Optically Active Triptycenes. IV.[1] Synthesis of Optically Active 2- or 5-Substituted 7-Carboxytriptycenes

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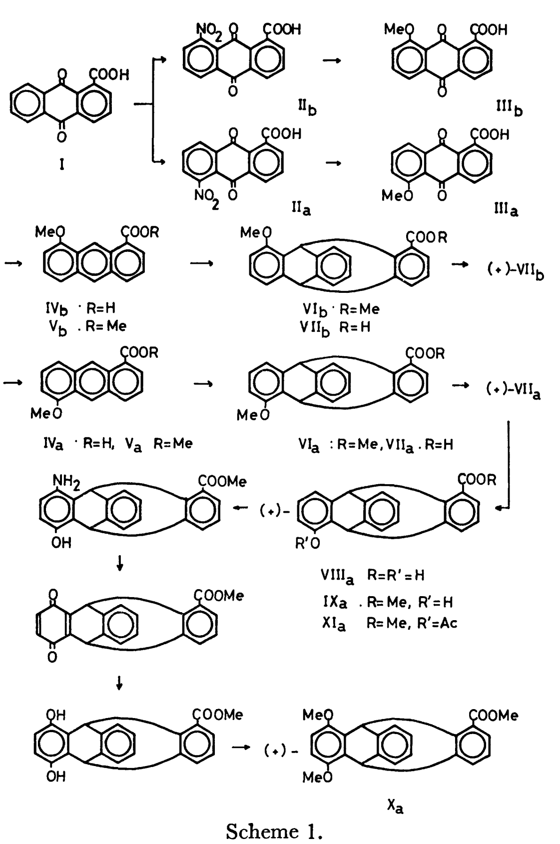
Starting from anthraquinone-1-carboxylic acid (I), 2-methoxy- and 5-methoxy-7-carboxytriptycenes (VIIa and VIIb) have been synthesized. Optical resolution of the triptycenecarboxylic acids with brucine afforded (+)-VIIa and (+)-VIIb. The absolute configuration of (+)-VIIa was determined to be 1R,6R by the chemical correlation with (+)-2,5-dimethoxy-7-methoxycarbonyltriptycene. From a comparison of the CD spectrum of (+)-5-methoxy-7-carboxytriptycene (VIIb) with that of (+)-2-acetoxy-5-methoxy-7-methoxycarbonyltriptycene (XIIIb), 1R,6R absolute configuration was assigned to (+)-VIIb. (+)-2-Hydroxy-5-phenylazo-7-carboxytriptycene (XIIa) was derived from (+)-VIIa. (+)-2-Chloro- and (+)-5-chloro-7-carboxytriptycenes (XVIIIa and XVIIIb) have been prepared from 5-chloro- and 8-chloro-1-carboxyanthraquinones (XIVa and XIVb). The absolute configuration of (+)-XVIIIa was determined to be 1R,6R by the chemical correlation with (—)-VIIa *via* (+)-2-chloro-5-methoxytriptycene (XIX).

The synthesis and optical resolution of 2,5,7-trisubstituted triptycenes have been reported in previous papers of this series,[2-4] and studies on C_2-symmetrical 2,7-disubstituted derivatives will be reported in the following paper.[5]

The present paper deals with the synthesis, optical resolution of 2- and 5-substituted 7-carboxytriptycenes and the determination of their absolute configuration by chemical correlation.

Anthraquinone-1-carboxylic acid (I) obtained by chromium trioxide oxidation of benzanthrone[6] was nitrated by the reported method[7] to yield 1-carboxy-5-nitro-anthraquinone (IIa) and 1-carboxy-8-nitro-anthraquinone (IIb). Treatment of the nitro compounds (IIa and IIb) with potassium hydroxide in methanol afforded methyl ether derivative (IIIa or IIIb). Carboxymethoxyanthracene (IVa or IVb) obtained by reduction of IIIa or IIIb with zinc dust and aqueous ammonia was converted into methyl ester (Va or Vb) by the usual method. Reaction of benzyne generated by the decomposition of benzenediazonium carboxylate[8] with Va or Vb gave 2-methoxy-7-methoxycarbonyl or 5-methoxy-7-methoxycarbonyltriptycene (VI or VIb). 2-Methoxy-7-carboxytriptycene (VIIa) obtained by the hydrolysis of VIa was treated with 0.5 equivalent of brucine dihydrate in ethanol. Recrystallization of the brucine salt from ethanol yielded (+)-VIIa with positive rotation in the visible region. The triptycene derivatives derived from (+)-VIIa will be referred to the (+)-series. The brucine salt of VIIb was recrystallized from acetone to afford (+)-VIIb. (+)-Hydroxycarboxylic acid (VIIIa) obtained on treatment of (+)-VIIa with a mixture of hydrobromic acid and hydriodic acids in acetic acid was converted into methyl ester (+)-IXa. Acetylation of (+)-IXa gave (+)-acetoxy methyl ester (+)-XIa, and coupling of benzenediazonium salt with (+)-VIIIa afforded (+)-azocarboxylic acid (+)-XIIa.



Scheme 1.

Coupling of diazotized sulfanilic acid with (+)-IXa followed by reduction afforded *p*-aminophenol derivative which was oxidized to yield *p*-benzoquinone derivative. Hydroquinone derivative obtained from the quinone was converted into dimethyl ether(+)-Xa. The dimethyl ether derivative (+)-Xa thus prepared was found to be identical with (+)-2,5-dimethoxy-7-meth-

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[1] For Part III of this series, see Ref. 4.

[2] A. Sonoda, F. Ogura, and M. Nakagawa, This Bulletin, **35**, 853 (1962).

[3] F. Ogura, Y. Sakata, and M. Nakagawa, *ibid.*, **45**, 3646 (1972).

[4] F. Ogura and M. Nakagawa, This Bulletin, **46**, 651 (1973).

[5] M. Kuritani, Y. Sakata, F. Ogura, and M. Nakagawa, *ibid.*, **46**, 605 (1973).

[6] E. B. Barnett, J. W. Cook, and H. H. Grainger, *Ber.*, **57**, 1775 (1924).

[7] F. Ullmann and W. van der Schalk, *Ann. Chem.*, **388**, 199 (1912).

[8] L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, **85**, 1549 (1963).

oxycarbonyltriptycene (+)-X, derived from 1-methoxycarbonylanthracene and *p*-benzoquinone.[3] Since the absolute configuration of (+)-2,5-dimethoxy-7-dimethylaminotriptycene hydrobromide prepared from (+)-2, 5-dimethoxy-7-methoxycarbonyltriptycene (+)-X has been proved to be 1R,6S using the Bijvoet method,[9] the absolute configuration of (+)-Xa now prepared can be determined as 1R,6S. Consequently, the 2,7-disubstituted triptycenes of (+)-series derived from (+)-VIIa should have the same 1R,6R absolute configuration.

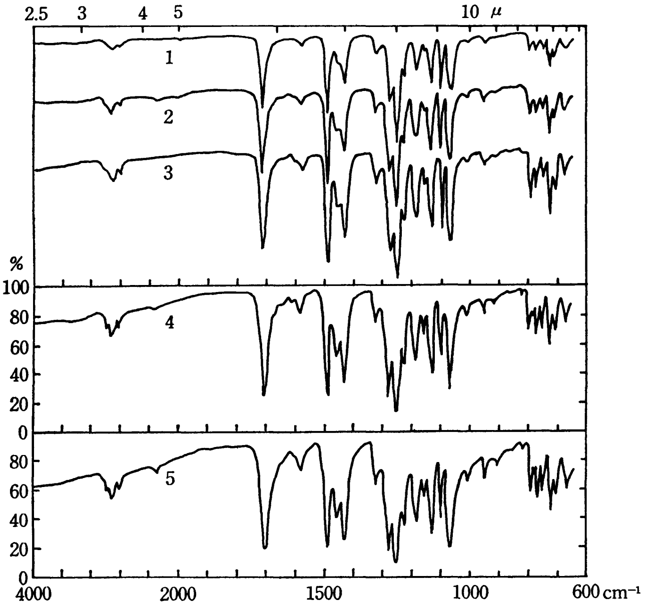


Fig. 1. IR spectra (KBr-disk) of (+)- and (—)-2,5-dimethoxy-7-methoxycarbonyltriptycene prepared by different process.
1: *dl*-Xa, 2: *dl*-Xb, 3: *dl*-X, 4: (+)-X, 5: (+)-Xa

dl-2-Methoxy-7-methoxycarbonyltriptycene (VIa) and *dl*-5-methoxy-7-methoxycarbonyltriptycene (VIb) could be transformed into *dl*-2,5-dimethoxy-7-methoxycarbonyltriptycene (*dl*-Xa and *dl*-Xb) according to the same reaction sequence used in the preparation of (+)-Xa from (+)-VIa. *dl*-2,5-Dimethoxy-7-methoxycarbonyltriptycene (*dl*-Xa, *dl*-Xb, and *dl*-X[3]) showed identical melting point (mp 227.0—228.5°C) and the mixed melting points showed no depression. As illustrated in Fig. 1, their IR spectra were found to be superimposable.

(+)-VIIb showed a negative Cotton effect in the longest wavelength region of the CD spectrum in contrast with the positive Cotton effect of (+)-VIIa in the same wavelength region. However, (+)-2-methoxy-5-acetoxy- and (+)-2-acetoxy-5-methoxy-7-methoxycarbonyltriptycenes (XIIIa and XIIIb) showed UV and CD spectra closely related with those of (+)-VIa and (+)-VIIb, respectively (Figs. 2 and 3). Since the absolute configuration of (+)-XIII has been established to be 1R,6S in relation to (+)-X,[4] 1R,6R absolute configuration may reasonably be assigned to

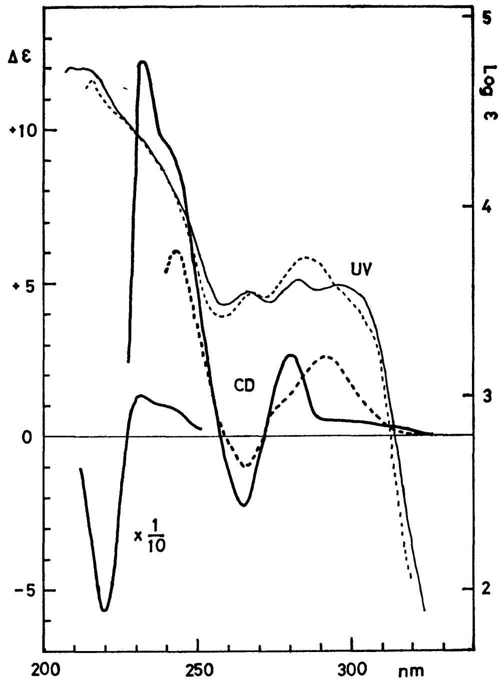


Fig. 2. UV and CD spectra of (+)-VIa (——) and (+)-XIIIa (····) in dioxane

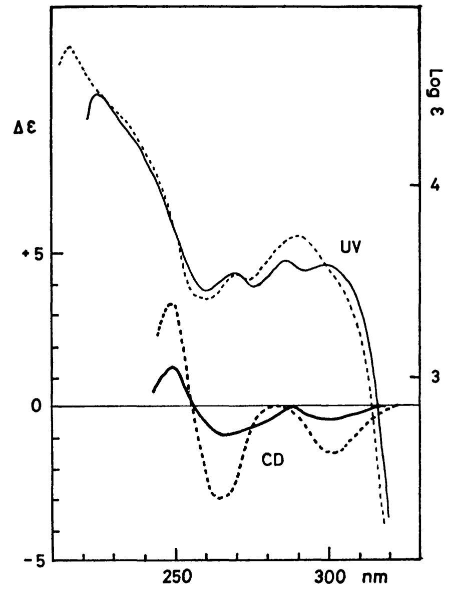
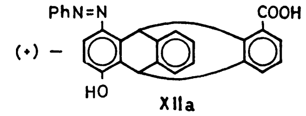
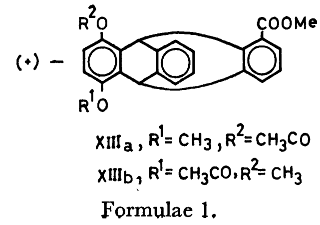


Fig. 3. UV and CD spectra of (+)-VIIb (——) and (+)-XIIIa (····) in dioxane



XIIa



XIIIa, $R^1 = CH_3$, $R^2 = CH_3CO$
XIIIb, $R^1 = CH_3CO$, $R^2 = CH_3$

Formulae 1.

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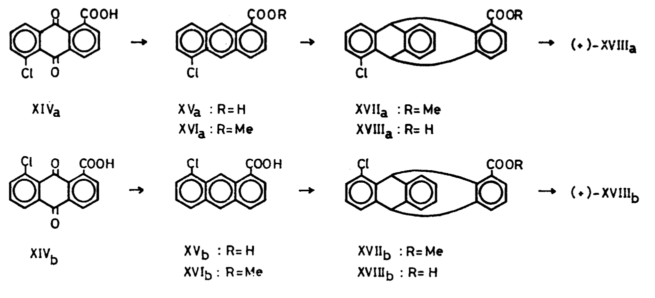
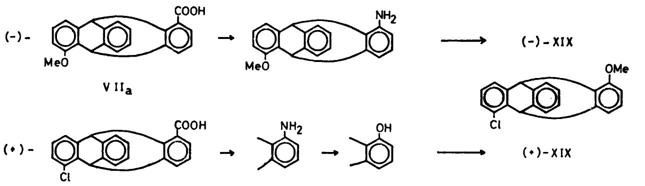
[9] N. Sakabe, K. Sakabe, K. Ozeki-Minakata, and J. Tanaka, presented at the 9th International Congress of Crystallography (1972) and *Acta Crystallogr.*, **B 82**, 3441 (1972).



Scheme 2.

(+)-VIIb. The CD spectrum of (+)-XIa also showed a negative Cotton effect in the longest wavelength region.

In order to get information on the effect of magnitude of electric transition moment on the rotatory properties, replacement of the methoxyl group (spectroscopic moment 30)[10] in VIIa and VIIb with chlorine atom (spectroscopic moment 6)[10] was undertaken. 5-Chloroanthraquinone-1-carboxylic acid (XIVa) and 8-chloroanthraquinone-1-carboxylic acid (XIVb) prepared from anthraquinone-1-sulfonic acid by the reported method[11] were reduced to anthracene derivatives (XVa and XVb) by the procedure used in the preparation of IVa and IVb. The reaction of its methyl ester (XVIa or XVIb) with benzyne afforded chlorotriptycenecarboxylate (XVIIa or XVIIb). Chlorotriptycenecarboxylic acid (XVIIIa or XVIIIb) derived from XVIIa or XVIIb were resolved by means of brucine to yield optically pure (+)-5-chlorotriptycene-1-carboxylic acid, (+)-XVIIIa or 7-chlorotriptycene-1-carboxylic acid, (+)-XVIIIb.



Scheme 3.

(+)-2-Chloro-7-carboxytriptycene (XVIIIa) was converted by the Curtius reaction into 2-chloro-7-hydroxytriptycene *via* 2-chloro-7-amino derivative. Methylation of the phenolic derivative afforded (+)-2-chloro-5-methoxytriptycene (XIX). On the other hand, the Curtius reaction of (−)-2-methoxy-7-carboxytriptycene (VIIa) obtained from the mother liquor of the optical resolution of *dl*-VIIa by means of brucine in *ca.* 60% optical purity, yielded 2-methoxy-7-aminotriptycene which could be converted into (−)-2-chloro-5-methoxytriptycene (XIX) by the Sandmeyer reaction. The IR spectra of (+)-XIX and (−)-XIX thus prepared were found to be superimposable and their CD spectra showed antipodal curves. The absolute configuration of (−)-VIIa has been estimated to be 1S,6S on the bases of X-ray structure analysis by the Bijvoet method and the chemical correlation. Consequently, the absolute configuration of (+)-2-chloro-7-carboxytriptycene (XVIIIa) could be concluded to be 1R,6R on the same ground.

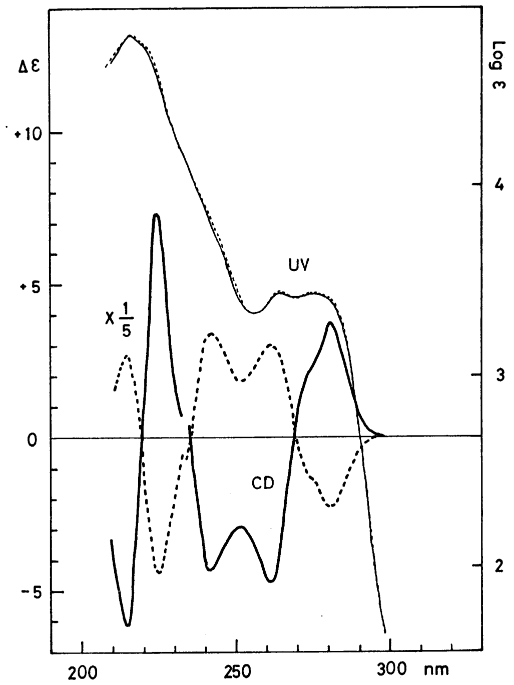


Fig. 4. UV and CD spectra of (+)-XIX (——) and (−)-XIX (····, optical purity 60%) in dioxane

The bridgehead proton (C¹–H) proximate to carbomethoxy group and chlorine atom in XVIIb exhibited NMR signal at τ 2.57, whereas the signal of bridgehead proton (C⁶–H) proximate to carbomethoxy group in XVIIa appeared at τ 3.00. The down-field shift of signal of the former compound could be attributed to magnetic anisotropy, van der Waals effect and electric field effect of the substituent groups.[12] The down-field shift of signal of bridgehead proton proximate to methoxycarbonyl group in VIb (τ 2.55) as compared with that of VIa (τ 3.00) indicates that the methoxyl group in VIb should occupy the 10-position. Consequently, the structure of IIb was firmly established to be 8-nitroanthraquinone-1-carboxylic acid.[13] The same effect of substituent groups on NMR spectrum was observed in the anthracene derivatives (Va and Vb) (see Experimental).

Experimental

All the melting points are not corrected. The IR (KBr-disk method) and UV spectra were measured with JASCO-402 and Hitachi EPS-3T spectrophotometers, respectively. The NMR spectra in deuteriochloroform were obtained on a Varian A-60 spectrometer using TMS as an internal standard. The CD spectra were measured with a Roussel-Jouan Dichrograph B and II CD-185.

5-Nitroanthraquinone-1-carboxylic Acid (IIa) and 8-Nitroanthra-

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[10] J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951).

[11] F. Ullmann and P. Kerteoz, *Ber.*, **52**, 545 (1919); R. S. Cahn, W. O. Jones, and J. L. Simonsen, *J. Chem. Soc.*, **1933**, 444; T. Maki and Y. Nagai, *Kogyo Kagaku Zasshi*, **33**, 1310 (1930).

[12] I. Mori, T. Kadosaka, Y. Sakata, and S. Misumi, This Bulletin, **44**, 1649 (1971).

[13] The position of nitro group in IIb was presumed to be the 8-position without firm experimental evidence.[7]

quinone-1-carboxylic Acid (IIb). Anthraquinone-1-carboxylic acid obtained from benzanthrone[5] was nitrated by the reported method.[12] IIa was obtained from the fraction less soluble in ethanol. The residue obtained on evaporating the ethanolic mother liquor was recrystallized from water to yield yellow crystals, mp 288—295°C. The IR spectrum of this substance showed absorptions characteristic of 1,8-disubstituted anthraquinone[14] at 810 and 755 cm^{-1}. The yellow crystals (IIb) were converted into methyl ester in the usual way, mp 147.0—148.4°C (from methanol), IR: 1723 ($\nu_{C=O}$, -COOCH$_3$), 1678 ($\nu_{C=O}$, quinone), 1540, 1328 (C-NO$_2$) 802, 743 (1,8-disubstituted anthraquinone) cm^{-1}.

Found: C, 62.53; H, 3.08; N, 4.26%. Calcd for $C_{16}H_9O_6N$: C, 61.74; H, 2.91; N, 4.50%.

5-Methoxyanthraquinone-1-carboxylic Acid (IIIa) and the Methyl Ester. A mixture of crude IIa (10 g), sodium hydroxide (15 g) and methanol (300 ml) was refluxed for 8 hr. The residue obtained by concentration of the dark red reaction mixture was mixed with water (300 ml). The insoluble material was removed by filtration. The filtrate was acidified with concentrated hydrochloric acid to yield crude IIIa as yellow solid, mp 270—280°C (decomp), 9.2 g (97%). Treatment of crude IIIa with methanol containing sulfuric acid afforded methyl ester, yellow needles, mp 184.5—186.0°C (from methanol), IR (KBr-disk): 2840 (ν_{C-H}, -OCH$_3$), 1727 ($\nu_{C=O}$, -COOCH$_3$), 1664 ($\nu_{C=O}$, quinone), 815, 707 (1,5-disubstituted anthraquinone) cm^{-1}.

Found: C, 68.60; H, 4.06%. Calcd for $C_{17}H_{12}O_5$: C, 68.91; H, 4.08%.

8-Methoxyanthraquinone-1-carboxylic Acid (IIIb) and the Methyl Ester. According to the procedure used for IIIa, crude IIb (69.4 g) was converted into crude IIIb (49.6 g, 75.3%) which was recrystallized from acetic acid, mp 270—285°C (decomp). Methyl ester, yellow needles, mp 228.5—229.5°C (from methanol) was obtained by the usual method, IR: 2840 (ν_{C-H}, -OCH$_3$), 1720, 1664 ($\nu_{C=O}$, -COOCH$_3$, quinone), 800, 745 (1,8-disubstituted anthraquinone) cm^{-1}.

Found: C, 69.05; H, 3.85%. Calcd for $C_{17}H_{12}O_5$: C, 68.91; H, 4.08%.

5-Methoxyanthracene-1-carboxylic Acid (IVa). A mixture of crude IIIa (33 g), 15% aqueous ammonia (1.1 liter) and zinc dust (55 g) was heated with stirring on a boiling water-bath for 8 hr. At 2 hr intervals, zinc dust (4 g) and concentrated aqueous ammonia (30 ml) were added to the reaction mixture. Excess zinc dust was removed by filtration and washed with aquous ammonia. The combined filtrate and washings were treated twice with active charcoal. The hot filtrate was made acid to Congo red with concentrated hydrochloric acid, yielding crude IVa as yellow precipitate, 26.0 g (88.1%), mp *ca.* 215°C (decomp.).

5-Methoxy-1-methoxycarbonylanthracene (Va). A mixture of crude IVa (25.0 g), anhydrous methanol (880 ml) and concentrated sulfuric acid (14 ml) was refluxed for 8 hr. After the solvent had been removed, the residue was mixed with water and extracted with benzene. The concentrated extract was subjected to a chromatography on alumina (700 g). Elution with benzene afforded crude methyl ester (Va, 17.9 g, 67.8%). The crude material was recrystallized from methanol to yield pure Va, yellow needles, mp 130.5—131.5°C, IR: 2830 (ν_{C-H}, -OCH$_3$), 1700 ($\nu_{C=O}$, -COOCH$_3$) cm^{-1}, NMR: τ 0.48 (C^9-H), 1.15 (C^{10}-H), 5.97 (-COOCH$_3$ and -OCH$_3$).

Found: C, 76.65; H, 5.22%. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30%.

8-Methoxyanthracene-1-carboxylic Acid (IVb). Reduction of crude IIIb (49.0 g) by the method used for IVa afforded crude IVb (39.3 g, 81.7%), mp *ca.* 180°C (decomp.). The crude material was used in the following reaction.

8-Methoxy-1-methoxycarbonylanthracene (Vb). Esterification of crude IVb (38 g) according to the method used for IVa followed by chromatography on alumina afforded crude Vb (17.0 g, 42.5%). The crude material was recrystallized from methanol to yield pure Vb, yellow leaflets, mp 132—132.5°C, IR: 2835 (ν_{C-H}, -OCH$_3$) 1705 ($\nu_{C=O}$, -COOCH$_3$), cm^{-1}. NMR: τ 0.05 (C^9-H), 1.63 (C^{10}-H), 5.93 (-COOCH$_3$ and -OCH$_3$).

Found: C, 76.76; H, 5.33%. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30%.

2-Methoxy-7-methoxycarbonyltriptycene (VIa). To a mixture of Va (3.0 g, 11 mmol), isoamyl nitrite (2 ml, 15 mmol) and 1,2-dimethoxyethane (20 ml), stirred under gentle reflux, was added over 20 min period a solution of anthranilic acid (2.6 g, 19 mmol) in the same solvent (10 ml), and then an additional amount of isoamyl nitrite (2 ml). A solution of anthranilic acid (2.6 g) in the same solvent (10 ml) was again added to the mixture over a period of 20 min. The mixture was stirred for further 10 min under reflux. Crystals deposited on cooling the mixture on an ice-salt bath were collected by filtration and washed 4 times with cold methanol–water (4: 1, 10 ml), yielding crystalline material (1.6 g). The material in xylene (20 ml) was refluxed for 5 min with maleic anhydride (1.0 g, 10 mmol) to remove the unreacted anthracene derivative. After the solvent had been removed under reduced pressure, the residue was dissolved in benzene and chromatographed on alumina (100 g) to afford VIa as colorless crystals, mp 232—232.5°C, IR: 2836 (ν_{C-H}, -OCH$_3$), 1713 ($\nu_{C=O}$, -COOCH$_3$) cm^{-1}, UV: $\lambda_{\max}^{\text{dioxane}}$ (ε) 209.5 (53400), 215 (51000), 267 (3550), 283.5 (4100), 296 (3810) nm, NMR: τ 2.33—3.17 (m, 11H, aromatic and C^1-H), 4.07 (s, 1H, C^6-H), 6.05 (s, 3H, -COOCH$_3$).

Found: C, 80.72; H, 5.33%. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30%.

5-Methoxy-7-methoxycarbonyltriptycene (VIb). To a solution of Vb (4.286 g, 16.1 mmol) and isoamyl nitrite (1.9 g, 16 mmol) in dichloromethane (20 ml), stirred under reflux, was added a solution of anthranilic acid (2.3 g, 16.8 mmol) in tetrahydrofuran (60 ml) over a period of 5 hr. Pale yellow residue obtained on evaporation of the solvent was mixed with xylene (50 ml) and maleic anhydride (3.5 g, 36 mmol). After refluxing for 1 hr, water (70 ml) and dichloromethane (70 ml) were added to the reaction mixture. The organic layer was washed successively with cold 5% aqueous potassium hydroxide (20 ml × 5) and water, and dried (sodium sulfate). The residue obtained on evaporating the solvent was dissolved in benzene and chromatographed on alumina (120 g), yielding VIb (1.843 g, 33.4%) which was recrystallized from ethyl acetate to give pure VIb, colorless crystals, mp 220—221.5°C, IR: 2835 (ν_{C-H}, -OCH$_3$), 1708 ($\nu_{C=O}$, -COOCH$_3$) cm^{-1}, UV: $\lambda_{\max}^{\text{dioxane}}$ (ε) 220 (44600), 268 (3740), 285 (4680), 295 (4260) nm, NMR: τ 2.55 (C^1-H), 4.55 (C^6-H), 6.00 (-COOCH$_3$).

Found: C, 80.52; H, 4.72%. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30%.

2-Methoxy-7-carboxytriptycene (VIIa). A mixture of VIa (1.231 g), acetic acid (30 ml) and 10% aqueous sulfuric acid (45 ml) was refluxed for 25 hr. VIIa (1.067 g) was obtained on cooling the reaction mixture. The filtrate gave a second crop of VIIa (94 mg) (total yield, quantitative). Pure VIIa, mp 299.0—300°C was obtained on recrystallization from acetic acid, IR: 2830 (ν_{C-H}, -OCH$_3$), 1677 ($\nu_{C=O}$, -COOH) cm^{-1}, UV: $\lambda_{\max}^{\text{dioxane}}$ (ε) 298 (3810), 285 (4010), 269 (3460), 224 (31100) nm.

Found: C, 80.27; H, 4.83%. Calcd for $C_{22}H_{16}O_3$: C,

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[14] N. Oi, *Chem. Pharm. Bull.* (Tokyo), **5**, 153 (1957).

80.47; H, 4.91%.

5-Methoxy-7-carboxytriptycene (VIIb). Hydrolysis of VIb (790 mg) according to the above method afforded VIIb (660 mg, 95%) which was recrystallized from aqueous acetic acid, yielding pure VIIb, mp 305—308°C, IR: 2830 (ν_{C-H}, -OCH$_3$), 1680 ($\nu_{C=O}$, -COOH) cm^{-1}.

Found: C, 80.20; H, 4.61%. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91%.

Optical Resolution of 2-Methoxy-7-carboxytriptycene (VIIa). To a hot solution of VIIa (4.70 g, 14.3 mmol) in 99% ethanol (270 ml) was added brucine dihydrate (3.08 g, 7.80 mmol) in one portion. After refluxing for 15 min, the mixture was allowed to stand overnight to deposit brucine salt (5.1 g). The salt was recrystallized twice from 99% ethanol to yield pure material, mp 196.0—198.0°C, IR: 3510 (ν_{N-H}), 1655 ($\nu_{C=O}$, -COO$^-$) cm^{-1}, $[\alpha]^{20}_{350}$ −268° (*c* 0.117, dioxane).

The pure salt (1.125 g) was dissolved in acetic acid (10 ml) on warming up to 90—95°C for 5 min. White precipitate (478 mg) obtained on addition of water (30 ml) to the acetic acid solution was recrystallized from acetic acid to give pure (+)-VIIa mp 267°C (decomp.), IR: 2830 (ν_{C-H}, -OCH$_3$), 1673 ($\nu_{C=O}$, -COOH) cm^{-1}, $[\alpha]^{20}_{D}$ +15.4°, $[\alpha]^{20}_{405}$ −74.4° (*c* 0.187, dioxane).

Found: C, 80.26; H, 4.76%. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91%.

(+)-2-Methoxy-7-methoxycarbonyltriptycene (VIa). A mixture of (+)-VIIa (35 mg), methanol (5 ml) and concentrated sulfuric acid (0.2 ml) was refluxed for 5 hr. Crystals (33 mg) deposited on cooling the reaction mixture were washed with a small amount of methanol and recrystallized from the same solvent to yield pure ester, (+)-VIa as colorless, rods, mp 240—241°C, IR: 2830 (ν_{C-H}, -OCH$_3$), 1714 ($\nu_{C=O}$, -COOCH$_3$) cm^{-1}, CD: $\lambda^{\text{dioxane}}_{\text{max}}$ ($\Delta\varepsilon$) 325—288 (+0.4), 280 (+2.6), 265 (−2.5), 242* (+8.3), 232 (+12.2), 220 (−56.8) nm.

Found: C, 80.81; H, 5.34%. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30%.

Optical Resolution of 5-Methoxy-7-carboxytriptycene (VIIb). To a hot solution of VIIb (170 mg, 0.518 mmol) in acetone (5 ml) was added brucine dihydrate (111 mg, 0.258 mmol). After refluxing for 15 min, crystals deposited (84 mg) were recrystallized from acetone (6 ml) to give brucine salt, 31 mg, $[\alpha]^{15}_{350}$ −206° (*c* 0.34, chloroform). (+)-VIIb obtained from an acetic acid solution of the brucine salt on dilution with water was sublimed *in vacuo* to give pure (+)-VIIb, mp 310—313°C, $[\alpha]_{600}$ +21.1°, $[\alpha]_D$ +23.7°, $[\alpha]_{400}$ +55.3°.

Found: C, 80.00; H, 4.85%. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91%.

The residue obtained on concentrating the mother liquor of recrystallization of brucine salt was decomposed to yield (−)-VIIb with unknown optical purity (negative rotation in the visible wavelength region).

The experiments were repeated under the same and different conditions, but no optical resolution could be achieved except for the above described run. The cause of the poor reproducibility is not clear.

(+)-2-Hydroxy-7-carboxytriptycene (VIIIa). A mixture of (+)-VIIa (467 mg), acetic acid (10 ml), 48% hydrobromic acid (10 ml) and 52% hydriodic acid (1 ml) was refluxed for 15 hr. The resulting red reaction mixture was poured onto water (80 ml) containing sodium hydrogen sulfite, and extracted with chloroform (20 ml×4). The extract was washed with water and dried (sodium sulfate). The residue (426 mg, 95.3%) obtained by evaporation of the solvent was recrystallized from petroleum ether–methyl acetate to yield pure (+)-VIIIa, mp 269—271°C (*dl*-VIIIa, mp 263.0—264.0°C), IR: 3020, 3200 (ν_{C-H}), 1683 ($\nu_{C=O}$, -COOH) cm^{-1}, UV: $\lambda^{95\%\text{EtOH}}_{\text{max}}$ (ε) 300* (3400), 286 (4350), 269 (3410), 214* (46200) nm.

Found: C, 80.05; H, 4.36%. Calcd for $C_{21}H_{14}O_3$: C, 80.24; H, 4.39%.

(+)-2-Hydroxy-7-methoxycarbonyltriptycene (IXa). The reaction mixture obtained on refluxing a mixture of (+)-VIIIa (393 mg), anhydrous methanol (7 ml) and concentrated sulfuric acid (0.4 ml) for 8 hr was poured onto water (40 ml). The crude ester (404 mg, 98.5%) obtained as a white precipitate was recrystallized from cyclohexane–methyl acetate to give pure (+)-IXa, mp 217—225°C (*dl*-IXa, mp 231—234°C), IR: 3400 (ν_{O-H}), 1697 ($\nu_{C=O}$) cm^{-1}.

Found: C, 80.20; H, 4.76%. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91%.

(+)-2,5-Dimethoxy-7-methoxycarbonyltriptycene (Xa). A mixture of concentrated hydrochloric acid (0.14 ml) and ice-water (5 ml) was added to an ice-cooled solution of sulfanilic acid (185 mg, 0.97 mmol), sodium carbonate (57 mg) and sodium nitrite (82 mg) in water (5 ml), and the mixture was stirred for 30 min at 0°C. To the resulting solution of diazotized sulfanilic acid was added a solution of (+)-IXa (219 mg, 0.667 mmol) in methanol (20 ml) and water (4 ml) containing sodium hydroxide (147 mg). After being stirred for 1 hr at room temperature, the deep red reaction mixture was poured onto water (40 ml). Sodium hydrosulfite was added in small portions at 40—50°C until the color of the mixture turned light yellow, and then extracted with ethyl acetate (20 ml×4). The extract was washed with a saturated sodium chloride solution (20 ml×2) and dried (sodium sulfate). Aminophenol derivative (195 mg) obtained by evaporating the solvent was mixed with 2N sulfuric acid (35 ml). Ethanol was then added to result in a homogeneous solution. Ferric sulfate (3.3 g) was added to the solution and the mixture was kept for 2 hr on a boiling water-bath. After cooling, the reaction mixture containing yellow precipitate was extracted with chloroform (20 ml×4). The extract was worked up in the usual way to yield crude quinone derivative. The crude quinone in ethanol (10 ml) was reduced with a saturated aqueous solution of sodium hydrosulfite. Water was added to the resulting pale yellow mixture and extracted with ether. The dried extract was concentrated to yield crude hydroquinone derivative (116 mg). A mixture of the hydroquinone, acetone (5 ml), anhydrous potassium carbonate (1.0 g) and dimethyl sulfate (0.4 ml) was refluxed for 5 hr. The reaction mixture was mixed with water (50 ml) and extracted with benzene (20 ml×4). After washing and drying, the extract was concentrated to *ca.* 20 ml and chromatographed on alumina (5 g) to yield (+)-Xa (83 mg). Pure (+)-Xa was obtained by recrystallization from benzene, mp 261.5—262.5°C. (+)-Xa thus obtained showed no depression of melting point [mixed mp 261.5—262.3°C] on admixture with (+)-2,5-dimethoxy-7-methoxycarbonyltriptycene [(+)-X, mp 261.5—262.5°C] prepared by a different route.[3] Both compounds showed identical IR spectra. The optical purity of (+)-Xa was confirmed by comparison of $\Delta\varepsilon$ value at 267 nm in dioxane [(+)-Xa: $\Delta\varepsilon = -3.15$, (+)-X: $\Delta\varepsilon = -3.06$[3]].

Found: C, 77.55; H, 5.46%. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41%.

(+)-2-Acetoxy-7-methoxycarbonyltriptycene (XIa). A mixture of (+)-IXa (70 mg), acetic anhydride (3 ml) and a small amount of anhydrous sodium acetate was heated on a boiling water-bath for 3 hr. After cooling, water was added to the reaction mixture. Crystals deposited were recrystallized from methanol to yield (+)-XIa, colorless rods, mp 175.5—176.5°C, IR: 1767 ($\nu_{C=O}$, -OCOCH$_3$), 1723 ($\nu_{C=O}$, -COOCH$_3$) cm^{-1}, UV: $\lambda^{\text{dioxane}}_{\text{max}}$ (ε) 294 (3830), 276.5 (2170),

215 (53300) nm, CD: $\lambda_{\max}^{\text{dioxane}}$ ($\Delta\varepsilon$) 285 (−0.6), 272.5 (+1.5), 260 (−1.16) nm.

Found: C, 78.43; H, 4.77%. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90%.

dl-XIa: mp 189.0—191.5°C, IR: 1755 ($\nu_{C=O}$, -$OCOCH_3$), 1708 ($\nu_{C=O}$, -$COOCH_3$) cm^{-1}.

(+)-2-Hydroxy-5-phenylazo-7-carboxytriptycene (XIIa). To a solution of (+)-VIIIa (93 mg, 0.30 mmol) in methanol (5 ml) and 10% aqueous potassium hydroxide solution (1.5 ml) was added a solution of benzenediazonium chloride prepared from aniline (46 mg, 0.49 mmol), concentrated hydrochloric acid (0.15 ml), water (0.5 ml) and sodium nitrite (36 ml). After the mixture had been stirred for 10 min at 0°C, water (20 ml) was added to the resulting red solution and extracted with dichloromethane. The residue obtained by working up the extract was dissolved in ether–benzene (1: 1) and chromatographed on silica gel. Pure (+)-XIIa, red crystals, mp 279—280°C, was obtained by recrystallization from benzene–cyclohexane (1: 1), IR: 3100—3600 (broad), 3040, 1685 ($\nu_{C=O}$, -COOH) cm^{-1}, UV: $\lambda_{\max}^{95\%\text{EtOH}}$ (ε) 466 (3700), 359 (17700), 269 (10200) nm, CD: $\lambda_{\max}^{\text{dioxane}}$ ($\Delta\varepsilon$) 450 (−2.9), 319 (−0.9), 277 (+6.1) nm.

The azotriptycene (XIIa) gave no satisfactory elemental analysis presumably owing to its incomplete combustion.

Found: C, 78.11; H, 4.73; N, 5.91%. Calcd for $C_{27}H_{18}O_3N_2$: C, 77.50; H, 4.34; N, 6.69%.

5-Chloroanthraquinone-1-carboxylic Acid (XIVa) and 8-Chloroanthraquinone-1-carboxylic Acid (XIVb). Anthraquinone-1-sulfonic acid was converted into XIVa and XIVb according to the reported method.[11)]

5-Chloroanthracene-1-carboxylic Acid (XVa). A mixture of crude XIVa (6 g), 14% aqueous ammonia (350 ml) and zinc dust (10.5 g) was stirred on a water-bath at 90°C. Zinc dust and aqueous ammonia were further added in small portions during the course of reaction until the deep red color of the reaction mixture turned greenish grey. Excess zinc dust was removed by filtration. The filtrate was treated with active charcoal and the hot filtrate was made acidic to Congo red with concentrated hydrochloric acid to precipitate crude XVa as yellowish brown solid, 4.5 g, mp >300°C.

8-Chloroanthracene-1-carboxylic Acid (XVb). Crude XIVb (9.9 g) was converted into XVb (6.9 g, 78%) according to the procedure given above.

Methyl 5-Chloroanthracene-1-carboxylate (XVIa). A mixture of crude XVa (21.7 g), anhydrous methanol (680 ml) and concentrated sulfuric acid (10.8 ml) was refluxed. The reaction mixture was worked up in the usual way and extracted with benzene. The benzene solution was chromatographed on alumina to yield XVIa (11.0 g, 48%) which was recrystallized from methanol to give pure XVIa, light yellow needles, mp 131.5—132.5°C, IR: 1690 ($\nu_{C=O}$, -CO_2CH_3) cm^{-1}, NMR: τ 0.40 (C^9-H), 1.70 (C^{10}-H), 5.95 (-CO_2CH_3).

Found: C, 71.24; H, 4.16; Cl, 13.26%. Calcd for $C_{16}H_{11}O_2Cl$: C, 70.99; H, 4.10; Cl, 13.10%.

Methyl 8-Chloroanthracene-1-carboxylate (XVIb). Crude XVb was converted into XVIb according to the method used for the 5-chloro isomer. Pure XVIb was obtained by repeated recrystallization from methanol and petroleum ether–methyl acetate, light yellow leaflets, mp 126.0—126.8°C, IR: 1700 ($\nu_{C=O}$, -CO_2CH_3) cm^{-1}, NMR: τ 0.00 (C^9-H), 1.58 (C^{10}-H), 5.93 (-CO_2CH_3).

Found: C, 70.75; H, 4.07; Cl, 13.23%. Calcd for $C_{16}H_{11}O_2Cl$: C, 70.99; H, 4.10; Cl, 13.10%.

2-Chloro-7-methoxycarbonyltriptycene (XVIIa). To a mixture of XVIa (4.7 g, 17 mmol), dichloromethane (94 ml) and isoamyl nitrite (2.9 ml, 22 mmol), stirred vigorously under gentle reflux, was added a solution of anthranilic acid (2.72 g, 20 mmol) in tetrahydrofuran (62 ml) over a period of 5 hr. After being refluxed for further 1 hr, the solvent was removed under reduced pressure. Maleic anhydride (3.6 g, 37 mmol) and xylene (55 ml) were added to the residue and refluxed for 3.5 hr. The reaction mixture was mixed with dichloromethane (100 ml) and water (100 ml). The organic layer was washed with 5% aqueous potassium hydroxide solution (30 ml×5) and water, successively, and dried. The dichloromethane was removed by distillation and the residue was chromatographed on alumina. Slightly crude XVIIa (1.75 g, 29.1%) obtained from benzene eluate was recrystallized from cyclohexane to yield pure XVIIa, mp 164—165°C, IR: 1710 ($\nu_{C=O}$, -$COOCH_3$) cm^{-1}, UV: $\lambda_{\max}^{\text{EtOH}}$ (ε) 216 (56600), 263 (1550), 280* (2710), 295 (3990) nm, NMR: τ 3.00 (C^6-H), 4.04 (C^1-H), 6.03 (-$COOCH_3$).

Found: C, 76.30; H, 4.30; Cl, 10.02%. Calcd for $C_{22}H_{15}O_2Cl$: C, 76.19; H, 4.36; Cl, 10.22%.

5-Chloro-7-methoxycarbonyltriptycene (XVIIb). The product obtained by the reaction of XVIb (3.0 g) with benzyne generated by the above method was chromatographed on alumina, yielding slightly crude XVIIb (1.2 g, 31.2%). Pure XVIIb was obtained by recrystallization from cyclohexane, mp 248—249°C, IR: 1710 ($\nu_{C=O}$, -$COOCH_3$) cm^{-1}, UV: $\lambda_{\max}^{\text{EtOH}}$ (ε) 216 (55000), 263 (1550), 280* (2590), 295 (3740) nm, NMR: τ 2.57 (C^6-H), 4.57 (C^1-H), 6.00 (-$COOCH_3$).

Found: C, 76.16: H, 4.12; Cl, 10.54%. Calcd for $C_{22}H_{15}O_2Cl$: C, 76.19; H, 4.36; Cl, 10.22%.

2-Chloro-7-carboxytriptycene (XVIIIa). A mixture of XVIIa (979 mg), acetic acid (100 ml) and 10% aqueous sulfuric acid (30 ml) was refluxed for 10 hr. The crystals deposited on cooling the reaction mixture were combined with the second crop obtained from the concentrated filtrate. The combined crystals (quantitative yield) were recrystallized from benzene–cyclohexane to give pure XVIIIa, mp 295—296°C, IR: 1680 ($\nu_{C=O}$, -COOH) cm^{-1}.

Found: C, 75.80; H, 3.79; Cl, 10.39%. Calcd for $C_{21}H_{13}O_2Cl$: C, 75.79; H, 3.94; Cl, 10.66%.

5-Chloro-7-carboxytriptycene (XVIIIb). XVIIb was converted into XVIIIb according to the method given above, mp 217°C (from methanol), IR: 1680 ($\nu_{C=O}$, -CO_2CH_3) cm^{-1}.

Found: C, 75.76; H, 4.24; Cl, 10.86%. Calcd for $C_{21}H_{13}O_2Cl$: C, 75.79; H, 3.94; Cl, 10.66%.

Optical Resolution of 2-Chloro-7-carboxytriptycene (XVIIIa). Brucine dihydrate (1034 mg, 2.40 mmol) was added to a solution of XVIIIa (796 mg, 2.40 mmol) in 99% ethanol (30 ml). After the mixture had been refluxed for 10 min, the solvent was removed under reduced pressure. The residue was recrystallized twice from acetone to yield pure brucine salt, mp 195—199°C, $[\alpha]_{350}$ −154°, $[\alpha]_{400}$ −54.0°, $[\alpha]_{500}$ −6.00°, $[\alpha]_D$ +4.00° (*c* 0.50, $CHCl_3$).

Found: C, 72.76; H, 5.32; N, 3.85; Cl, 4.62%. Calcd for $C_{44}H_{39}O_6N_2Cl$: C, 72.66; H, 5.41; N, 3.85; Cl, 4.88%.

The brucine salt was dissolved in hot acetic acid and diluted with water to precipitate (+)-XVIIIa, mp 289—291°C (decomp.), $[\alpha]_{350}^{15}$ +103°, $[\alpha]_D^{15}$ +19.4° (*c* 0.515, dioxane), CD: $\lambda_{\max}^{\text{dioxane}}$ ($\Delta\varepsilon$) 287 (−1.2), 275 (+3.2), 259 (−1.3) nm.

Found: C, 75.30; H, 3.75%. Calcd for $C_{21}H_{13}O_2Cl$: C, 75.79; H, 3.94%.

Optical Resolution of 5-Chloro-7-carboxytriptycene (XVIIIb). To a solution of XVIIIb (128 mg, 0.4 mmol) in ethanol (6 ml) was added brucine dihydrate (172 mg, 0.4 mmol) and the mixture was refluxed for 30 min. The mixture was allowed to stand overnight. The crystals deposited were recrystallized from methyl acetate to afford pure brucine salt, mp 225—231°C.

Found: C, 72.56; H, 5.43; N, 3.83; Cl, 4.62%. Calcd for $C_{44}H_{39}O_6N_2Cl$: C, 72.66; H, 5.41; N, 3.85; Cl, 4.88%.

A hot acetic acid solution of the brucine salt was diluted with water to result in the precipitation of (+)-XVIIIb, mp 285—277°C, CD: $\lambda_{\max}^{\text{dioxane}}$ $(\Delta\varepsilon)$ 285 (−0.8), 275 (+1.3) nm.

Found: C, 75.64; H, 3.75%. Calcd for $C_{21}H_{13}O_2Cl$: C, 75.79; H, 3.94%.

(+)-2-Chloro-7-methoxytriptycene (XIX). A mixture of (+)-2-chloro-7-carboxytriptycene (XVIIIa, 0.330 g), thionyl chloride (0.4 ml) and tetrahydrofuran (10 ml) was refluxed for 2 hr. The volatile material was removed under reduced pressure to give crude acid chloride (0.350 g). To an ice-cooled solution of the crude acid chloride in tetrahydrofuran (15 ml) was added a solution of sodium azide (130 mg, 2.0 mmol) in water (1 ml). After the mixture had been stirred for 2 hr, the reaction mixture was poured onto water (100 ml). The solid deposited was washed thoroughly with water and dried *in vacuo*. The well-dried acid azide (0.304 g) was spread on the bottom of a 100 ml Erlenmeyer flask in a thin layer and gradually heated to 120°C avoiding the atmospheric moisture. After being kept at the same temperature for 2 hr, 99% ethanol (30 ml) containing potassium hydroxide (2.0 g) was added to the resulting isocyanate. After being refluxed for 6 hr, the ethanol was removed under reduced pressure. The residue was mixed with water (100 ml) and extracted with benzene. The extract, after being washed with a saturated sodium chloride solution and dried, was concentrated under reduced pressure to give amino derivative (0.250 g). The chloro-aminotriptycene thus obtained was dissolved in acetic acid (10 ml) and a solution of sodium nitrite (0.058 g) in water (2 ml) was added to the solution in small portions over 20 min period under stirring at 10—15°C. After being stirred for further 30 min, the resulting red solution of diazonium salt was added dropwise to boiling 6N sulfuric acid (30 ml). After further boiling for 10 min, water was added to the reaction mixture to make 100 ml of mixture and extracted with benzene. After being washed and dried, the extract was concentrated under reduced pressure to give phenolic derivative (0.263 g). A mixture of the crude phenol, acetone (15 ml), anhydrous potassium carbonate (1.2 g) and dimethyl sulfate (0.3 ml) was refluxed for 8 hr under stirring. The residue obtained by evaporation of the solvent under reduced pressure was mixed with water (40 ml) and extracted with benzene. The extract was worked up in the usual way. A benzene solution of the crude methyl ether was passed through a column of alumina (10 g). The crystals (186 mg) obtained from the initial filtrate (110 ml) were chromatographed on alumina (30 g). Elution with ligroin–benzene (2: 3) afforded colorless crystals (58 mg) which were recrystallized from methanol and then sublimed *in vacuo* to give pure (+)-XIX, mp 235—236.0°C, UV: $\lambda_{\max}^{\text{dioxane}}$ (ε) 280 (2500), 276 (2620), 273* (2600), 268* (2580), 264 (2600), 217 (60500) nm, CD: $\lambda_{\max}^{\text{dioxane}}$ $(\Delta\varepsilon)$ 280 (+3.74), 275* (+2.28), 262 (−4.71), 242 (−4.31), 224 (+36.8), 216 (−31.0) nm.

Found: C, 78.93; H, 4.74; Cl, 11.00%. Calcd for $C_{21}H_{15}OCl$: C, 79.12; H, 4.74; Cl, 11.12%.

(+)-XIX thus prepared was admixed with approximately the same amount of (−)-XIX. The mixed melting point was found to be 240.5—241.4°C indicating the formation of a racemic compound.

(−)-2-Chloro-7-methoxytriptycene (XIX). Thionyl chloride (0.8 ml) was added to a solution of (−)-2-methoxy-7-carboxytriptycene (VIIa, 604 mg) with *ca.* 60% optical purity, obtained from the mother liquor of optical resolution of *dl*-VIIa with brucine, in tetrahydrofuran (20 ml). After the mixture had been refluxed for 2 hr, the volatile material was removed under reduced pressure to give crude acid chloride [659 mg, IR: 1750 ($\nu_{C=O}$, -COCl) cm^{-1}]. To an ice-cooled solution of the acid chloride in tetrahydrofuran (30 ml) was added a solution of sodium azide (254 mg) in water (2 ml). After being stirred for further 2 hr at the same temperature, the reaction mixture was poured onto ice-water (200 ml). Thoroughly dried acid azide [88 mg, IR: 2130 ($\nu_{N=N^+=N^-}$), 1680 ($\nu_{C=O}$) cm^{-1}] was heated to 180°C as previously to give isocyanate [66 mg, IR: 2250 ($\nu_{N=C=O}$) cm^{-1}]. A mixture of the crude isocyanate (343 mg), potassium hydroxide (2.0 g), water (10 ml) and 99% ethanol (50 ml) was refluxed for 6 hr. After the solvent had been removed under reduced pressure, the residue was mixed with water (200 ml) and extracted with benzene. Concentration of the extract, after washing and drying, under reduced pressure afforded amino derivative [338 mg, IR: 3480, 3390 (ν_{N-H}) cm^{-1}]. A solution of sodium nitrite (925 mg) in water (2 ml) was added to an ice-cooled mixture of the amine (402 mg) in concentrated hydrochloric acid (5 ml). Freshly prepared cuprous salt [from cupric sulfate pentahydrate (500 mg), sodium chloride (130 mg), sodium hydrogen sulfite (106 mg), sodium hydroxide (70 mg) and water (24 ml)] was dissolved in concentrated hydrochloric acid (5 ml). To the solution of cuprous chloride in hydrochloric acid was added the diazotized amine in the same acid, and the mixture was kept at 80°C for 1 hr. Crude crystals (377 mg) obtained by diluting the reaction mixture with water were dissolved in *n*-hexane–benzene (1: 1) and percolated through a column of alumina. Crystals (260 mg) obtained from the initial filtrate (100 ml) were recrystallized from methanol and then sublimed *in vacuo* (bath temp. 200°C/2 mmHg) to give (−)-XIX, mp 234.0—235.0°C, UV: $\lambda_{\max}^{\text{dioxane}}$ (ε) 280 (2530), 276 (2770), 273* (2670), 268* (2570), 264 (2750), 217 (60000) nm, CD: $\lambda_{\max}^{\text{dioxane}}$ $(\Delta\varepsilon)$ 281 (−2.23), 275* (−1.39), 269 (+3.00), 242 (+3.42), 225 (−22.0), 215 (+13.0) nm.

The optical purity of (−)-XIX thus obtained was found to be 60%.

Found: C, 78.99; H, 4.59; Cl, 11.10%. Calcd for $C_{21}H_{15}OCl$: C, 79.12; H, 4.74; Cl, 11.12%.