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Synthetic Studies on Lignans and Related Compounds. V.[1] Regiospecificity in the Photocyclization of 2,3-Dibenzylidenebutyrolactones[2]

Takefumi Momose, Ken-ichi Kanai, Takeshi Nakamura, and Yukiko Kuni

Faculty of Pharmaceutical Sciences, Osaka University[3]

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The photocyclization of 2,3-dibenzylidenebutyrolactones (**5**) was investigated in association with the possible biogenetic pathway to natural naphthalide lignans in which 1-phenyl-2,3-naphthalide types predominate over 4-phenyl-2,3-naphthalide ones. The butyrolactones (**5**) were prepared *via* Stobbe condensation of benzylidenesuccinates (**6**) followed by the selective reduction of the resulting half esters (**7**) to hydroxy acids (**8**) and subsequent lactonization, and their *cis,cis*-configuration was assigned on the basis of comparative proton magnetic resonance (^{1}H–NMR) data. Irradiation of **5** afforded selectively β-apolignans (**11**) of the 1-phenyl-2,3-naphthalide types irrespectively of the ring substituents, and none of the 4-phenyl-2,3-naphthalide types was formed in the reaction.

Keywords——2,3-dibenzylidenebutyrolactone lignan; taiwanin A; *cis,cis*-geometry of double-Stobbe products; regiospecific photocyclization; β-aponaphthalide lignan; 1-phenyl-2,3-naphthalide lignan; biosynthetic model; *cis*- and *trans*-cinnamate; (*Z*)- and (*E*)-arylmethylenesuccinate

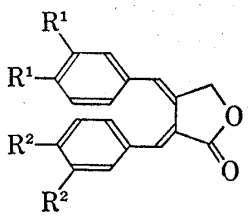
In the preceding paper,[1] we described the synthesis of naphthalide lignans related to taiwanin C (**1**) and E (**2**),[4] and revealed that our prediction[5] concerning the photoproducts from taiwanin A (**3**)[4] was actually the case: only 1-aryl-2,3-naphthalides (**1** and **2**) instead of 4-aryl-2,3-naphthalides (**4**) were formed from a 2,3-dibenzylidenebutyrolactone (**3**) on photocyclization. The result suggests that a preferential activation of the olefinic system conjugated with the carbonyl group in 2,3-dibenzylidenebutyrolactones in the light is responsible for the selective formation of **1** or **2** instead of **4**, and appears to be associated with the fact that most of natural naphthalide lignans belong to type **1** or **2** rather than type **4**.

In this paper, we give details of regiospecific photocyclization[6] of 2,3-dibenzylidenebutyrolactones in the absence of oxygen.

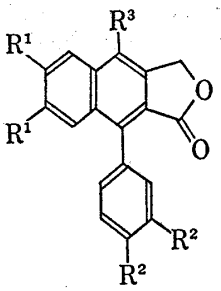
Preparation of 2,3-Dibenzylidenebutyrolactones

Our approach to the lactones (**5a** and **b**) is outlined in Chart 1. The Stobbe condensation of dimethyl *trans*-veratrylidenesuccinate (**6a**) with benzaldehyde afforded a half ester (**7a**), which was reduced to a hydroxy acid (**8a**) by treatment with lithium aluminum hydride at $-20°$——$-15°$. Treatment of **8a** with *p*-toluenesulfonic acid in the dark completed the synthesis of **5a**. Another lactone (**5b**) was prepared in the same manner starting from dimethyl *trans*-benzylidenesuccinate (**6b**).

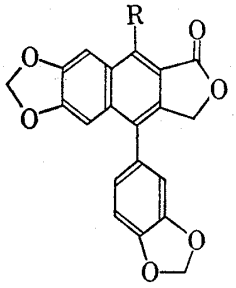
1) Part IV: Z. Horii, M. Tsujiuchi, K. Kanai, and T. Momose, *Chem. Pharm. Bull.* (Tokyo), **25**, 1803 (1977).
2) Presented in part at the 23rd Meeting of Kinki Branch, Pharmaceutical Society of Japan, Kyoto, Nov. 1973, Abstracts of Papers, p. 47. The preliminary communication has appeared in *Heterocycles*, **4**, 1481 (1976).
3) Location: 133–1, *Yamada-kami, Suita, Osaka* 565, *Japan*.
4) Y.-T. Lin, T.-B. Lo, K.-T. Wang, and B. Weinstein, *Tetrahedron Lett.*, **1967**, 849.
5) Z. Horii, M. Tsujiuchi, and T. Momose, *Tetrahedron Lett.*, **1969**, 1079.
6) Shortly before the publication of our preliminary communication[2] concerning a series of experiments on the selective photocyclization of 2,3-dibenzylidenebutyrolactones, a report on the similar subject has appeared; H.G. Heller and P.J. Strydom, *J. Chem. Soc., Chem. Commun.*, **1976**, 50.



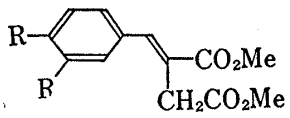
3: $R^1=R^2=OCH_2O$
5a: $R^1=H$, $R^2=OMe$
5b: $R^1=OMe$, $R^2=H$



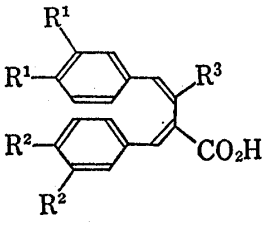
1: $R^1=R^2=OCH_2O$, $R^3=H$
2: $R^1=R^2=OCH_2O$, $R^3=OH$
12: $R^1=R^3=H$, $R^2=OMe$



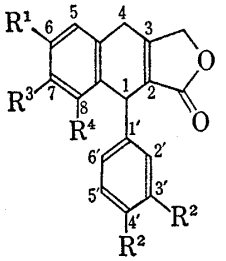
4
(R=H or OH)



6a: R=OMe
6b: R=H



7a: $R^1=H$, $R^2=OMe$
$R^3=CO_2Me$
7b: $R^1=OMe$, $R^2=H$
$R^3=CO_2Me$
8a: $R^1=H$, $R^2=OMe$
$R^3=CH_2OH$
8b: $R^1=OMe$, $R^2=H$
$R^3=CH_2OH$



11a: $R^1=R^3=R^4=H$, $R^2=OMe$
11b: $R^1=R^3=OMe$, $R^2=R^4=H$
11c: $R^1=R^2=H$, $R^3=R^4=OMe$

Chart 1

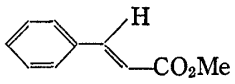
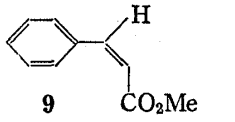
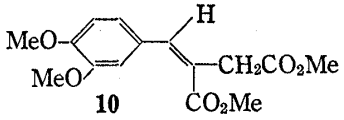
The *cis,cis*-configuration[7] for **5** was assigned based on comparative proton magnetic resonance (^{1}H-NMR) data (see Table I) as in the case of taiwanin A (**3**).[8] The *cis*-cinnamate (**9**), one of the model compounds, was prepared by methylation of *cis*-cinnamic acid which was prepared in a manner similar to that reported for the *p*-methoxy analogue.[9] Dimethyl *cis*-veratrylidenesuccinate (**10**), another model compound, was prepared in the same manner[10] starting from *trans*-veratrylidenesuccinic acid.[11] The olefinic protons in **7** and one of those in **8** and **5** resonate at the field closely similar to that for the β-proton in methyl *trans*-cinnamate[12] (δ 7.69) rather than in **9** (δ 6.93) and **10** (δ 6.76): the β-proton in the *trans*-cinnamate is deshielded by the carbonyl group of the ester, while those in **9** and **10** are not. The assignment coincides with the results obtained for isomeric bisbenzylidenesuccinic acids and related compounds.[13]

Photoreaction

A solution of **5a** in dimethyl formamide (DMF) was irradiated with a 100 W high-pressure mercury lamp through a filter of ordinary borosilicate glass in the presence of 1,4-diazabicyclo-

7) The term "*cis*" means that the phenyl moieties are located *cis* to the central carbon-carbon linkage of the butadiene system.
8) R.J. Hart and H.G. Heller, *J. Chem. Soc., Perkin Trans. I*, **1972**, 1321, and references therein.
9) J. Bregman, K. Osaki, G.M.J. Schmidt, and F.I. Sonntag, *J. Chem. Soc.*, **1964**, 2021.
10) The anisylidene analogue has been prepared by House and Larson [H.O. House and J.K. Larson, *J. Org. Chem.*, 33, 448 (1968)].
11) E.C. Horning and G.N. Walker, *J. Am. Chem. Soc.*, **74**, 5147 (1952).
12) H.A. Szymanski and R.E. Yelin, "NMR Band Handbook," IFI/Plenum Data Corporation, New York, 1968, p. 266.
13) H.-L. Elbe and G. Köbrich, *Chem. Ber.*, **107**, 1654 (1974).

TABLE I. Chemical Shifts (δ Values for the $CDCl_3$ Solution) for the Olefinic Protons in **5a** and Related Model Compounds

Compound	Olefinic H
	7.69(d, J=16 Hz)[a]
 **9**	6.93(d, J=12 Hz)
 **10**	6.76(fused t, J=1 Hz)
6a	7.83(s)
7a	7.92(s) 7.94(s)
8a[b]	7.83(s)
5a	7.64(s) 6.62(t, J=2 Hz)
3[c] (Taiwanin A)	7.54(s) 6.72(t, J=2 Hz)

a) Reported value: δ 7.71.[12]
b) Another olefinic proton signal is masked by aromatic proton signals.
c) Reported values for the d_6-DMSO solution: δ 7.47 and 6.68.[d]
d) Taiwanin A (**3**) was prepared according to the procedure described by Swoboda, *et al.* [G. A. Swoboda, K.-T. Wang, and B. Weinstein, *J. Chem, Soc.* (*C*), **1967**, 161].

[2.2.2]octane (DABCO),[14] and simultaneously bubbled with dry, oxygen-free nitrogen. Chromatography of the crude product gave a β-apolignan (**11a**) in 41% yield. Similar irradiation of **5a** in benzene afforded **11a** in 46% yield, but was accompanied by a secondary product.[15] Lack of the secondary product in the run using DMF as solvent can be explained as follows. The ultraviolet (UV) spectrum of **11a** showed λ_{max} 284.2 nm (log ε 3.62) in benzene and λ_{max} 283.8 nm (log ε 3.59) in DMF, respectively. The hyperchromic shift in DMF prevents **11a** from absorbing the light of wave length essential to the degenerate rearrangement of **11a** in the presence of a filter of ordinary borosilicate glass. In the absence of DABCO, **11a** was obtained in low yields. The structure of **11a** was established on the basis of the following observations. The photoproduct showed infrared spectrum (IR) absorption at 1752 (C=O) and 1694 (C=C) cm^{-1}, and ^{1}H-NMR signals at δ *ca.* 3.84 (2H, m, C_4–H), 4.85 (2H, s, $-CH_2$-OCO–), and *ca.* 4.93 (1H, m, C_1–H), which were closely similar to those of β-apopicropodophyllin.[15] The carbon skeleton of **11a** was confirmed by its aromatization with lead tetraacetate into a known lignan (**12**).[17]

Similar irradiation of **5b** afforded a mixture of **11b** (mp 136—137°; 30%) and **11c** (mp 184.5—185°; 20%). These products exhibited IR bands characteristic of β-apolignans at *ca.* 1750 (C=O) and *ca.* 1690 (C=C) cm^{-1}, and their substitutional isomerism was deduced from their ^{1}H-NMR spectra. The structure of **11b** was assigned from the presence of two singlet ^{1}H-NMR signals due to aromatic protons at δ 6.58 and 6.72. The assignment of another one

14) A quencher of singlet oxygen: see R.S. Atkinson, D.R.G. Brimage, R.S. Davidson, and E. Gray, *J. Chem. Soc., Perkin Trans. I*, **1973**, 960.
15) Found to be a product of photorearrangement of **11a** (see Ref. 2). This will be described in another paper.
16) D.C. Ayres, *Can. J. Chem.*, **47**, 2075 (1969).
17) L.H. Klemm, K.W. Gopinath, D.H. Lee, F.W. Kelly, E. Trod, and T.M. McGuire, *Tetrahedron*, **22**, 1797 (1966).

(**11c**) was furnished based on the presence of two doublet signals of AB type at δ 6.87 and 6.98 (J= 8 Hz) ascribed to C_6–H and C_5–H, respectively. The C_1–H signal at δ 5.23 for **11c** appeared at considerably lower field than for **11a** (δ *ca.* 4.93) and **11b** (δ *ca.* 4.90) owing to the deshielding effect of the C_8-methoxyl group, the feature supporting the structure for **11c**.

Consequently, the photocyclization of the 2,3-dibenzylidenebutyrolactones (**5**) was found to proceed regiospecifically, giving only the β-apolignans (**11**) of the 1-aryl-2,3-naphthalide types.

In the photocyclization of α,α'-dibenzylidenesuccinic anhydrides,[18] the ring closure is known to occur at both phenyl rings irrespectively of the ring substituents, whose effects on the cyclization selectivity have been observed significantly for 1,4-diphenyl-1,3-butadienes.[19] The leading role of the cinnamoyl system (Ar–C=C–C=O) in the cyclization of the succinic anhydrides[20] seems to operate also for the present butyrolactone system, resulting in the high specificity.

Experimental

All melting points and boiling points are uncorrected. ^{1}H–NMR spectra were obtained with a Hitachi R-22 (90 MHz) spectrometer with tetramethylsilane as an internal standard, IR spectra with a Hitachi EPI-G3 spectrophotometer, UV spectra with a Shimadzu MPS-50L spectrophotometer, and mass spectra with a Hitachi RMU-6E spectrometer (direct inlet, at 70 eV). Column chromatography was effected using Mallinckrodt silicic acid. Preparative thin-layer chromatography (TLC) was performed on Merck Kieselgel 60 PF_{254}. The photochemical reactions were carried out in an immersion apparatus fitted with an Eikosha 100 W high-pressure mercury lamp.

Dimethyl *trans*-Veratrylidenesuccinate (6a)[22]——*trans*-Veratrylidenesuccinic acid[11] (29.0 g) was methylated with CH_2N_2 in AcOEt in a usual manner to give **6a** (30.2 g, 93%) as a pale yellow oil, bp 158—161° (0.002 mmHg) [lit.[22] bp 188—192° (0.5 mmHg)]. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1747, 1717 (C=O), 1635 (C=C), 1600, 1582 (arom.). ^{1}H–NMR ($CDCl_3$) δ: 3.57 (2H, s, –C<u>H</u>$_2$CO$_2$Me), 3.69 (3H, s, –CO$_2$Me), 3.78 (3H, s, –CO$_2$Me), 3.83 (3H, s, OMe), 3.87 (3H, s, OMe), 6.93 (3H, s, Ar–H), 7.83 (1H, s, –CH=C–). MS *m/e*: 294 (M$^+$). *Anal.* Calcd. for $C_{15}H_{18}O_6$: C, 61.21; H, 6.17. Found: C, 61.16; H, 6.21.

Dimethyl *trans*-Benzylidenesuccinate (6b)[23]——*trans*-Benzylidenesuccinic acid[11] (5.5 g) was converted into **6b** (5.9 g, 94%) in a similar manner to that for **6a**. A pale yellow oil, bp 130—135° (1 mmHg) [lit.[23] bp 235—240° (4 mmHg)]. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1747, 1726 (C=O), 1644 (C=C). ^{1}H–NMR ($CDCl_3$) δ: 3.56 (2H, s, –C<u>H</u>$_2$CO$_2$Me), 3.74 (3H, s, –CO$_2$Me), 3.84 (3H, s, –CO$_2$Me), 7.37 (5H, s, Ar–H), 7.92 (1H, s, –CH=C–). *Anal.* Calcd. for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.40; H, 5.99.

Methyl Hydrogen α-Benzylidene-β-veratrylidenesuccinate (7a)——Metallic K (4.0 g) was dissolved in dry *t*-butanol (60 ml), and to this was added a solution of **6a** (21.6 g) and benzaldehyde (7.6 g) in dry *t*-butanol (27 ml) with stirring at room temperature over 1 hr. After heating under reflux for 2 hr, the solution was poured into ice-water (800 ml), and the separated oil was taken in ether. The aqueous layer was acidified with 5% H_2SO_4, and the separated oil was extracted with AcOEt. The extract was washed with satd. NaCl, dried over Na_2SO_4, and evaporated to give a brown glass (28.6 g), which was chromatographed on silica gel (570 g) in $CHCl_3$ to give **7a** (17.0 g, 66%) as pale yellow crystals (from ether–CCl_4), mp 153—154°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1717, 1685 (C=O), 1633 (C=C), 1597, 1580 (arom.). ^{1}H–NMR ($CDCl_3$) δ: 3.70 (6H, s, –CO$_2$Me and OMe), 3.82 (3H, s, OMe), 6.7—7.7 (8H, m, Ar–H), 7.92 (1H, s, –CH=C–), 7.94 (1H, s, –CH=C–), 9.30 (1H, broad, –CO$_2$H). MS *m/e*: 368 (M$^+$, 33%), 336 (100%). *Anal.* Calcd. for $C_{21}H_{20}O_6$: C, 68.47; H, 5.47. Found: C, 68.19; H, 5.44.

18) F.G. Baddar, L.S. El-Assal, N.A. Doss, and A.H. Shehab, *J. Chem. Soc.*, **1959**, 1016.
19) C.C. Leznoff and R.J. Hayward, *Can. J. Chem.*, **48**, 1842 (1970).
20) Heller and Szewczyk have mentioned non-planarity of the butadiene system in the *cis,cis*-diarylidenesuccinic anhydrides on the basis of the X-ray crystallographic analysis of the bis-*p*-anisylidene analogue[21] and of the UV spectroscopic studies on isomeric bis(α-substituted benzylidene) analogues, and have ascribed the regiospecific photocyclization of these anhydrides to $n\rightarrow\pi^*$ excitation of one of two independent cinnamoyl chromophores; H.G. Heller and M. Szewczyk, *J. Chem. Soc., Perkin Trans. I*, **1974**, 1487.
21) M.D. Cohen, H.W. Kaufman, D. Sinnreich, and G.M.J. Schmidt, *J. Chem. Soc.* (*B*), **1970**, 1035.
22) The diester (**6a**) has been prepared, by Schrecker, from veratrylidenesuccinic acid by the Fischer esterification [A.W. Schrecker, *J. Am. Chem. Soc.*, **79**, 3823 (1957)].
23) The diester (**6b**) has been prepared, by El-Assal and Shehab, from benzylidenesuccinic acid by methylation with dimethyl sulfate (L.S. El-Assal and A.H. Shehab, *J. Chem. Soc.*, **1963**, 2983).

Methyl Hydrogen α-Veratrylidene-β-benzylidenesuccinate (7b)——A solution of **6b** (9.2 g) and veratraldehyde (10.4 g) in dry *t*-butanol (50 ml) was added to a stirred solution of potassium *t*-butoxide [from metallic K (2.8 g)] in dry *t*-butanol (60 ml) at room temperature over 40 min, and the solution was refluxed for 2 hr. Working-up similar to that for **7a** afforded a brown glass (16.5 g), which was chromatographed on silica gel (495 g) in $CHCl_3$ to give **7b** (13.9 g, 95%) as pale yellow crystals (from ether–CCl_4), mp 136—138°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1709, 1692 (C=O), 1633 (C=C), 1598 (arom.). ^{1}H-NMR ($CDCl_3$) δ: 3.71 (3H, s, OMe or –COOMe), 3.74 (3H, s, OMe or $-CO_2Me$), 3.86 (3H, s, OMe), 6.24 (1H, broad, $-CO_2H$), 6.7—7.6 (8H, m, Ar–H), 7.87 (1H, s, –CH=C–), 7.99 (1H, s, –CH=C–). MS *m/e*: 368 (M^+, 100%). *Anal.* Calcd. for $C_{21}H_{20}O_6$: C, 68.47; H, 5.47. Found: C, 68.09; H, 5.42.

2-Veratrylidene-3-benzylidene-4-hydroxybutyric Acid (8a)——A solution of **7a** (10.0 g) in dry tetrahydrofuran (42 ml) and dry ether (260 ml) was added to a stirred suspension of $LiAlH_4$ (15 g) in dry ether (448 ml) at −50° over 1.5 hr, and the suspension was stirred at −15°[24] for 5 hr. After addition of AcOEt (60 ml) and subsequently of 5% H_2SO_4, the organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined extracts were washed with satd. NaCl, dried over Na_2SO_4, and evaporated *in vacuo* below room temperature to give a pale yellow glass (10.6 g), which was crystallized from benzene to afford **8a** (5.4 g, 59%).[24] Recrystallization from ether–benzene gave an analytical sample as colorless prisms, mp 102—105°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1682 (C=O), 1599, 1581 (arom.). ^{1}H-NMR ($CDCl_3$) δ: 3.70 (3H, s, OMe), 3.80 (3H, s, OMe), 4.24 (2H, broad s, $-C\underline{H}_2OH$), 6.30 (2H, broad s, $-CH_2O\underline{H}$ and $-CO_2\underline{H}$), 6.7—7.7 (9H, m, Ar–H and –CH=C–), 7.83 (1H, s, –CH=C–). *Anal*, Calcd. for $C_{20}H_{20}O_5 \cdot 1/2\ C_6H_6$: C, 72.80; H, 6.10. Found: C, 72.94; H, 6.21.

2-Benzylidene-3-veratrylidene-4-hydroxybutyric Acid (8b)——The half ester (**7b**, 1.0 g) was reduced with $LiAlH_4$ in a similar manner to that for **8a** to give a pale yellow glass (0.95 g), which was purified by preparative TLC on silica gel using benzene–acetone (3:1) as a developing solvent to give **8b** (0.49 g, 53%) as a pale yellow glass. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1687 (C=O), 1603, 1584 (arom.). ^{1}H-NMR ($CDCl_3$) δ: 3.71 (3H, s, OMe), 3.80 (3H, s, OMe), 4.27 (2H, broad s, $-C\underline{H}_2OH$), 5.41 (2H, broad s, $-CH_2O\underline{H}$ and $-CO_2\underline{H}$), 6.6—7.7 (9H, m, Ar–H and –CH=C–), 7.82 (1H, s, –CH=C–).

2-Veratrylidene-3-benzylidene-4-hydroxybutyric Acid γ-Lactone (5a)——A solution of **8a** (0.20 g) and *p*-toluenesulfonic acid (0.30 g) in dry ether (75 ml) was stirred in the dark for 47 hr at room temperature. The solution was washed with satd. $NaHCO_3$ and then satd. NaCl, dried over Na_2SO_4, and evaporated *in vacuo* below room temperature to give **5a** (0.17 g, 93%) as a yellow solid, mp 87—93°. IR ν_{max}^{KBr} cm^{-1}: 1765 (C=O), 1624 (C=C), 1592, 1580 (arom.). ^{1}H-NMR ($CDCl_3$) δ: 3.54 (3H, s, OMe), 3.78 (3H, s, OMe), 5.02 (2H, d, J=2 Hz, $-CH_2OCO-$), 6.3—7.4 (8H, m, Ar–H), 6.62 (1H, t, J=2 Hz, –CH=C–), 7.64 (1H, broad s, –CH=C–). UV λ_{max}^{EtOH} nm (log ε): 266 (3.98), 390 (3.64).

2-Benzylidene-3-veratrylidene-4-hydroxybutyric Acid γ-Lactone (5b)——The hydroxy acid (**8b**, 0.25 g) in dry ether (85 ml) was lactonized with *p*-toluenesulfonic acid (0.30 g) in a similar manner to that for **5a** to give **5b** (0.20 g, 83%) as a yellow solid, mp 125—130°. IR ν_{max}^{KBr} cm^{-1}: 1770 (C=O), 1622 (C=C), 1590 (arom.). ^{1}H-NMR ($CDCl_3$) δ: 3.50 (3H, s, OMe), 3.73 (3H, s, OMe), 5.02 (2H, d, J=2 Hz, $-CH_2OCO-$), 6.59 (1H, m, –CH=C–), 6.2—7.4 (8H, m, Ar–H), 7.67 (1H, broad s, –CH=C–). UV λ_{max}^{EtOH} nm (log ε): 276 (3.56), 389 (2.85).

Methyl *cis*-Cinnamate (9)——A solution of *trans*-cinnamic acid (1.2 g) and Na_2CO_3 (1.2 g) in H_2O (180 ml) was irradiated through Pyrex sleeve (1.5 mm wall thickness) for 13 hr under a stream of oxygen-free N_2. The solution was acidified with 5% H_2SO_4, and the separated solid was filtered off, and the filtrate was extracted with AcOEt. The extract was washed with satd. NaCl, dried over Na_2SO_4, and evaporated to give a colorless solid (1.2 g), which was recrystallized from petroleum ether (bp 40—47°) to give *cis*-cinnamic acid (0.16 g, 13%) as colorless crystals, mp 66—68° (lit.[25] mp 68°).

The *cis*-acid (0.16 g) was methylated with CH_2N_2 in ether in a usual manner to give **9** (0.17 g, 95%) as a colorless oil, bp 114—115° (bath temperature, 1 mmHg) [lit.[26] bp 129—130° (17 mmHg)]. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735 (C=O), 1631 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 3.74 (3H, s, $-CO_2Me$), 5.98 (1H, d, J=12 Hz, –CH=C–), 6.93 (1H, d, J=12 Hz, –CH=C–), 7.2—7.7 (5H, m, Ar–H). *Anal.* Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 73.56; H, 6.16.

Dimethyl *cis*-Veratrylidenesuccinate (10)——A solution of *trans*-veratrylidenesuccinic acid[11] (10.0 g) and Na_2CO_3 (12.0 g) in H_2O (300 ml) was irradiated through Pyrex sleeve (1.5 mm wall thickness) for 26 hr under a stream of oxygen-free N_2. The solution was acidified with 5% H_2SO_4, and extracted with AcOEt. The extract was washed with satd. NaCl, dried over Na_2SO_4, and evaporated to give a pale yellow solid (9.4 g). The crude acid was contaminated with *trans*-acid (*ca.* 30% in ^{1}H-NMR spectrum), and further purification was unsuccessful.

The crude acid (9.4 g) was methylated with CH_2N_2 in AcOEt in a usual manner to give a pale yellow solid (10.6 g), which was recrystallized from isopropyl ether to give **10** (6.2 g, 56%) as colorless needles, mp

24) The yield on the run at −20° was 41%.
25) A method using photoisomerization of the free acid in benzene has been described: H. Stobbe and F.K. Steinberger, *Ber.*, **55**, 2225 (1922).
26) S. Sugden and H. Whittaker, *J. Chem. Soc. London*, **127**, 1868 (1925).

69.5—70°. IR ν_{max}^{KBr} cm^{-1}: 1729, 1718 (C=O), 1640 (C=C), 1604, 1579 (arom.). ^{1}H-NMR ($CDCl_3$) δ: 3.44 (2H, d, J=1 Hz, $-CH_2CO_2Me$), 3.69 (3H, s, $-CO_2Me$), 3.71 (3H, s, $-CO_2Me$), 3.87 (3H, s, OMe), 3.89 (3H, s, OMe), 6.76 (1H, fused t, J=1 Hz, -CH=C-), 6.7—7.0 (3H, m, Ar-H). MS *m/e*: 294 (M^+, 36%), 175 (100%). *Anal.* Calcd. for $C_{15}H_{18}O_6$: C, 61.21; H, 6.17. Found: C, 61.29; H, 6.20.

1,4-Dihydro-1-(3,4-dimethoxyphenyl)-3-hydroxymethyl-2-naphthoic Acid γ-Lactone (11a)——A solution of **5a** (99 mg) and DABCO (23 mg) in DMF (90 ml) was irradiated through an ordinary borosilicate glass sleeve (1.5 mm wall thickness) at 5° under a stream of dry, oxygen-free N_2. The reaction went to completion after 20 min's irradiation (checked by TLC). Evaporation of the solution *in vacuo* afforded a pale brown viscous oil (106 mg), which was purified by preparative TLC on silica gel using $CHCl_3$ as solvent to give **11a** (41 mg, 41%) as colorless rhombs (from EtOH), mp 168—169°. IR ν_{max}^{KBr} cm^{-1}: 1752 (C=O), 1694 (C=C), 1604, 1593, 1578 (arom.). ^{1}H-NMR ($CDCl_3$) δ: 3.80 (3H, s, OMe), 3.82 (3H, s, OMe), *ca.* 3.84 (2H, m, C_4-H), 4.85 (2H, s, $-CH_2OCO-$), *ca.* 4.93 (1H, m, C_1-H), 6.50 (1H, dd, J=9, 2 Hz, C_6'-H), 6.70 (1H, d, J=9 Hz, C_5'-H), 6.82 (1H, d, J=2 Hz, C_2'-H), 7.1—7.2 (4H, m, Ar-H). MS *m/e*: 322 (M^+, 100%). UV λ_{max}^{EtOH} nm (log ε): 282.0 (3.57). *Anal.* Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.31; H, 5.56.

1,4-Dihydro-6,7-dimethoxy-3-hydroxymethyl-1-phenyl-2-naphthoic Acid γ-Lactone (11b) and 1,4-Dihydro-7,8-dimethoxy-3-hydroxymethyl-1-phenyl-2-naphthoic Acid γ-Lactone (11c)——A solution of **5b** (100 mg) and DABCO (20 mg) in DMF (91 ml) was irradiated for 30 min in a similar manner to that for **11a**. After evaporation of the solution, the crude product (155 mg) was purified by preparative TLC on silica gel using dry ether as solvent to give **11b** (30 mg, 30%) and **11c** (20 mg, 20%).

Compound **11b**: Colorless micro needles (from EtOH), mp 136—137°. IR ν_{max}^{KBr} cm^{-1}: 1748 (C=O), 1691 (C=C), 1611 (arom.). ^{1}H-NMR ($CDCl_3$) δ: 3.76 (3H, s, OMe), 3.90 (3H, s, OMe), 3.7—4.0 (2H, m, C_4-H), 4.84 (2H, s, $-CH_2OCO-$), *ca.* 4.90 (1H, m, C_1-H), 6.58 (1H, s, C_8-H), 6.72 (1H, s, C_5-H), 7.0—7.3 (5H, m, Ar-H). MS *m/e*: 322 (M^+, 30%). UV λ_{max}^{EtOH} nm (log ε): 286.4 (3.46). *Anal.* Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.42; H, 5.63.

Compound **11c**: Colorless leaflets (from EtOH), mp 184.5—185°. IR ν_{max}^{KBr} cm^{-1}: 1749 (C=O), 1690 (C=C), 1604 (arom.). ^{1}H-NMR ($CDCl_3$) δ: 3.36 (3H, s, OMe), 3.81 (3H, s, OMe), 3.70—3.90 (2H, m, C_4-H), 4.78 (2H, broad s, $-CH_2OCO-$), 5.23 (1H, m, C_1-H), 6.87 (1H, d, J=8 Hz, C_6-H), 6.98 (1H, d, J=8 Hz, C_5-H), 7.1—7.3 (5H, m, Ar-H). MS *m/e*: 322 (M^+, 100%). UV λ_{max}^{EtOH} nm (log ε): 282 (3.05). *Anal.* Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.67; H, 5.66.

1-(3,4-Dimethoxyphenyl)-3-hydroxymethyl-2-naphthoic Acid γ-Lactone (12)——A mixture of **11a** (60 mg), lead tetraacetate (181 mg), and dry AcOH (2 ml) was heated at 90° for 20 min under a stream of dry N_2. After evaporation of the solution, the crude material was purified by preparative TLC on silica gel using $CHCl_3$–EtOH (30: 1) as solvent to give **12** (20 mg, 33%) as colorless needles (from EtOH), mp 213—214°. The product was identical with the authentic sample prepared according to the Klemm's procedure[17] on IR and ^{1}H-NMR spectral comparison.