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Synthetic Studies on Lignans and Related Compounds. VI.[1] Photochemical Rearrangement of β-Apolignans[2]

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The photochemistry of the β-apolignan (**1**) was investigated, and a specific rearrangement was found to occur on irradiation of **1**. The photoproduct was identified as a tetrahydrocycloprop(a)indene (**2b**) based on an unambiguous synthesis of the dihydro product (**3b**) derived from its hydrogenolysis. Similar irradiation of taiwanin A gave two isomeric tetrahydrocycloprop(a)indenes (**10a** and **10b**) *via* the cyclization into β-apolignans followed by their degenerate rearrangement. Consequently, this type of photo-transformation was found to be a common feature of β-apolignans irrespective of ring substituents, and was characterized as a vinyl-aryl di-π-methane rearrangement. Mechanistic aspects of the rearrangement are briefly described.

Keywords——β-apolignan; taiwanin A; photorearrangement; tetrahydrocycloprop-(a)indene system; indan-2-spiro-γ-lactone; synthesis of indan derivatives; vinyl-aryl di-π-methane rearrangement

In the preceding paper,[1] we reported the regiospecific photocyclization of 2,3-dibenzylidenebutyrolactones to β-apolignans which was investigated as a possible model for the biogenetic pathway to natural naphthalide lignans. We now report a di-π-methane rearrangement of the β-apolignans which was encounted concurrently in the above photo-transformation.

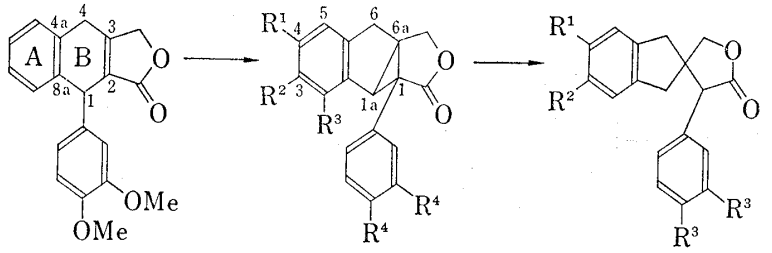
Photorearrangement

Irradiation of 1,4-dihydro-1-(3,4-dimethoxyphenyl)-3-hydroxymethyl-2-naphthoic acid γ-lactone (**1**)[1] in benzene with Pyrex-filtered light for 3.5 hr resulted in quantitative conversion to a crystalline product.

Elemental analysis showed the photoproduct to be isomeric with **1**. The photoproduct exhibited a benzenoid ultraviolet (UV) absorption at λ_{max} 278.8 nm (log ε 3.50) and an infrared (IR) absorption for the lactone carbonyl at 1750 cm^{-1}. The proton magnetic resonance (^1H-NMR) spectrum showed a pair of one-proton doublets (J=18 Hz), at δ 2.96 and 3.38, indicative of a benzylic methylene group,[4] a one-proton singlet due to a benzylic hydrogen at 3.09, and a two-proton singlet due to a lactone methylene at 4.63. These observations showed that structural modifications had taken place only in ring B of **1**. By analogy with the di-π-methane rearrangement of 3,3-diphenylcyclohexene,[5] there were postulated two possible structures, (**2a**) and (**2b**), for the photoproduct. The rearrangement of **1** to **2a** would involve cleavage of the C_1–C_{8a} bond accompanied by bond formation at C_2–C_{8a} and C_1–C_3. The $C_1 \rightarrow C_2$ dimethoxyphenyl migration and the C_1–C_3 bond formation would give **2b**. This assumption was supported by the degradation experiments on the photoproduct. Catalytic hydrogena-

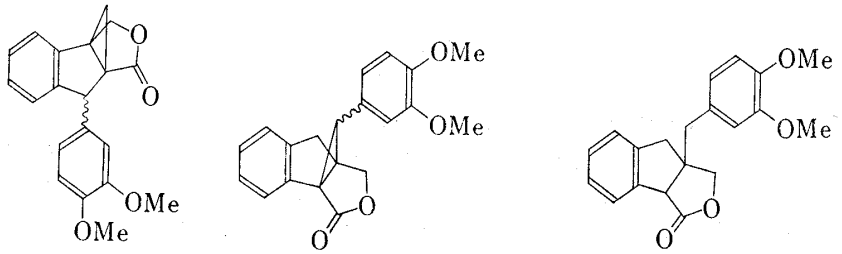
1) Part V: T. Momose, K. Kanai, T. Nakamura, and Y. Kuni, *Chem. Pharm. Bull.* (Tokyo), **25**, 2755 (1977).
2) Presented in part at the 26th Meeting of Kinki Branch, Pharmaceutical Society of Japan, Osaka, Oct. 1976, Abstracts of Papers, p. 46. The preliminary communication has appeared in *Heterocycles*, **4**, 1481 (1976).
3) Location: *133–1, Yamada-kami, Suita, Osaka 565, Japan.*
4) R.M. Silverstein and G.C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, 1963, p. 87.
5) *a*) W.G. Dauben and W.A. Spitzer, *J. Am. Chem. Soc.*, **92**, 5817 (1970); *b*) For a review, see S.S. Hixson, P.S. Mariano, and H.E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

tion[6] of the photoproduct over palladium chloride on carbon gave quantitatively a dihydro derivative, which showed a lactone IR absorption at 1768 cm^{-1}, and ^1H-NMR signals for benzylic hydrogen as a pair of one-proton singlets at δ 2.68 and 2.71, a pair of one-proton doublets (J=16 Hz) at 3.02 and 3.20, and one-proton singlet at 3.76, together with those for lactone methylene protons as a pair of one-proton doublets (J=9 Hz) at 4.20 and 4.27. In addition, the dihydro-photoproduct displayed a mass fragment peak due to dimethoxytropylium at *m/e* 151 (18%). These data seems to be consistent with the structures (**3a** and **3b**) expected to arise from the hydrogenolysis of **2a** and **2b**, respectively. Potassium permanganate oxidation of the dihydro derivative and subsequent methylation of the resulting mixture of acids with diazomethane gave methyl veratrate (33%) and dimethyl phthalate (43%). The formation of these esters rather than of methyl 2-(3,4-dimethoxybenzoyl)benzoate indicates that the photoproduct has an aryl-rearranged structure (**2a** or **2b**). Since it was difficult to discriminate between **2a** and **2b** from the spectral and degradative evidences, the synthesis of **3a** and **3b** was undertaken.



1

2b : $R^1=R^2=R^3=H$, $R^4=OMe$ **3b** : $R^1=R^2=H$, $R^3=OMe$
10a : R^1 $R^2=R^4=OCH_2O$, $R^3=H$ **11** : $R^1R^2=R^3=OCH_2O$
10b : $R^1=H$, R^2 $R^3=R^4=OCH_2O$



2c **2a** **3a**

Chart 1

Synthesis of 3a and 3b

Our approach to **3a** is outlined in Chart 2. The Claisen-Schmidt condensation of methyl 3-oxo-1-indancarboxylate[7] with veratraldehyde and subsequent methylation of the resulting veratrylidene keto acid with diazomethane afforded a veratrylideneindanone (**4**) in 90% yield. The *trans* configuration of **4** was assigned based on ^1H-NMR spectral analysis. The olefinic proton in **4** (δ 7.68) resonates at the field closely similar to that for the protons in *trans*-2-benzylidene-1-indanone derivatives (for example, δ 7.65 in the case of *trans*-2-benzylidene-3,3-dimethyl-1-indanone[8]) rather than in *cis* compounds (δ 6.78—6.96[8]): the olefinic protons

6) Popovici *et al.* have described the hydrogenolysis of 6-phenyl-2: 3-benzobicyclo[3.1.0]hex-2-ene; M. Popovici, V. Ioan, M. Elian, and C.D. Nenitzescu, *Rev. Roum. Chim.*, **12**, 583 (1967).
7) K. Mori, M. Matsui, and Y. Sumiki, *Agr. Biol. Chem.* (Tokyo), **27**, 27 (1963).
8) J.-L. Imbach, A.E. Pohland, E.D. Weiler, and N.H. Cromwell, *Tetrahedron*, **23**, 3931 (1967).

in the *trans* compounds are deshielded by the carbonyl group while those in the *cis* compounds are not. The ester (**4**) was hydrogenated over palladium chloride on carbon to give a 3,4-dimethoxybenzylindanone (**5**) whose stereochemistry remained unsolved. Condensation of **5** with aqueous formaldehyde in the presence of potassium hydroxide gave a keto lactone (**6**) in 42% yield. Hydrogenolysis of **6** over palladium chloride on carbon gave **3a**. The IR and ^{1}H–NMR spectra of **3a** are quite different from those of the dihydro-photoproduct.

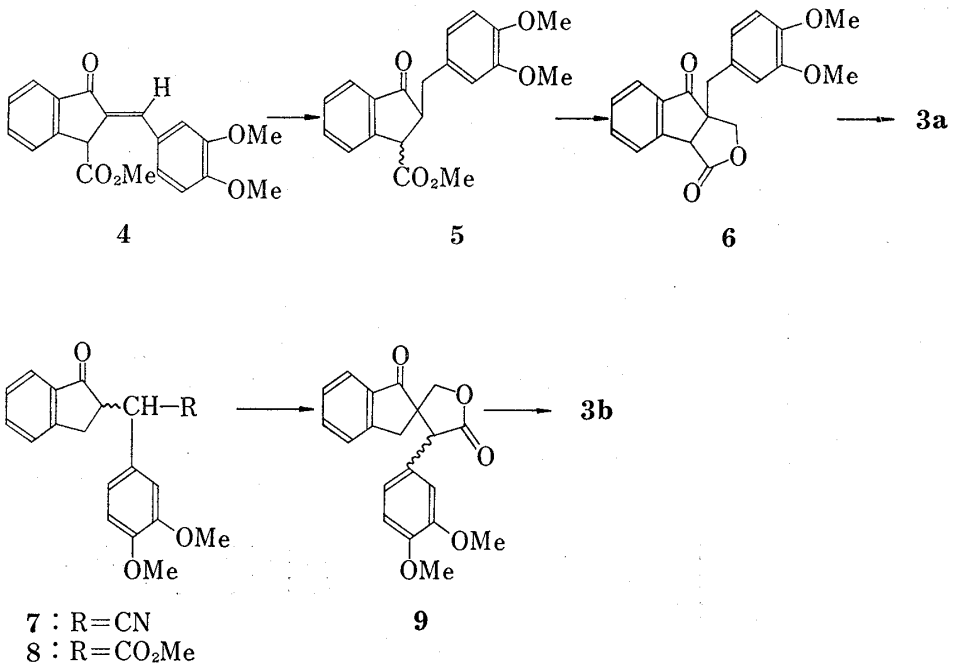


Chart 2

The synthesis of **3b** was carried out as delineated in Chart 2. Hydrocyanation of 2 veratrylidene-1-indanone[9] and subsequent treatment of the resulting keto nitrile (**7**) (a diastereomeric mixture) with methanolic hydrogen chloride gave a keto ester (**8**) (a diastereomeric mixture). Condensation of **8** with aqueous formaldehyde in the presence of potassium carbonate gave a keto lactone (**9**) in 41% yield. Hydrogenolysis of **9** over palladium chloride on carbon yielded **3b**, which showed the mp and IR and ^{1}H–NMR spectra identical with those of the dihydro-photoproduct.

Consequently, it was found that the β-apolignan (**1**) was phototransformed into the tetrahydrocycloprop(*a*)indene system (**2b**) *via* a vinyl-aryl di-π-methane rearrangement.

Photorearrangement of Taiwanin A

A similar rearrangement was also encountered in the irradiation of taiwanin A[10] with Pyrex-filtered light in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO). Preparative high-performance liquid chromatography (HPLC) of the crude product gave (**10a**) (mp 246—247°; 18%) and (**10b**) (mp 213—214°; 3%) (see Chart 1) presumably *via* respective β-apolignans. The ^{1}H–NMR spectra of these products exhibited a pair of doublets and a singlet in the δ *ca.* 3.0—3.4 region, characteristic of the tetrahydrocycloprop(*a*)indene system, and their substitutional isomerism was also deduced from their ^{1}H–NMR spectra. Especially, the structure of **10b** was assigned from the presence of a pair of one-proton doublet signals at δ 5.92, 5.93, 5.97, and 5.98 ascribed to the C_2,C_3-methylenedioxy protons, which were not symmetrically

9) Y. Poirier and N. Lozac'h, *Bull. Soc. Chim. France*, **1966**, 1062.
10) G.A. Swoboda, K.-T. Wang, and B. Weinstein, *J. Chem. Soc.* (*C*), **1967**, 161.

arranged with respect to the pendant phenyl ring and were similar in its ^{1}H–NMR pattern to that in otobain.[11] The assignment of another one (**10a**) was furnished based on the close proximity of two singlet signals due to methylenedioxy protons at δ 5.84 and 5.86. Catalytic hydrogenation of **10a** over palladium chloride on carbon gave quantitatively **11**, the conversion supporting the tetrahydrocycloprop(*a*)indene structure for **10a**.

Hence, β-apolignans were found to undergo a di-π-methane rearrangement irrespectively of the ring substituents.

Mechanistically, a di-π-methane rearrangement of the β-apolignan (**1**) could give **2a** and **2c** (see Chart 1). Above all, the formation of the latter from **1** seems not to be ruled out on the analogy of the di-π-methane reaction of 4-benzyl-5,5-dimethyl-2(5*H*)-furanone[12]: the rearrangement of **1** to **2c** would involve cleavage of the C_4–C_{4a} bond accompanied by bond formation at C_3–C_{4a} and C_2–C_4. The specific rearrangement of **1** into **2b** in the present study can be rationalized by stereoelectronic control: only migrates the phenyl on the *quasi*-axial linkage capable of the maximum orbital overlap with the butenolide olefinic bond.

Meanwhile, sensitized irradiation[13] of **1** using excess molar amounts of acetophenone as a sensitizer through a filter of ordinary borosilicate glass (*i.e.*, acetophenone essentially absorbs all the light) gave **2b** (45%) and dehydrogenation product[1] (6%). The result indicates that the rearrangement proceeds *via* the triplet state of **1**, and coincides with the suggestion[5b] that di-π-methane systems in a sterially constrained situation rearrange preferentially by way of their triplet excited states.

Experimental

Melting points and boiling point 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 (MS) with a Hitachi RMU-6E spectrometer (direct inlet, at 70 eV). All organic extracts were dried over Na_2SO_4 before evaporation. Preparative thin-layer chromatography (TLC) was performed on Merck Kieselgel 60 PF_{254}. Column chromatography was effected using Mallinckrodt silicic acid. Preparative HPLC was performed on a Hitachi 635 Liquid Chromatograph employing a LiChrosorb SI-100 column (8 mmϕ × 50 cm) with $CHCl_3$–*n*-hexane (17: 8) as the eluent and a flow rate of 2.5 ml/min. The photochemical reactions were carried out in an immersion apparatus fitted with an Eikosha 100 W high-pressure mercury lamp.

Photolysis of 1,4-Dihydro-1-(3,4-dimethoxyphenyl)-3-hydroxymethyl-2-naphthoic Acid γ-Lactone (1)[1]——A solution of **1** (50 mg) in benzene (50 ml) was irradiated through a Pyrex sleeve (1.5 mm wall thickness) at 5° under a stream of dry, oxygen-free N_2. The reaction went to completion after 3.5 hr's irradiation (checked by ^{1}H–NMR spectrum). Evaporation of the solution *in vacuo* afforded quantitatively 1-(3,4-dimethoxyphenyl)-6a-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop(*a*)indene-1-carboxylic acid γ-lactone (**2b**) as colorless leaflets (from EtOH), mp 195—196°. IR ν_{max}^{KBr} cm^{-1}: 1750 (C=O), 1588, 1608 (arom.). ^{1}H–NMR ($CDCl_3$) δ: 2.96 (1H, d, J=18 Hz, C_6–H), 3.38 (1H, d, J=18 Hz, C_6–H), 3.09 (1H, s, C_{1a}–H), 3.64 (3H, s, OMe), 3.73 (3H, s, OMe), 4.63 (2H, s, $-CH_2OCO-$), 6.3—7.4 (7H, m, Ar–H). MS *m/e*: 322 (M^+, 48%), 202 (100%). UV λ_{max}^{EtOH} nm (log ε): 273 sh. (3.42), 278.8 (3.50), 287 sh. (3.40). *Anal.* Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.24; H, 5.62.

Catalytic Hydrogenation of the Photoproduct (2b)——A suspension of 5% $PdCl_2$–C (0.30 g) in dioxane (30 ml) was pre-equilibrated with hydrogen. The photoproduct (**2b**, 0.23 g) in dioxane (15 ml) was added to this, and hydrogenated at room temperature and atmospheric pressure until the uptake of hydrogen ceased. The catalyst was filtered off, and the filtrate was evaporated *in vacuo* to give quantitatively α-(3,4-dimethoxyphenyl)-2-hydroxymethyl-2-indanacetic acid γ-lactone (**3b**) as colorless micro needles (from isopropyl ether), mp 105—106°. IR ν_{max}^{KBr} cm^{-1}: 1768 (C=O), 1589, 1604 (arom.). ^{1}H–NMR ($CDCl_3$) δ: 2.68 and 2.71 (2H, each s, C_1–H), 3.02 (1H, d, J=16 Hz, C_3–H), 3.20 (1H, d, J=16 Hz, C_3–H), 3.76 (1H, s, C_α–H), 3.82 (3H, s, OMe), 3.84 (3H, s, OMe), 4.20 (1H, d, J=9 Hz, $-CH_2OCO-$), 4.27 (1H, d, J=9 Hz, $-CH_2OCO-$), 6.5—

11) T. Gilchrist, R. Hodges, and A.L. Porte, *J. Chem. Soc.*, **1962**, 1780.
12) P.C.M. van Noort and H. Cerfontain, *Tetrahedron Lett.*, **1977**, 3899.
13) A solution of **1** (31 mg) and acetophenone (375 mg) in benzene (30 ml) was irradiated through an ordinary borosilicate glass sleeve (1.5 mm wall thickness) in a similar manner to that for **2b** in Experimental to give **2b** (14 mg, 45%) and 1-(3,4-dimethoxyphenyl)-3-hydroxymethyl-2-naphthoic acid γ-lactone[1] (2 mg, 6%).

7.2 (7H, m, Ar–H). MS *m/e*: 324 (M^+, 29%), 151 (18%), 129 (100%). UV λ_{max}^{EtOH} nm (log ε): 268 (3.42), 273.5 (3.56), 280 sh. (3.48). *Anal.* Calcd. for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 73.98; H, 6.20.

Oxidation of the Dihydro-photoproduct (3b)——A mixture of **3b** (0.12 g), $KMnO_4$ (0.60 g), and acetone (10 ml) was refluxed for 4 hr, during which time an additional portion of $KMnO_4$ (0.50 g) was added. After removal of acetone, the residual solid was suspended in H_2O, and treated with sulfur dioxide until the disappearance of MnO_2. The aqueous solution was acidified (Congo Red) with 5% H_2SO_4, and extracted with AcOEt. The extract was washed with satd. NaCl and evaporated to give a colorless solid (0.08 g). The solid (0.08 g) was methylated with CH_2N_2 in AcOEt in a usual manner to give a colorless oil (0.09 g), which was purified by preparative TLC on silica gel using $CHCl_3$ as solvent to give methyl veratrate (0.02 g, 33%), mp 59—59.5° (from petroleum ether), identical with an authentic sample[14] on IR and ^{1}H-NMR spectral comparison, and dimethyl phthalate (0.03 g, 43%), bp 120° (bath temperature, 1 mmHg), identical with an authentic sample[15] on IR and ^{1}H-NMR spectral comparison.

Methyl *trans*-2-Veratrylidene-3-oxo-1-indancarboxylate (4)——A solution of KOH (11.0 g) in EtOH (100 ml) was added to an ice-cooled solution of methyl 3-oxo-1-indancarboxylate[7] (11.0 g) and veratraldehyde (16.0 g) in EtOH (40 ml) with stirring over 1 hr, and the mixture was further stirred at room temperature for 2 hr. The mixture was diluted with H_2O (700 ml), and then acidified with conc. HCl, and the deposited yellow solid (19.2 g) was collected by filtration. The solid (19.2 g) was methylated with CH_2N_2 in MeOH (40 ml) in a usual manner. The deposited solid was collected and recrystallized to give **4** (17.6 g, 90%) as pale yellow rhombs (from MeOH), mp 136—137°. IR ν_{max}^{KBr} cm^{-1}: 1727, 1697 (C=O), 1618 (C=C), 1596, 1588 (arom.). ^{1}H-NMR ($CDCl_3$) δ: 3.56 (3H, s, $-CO_2CH_3$), 3.91 (3H, s, OMe), 3.96 (3H, s, OMe), 5.09 (1H, d, J=2 Hz, C_1–H), 6.8—8.0 (7H, m, Ar–H), 7.68 (1H, d, J=2 Hz, $-CH=\overset{|}{C}-$). MS *m/e*: 338 (M^+), 279 (100%). *Anal.* Calcd. for $C_{20}H_{18}O_5$: C, 70.99; H, 5.36. Found: C, 71.13; H, 5.41.

Methyl 2-(3,4-Dimethoxybenzyl)-3-oxo-1-indancarboxylate (5)——The veratrylidene ester (**4**, 2.0 g) was hydrogenated over 5% $PdCl_2$–C (1.0 g) in MeOH (220 ml) at room temperature and atmospheric pressure until 148 cc of hydrogen (theoretically 132 cc) was consumed. The catalyst was filtered off, and the filtrate was evaporated to give **5** (1.4 g, 68%) as colorless needles (from isopropyl ether), mp 77—79°. IR ν_{max}^{KBr} cm^{-1}: 1742, 1727 (C=O), 1599, 1592 (arom.). ^{1}H-NMR ($CDCl_3$) δ: 2.7—4.2 (3H, m, benzylic H and C_2–H), 3.67 (3H, s, $-CO_2CH_3$), 3.79 (3H, s, OMe), 3.80 (3H, s, OMe), 3.96 (1H, d, J= 4 Hz, C_1–H), 6.69 (3H, s, Ar–H), 7.2—7.8 (4H, m, Ar–H). MS *m/e*: 340 (M^+), 151 (100%). *Anal.* Calcd. for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.61; H, 5.93.

2-(3,4-Dimethoxybenzyl)-2-hydroxymethyl-3-oxo-1-indancarboxylic Acid γ-Lactone (6)——To a stirred solution of **5** (1.1 g) and KOH (0.44 g) in MeOH (35 ml)–H_2O (14 ml) was added 37% formalin (5 ml) over 30 min at room temperature. The solution was diluted with satd. NaCl (300 ml), and acidified with 5% H_2SO_4, and the separated oil was extracted with ether. The extract was washed with satd. $NaHCO_3$, then with satd. NaCl, and evaporated to give **6** (0.47 g, 42%) as colorless leaflets (from isopropyl ether), mp 105—106°. IR ν_{max}^{KBr} cm^{-1}: 1771, 1724 (C=O), 1602, 1590 (arom.). ^{1}H-NMR ($CDCl_3$) δ: 2.98 (1H, d, J=14 Hz, benzylic H), 3.40 (1H, d, J=14 Hz, benzylic H), 3.73 (3H, s, OMe), 3.76 (3H, s, OMe), 4.11 (1H, s, C_1–H), 4.37 (1H, d, J=10 Hz, $-CH_2OCO-$), 4.42 (1H, d, J=10 Hz, $-CH_2OCO-$), 6.5—6.7 and 7.2—7.8 (7H, each m, Ar–H). MS *m/e*: 338 (M^+, 41%), 151 (100%). *Anal.* Calcd. for $C_{20}H_{18}O_5$: C, 70.99; H, 5.36. Found: C, 71.00; H, 5.24.

2-(3,4-Dimethoxybenzyl)-2-hydroxymethyl-1-indancarboxylic Acid γ-Lactone (3a)——The keto lactone (**6**, 100 mg) was hydrogenated over 5% $PdCl_2$–C (200 mg) in AcOH (20 ml) at 50° and 95 atmospheric pressure for 3 hr. The catalyst was filtered off, and the filtrate was evaporated *in vacuo* to give a brown glass, which was purified by preparative TLC on silica gel using $CHCl_3$ as solvent to give **3a** (85 mg, 88%) as a colorless viscous oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770 (C=O), 1605, 1590 (arom.). ^{1}H-NMR ($CDCl_3$) δ: 2.88 (1H, d, J=16 Hz, C_3–H), 3.19 (1H, d, J=16 Hz, C_3–H), 2.98 (2H, s, benzylic H), 3.87 (3H, s, OMe), 3.88 (3H, s, OMe), *ca.* 3.91 (1H, d, J=9 Hz, $-CH_2OCO-$), 4.41 (1H, d, J=9 Hz, $-CH_2OCO-$), 3.93 (1H, s, C_1–H), 6.6—6.9 and 7.1—7.5 (7H, each m, Ar–H). MS *m/e*: 324 (M^+, 52%), 151 (100%). UV λ_{max}^{EtOH} nm (log ε): 267 (3.32), 273 (3.48), 281 (3.46). *Anal.* Calcd. for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 73.91; H, 6.46. Compound **3a** was not identical with the dihydro derivative from the photoproduct on ^{1}H-NMR spectral comparison.

α-(3,4-Dimethoxyphenyl)-1-oxo-2-indanacetonitrile (7)——A solution of NaCN (2.2 g) in H_2O (11 ml) was added to a stirred solution of 2-veratrylidene-1-indanone[9] (3.0 g) and NH_4Cl (1.8 g) in dimethylformamide (45 ml) at 100° over 10 min, and the solution was further stirred for 3.5 hr. The iced solution was diluted with satd. NaCl (250 ml), and the separated oil was extracted with benzene. The extract was washed with satd. $NaHCO_3$ and then satd. NaCl and evaporated to give a brown viscous oil (3.4 g), which was chromatographed on silica gel (70 g) in $CHCl_3$ to give **7** (3.1 g, 91%) as a colorless glass. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2250, 2327 (CN), 1718 (C=O), 1608, 1595 (arom.). ^{1}H-NMR ($CDCl_3$) δ: 2.9—3.5 (3H, m, C_2– and C_3–H), 3.76 and 3.78, and 3.89 and 3.91 (6H, each s, OMe, a mixture of *erythro* and *threo* isomer), 4.71 (1H, m, C_α–H), 6.5—8.0 (7H, m, Ar–H).

14) K.U. Matsmoto, *Ber.*, **11**, 122 (1878).
15) H. Meyer, *Monatsh. Chem.*, **25**, 1201 (1904).

Methyl α-(3,4-Dimethoxyphenyl)-1-oxo-2-indanacetate (8)——An ice-cooled solution of **7** (1.6 g) in dry MeOH (15 ml) was saturated with dry HCl. After being allowed to stand overnight at room temperature, the solution was poured into satd. NaCl (75 ml), and the separated oil was extracted with AcOEt. The extract was washed with satd. $NaHCO_3$ and then satd. NaCl and evaporated to give a pale yellow glass (1.5 g), which was chromatographed on silica gel (30 g) in $CHCl_3$ to give **8** (1.3 g, 75%) as a colorless glass. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1735, 1714 (C=O), 1608, 1591 (arom.). ^1H-NMR ($CDCl_3$) δ: 2.6—4.0 (4H, m, C_α–, C_2–, and C_3–H), 3.61 and 3.88, and 3.78 and 3.84 (9H, each s, OMe and $-CO_2CH_3$, a mixture of *erythro* and *threo* isomer), 6.7—6.9 (3H, m, Ar–H), 7.2—7.8 (4H, m, Ar–H). The mixture afforded a colorless solid on addition of isopropyl ether. Recrystallization from EtOH-isopropyl ether gave one isomer of **8** (0.55 g) as colorless rhombs, mp 128—129°. IR ν_{max}^{KBr} cm^{-1}: 1732, 1710 (C=O), 1604, 1587 (arom.). ^1H-NMR ($CDCl_3$) δ: 2.6—4.0 (4H, m, C_α–, C_2–, and C_3–H), 3.78 (3H, s, $-CO_2CH_3$ or OMe), 3.84 (6H, s, OMe, or $-CO_2CH_3$ and OMe), 6.7—6.9 (3H, m, Ar–H), 7.2—7.8 (4H, m, Ar–H). MS *m/e*: 340 (M^+, 40%), 308 (100%). *Anal.* Calcd. for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.51; H, 5.90.

α-(3,4-Dimethoxyphenyl)-2-hydroxymethyl-1-oxo-2-indanacetic Acid γ-Lactone (9)——To a stirred solution of **8** (0.52 g) and K_2CO_3 (0.03 g) in MeOH (25 ml)–H_2O (5 ml) was added 37% formalin (0.25 ml) at room temperature. The solution was further stirred for 4.5 hr, during which time an additional portion of formalin (0.25 ml) was added. The deposited solid was collected by filtration to give **9** (0.21 g, 41%) as colorless needles (from $CHCl_3$–EtOH), mp 206—207°. IR ν_{max}^{KBr} cm^{-1}: 1767, 1707 (C=O), 1607, 1590 (arom.). ^1H-NMR ($CDCl_3$) δ: 3.31 (1H, d, J=18 Hz, C_3–H), 3.49 (1H, d, J=18 Hz, C_3–H), 3.76 (3H, s, OMe), 3.78 (3H, s, OMe), 3.93 (1H, s, C_α–H), 4.30 (1H, d, J=10 Hz, $-CH_2OCO-$), 4.58 (1H, d, J=10 Hz, $-CH_2OCO-$), 6.64 (3H, s, Ar–H), 7.1—7.7 (4H, m, Ar–H). MS *m/e*: 338 (M^+, 100%), 279 (100%). *Anal.* Calcd. for $C_{20}H_{18}O_5$: C, 70.99; H, 5.36. Found: C, 70.75; H, 5.27. The acetate (**8**) (0.10 g) was recovered.

α-(3,4-Dimethoxyphenyl)-2-hydroxymethyl-2-indanacetic Acid γ-Lactone (3b)——The keto lactone (**9**, 50 mg) was hydrogenated in a similar manner to that for **3a** to give a brown viscous oil, which was purified by preparative TLC on silica gel using $CHCl_3$ as solvent to give **3b** (44 mg, 90%) as colorless micro needles (from isopropyl ether), mp 105—106°. The product was identical with the dihydro derivative from the photoproduct on mp and IR and ^1H-NMR spectral comparison.

6a-Hydroxymethyl-3,4-methylenedioxy-1-(3,4-methylenedioxyphenyl)-1,1a,6,6a-tetrahydrocycloprop(a)-indene-1-carboxylic Acid γ-Lactone (10a) and 6a-Hydroxymethyl-2,3-methylenedioxy-1-(3,4-methylenedioxyphenyl)-1,1a,6,6a-tetrahydrocycloprop(*a*)-indene-1-carboxylic Acid γ-Lactone (10b)——A solution of taiwanin A[10] (147 mg) and DABCO (36 mg) in acetone (130 ml) was irradiated for 10.5 hr in a similar manner to that for **2b**. After evaporation of the solution, the crude product was subjected to preparative TLC on silica gel using $CHCl_3$ as solvent to give a colorless solid (53 mg), which was purified by preparative HPLC to give **10a** (26 mg, 18%) and **10b** (4 mg, 3%).

Compound **10a**: Colorless micro needles (from $CHCl_3$–EtOH), mp 246—247°. IR ν_{max}^{KBr} cm^{-1}: 1750 (C=O). ^1H-NMR ($CDCl_3$) δ: 2.98 (1H, d, J=18 Hz, C_6–H), 3.20 (1H, d, J=18 Hz, C_6–H), 2.94 (1H, s, C_{1a}–H), 4.58 (2H, s, $-CH_2OCO-$), 5.84 (2H, s, $-OCH_2O-$), 5.86 (2H, s, $-OCH_2O-$), 6.3—6.9 (5H, m, Ar–H). MS *m/e*: 350 (M^+, 100%). UV λ_{max}^{EtOH} nm (log ε): 295 (3.90). *Anal.* Calcd. for $C_{20}H_{14}O_6$: C, 68.57; H, 4.03. Found: C, 68.52; H, 4.10.

Compound **10b**: Colorless rhombs (from $CHCl_3$–EtOH), mp 213—214°. IR ν_{max}^{KBr} cm^{-1}: 1759 (C=O), 1608 (arom.). ^1H-NMR ($CDCl_3$) δ: 3.04 (1H s, C_{1a}–H), 3.06 (1H, d, J=18 Hz, C_6–H), 3.27 (1H, d, J=18 Hz, C_6–H), 4.60 (2H, s, $-CH_2OCO-$), 5.83 (2H, s, $-OCH_2O-$), 5.92, 5.93, 5.97, and 5.98 (2H, dd, $-OCH_2O-$), 6.3—6.7 (5H, m, Ar–H). MS *m/e*: 350 (M^+, 100%). UV λ_{max}^{EtOH} nm (log ε): 289 (3.74). *Anal.* Calcd. for $C_{20}H_{14}O_6$: C, 68.57; H, 4.03. Found: C, 68.30; H, 4.04.

2-Hydroxymethyl-5,6-methylenedioxy-α-(3,4-methylenedioxyphenyl)-2-indanacetic Acid γ-Lactone (11)——The photoproduct (**10a**, 50 mg) was hydrogenated over 5% $PdCl_2$–C (100 mg) in dioxane (20 ml) at 50° and 50 atmospheric pressure for 3 hr. The catalyst was filtered off, and the filtrate was evaporated *in vacuo* to give quantitatively **11** as colorless crystals (from EtOH), mp 150—151°. IR ν_{max}^{KBr} cm^{-1}: 1770 (C=O), 1613 (arom.). ^1H-NMR ($CDCl_3$) δ: 2.54 (1H, d, J=16 Hz, C_1–H), 2.64 (1H, d, J=16 Hz, C_1–H), 2.90 (1H, d, J=15 Hz, C_3–H), 3.07 (1H, d, J=15 Hz, C_3–H), 3.72 (1H, s, C_α–H), 4.19 (1H, d, J=9 Hz, $-CH_2OCO-$), 4.27 (1H, d, J=9 Hz, $-CH_2OCO-$), 5.88 (2H, s, $-OCH_2O-$), 5.93 (2H, s, $-OCH_2O-$), 6.5—6.9 (5H, m, Ar–H). MS *m/e*: 352 (M^+, 36%), 173 (100%). UV λ_{max}^{EtOH} nm (log ε): 294.5 (3.94). *Anal.* Calcd. for $C_{20}H_{16}O_6$: C, 68.18; H, 4.58. Found: C, 68.07; H, 4.59.