}_2-CH_2-$), 3.83, 3.86, 3.90 (each 3H, s, OMe×3), 6.44 (H, s, arom. H), 7.32 (H, s, arom. H). *Anal.* Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.35; H, 7.56.

$NaBH_4$ Reduction of 16——A solution of the ketone (**16**, 700 mg) and $NaBH_4$ (180 mg) in MeOH (10 ml) was stirred for 1 hr at room temperature. The reaction mixture was poured into water and extracted with ether. The ether layer was washed with water and dried over Na_2SO_4, then the ether was evaporated off to

give a colorless oil (620 mg), which was recrystallized from *n*-hexane to provide **18** (500 mg), mp 58—59°, IR ν_{max}^{KBr} cm^{-1}: 3390, 1608, 1596, 1522, 1458, 1423, 1265, 1242, 1162, 1140, 1027; PMR (δ in $CDCl_3$): 0.92 (3H, t, $J=6$ Hz, CH_3), 1.35 (2H, m, $-CH_2-CH_2-CH_3$), 1.69 (2H, q, $J=6$ Hz, $-CHOH-CH_2-CH_2-$), 2.13 (1H, br. s, OH), 3.81, 3.82 (each 3H, s, OMe×2), 4.54 (H, t, $J=6$ Hz, ph-CHOH–), 6.78 (3H, br. s, arom. H). *Anal.* Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.74; H, 8.63.

$NaBH_4$ Reduction of 17——The ketone (**17**, 500 mg) was reduced with $NaBH_4$ (150 mg) to give a crystalline product, which was recrystallized from *n*-hexane as colorless needles, **19** (350 mg), mp 85—86°, IR ν_{max}^{KBr} cm^{-1}: 3400, 1611, 1510, 1461, 1402, 1324, 1208, 1135, 1033; PMR (δ in $CDCl_3$): 0.93 (3H, t, CH_3), 1.40 (2H, m, $-CH_2-CH_2-CH_3$), 1.70 (2H, q, $J=6$ Hz, $-CHOH-CH_2-CH_2-$), 2.44 (1H, br. s, OH), 3.79, 3.81, 3.85 (each 3H, s, OMe×3), 4.86 (1H, t, $J=6$ Hz, ph-CHOH–CH_2-), 6.46 (1H, s, arom. H), 6.84 (1H, s, arom. H). *Anal.* Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.05; H, 8.31.

Dehydration of 18——Three drops of conc. H_2SO_4 were added to a solution of **18** (340 mg) in dioxane (8 ml), and the mixture was refluxed for 1 hr. The reaction mixture was poured into ice-water and extracted with ether. The ethereal solution was washed with water and dried over Na_2SO_4, then the ether was evaporated off to give colorless oil, which was purified by PLC to give **10** (150 mg). This material was identical with the natural product as judged by TLC, IR and PMR.

Dehydration of 19——The alcohol (**19**, 200 mg) in dioxane (5 ml) was dehydrated with two drops of conc. H_2SO_4 and the reaction product was purified by PLC to give chromatographically pure **11** (80 mg) as an oil, which was identical with the natural **11** (TLC, IR, and PMR).

The Grignard Reaction of Veratrum Aldehyde (20)——Some iodine crystals were added to a solution of allyl chloride (500 mg) and magnesium turnings (1.9 g) in dry ether (15 ml) under stirring at −5°. Allyl chloride (4.5 g) and veratrum aldehyde (2 g) in ether (20 ml) were then added gradually with cooling on an ice bath. After the addition, the reaction mixture was stirred for 30 min at room temperature, then saturated NH_4Cl solution was added in small portions under cooling and the whole was extracted with ether. The ether layer was washed with water and dried over Na_2SO_4, then the ether was evaporated off to give a crystalline product (2.3 g), which was recrystallized from *n*-hexane as pale yellow needles (**21**, 1.6 g), mp 73—74°, IR ν_{max}^{KBr} cm^{-1}: 3370, 1642, 1596, 1525, 1422, 1365, 1268; PMR (δ in $CDCl_3$): 2.45 (2H, br. t, $J=6.5$ Hz, $-CHOH-CH_2-CH=$), 3.81 (6H, s, OMe×2), 4.59 (1H, t, $J=6.5$ Hz, ph-CHOH–CH_2-), 4.85—5.25 (2H, m, $-CH_2-CH=CH_2$), 5.45—6.10 (1H, m, $-CH_2-CH=CH_2$), 6.80 (3H, br. d, arom, H). *Anal.* Calcd for $C_{13}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.27; H, 7.68.

Dehydration of 21——A mixture of the alcohol (**21**, 200 mg) and conc. H_2SO_4 (2 drops) in dioxane (10 ml) was refluxed for 30 min. Ether was added to the cooled reaction solution and the ethereal extract was washed with water and dried over Na_2SO_4. The ether was evaporated off to give a brown oil which was purified by PLC to give chromatographically pure **12** (50 mg); this was identical with the natural product as judged by TLC, IR and PMR.

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Note added in Proof (August 20, 1980) Quite recently synthesis of the compounds **1**—**4** was reported (P. Tuntiwachwuttikul, B. Limchawfar, V. Reutrakul, O. Pancharoen, K. Kusamran, and L.T. Bryne, *Aust. J. Chem.*, **33**, 913 (1980)). The isolation and structure elucidation of the compounds **9**—**12**, and **29** were recently performed by the same Thai group (Dr. Vichai Reutrakul, private communication; *cf.* P. Tuntiwachwuttikul and V. Reutrakul, the paper presented at Third Symposium on the Development and Application of Naturally Occurring Drug Materials, the Pharmaceutical Society of Japan and UNESCO, Tokyo, August 2, 1980).