Constituents of *Geranium thunbergii* Sieb. et Zucc. IV.1) 
Ellagitannins. (2). Structure of Geraniin2)

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(Received November 9, 1976)

The main tannin of *Geranium thunbergii* has been isolated as yellow crystals, and named geraniin. Geraniin gave upon hydrolysis in boiling water, gallic acid, hexahydroxydiphenic acid, ellagic acid, and corilagin, and is shown by the proton nuclear magnetic resonance spectra to be a corilagin derivative esterified at O-2 and O-4 of D-glucopyranose in the molecule. Upon condensation with o-phenylenediamine, geraniin yielded a phenazine derivative, named phenazine A (X), which was transformed into phenazine B (XI) upon prolonged reaction. These two phenazine derivatives gave phenazine C (XII) by further prolonged reaction, or by hydrolysis of X or XI in boiling water. Corilagin was also isolated from the hydrolysis products mixture. The structure of phenazine C was proved by identification of its hydrolyzed product XV with synthetic specimen which was prepared via hydrogenolysis of dimethyl dimethoxytetrahydroxydiphenolate. These data along with the PMR spectra show that the structure of geraniin to be I. The carbon nuclear magnetic resonance spectra of geraniin indicate partial hydration to form geminal diol at the cyclohexenetrione moiety.

**Keywords** —dehydrohexahydroxydiphenoyl ester of corilagin; PMR and CMR spectra; hydrolysis; phenazine derivatives from geraniin; synthesis of phenazines; tannin structure determination

Preparation of a crude ellagitannin, temporarily named tannin 1, from the extract of *Geranium thunbergii* Sieb. et Zucc. was reported in Part II4) of this series. Upon further purification, we have isolated a pure ellagitannin, named geraniin, which is regarded as the main tannin of this plant, and determined its structure to be I.

Geraniin, when repeatedly recrystallized from a mixture of MeOH and H$_2$O, formed yellow crystals, C$_{44}$H$_{46}$O$_{27}$·3H$_2$O, [α]$_D^{-}$ = 141° (hexahydrate, c=0.5, MeOH). A single spot was shown on paper-partition chromatography (PPC) and paper electrophoresis, and the characteristic color of ellagitannin1) was given by the reaction with NO$_2^{-}$. The products of hydrolysis of tannin 1 in boiling water,5) i.e., gallic acid (II), ellagic acid (III), hexahydroxydiphenic acid (IV) and corilagin (V), were produced upon analogous hydrolysis of geraniin, and the products were fractionated by preparative thin-layer chromatography (prep. TLC) after methylation with diazomethane to give methyl tri-O-methylgallate (VI), tetra-O-methylellagic acid (VII), dimethyl hexamethoxydiphenolate (VIII), and nonamethylcorilagin (IX).4) Proton nuclear magnetic resonance (PMR) spectrum of geraniin measured in acetone-$d_6$ (Table I) shows seven protons including that of anomic proton of sugar, in the region of aromatic and vinyl protons, among which four protons can be regarded as due to the identical protons as the aromatic protons in corilagin.5) Downfield shifts of H-2 and H-4 of glucopyranose to $\delta$ 5.4—5.6 ppm from those of corilagin ($\delta$ 4.06 and 4.42) are observed. A one-proton singlet is exhibited at $\delta$ 5.16. These spectral evidences along with

3) Location: 1-1-1 Tsushima-naka, Okayama, 700, Japan.
the results of hydrolysis show that geraniin is a derivative of V esterified at O-2 and O-4 of d-glucopyranose.

The solution of geraniin was turned red by phenylhydrazine–AcOH, and gave pale yellow precipitate upon the reaction with o-phenylenediamine solution in 15% AcOH at room temperature. This precipitate was purified by reprecipitation from MeOH–CHCl₃ to give amorphous powder, C₄₇H₃₀N₅O₂₄·6H₂O, (X), [α]D²₅ = -163° (c=0.5, MeOH), which was named phenazine A. Upon the reaction of geraniin with o-phenylenediamine in 50% AcOH, yellow precipitate was produced, and this product was purified by analogous reprecipitation to give amorphous powder, C₄₇H₃₀N₅O₂₄·5H₂O, (XI), [α]D²₅ = -90° (c=0.5, dioxane), which was named phenazine B. Phenazine B was also obtained when the reaction mixture producing X or an acetone solution of X was left stand or warmed. When aqueous solution of either X or XI was kept at boiling temperature for 1.5 hr, or the reaction mixture yielding phenazine B was
kept for longer time or at higher temperature, dark brown-red precipitate was produced, and was recrystallized from tetrahydrofuran to give needles of phenazine C, C_{20}H_{24}N_{6}O_{6}, H_2O, (XII), m/e 372 (M^+). The mother liquor of XII gave, upon evaporation followed by fractionation of methylated residue, VI, VII, VIII and IX. Phenazine C yielded dibenzoate, C_{24}H_{16}N_{2}O_{8}, diacetate, C_{26}H_{12}N_{2}O_{6}, and di-O-methyl derivative, XIII, C_{22}H_{12}N_{2}O_{6}, which yielded upon hydrolysis, hydroxy acid XIV. This acid was converted by the treatment with diazomethane, to dimethyl ester of tetra-O-methyl derivative, XV, C_{26}H_{26}N_{2}O_{8}, mp 130°. This ester was also produced upon the reaction of XIII with dimethyl sulfate in alkali, but the main product, XVI, C_{27}H_{26}N_{2}O_{6}, was found to have a C-methyl group (PMR, CDCl_3, δ 2.76) which is presumed to have replaced the hydrogen near a pyrazine nitrogen in XV (δ 8.75). These reaction sequences, the properties of the products, and the result of acid hydrolysis of geraniin, which yielded more than 1 mole equivalent of hexahydroxydiphenic acid, indicate structures of these esters to be XV and XVI, and determination of XV structure was accomplished by synthesis. As the synthesis of XV via acetate of tribenzylellagic acid⁶ was retarded by extreme low yield of this compound from tetraacetyllellagic acid, present synthesis was carried out as follows. Hydrogenolysis of dimethyl dimethoxytetra benzoxoxydiphenoate (XVII)⁷ followed by methylation with diazomethane yielded, via XVIII, tri-

![Chemical structures](image)

Chart 2

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benzyl derivative XIX, C_{40}H_{38}O_{10}, mp 146–147°, which was hydrogenolyzed to give XX, C_{19}H_{20}O_{10}, mp 152–154°. Oxidation of XX with o-chloranil yielded diketone XXI which was condensed with o-phenylenediamine to give XXII. Methylation of XXII with diazomethane gave XV. The production of XVIII by hydrogenolysis of XVII was accompanied by formation of a small amount of an isomer of XVIII. Comparisons of the properties of the product obtained by methylation of this isomer followed by hydrogenolysis, and those of XX, with the properties of XXIV which had been reported to be produced via XXIII, support the assignments of structure XVIII to the main product of the hydrogenolysis of XVII, and structure XXIII to the isomeric minor product, although XV should be produced from either XVIII or XXIII.

![Chemical Structures](https://example.com/structure.png)

The process of phenazine C formation via phenazine A and phenazine B, and comparison of the signals in PMR spectra of these compounds, indicate structures X, XI and I for phenazine A, phenazine B and geraniin, respectively. The marked downfield shift of H₄ in the PMR spectrum, upon the formation of XI (δ 8.24, s) from X (δ 7.07, d, J=2 Hz) is presumed to be due to aromatization of the ring, and the downfield shift of the same proton in X from that in geraniin (δ 6.53, s) would be the result of pyrazine ring formation. The decoupling experiment showed the allylic coupling between H₄ and H₉ (δ 5.53, d, J=2 Hz) in X, which is presumed to be due to conformational change occurred upon the production of X from geraniin.

As for the ester linkages at O-2 and O-4 of β-glucopyranose in geraniin, the one at O-2 rather than that at O-4, is presumed to be on the cyclohexenetrione moiety because of the significant upfield shift of the anomeric proton of β-glucopyranose from δ 6.55 to 6.14, upon the formation of XI from X, as this shift indicates nearby location of the phenazine ring.

The ¹³C-NMR (CMR) spectra of geraniin generally show two peaks in the region of conjugated ketone, at δ 191–192 and at δ 194–195, and also peaks assignable to geminal diols at δ 91–97 alongside of C-1 signal of glucose, their shifts and patterns being varied depending on the water content and the solvent. These signals indicate geminal diol formation by partial hydration at cyclohexenetrione moiety of geraniin. The above mentioned shifts of ketone carbon peaks may occur either for conjugated ketone or for isolated ketone having geminal diols at α-carbon. The ketone group in phenazine A may also be hydrated to retard.
enolization. Further investigations of hydration of cyclohexenetrione in geraniin molecule are in progress.

Geraniin was obtained in the yield of up to 1.6% from fresh plant collected in summer.\textsuperscript{8} Comparison of this yield with the data of tannin analysis of the plant,\textsuperscript{3} and the results of fractionation of the plant extract show that geraniin is the main tannin of \textit{G. thunbergii}, and that appreciable parts of the phenolic compounds of smaller molecules reported previously\textsuperscript{5,9} could be products of hydrolysis of geraniin occurred during extraction and fractionation. Among these phenolic compounds, brevifolin (XXV)\textsuperscript{3} would presumably be decarboxylated product from brevifolin carboxylic acid (XXVI) which could be produced from the dehydrohexahydroxydiphenoyl residue upon the hydrolysis of geraniin. This presumption has been supported by combined gas chromatography–mass spectrometry (GC–MS) of methylated hydrolysis product of geraniin in boiling water, which showed presence of a product presumed to be XXVIII which is the fully methylated derivative of XXVI, based on the analogy of its fragmentation pattern to that of tri-O-methylbrevifolin (XXVII), in addition to \textbf{M}\textsuperscript{+} ion (\textit{m/e} 348) and [\textbf{M}–COOMe]\textsuperscript{+} ion (\textit{m/e} 289).

\begin{center}
\begin{tikzpicture}
  \node at (0,0) {
    \begin{tikzpicture}
      \node[shape=circle,draw=black,font=\scriptsize] (A) at (0,0) {RO-\CO-O-RO};
      \node[shape=circle,draw=black,font=\scriptsize] (B) at (1,0) {O};
      \draw[thick,black] (A) -- (B);
    \end{tikzpicture}
  };
  \node at (2,0) {
    \begin{tikzpicture}
      \node[shape=circle,draw=black,font=\scriptsize] (A) at (0,0) {RO-\CO-O-RO};
      \node[shape=circle,draw=black,font=\scriptsize] (B) at (1,0) {O};
      \draw[thick,black] (A) -- (B);
    \end{tikzpicture}
  };
  \node at (0,-1) {XXV: R=H};
  \node at (2,-1) {XXVI: R=H};
  \node at (0,-2) {XXVII: R=CH\textsubscript{3}};
  \node at (2,-2) {XXVIII: R=CH\textsubscript{3}};
\end{tikzpicture}
\end{center}

Chart 4

Crystalline geraniin shows almost no astringency on the tongue, and the weak astringency shown by its solution in aqueous ethanol is also incomparable to that of tannic acid of Japanese Pharmacopoeia, in spite of the appreciable astringency exhibited by geraniin when measured with hemoglobin.\textsuperscript{1,4} Such properties of geraniin would have been favoring the medicinal application of \textit{G. thunbergii}.

**Experimental**

Infrared (IR) spectra were recorded with JASCO IR-G, ultraviolet (UV) spectra were obtained with Shimadzu Double-40 Spectrophotometer, and [\textit{\alpha}]\textsubscript{D} was measured with JASCO DIP-4 Digital Polarimeter. PMR spectra were recorded with Hitachi R-22 at 90 MHz with tetramethylsilane as internal standard, and CMR spectra were measured with NEVA's NV-21 at 22.6 MHz with \textit{H} internal lock and tetramethylsilane as the internal standard in acetone-\textit{d}_4, tetrahydrofuran-\textit{d}_4 and methanol-\textit{d}_4. Gas liquid chromatography (GLC) was carried out with Shimadzu 5A gas chromatograph equipped with FID, using a glass column (2 m x 3 cm i.d.) packed with 1% OV-1 on 80–100 mesh Chromosorb W, AW-HMDS, at column temperature 220\textdegree. MS were obtained with Shimadzu-LKB-9000 Gas Chromatograph–Mass Spectrometer by GC–MS or direct inlet system. Temperature of ion source 270\textdegree, ion accelerating voltage 3.5 kV, ionizing potential 70 eV, trap current 60 \textmu A. Paper chromatography was performed on Toyo Filter Paper No. 50, and column chromatography was carried out on silica gel, Wako C-200. Paper electrophoresis was performed on Toyo Kagaku Sangyo FS-1510 at 600 V with 1% borax. Thin-layer chromatography (TLC) and prep. TLC were performed on Kieselgel PF\textsubscript{254} (Merck). Solvents for TLC and prep. TLC: A, ligroin–CHCl\textsubscript{3}–MeOH (7: 4: 1.5); B, benzene–CHCl\textsubscript{3}–acetone (3: 1: 1); C, benzene–EtOAc (9: 1); D, CHCl\textsubscript{3}–acetone (3: 1). Evaporation of solvents was carried out at the temperature lower than 40\textdegree.

**Geraniin (1)——**The crude ellagitannin temporarily named tannin 1\textsuperscript{9} was recrystallized several times from MeOH–H\textsubscript{2}O treating with activated charcoal to give yellow crystals.\textsuperscript{7} Seeding of MeOH–H\textsubscript{2}O solution of the EtOAc extract from the aqueous acetone extract of the plant\textsuperscript{9} with the crystals obtained above, after treating the EtOAc extract with ether and activated charcoal, yielded the same yellow crude crystals which were recrystallized from MeOH–H\textsubscript{2}O to give geraniin, mp >360\textdegree (yield: 1.6% from fresh plant). FPC

\textsuperscript{8} The yield from dried herb described in the preliminary paper may be improved by proper treatment of the herb.

\textsuperscript{9} Y. Asahina and K. Tomimura, \textit{Yakugaku Zasshi}, 38, 405 (1918).
(colored with aq. FeCl₃ solution): RF 0.41 (n-BuOH–AcOH–H₂O, 4:1:5, upper (BAW)): 0.18 (7% AcOH). [α]₂⁰° = −141° (c=0.5, MeOH). UV λ[lim] nm (log ε): 222 (4.74), 285 (4.45). IR ν[max] cm⁻¹: 3400, 1735 (shoulder), 1750, 1710, 1700 (sh.), 1620, 1340, 1205. NMR (acetone-d₆): δ: 4.28 (m, 1H, glu-H₂), 4.67–5.00 (m, 2H, glu-H₂, H₆). 5.16 (s, 1H, H₆). 5.40–5.60 (m, 3H, glu-H₂, H₆, H₇). 6.53 (s, 1H, H₄). 6.55 (br, s, 1H, glu-H₂). 6.67 (s, 1H, hexahydroxydiphenyl (HHDHP)). 7.13 (s, 1H, HHDHP). 7.20 (s, 2H, galloyl (gall)). 7.21 (s, 1H, H₆). Anal. Calcd. for C₄₇H₄₀O₈·5H₂O: C, 47.22; H, 3.67. Found: C, 47.33; H, 3.57.¹⁰

**Hydrolysis of Geraniin in Boiling Water**—Geraniin (300 mg) in H₂O (150 ml) was refluxed in N₂ atmosphere for 1.5 hr, and H₂O was distilled in vacuo. The residue was dissolved in MeOH and treated with a solution of diazomethane in ether (CH₃₂N₂-ether). The solvent was distilled 12 hr later, and the CH₃₂N₂ treatment was repeated. After distilling the solvent, CHCl₃ was added to the residue, and insoluble material was recrystallized from pyridine to give pale yellow needles (40 mg) which were identified with tetra-O-methyllellagic acid (VII) by IR spectra. The CHCl₃-soluble material was fractionated by prep. TLC (solvent A), and the constituent of RF 0.50 was recrystallized from H₂O to give colorless needles, mp 83–84° (51.7 mg), which were identified with methyl tri-O-methylgallate (VI) by mixed mp and IR spectra. The fraction of RF 0.42 gave pale yellow syrup (11 mg) which was identified with dimethyl hexamethoxydiphenoate (VIII) by GLC, MS and PMR. The fraction of RF 0.30 showed upon GC–MS analysis, a GLC peak (tR 8.5 min) which exhibited m/e 348 (M⁺), 289 (M–COOMe)⁺, 261, 247, 233, 219 and 212 ions. The fragment ions lower than 261 were almost identical with those of tri-O-methyl brevifolin (XXVII). The fraction of RF 0.18 was recrystallized from MeOH to give colorless needles, mp 240–241°, which were identified with nona-O-methylcorilagin (IX) by mixed mp and IR spectra (35.6 mg).

**Hydrolysis of Geraniin in 5% H₂SO₄**—Geraniin (500 mg) in 5% H₂SO₄ (50 ml) was refluxed for 10 hr, precipitate was filtered and washed with H₂O. Recrystallization from pyridine yielded yellow needles (212 mg) which were identified as ellagic acid by IR spectra. The mother liquor was extracted with EtOAc (50 ml×3). The residue obtained by distillation of EtOAc solution was treated with CH₃₂N₂-ether for 5 hr, and after evaporation, the product was fractionated by prep. TLC (solvent A) to give the main product (RF 0.50) which was extracted with CHCl₃ and recrystallized from H₂O to give colorless needles, mp 83–84° (90 mg), which were identified as methyl tri-O-methylgallate by mixed mp and IR spectra.

**Phenazine A (X)**—A solution of o-phenylenediamine (60 mg) in 15% AcOH (15 ml) was added to a solution of I (250 mg) in MeOH (5 ml) and was washed with H₂O, and the mixture was stirred for 5 min at room temperature. Pale yellow precipitate was filtered and washed with H₂O, and then recrystallized from MeOH–CHCl₃ to give pale yellow amorphous powder (243 mg), mp >360°. PPC: RF 0.48 (BAW, FeCl₃). λ[lim] nm (log ε): 220 (4.93), 265 (4.73). ν[max] cm⁻¹: 3380, 1730 (sh.), 1720, 1610, 1355, 1325, 1220. [α]₂⁰° = −103° (c=0.5, MeOH). NMR (acetone-d₆): δ: 4.39 (m, 1H, glu-H₂), 4.24 (m, 2H, H₆) (1H, H₆) (1H, H₆). 5.56 (d, 1H, J=1 Hz, H₇). 6.62 (d, 1H, J=2 Hz, glu-H₂). 6.67 (s, H₆), 7.06 (s, 1H) (HHDHP). 7.07 (d, 1H, J=2 Hz, H₆), 7.19 (s, 2H, gall), 7.33 (s, 1H, H₆), 7.78–8.22 (m, 4H, ar. am.). Anal. Calcd. for C₄₇H₄₀N₄O₄·5H₂O: C, 50.63; H, 3.79; N, 2.51. Found: C, 50.66; H, 3.75; N, 2.08.

**Phenazine B (XI)**—A solution of o-phenylenediamine (60 mg) in 50% AcOH (15 ml) was added to a solution of I (250 mg) in MeOH (5 ml), and the mixture was left stand for 5 hr. The solvent was distilled, and the residue was washed with H₂O, and recrystallized from MeOH–CHCl₃ to give pale orange-yellow amorphous powder (250 mg), mp >360°. PPC: RF 0.48 (BAW, FeCl₃). [α]₂⁰° = −90° (c=0.5, dioxane). λ[lim] nm (log ε): 220 (4.83), 280 (4.70). ν[max] cm⁻¹: practically identical with the IR spectrum of X. NMR (acetone-d₆): δ: 4.03 (dd, 1H, J=4, 12 Hz, glu-H₂), 4.27 (dd, 1H, J=8, 12 Hz, glu-H₆), 4.99 (dd, 1H, J=4, 8 Hz, glu-H₆), 5.48 (br, s, 2H, glu-H₂, H₆), 5.63 (d, 1H, J=6 Hz, glu-H₂), 6.14 (d, 1H, J=6 Hz, glu-H₂), 6.70 (s, 1H, HHDHP), 6.99 (s, 3H, gall, H₋2, HHDHP-H₋1). 7.46 (s, 1H, H₂O), 7.84–8.44 (m, 4H, ar. am.), 8.24 (s, 1H, H₆). Anal. Calcd. for C₄₇H₄₀N₂O₄·5H₂O: C, 51.47; H, 3.68; N, 2.55. Found: C, 51.65; H, 3.72; N, 2.27.

**Phenazine C (XII)**—The same reaction mixture as that afforded phenazine B by 5 hr reaction was left stand for 24 hr. The residue obtained by distillation solvent was treated with MeOH, and insoluble material was filtered and washed with H₂O. Recrystallization from tetrahydrofuran yielded dark brown-red needles, mp >360°. λ[lim] nm (log ε): 282 (4.73), 335 (4.46), 405 (3.63). ν[max] cm⁻¹: 3400, 1737, 1616, 1595, 1515, 1350, 1300, 1210. NMR (CDCl₃): δ: 8.66 (s, 1H), 8.26–8.89 (m, 4H), 9.61 (s, 1H). MS m/e 572 (M⁺). Anal. Calcd. for C₄₇H₄₀N₂O₄·5H₂O: C, 61.55; H, 2.58; N, 7.18. Found: C, 61.16; H, 2.61; N, 6.92.

Upon acetylation of XII with Ac₂O–pyridine, a lemon-yellow amorphous diacetate, mp>360°, MS m/e 456 (M⁺) was obtained. Benzoylation of XII with benzoyl chloride–dimethylformamide–pyridine yielded yellow amorphous dibenzoate, mp>360°, MS m/e 580 (M⁺).

**Hydrolysis of Phenazine A (X) and Phenazine B (XI)**—Phenazine A or B (500 mg) in H₂O (500 ml) was refluxed in N₂ atmosphere for 1.5 hr. The precipitate from hot solution was filtered, washed with MeOH, and recrystallized from tetrahydrofuran to give dark brown-red needles which were identified with XII. The mother liquor and washing were combined, concentrated to dryness, and the residue was taken up in

¹⁰ The water content varied depending on the way of drying and storage. The sample for these data were dried in vacuo at 50°, over P₂O₅, and kept in a desiccator over silica gel at ordinary pressure for 3 days—1 week.
MeOH. The MeOH solution was treated with CH$_2$N$_2$-ether, and after evaporation of the solvent, the residue was fractionated by prep. TLC (solvent A). The fractionated products were identified with VI (82 mg), VIII (10.5 mg), IX (72.2 mg), and VII (70 mg), respectively.

**Methyl 4-Methoxy-3-(4,5,6-trimethoxy-2-methoxybenzylidenephenoxy-2-carboxylate (XV) from Phenazine C**—Phenazine C (55 mg) was treated with excess CH$_2$N$_2$-ether twice for 12 hr each. The resulting dark brown precipitate was filtered, washed with MeOH, and recrystallized from dimethylformamide to give dark brown amorphous powder (XIII), mp >360°, MS m/e 400 (M$^+$). This powder was dissolved in warm 10% NaOH (5 ml), and after heating, H$_2$O (20 ml) was added. The resulting solution was neutralized with conc. HCl (9%) under ice-cooling to give orange-red precipitate which was filtered, washed with H$_2$O, and treated with CH$_2$N$_2$-ether for 12 hr after dissolving in MeOH (5 ml). The solvent was distilled and the residue which showed two spots ($R_f$ 0.57, 0.55) on TLC (solvent B) was fractionated by prep. TLC (solvent B) to give the main product, $R_f$ 0.55 (XV). Recrystallization from MeOH-H$_2$O gave yellow needles, mp 130–131°, yield 28 mg (35.5%). $\lambda$$_{max}$ nm (log e): 267 (4.79), 370 (3.84). $\beta$$_{max}$ cm$^{-1}$: 2950, 1727, 1710, 1330, 1208, 1213, 1092. NMR (CDCl$_3$): $\delta$: 3.56, 3.67, 3.77, 3.90, 4.00, 4.02 (OMe x 6), 7.48 (s, 1H), 7.75–8.44 (m, 4H), 8.75 (s, 1H). MS m/e 492 (M$^+$). *Anal. Calcd. for C$_{38}$H$_{42}$N$_2$O$_8$: C, 63.41; H, 4.91; N, 5.69. Found: C, 63.46; H, 5.18; N, 5.54.

**The Product Having C-methyl Group (XVI)**—To a solution of dimethyl ether (XIII) (70 mg) in 20% NaOH (2 ml) was added dimethyl sulfate (1 ml), and the solution was refluxed for 1 hr. 10% NaOH (10 ml) was added, and refluxing was continued for additional 2 hr. After cooling, the reaction mixture was neutralized with 10% HCl, precipitate was filtered, and washed with H$_2$O. The precipitate was dissolved in MeOH (10 ml) and treated with excess CH$_2$N$_2$-ether for 12 hr, and after distilling, the solvent was fractionated by prep. TLC (solvent B) to give the constituent of $R_f$ 0.57, which was recrystallized from MeOH–H$_2$O to afford yellow needles (XVI), mp 150–151°, yield 20 mg (21%). $\lambda$$_{max}$ nm (log e): 265 (4.88), 368 (4.05). $\beta$$_{max}$ cm$^{-1}$: 2900, 1730, 1715, 1360, 1255, 1200, 1110. NMR (CDCl$_3$) $\delta$: 2.76 (s, 3H, Me), 3.56 (MeO), 3.58 (MeO), 3.73 (MeO), 3.98 (MeO x 2), 4.07 (MeO), 7.44 (s, 1H), 7.78–8.35 (m, 4H). MS m/e 506 (M$^+$). *Anal. Calcd. for C$_{36}$H$_{41}$N$_2$O$_8$: C, 64.03; H, 5.17; N, 5.53. Found: C, 63.77; H, 5.25; N, 5.08.

**Debonylation of Dimethyl Dimethoxytetraybenzyloxido- phenylone (XVII)**—Hydrogenolysis of XVII (2.0 g) in AcOH (200 ml) over 10% Pd-C was carried out to absorb 1 mol equivalent of H$_2$ (60 ml). After removing the catalyst and the solvent, the residue was dissolved in CHCl$_3$ and chromatographed on a silica gel column (3 x 30 cm) eluting with CHCl$_3$ to give colorless syrup (XVIII) from fractions No. 20–25 (5 ml portions), yield 516 mg (25.8%). TLC: $R_f$ 0.54 (solvent C). NMR (CDCl$_3$) $\delta$: 3.51, 3.53, 3.58, 3.61 (MeO x 4), 5.14 (s, 4H, C$_2$H$_4$CH$_2$=C), 5.19 (s, 2H, C$_2$H$_4$CH$_2$-), 5.91 (br. s, 1H, OH), 7.25–7.51 (m, 17H). Fractions No. 26–28 yielded a colorless syrup (XXII), yield 200 mg (10%). TLC: $R_f$ 0.52. NMR (CDCl$_3$) $\delta$: 3.49, 3.52, 3.55, 3.59 (MeO x 4), 5.12 (s, 4H, C$_2$H$_4$CH$_2$=C), 5.17 (s, 2H, C$_2$H$_4$CH$_2$-). *Anal. Calcd. for C$_{36}$H$_{40}$O$_8$: C, 70.79; H, 5.04. Found: C, 70.65; H, 5.61.

**Hydrogenolysis of Dimethyl Trimethoxybenzyloxido- phenylone (XIX)**—Hydrogenolysis of XIX (300 mg) was carried out in AcOH (100 ml) over Pd which had been activated by hydrogenation of PdCl$_2$ (50 mg) in MeOH (100 ml). The catalyst and the solvent were removed when absorption of H$_2$ ceased, and the residue was recrystallized from H$_2$O to yield colorless prisms (XX), mp 152–154°, yield 100 mg (56%). $\beta$$_{max}$ cm$^{-1}$: 2300, 1630, 1590, 1340, 1315, 1245 (broad), 1067, 1017. NMR (CD$_2$OD) $\delta$: 3.43 (MeO), 3.54 (MeO x 3), 3.89 (MeO), 7.25 (s, 1H), 7.30 (s, 1H). *Anal. Calcd. for C$_{36}$H$_{42}$O$_8$: C, 55.88; H, 4.94. Found: C, 55.08; H, 4.95, 4.90. The carbon value was not raised by repeated experiments. However, crude XX was supported by production of VIII upon the treatment with CH$_2$N$_2$-ether.

**Oxidation of Dimethyl Trimethoxybenzyloxido- phenylone (XX) and Condensation of the Product with o-Phenlenediamine**—A solution of o-chloranil (30 mg) in dioxane (0.5 ml) was added to a solution of XX (50 mg) in dioxane (1 ml), and the mixture was stirred for 1 hr at room temperature. Petroleum ether was added to deposit red oil, and the upper layer was removed by decantation. The oil was recrystallized from ether–petr., ether repeatedly to give a viscous oil (XXI), which was dissolved in ether (2 ml), and a solution of o-phenlenediamine (13.5 mg) in ether (2 ml) and a few drops of AcOH were added. The mixture was left stand at room temperature for 18 hr. The solvent was distilled, and the residue was fractionated by prep. TLC (solvent D), upon which the yellow zone of $R_f$ 0.5 afforded by extraction with CHCl$_3$ a yellow syrup (XXII), yield 15 mg (25.6%). NMR (acetone-d$_4$) $\delta$: 3.49, 3.59, 3.71, 3.92, 4.04 (MeO x 5), 7.46 (s, 1H), 7.93–8.37 (m, 4H), 8.59 (s, 1H).

**Methyl 4-Methoxy-3-(4,5,6-trimethoxy-2-methoxybenzylidenephenoxy-2-carboxylate by Methylation of XXII**—Excess CH$_2$N$_2$-ether was added to a solution of XXII (25 mg) in MeOH. The solvent was distilled 12 hr later, and the residue was fractionated by prep. TLC extracting with CHCl$_3$ to give the product of $R_f$ 0.52, which was recrystallized from MeOH–H$_2$O to afford yellow needles, mp 160–161°, yield
21 mg (81.6%). When recrystallized from the solvent seeding with XV prepared from I, needles, mp 130—131°, were obtained, which were identified with XV by mixed mp and spectra. Anal. Calcd. for C_{26}H_{24}N_{4}O_{3}: C, 63.41; H, 4.91; N, 5.69. Found: C, 63.45; H, 4.93; N, 5.52.

Acknowledgement The authors wish to thank Dr. N. Nagakura of Kobe Women's College of Pharmacy for the CMR spectral measurements. This work was supported in part by a grant from the Ministry of Education, Japan, which is greatly acknowledged.