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Synthetic Studies on Lythraceae Alkaloids. III.[1] Stereoselective Total Synthesis of (±)-Decaline

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The first stereoselective total synthesis of one of Lythraceae alkaloids, decaline, was described. The Mannich condensation of isopelletierine (III) with 6-bromoisovanillin (IV) afforded stereoselectively the *trans* quinolizidine (V) which was converted to the methyl ether (VI). Stereoselective reduction of VI with the Henbest catalyst gave the axial alcohol (VII) along with the equatorial alcohol (VIII). The Ullmann condensation of the acetyl derivative (IX) from VII with the ester (XI) furnished the biphenyl ether (XII). Hydrolysis of XII and lactonization of the resulting hydroxy-acid (XIV) provided (±)-decaline (II).

Lythraceae alkaloids are classified into two groups, the lactone[3] and metacyclophan[4] type. Over twenty alkaloids belonging to the former type have been hitherto isolated and are further classified into the biphenyl and biphenyl ether alkaloids, as shown in lythrine (I) and decaline (II). These alkaloids have attracted considerable attention because of their unique structures and a few attempted syntheses[5-7] have been reported. We published the first total synthesis of one of these alkaloids, decaline in a preliminary communication.[8] Decaline, a representative of the biphenyl ether alkaloids, was isolated in 1962 from *Decodon verticillatus* (L.) Ell.[9] and characterized as the structure (II) by Ferris, *et al.*[10] Recently total synthesis of (±)-decaline was reported.[11] The present paper is concerned another with a full account of our experiments.

One of the possible biosynthetic pathways for the lactonic Lythraceae alkaloids has been suggested[12] to proceed *via* 4-arylquinolizidin-2-one produced by the condensation of isopelletierine with arylaldehyde. In the previous paper,[1] this Mannich condensation under an alkaline condition has been clarified to afford initially *cis*-4-arylquinolizidin-2-one which then isomerizes to the corresponding *trans* isomer, and especially, the *trans* isomer is stereoselectively obtained by the reaction with an arylaldehyde having a phenolic hydroxyl group in its molecule.

On the basis of the above observation, the condensation of isopelletierine[13] (III) with 6-bromoisovanillin[14] (IV) in an aqueous sodium hydroxide solution afforded the expected

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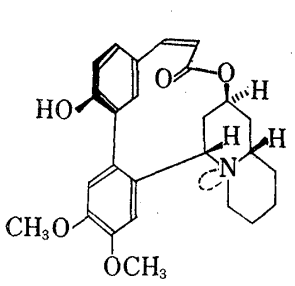

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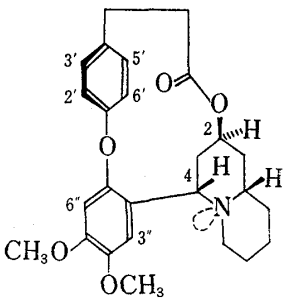

II

Chart 1

trans-quinolizidine (V), *m/e* 355, 353 (M^+, 1: 1), as a sole isolated product. The product showed bands at 3530 (OH), 2780, 2750 (Bohlmann bands), and 1720 cm^{-1} (C=O) in its infrared (IR) spectrum. Methylation of V with dimethyl sulfate and sodium hydroxide gave the methyl ether (VI), *m/e* 369, 367 (M^+, 1: 1), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2800, 2760 (Bohlmann bands), 1719 (C=O), in 76% overall yield from III. Since the signal due to C_4–H overlapped with that of the methoxyl group in the nuclear magnetic resonance (NMR) spectra of V and VI, substantiating evidence for their configuration at C_4 could not be obtained from their NMR spectra, however, the stereochemistry of V and VI would be deduced as depicted from the presence of the Bohlmann bands in their IR spectra and the fact that 4-aryl substituents exist in an equatorial position in 4-(3-methoxyphenyl)- and 4-(3-hydroxyphenyl)-*trans*-quinolizidin-2-one.[1)]

It is necessary to get an axial alcohol from the ketone (VI) for the synthesis of the alkaloid, because all lactonic Lythraceae alkaloids have an axial C_2–O bond. It has been reported that the reduction of a quinolizidin-2-one gives a mixture of two epimers in which the equatorial isomer predominates by the ratio from 9: 1 to 1: 1 according to the reduction methods employed.[5,6,15)] On the other hand, Henbest, *et al.*[16)] have recently reported that the reduction of a non-hindered cyclohexanone with an iridium-containing catalyst affords stereoselectively an axial alcohol. The purpose to get an axial alcohol was successfully realized by the stereoselective reduction of VI with the Henbest catalyst.[16,17)] The quinolizidin-2-one (VI) was heated with iridium tetrachloride and hydrochloric acid in the presence of trimethyl phosphite in aqueous 2-propanol, and the resulting crude product was separated by column chromatography into the axial alcohol (VII), mp 112—113°, *m/e* 371, 369 (M^+, 1: 1), and the equatorial alcohol (VIII), mp 71—74°, *m/e* 371, 369 (M^+, 1: 1), in the ratio of 9: 1 in 84% yield. In contrast, reduction of VI with sodium borohydride afforded VII and VIII in the ratio of 3: 7 in 85% yield.

In order to verify unambiguously the stereochemistry of the hydroxyl group of VII and VIII, both alcohols (VII and VIII) were acetylated with acetic anhydride in pyridine to furnish quantitatively the acetyl derivative (IX), mp 118—119°, and the epimeric acetyl derivative (X), mp 131—132°, respectively. The NMR spectra of IX and X revealed the signal due to C_2–H at 5.05 (quintet, J=3 Hz) and 4.84 ppm (triplet of triplets, J=11; 4.5 Hz), respectively, supporting well the assigned stereochemistry of the acetoxyl group in IX and X.

The signal due to C_4–H of VIII and X appeared at 3.52 (doublet of doublets, J=12; 3 Hz) and 3.55 ppm (doublet of doublets, J=11; 3 Hz), respectively, in their NMR spectra. These data offered an unequivocal evidence for confirming the stereochemistry at C_4 of V and VI assigned above.

The Ullmann condensation of IX with methyl 3-(4-hydroxyphenyl)propionate[18)] (XI) in pyridine using copper oxide in the presence of potassium carbonate afforded the biphenyl ether (XII), *m/e* 511 (M^+), in 34% yield along with the debrominated product (XIII), *m/e* 333

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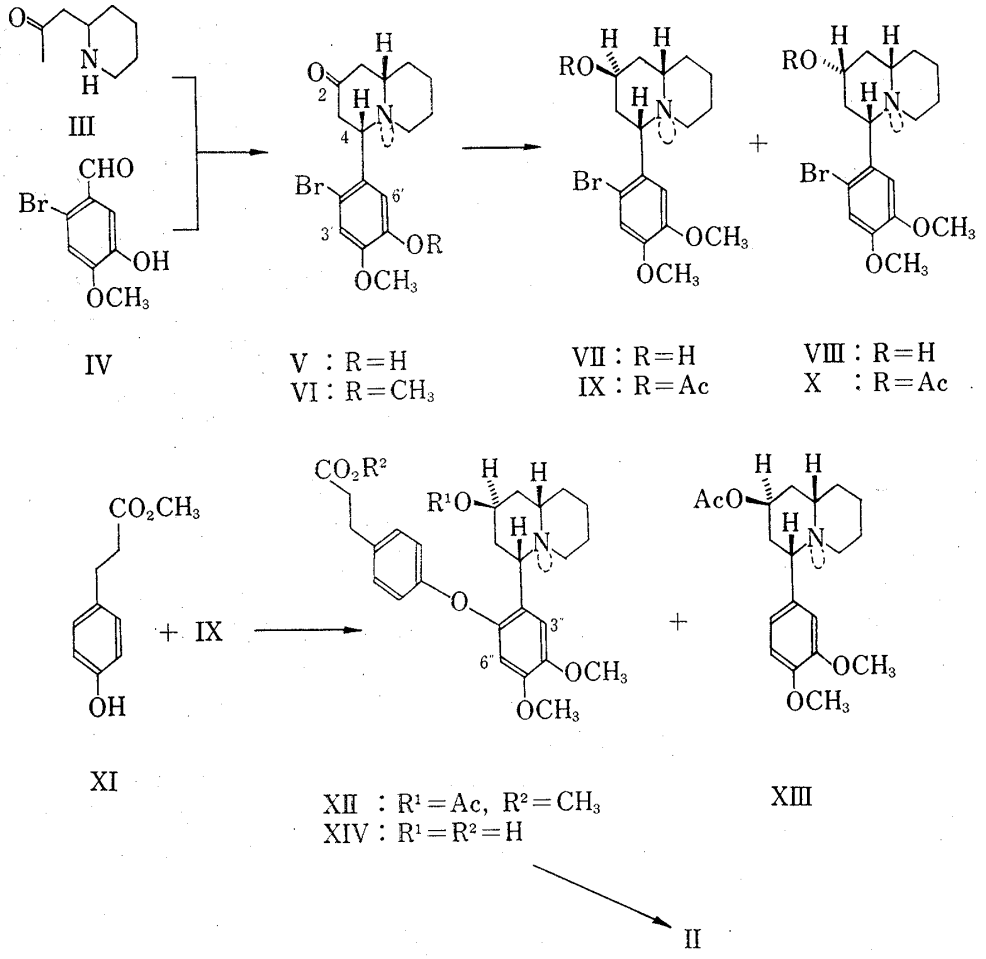

Chart 2

(M^+), in 7% yield. In agreement with the structure XII, the major product showed bands at 2790, 2760, 2730 (Bohlmann bands), 1728 cm^{-1} (C=O) in its IR spectrum and signals at 1.85 (3H, singlet, $OCOCH_3$), 3.67, 3.77, 3.91 (each 3H, singlet, $OCH_3 \times 3$), 4.97 ppm (1H, quintet, $J=3$ Hz, CHOAc) in its NMR spectrum. Hydrolysis of XII with aqueous sodium hydroxide in methanol furnished quantitatively the hydroxy-acid (XIV), *m/e* 455 (M^+), which was shown to exist in a zwitterion from its IR spectrum: 2460 (broad, N^+H), 1578 cm^{-1} (CO_2^-).

On treatment with thionyl chloride in chloroform, the hydrolysis product of dimethyldecodine, derived from a biphenyl alkaloid decodine, has been reported to revert to dimethyldecodine in 18% yield.[19] Similar treatment of the hydroxy-acid (XIV) with thionyl chloride resulted in the lactone, *m/e* 437 (M^+), which could not be fully characterized because of its poor yield. The yield did not exceed 3%. In order to prevent the intermolecular reaction, a highly diluted solution of XIV in benzene was heated with *p*-toluenesulfonic acid to provide (±)-decaline (II), mp 196—197°, *m/e* 437 (M^+), in 55% overall yield from XII. The product showed bands at 2800, 2730 (Bohlmann bands), 1720 cm^{-1} (C=O) in its IR spectrum and signals at 3.88, 3.90 (each 3H, singlet, $OCH_3 \times 2$), 4.89 ppm (1H, quintet, $J=3$ Hz, CHOCO) in its NMR spectrum. The product was identical with the lactone obtained above by mass spectral comparison and thin-layer chromatographic (TLC) behaviour.

The synthetic (±)-decaline was proved to be completely identical with natural decaline by IR ($CHCl_3$), NMR ($CDCl_3$), ultraviolet (UV), and mass spectral comparison and TLC behaviour. Thus, the first stereoselective total synthesis of (±)-decaline was accomplished. This synthesis will provide a general synthetic route to the biphenyl ether Lythraceae alkaloids.

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Experimental[20]

4-(2-Bromo-5-hydroxy-4-methoxyphenyl)(*e*)-*trans*-quinolizidin-2-one (V)—A mixture of isopelletierine[13] (III, 14.1 g, 0.1 mole) and 6-bromoisovanillin[14] (IV, 22.4 g, 0.09 mole) in 5% aq. NaOH (80 ml) was heated at 50° for 6 hr with stirring in a stream of N_2. The cooled reaction mixture was washed with ether. The aqueous layer was acidified with aq. HCl and washed with $CHCl_3$, giving the precipitate which was filtered. The aqueous filtrate was brought to pH 8 with aq. NaOH and extracted with $CHCl_3$. The extract was washed with H_2O, dried, and evaporated to give V (5.1 g) as a pale yellow amorphous solid. The collected precipitate was dissolved in aq. NaOH and the solution was brought to pH 8 with aq. HCl to give the precipitate, which was collected by filtration, washed with H_2O, and dissolved in $CHCl_3$. The $CHCl_3$ solution was washed with H_2O, dried, and evaporated to give V (26.5 g) as a pale yellow amorpous solid. The combined yield of V was quantitative. The compound thus obtained was used in the following reaction without further purification. The sample for measuring the spectra was purified with p-TLC (silica gel, $CHCl_3$–MeOH 30: 1). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3530 (OH), 2780, 2750 (Bohlmann bands), 1720 (C=O). NMR δ: 3.87 (3H, s, OCH_3), 6.94 (1H, s, Ar–H$^{3'}$), 7.22 (1H, s, Ar–H$^{6'}$). Mass Spectrum *m/e*: 355, 353 (M^+, 1: 1). High-resolution Mass Spectrum *m/e*: 355.070, 353.070. Calcd. for $C_{16}H_{20}O_3NBr$: 355.068, 353.070.

4-(2-Bromo-4,5-dimethoxyphenyl)(*e*)-*trans*-quinolizidin-2-one (VI)——To a solution of V (1.77 g) in 5% aq. NaOH (20 ml) was added dimethyl sulfate (2 ml) dropwise and a reaction mixture was heated at 60° for 1 hr with stirring. After the excess dimethyl sulfate was decomposed with aq. NH_3, the reaction mixture was extracted with $CHCl_3$. The extract was washed with H_2O, dried, and evaporated. The residue was recrystallized from EtOH to give VI (1.40 g, 76%) as colorless prisms, mp 143—144°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2800, 2760 (Bohlmann bands), 1719 (C=O). NMR δ: 3.90, 3.93 (each 3H, s, $OCH_3\times2$), 7.00 (1H, s, Ar–H$^{3'}$), 7.19 (1H, s, Ar–H$^{6'}$). Mass Spectrum *m/e*: 369, 367 (M^+, 1: 1). *Anal.* Calcd. for $C_{17}H_{22}O_3NBr$: C, 55.44; H, 6.02; N, 3.80. Found: C, 55.43; H, 6.01; N, 3.71.

4-(2-Bromo-4,5-dimethoxyphenyl)(*e*)-*trans*-quinolizidin-2-ol(*a*) (VII) and 4-(2-Bromo-4,5-dimethoxyphenyl) (*e*)-*trans*-quinolizidin-2-ol(*e*) (VIII)——1) With Henbest Catalyst: A solution of $IrCl_4\cdot H_2O$ (500 mg), conc. HCl (0.6 ml), H_2O (23 ml), and $(CH_3O)_3P$ (6.5 ml) was added to a solution of VI (10.1 g, 27.4 mmoles) in iso-PrOH (100 ml), and the reaction mixture was refluxed for 48 hr and evaporated. The residue was made alkaline with aq. NaOH and extracted with $CHCl_3$. The extract was washed with H_2O, dried, and evaporated. The residue was chromatographed on alumina using $CHCl_3$ as an eluent. The first fraction afforded the axial alcohol (VII, 7.65 g, 75.5%), which was recrystallized from AcOEt–*n*-hexane as colorless prisms, mp 112—113°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 2800, 2760 (Bohlmann bands). NMR δ: 3.86, 3.89 (each 3H, s, $OCH_3\times2$), 4.12 (1H, m, $W_H=7$ Hz, C_2–H), 6.93 (1H, s, Ar–H$^{3'}$), 7.12 (1H, s, Ar–H$^{6'}$). Mass Spectrum *m/e*: 371, 369 (M^+, 1: 1). *Anal.* Calcd. for $C_{17}H_{24}O_3NBr$: C, 55.14; H, 6.54; N, 3.78. Found: C, 55.35; H, 6.44; N, 3.68.

The second fraction afforded the equatorial alcohol (VIII, 0.85 g, 8.4%), which was recrystallized from AcOEt as colorless scales, mp 71—74°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 2790, 2750, 2720 (Bohlmann bands). NMR δ: 3.52 (1H, d-d, $J=12$; 3 Hz, C_4–H), 3.86, 3.89 (each 3H, s, $OCH_3\times2$), 6.93 (1H, s, Ar–H$^{3'}$), 7.14 (1H, s, Ar–H$^{6'}$). Mass Spectrum *m/e*: 371, 369 (M^+, 1: 1). *Anal.* Calcd. for $C_{17}H_{24}O_3NBr$: C, 55.14; H, 6.54; N, 3.78. Found: C, 55.35; H, 6.55, N, 3.78.

2) With $NaBH_4$: To a solution of VI (300 mg) in MeOH (10 ml) was added $NaBH_4$ (80 mg), and a reaction mixture was stirred at room temperature for 2 hr and evaporated. To the residue was added H_2O and the mixture was extracted with $CHCl_3$. The extract was washed with H_2O, dried, and evaporated. The residue was separated by the same procedure as that described in 1) to afford the axial alcohol (VII, 77 mg, 25.5%) and the equatorial alcohol (VIII, 179 mg, 59.5%), which were identical with the corresponding alcohols obtained in 1) in IR, TLC, and mixed melting points.

2-Acetoxy(*a*)-4-(2-bromo-4,5-dimethoxyphenyl)(*e*)-*trans*-quinolizidine (IX)——A solution of VII (2.0 g) and Ac_2O (7 ml) in pyridine (7 ml) was kept standing overnight at room temperature and evaporated. To the residue was added aq. HCl and the mixture was washed with ether. The aqueous layer was made alkaline with aq. $NaHCO_3$ and extracted with $CHCl_3$. The extract was washed with H_2O, dried, and evaporated. The residue (2.2 g, quantitative) was recrystallized from MeOH to give IX as colorless plates, mp 118—119°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2800, 2760 (Bohlmann bands), 1728 (C=O). NMR δ: 2.13 (3H, s, $COCH_3$), 3.86, 3.89 (each 3H, s, $OCH_3\times2$), 5.05 (1H, quin, $J=3$ Hz, C_2–H), 6.95 (1H, s, Ar–H$^{3'}$), 7.11 (1H, s, Ar–H$^{6'}$).

20) All melting points were measured with a Yanagimoto Micro Melting Point Apparatus and are uncorrected. The extracts were dried over anhyd. Na_2SO_4. Alumina (Brockmann grade II—III, Merck) and silica gel (Wako gel Q-23, 100—200 mesh, Wako) were used for column chromatography. Alumina (Aluminiumoxid GF_{254} Typ E, Merck) and silica gel (Kieselgel GF_{254} Typ 60, Merck) were used for TLC and preparative TLC (p-TLC). IR spectra were measured with a JASCO-IR-G, NMR spectra in $CDCl_3$ with a JEOL-PS-100 using TMS as an internal standard, mass spectra with a JEOL-JMS-01SG, and UV spectra in MeOH with a Hitachi Model 323.

Mass Spectrum *m/e*: 413, 411 (M^+, 1: 1). *Anal.* Calcd. for $C_{19}H_{26}O_4NBr$: C, 55.35; H, 6.34; N, 3.37. Found: C, 55.35; H, 6.35; N, 3.33.

2-Acetoxy(*e*)-4-(2-bromo-4,5-dimethoxyphenyl)(*e*)-*trans*-quinolizidine (X)——A solution of VIII (300 mg) and Ac_2O (3 ml) in pyridine (3 ml) was treated by the same procedure as that described for IX to give X (330 mg, quantitative) as colorless plates, mp 131—132° (MeOH). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2790, 2760, 2720 (Bohlmann bands), 1725 (C=O). NMR δ: 2.00 (3H, s, $COCH_3$), 3.55 (1H, d-d, $J=11$; 3 Hz, C_4–H), 3.84, 3.87 (each 3H, s, $OCH_3\times2$), 4.84 (1H, t-t, $J=11$; 4.5 Hz, C_2–H), 6.93 (1H, s, Ar–H$^{3'}$), 7.09 (1H, s, Ar–H$^{6'}$). Mass Spectrum *m/e*: 413, 411 (M^+, 1: 1). *Anal.* Calcd. for $C_{19}H_{26}O_4NBr$: C, 55.35; H, 6.34; N, 3.37. Found: C, 55.19; H, 6.13; N, 3.41.

Methyl 3-[4-{2-(2-Acetoxy(*a*)-*trans*-quinolizidin-4-yl(*e*))-4,5-dimethoxyphenoxy}phenyl]propionate (XII)——A mixture of IX (2.2 g, 5.3 mmoles) and methyl 3-(4-hydroxyphenyl)propionate[18] (XI, 1.9 g, 10.6 mmoles) and anhyd. K_2CO_3 (3.0 g) in pyridine (5 ml) was heated with stirring in a stream of N_2. To the mixture was added powdered CuO (1.5 g) at 130° and the mixture was heated at 150° for 5.5 hr with stirring. To the cooled reaction mixture was added H_2O and $CHCl_3$, and the mixture was filtered. To the filtrate was added aq. NaOH and the mixture was extracted with $CHCl_3$. The extract was washed with H_2O, dried, and evaporated. The residue was chromatographed on alumina using ether as an eluent. The first fraction afforded 2-acetoxy(*a*)-4-(3,4-dimethoxyphenyl) (*e*)-*trans*-quinolizidine (XIII, 120 mg, 6.8%) as a colorless viscous oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2790, 2750 (Bohlmann bands), 1727 (C=O). NMR δ: 2.12 (3H, s, $COCH_3$), 3.87, 3.89 (each 3H, s, $OCH_3\times2$), 5.05 (1H, quin, $J=3$ Hz, C_2–H), 6.80 (2H, br-s, Ar–H$^{5',6'}$), 6.88 (1H, s, Ar–H$^{2'}$). Mass Spectrum *m/e*: 333 (M^+). High-resolution Mass Spectrum *m/e*: 333.190. Calcd. for $C_{19}H_{27}O_4N$: 333.194.

The second fraction afforded XII (930 mg, 34%), which was recrystallized from EtOH as colorless needles, mp 113—114.5°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2790, 2760, 2730 (Bohlmann bands), 1728 (C=O). NMR δ: 1.85 (3H, s, $COCH_3$), 3.67, 3.77, 3.91 (each 3H, s, $OCH_3\times3$), 4.97 (1H, quin, $J=3$ Hz, C_2–H), 6.48 (1H, s, Ar–H$^{6''}$), 7.08 (1H, s, Ar–H$^{3''}$), 6.73, 7.09 (4H, AB-type-q, $J=9$ Hz, Ar-H$^{2',3',5',6'}$). Mass Spectrum *m/e*: 511 (M^+). UV nm (ε): λ_{max} 284 (5500), λ_{min} 259 (1730), λ_{infl} 279 (5020), 222 (22300). *Anal.* Calcd. for $C_{29}H_{37}O_7N$: C, 68.08; H, 7.29; N, 2.74. Found: C, 67.95; H, 7.35; N, 2.56.

3-[4-{2-(2-Hydroxy(*a*)-*trans*-quinolizidin-4-yl(*e*))-4,5-dimethoxyphenoxy}phenyl]propionic Acid (XIV)——A solution of XII (350 mg) in MeOH (15 ml) was refluxed with 5% aq. NaOH (9 ml) for 2 hr and evaporated. The residue was acidified with aq. HCl and washed with ether. The aqueous layer was brought to pH 6 with aq. NaOH and extracted with $CHCl_3$. The extract was dried and evaporated to give XIV (320 mg, quantitative) as a colorless amorphous solid. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2460 (br, N^+H), 1578 (CO_2^-). NMR δ: 3.87, 3.90 (each 3H, s, $OCH_3\times2$), 4.44 (1H, m, $W_H=18$ Hz, C_4–H), 6.63 (1H, s, Ar–H$^{6''}$), 7.70 (1H, s, Ar–H$^{3''}$), 6.72, 7.15 (4H, AB-type-q, $J=8$ Hz, Ar-H$^{2',3',5',6'}$). Mass Spectrum *m/e*: 455 (M^+).

(±)-Decaline (II)——1) With $SOCl_2$: A solution of XIV (82 mg, 0.18 mmole) and $SOCl_2$ (1 ml) in $CHCl_3$ (20 ml) was refluxed for 13 hr and evaporated. The residue was made alkaline with aq. Na_2CO_3 and extracted with $CHCl_3$. The extract was washed with H_2O, dried, and evaporated. The residue was chromatographed on p-TLC (alumina, ether–$CHCl_3$ 1: 1) to give colorless crystals (II, 2 mg, 2.5%). IR ν_{max}^{KBr} cm^{-1}: 1720 (C=O). Mass Spectrum *m/e*: 437 (M^+).

A solution of XIV (40 mg, 0.09 mmole) and $SOCl_2$ (0.5 ml) in benzene (100 ml) was treated in the same procedure as that described above to give II (1 mg, 2.5%), which was identical with that obtained above in TLC behaviour.

2) With *p*-TsOH: In a flask equipped with the Dean-Stark water-separator containing anhyd. Na_2SO_4 or molecular sieves (3A 1/16) a mixture of XIV (75 mg, 0.165 mmole) in benzene (500 ml) was heated. After XIV was completely dissolved, *p*-TsOH·H_2O (500 mg) was added to the solution and the solution was refluxed for 92 hr. The cooled reaction mixture was washed with 10% aq. K_2CO_3 (200 ml) and with H_2O. The combined aqueous layers were extracted with $CHCl_3$. The extract was washed with H_2O. The extract and the benzene layer were dried and evaporated. The residue was purified on p-TLC (alumina, ether–$CHCl_3$ 1: 1) to give colorless crystals (II, 40 mg, 55%), which was recrystallized from MeOH as colorless needles, mp 196—197°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2800, 2730 (Bohlmann bands), 1720 (C=O). NMR δ: 3.88, 3.90 (each 3H, s, $OCH_3\times2$), 4.89 (1H, quin, $J=3$ Hz, C_2–H), 6.45 (1H, d-d, $J=8.5$; 2.5 Hz, Ar–H$^{5'\text{ or }6'}$), 6.74 (1H, s, Ar–H$^{6''}$), 6.89 (1H, s, Ar–H$^{3''}$), 6.90 (1H, d-d, $J=8.5$; 2.0 Hz, Ar–H$^{6'\text{ or }5'}$), 7.15 (1H, d-d, $J=8.5$; 2.5 Hz, Ar–H$^{2'\text{ or }3'}$), 7.28 (1H, d-d, $J=8.5$; 2.0 Hz, Ar–H$^{3'\text{ or }2'}$). Mass Spectrum *m/e*: 437 (M^+). UV nm (ε): λ_{max} 293 (6100), λ_{min} 264 (2100), λ_{infl} 280 (4200), 241 (9950), 223 (16300). *Anal.* Calcd. for $C_{26}H_{31}O_5N$: C, 71.37; H, 7.14; N, 3.20. Found: C, 71.47; H, 7.01; N, 3.19.

The product was identical with that obtained in 1) in mass spectra and TLC, and identified with natural decaline by comparison with IR, NMR, mass, UV spectra and TLC behaviour.

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