Synthetic Studies on Lignans and Related Compounds. V.¹⁾
Regiospecificity in the Photocyclization of
2,3-Dibenzylidenebutylolactones²⁾

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The photocyclization of 2,3-dibenzylidenebutylolactones (**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 butylolactones (**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 (¹H-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-dibenzylidenebutylolactone 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 prediction⁵⁾ 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-dibenzylidenebutylolactone (**3**) on photocyclization. The result suggests that a preferential activation of the olefinic system conjugated with the carbonyl group in 2,3-dibenzylidenebutylolactones 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 photocyclization⁶⁾ of 2,3-dibenzylidenebutylolactones in the absence of oxygen.

Preparation of 2,3-Dibenzylidenebutylolactones

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 communication²⁾ concerning a series of experiments on the selective photocyclization of 2,3-dibenzylidenebutylolactones, a report on the similar subject has appeared; H.G. Heller and P.J. Strydom, *J. Chem. Soc., Chem. Commun.*, **1976**, 50.

The *cis,cis*-configuration⁷⁾ for **5** was assigned based on comparative proton magnetic resonance (¹H-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 manner¹⁰⁾ 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*-cinnamate¹²⁾ (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)}
6.93(d, $J=12$ Hz)
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 ($\log \epsilon$ 3.62) in benzene and λ_{max} 283.8 nm ($\log \epsilon$ 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 ^1H -NMR signals at δ ca. 3.84 (2H, m, $\text{C}_4\text{-H}$), 4.85 (2H, s, $-\text{CH}_2\text{-OCO-}$), and ca. 4.93 (1H, m, $\text{C}_1\text{-H}$), which were closely similar to those of β -apopicropodophyllin.¹³⁾ 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 ^1H -NMR spectra. The structure of **11b** was assigned from the presence of two singlet ^1H -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-dibenzylidenebutylolactones (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 ($Ar-\dot{C}=\dot{C}-\dot{C}=O$) in the cyclization of the succinic anhydrides²⁰⁾ seems to operate also for the present butylolactone system, resulting in the high specificity.

Experimental

All melting points and boiling points are uncorrected. 1H -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 PF₂₅₄. 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 acid¹¹⁾ (29.0 g) was methylated with CH_3N_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 $\nu_{max}^{CHCl_3}$ cm^{-1} : 1747, 1717 (C=O), 1635 (C=C), 1600, 1582 (arom.). 1H -NMR ($CDCl_3$) δ : 3.57 (2H, s, $-CH_2CO_2Me$), 3.69 (3H, s, $-CO_2Me$), 3.78 (3H, s, $-CO_2Me$), 3.83 (3H, s, OMe), 3.87 (3H, s, OMe), 6.93 (3H, s, Ar-H), 7.83 (1H, s, $-\dot{C}H=\dot{C}-$). 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 acid¹¹⁾ (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 $\nu_{max}^{CHCl_3}$ cm^{-1} : 1747, 1726 (C=O), 1644 (C=C). 1H -NMR ($CDCl_3$) δ : 3.56 (2H, s, $-CH_2CO_2Me$), 3.74 (3H, s, $-CO_2Me$), 3.84 (3H, s, $-CO_2Me$), 7.37 (5H, s, Ar-H), 7.92 (1H, s, $-\dot{C}H=\dot{C}-$). 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.). 1H -NMR ($CDCl_3$) δ : 3.70 (6H, s, $-CO_2Me$ and OMe), 3.82 (3H, s, OMe), 6.7–7.7 (8H, m, Ar-H), 7.92 (1H, s, $-\dot{C}H=\dot{C}-$), 7.94 (1H, s, $-\dot{C}H=\dot{C}-$), 9.30 (1H, broad, $-CO_2H$). 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 Szweczyk have mentioned non-planarity of the butadiene system in the *cis,cis*-diarylidene succinic anhydrides on the basis of the X-ray crystallographic analysis of the bis-*p*-anisylidene analogue²¹⁾ 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. Szweczyk, *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 $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 1709, 1692 (C=O), 1633 (C=C), 1598 (arom.). $^1\text{H-NMR}$ (CDCl_3) δ : 3.71 (3H, s, OMe or $-\text{CO}_2\text{Me}$), 3.74 (3H, s, OMe or $-\text{CO}_2\text{Me}$), 3.86 (3H, s, OMe), 6.24 (1H, broad, $-\text{CO}_2\text{H}$), 6.7–7.6 (8H, m, Ar-H), 7.87 (1H, s, $-\text{CH}=\text{C}-$), 7.99 (1H, s, $-\text{CH}=\text{C}-$). MS m/e : 368 (M^+ , 100%). Anal. Calcd. for $\text{C}_{21}\text{H}_{20}\text{O}_6$: 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 $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 1682 (C=O), 1599, 1581 (arom.). $^1\text{H-NMR}$ (CDCl_3) δ : 3.70 (3H, s, OMe), 3.80 (3H, s, OMe), 4.24 (2H, broad s, $-\text{CH}_2\text{OH}$), 6.30 (2H, broad s, $-\text{CH}_2\text{OH}$ and $-\text{CO}_2\text{H}$), 6.7–7.7 (9H, m, Ar-H and $-\text{CH}=\text{C}-$), 7.83 (1H, s, $-\text{CH}=\text{C}-$). Anal. Calcd. for $\text{C}_{20}\text{H}_{20}\text{O}_5 \cdot 1/2 \text{C}_6\text{H}_6$: 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 $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 1687 (C=O), 1603, 1584 (arom.). $^1\text{H-NMR}$ (CDCl_3) δ : 3.71 (3H, s, OMe), 3.80 (3H, s, OMe), 4.27 (2H, broad s, $-\text{CH}_2\text{OH}$), 5.41 (2H, broad s, $-\text{CH}_2\text{OH}$ and $-\text{CO}_2\text{H}$), 6.6–7.7 (9H, m, Ar-H and $-\text{CH}=\text{C}-$), 7.82 (1H, s, $-\text{CH}=\text{C}-$).

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 $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1765 (C=O), 1624 (C=C), 1592, 1580 (arom.). $^1\text{H-NMR}$ (CDCl_3) δ : 3.54 (3H, s, OMe), 3.78 (3H, s, OMe), 5.02 (2H, d, $J=2$ Hz, $-\text{CH}_2\text{OCO}-$), 6.3–7.4 (8H, m, Ar-H), 6.62 (1H, t, $J=2$ Hz, $-\text{CH}=\text{C}-$), 7.64 (1H, broad s, $-\text{CH}=\text{C}-$). UV $\nu_{\text{max}}^{\text{EtOH}}$ 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 $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1770 (C=O), 1622 (C=C), 1590 (arom.). $^1\text{H-NMR}$ (CDCl_3) δ : 3.50 (3H, s, OMe), 3.73 (3H, s, OMe), 5.02 (2H, d, $J=2$ Hz, $-\text{CH}_2\text{OCO}-$), 6.59 (1H, m, $-\text{CH}=\text{C}-$), 6.2–7.4 (8H, m, Ar-H), 7.67 (1H, broad s, $-\text{CH}=\text{C}-$). UV $\lambda_{\text{max}}^{\text{EtOH}}$ 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 $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 1735 (C=O), 1631 (C=C). $^1\text{H-NMR}$ (CDCl_3) δ : 3.74 (3H, s, $-\text{CO}_2\text{Me}$), 5.98 (1H, d, $J=12$ Hz, $-\text{CH}=\text{C}-$), 6.93 (1H, d, $J=12$ Hz, $-\text{CH}=\text{C}-$), 7.2–7.7 (5H, m, Ar-H). Anal. Calcd. for $\text{C}_{10}\text{H}_{10}\text{O}_2$: C, 74.05; H, 6.22. Found: C, 73.56; H, 6.16.

Dimethyl *cis*-Veratrylidenesuccinate (10)—A solution of *trans*-veratrylidenesuccinic acid¹¹ (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 $^1\text{H-NMR}$ 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 $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1729, 1718 (C=O), 1640 (C=C), 1604, 1579 (arom.). $^1\text{H-NMR}$ (CDCl_3) δ : 3.44 (2H, d, $J=1$ Hz, $-\text{CH}_2\text{CO}_2\text{Me}$), 3.69 (3H, s, $-\text{CO}_2\text{Me}$), 3.71 (3H, s, $-\text{CO}_2\text{Me}$), 3.87 (3H, s, OMe), 3.89 (3H, s, OMe), 6.76 (1H, fused t, $J=1$ Hz, $-\text{CH}=\text{C}-$), 6.7—7.0 (3H, m, Ar-H). MS m/e : 294 (M^+ , 36%), 175 (100%). *Anal.* Calcd. for $\text{C}_{15}\text{H}_{18}\text{O}_6$: 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 $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1752 (C=O), 1694 (C=C), 1604, 1593, 1578 (arom.). $^1\text{H-NMR}$ (CDCl_3) δ : 3.80 (3H, s, OMe), 3.82 (3H, s, OMe), *ca.* 3.84 (2H, m, $\text{C}_4\text{-H}$), 4.85 (2H, s, $-\text{CH}_2\text{OCO}-$), *ca.* 4.93 (1H, m, $\text{C}_1\text{-H}$), 6.50 (1H, dd, $J=9$, 2 Hz, $\text{C}_6\text{'-H}$), 6.70 (1H, d, $J=9$ Hz, $\text{C}_5\text{'-H}$), 6.82 (1H, d, $J=2$ Hz, $\text{C}_2\text{'-H}$), 7.1—7.2 (4H, m, Ar-H). MS m/e : 322 (M^+ , 100%). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 282.0 (3.57). *Anal.* Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_4$: 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 $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1748 (C=O), 1691 (C=C), 1611 (arom.). $^1\text{H-NMR}$ (CDCl_3) δ : 3.76 (3H, s, OMe), 3.90 (3H, s, OMe), 3.7—4.0 (2H, m, $\text{C}_4\text{-H}$), 4.84 (2H, s, $-\text{CH}_2\text{OCO}-$), *ca.* 4.90 (1H, m, $\text{C}_1\text{-H}$), 6.58 (1H, s, $\text{C}_6\text{-H}$), 6.72 (1H, s, $\text{C}_5\text{-H}$), 7.0—7.3 (5H, m, Ar-H). MS m/e : 322 (M^+ , 30%). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 286.4 (3.46). *Anal.* Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_4$: C, 74.52; H, 5.63. Found: C, 74.42; H, 5.63.

Compound 11c: Colorless leaflets (from EtOH), mp 184.5—185°. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1749 (C=O), 1690 (C=C), 1604 (arom.). $^1\text{H-NMR}$ (CDCl_3) δ : 3.36 (3H, s, OMe), 3.81 (3H, s, OMe), 3.70—3.90 (2H, m, $\text{C}_4\text{-H}$), 4.78 (2H, broad s, $-\text{CH}_2\text{OCO}-$), 5.23 (1H, m, $\text{C}_1\text{-H}$), 6.87 (1H, d, $J=8$ Hz, $\text{C}_6\text{-H}$), 6.98 (1H, d, $J=8$ Hz, $\text{C}_5\text{-H}$), 7.1—7.3 (5H, m, Ar-H). MS m/e : 322 (M^+ , 100%). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 282 (3.05). *Anal.* Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_4$: 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 procedure¹⁷⁾ on IR and $^1\text{H-NMR}$ spectral comparison.