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Optically Active Triptycenes. II.1) Synthesis of Optically Active 7-Substituted 2,5-Dimethoxytriptycenes

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A series of optically active 7-substituted 2,5-dimethoxytriptycenes has been prepared from (+)-2,5-diacetoxy-7-carboxytriptycene (I) as suitable model compounds for a study of the relationship between their structure and optical rotatory properties. The single crystal of 2,5-dimethoxy-7-dimethylaminotriptycene hydrobromide (VII) thus prepared was subjected to X-ray crystallographic analysis and proved to have 1*R*, 6*S* absolute configuration. Consequently, it became clear that all compounds of this series have the same 1*R*, 6*S* configuration. They showed without exception positive optical rotation in visible wavelength region.

Triptycene is a highly symmetrical cage compound and has a definite and rigid molecular structure confirmed by reactivities,2) various spectroscopic properties,3) electric dipole moments,4) and X-ray crystallographic analysis.5,6)

Triptycene derivatives bearing different substituent groups in two of the three benzene rings can be resolved into optical antipodes. We reported on the synthesis and optical resolution of 2,5-diacetoxy-7-carboxytriptycene (I).1) The optically active triptycene may be regarded as one of the most appropriate substances for studying the relation between structure and rotatory properties for the following reasons.

1. The difinite and rigid molecular structure should exclude the influence of complicated effects arising from the flexibility of the molecule.
2. The structural transformation necessary for the investigation can be accomplished without causing recemization and Walden inversion.
3. Theoretical approach to the analysis of the ORD and CD properties might be possible by utilizing the results of investigations on the electronic spectra of benzenoid chromophore.

We wish to report on the preparation of a series of 7-substituted 2,5-dimethoxytriptycenes with identical absolute configuration starting from (+)-2,5-diacetoxy-7-carboxytriptycene (I).1) The general scheme of the transformation is summarized in Fig. 1. Hydrolysis of I by means of aqueous acetic acid containing hydrogen bromide afforded 2,5-dihydroxy-7-carboxytriptycene (II). Methylation of II with dimethyl sulfate in acetone in the presence of anhydrous potassium carbonate resulted in the formation of 2,5-dimethoxy-7-methoxycarbonyltriptycene (III).7) 2,5-Dimethoxy-7-carboxytriptycene (IV) was obtained by hydrolysis of III in aqueous acetic acid containing sulfuric acid.8)

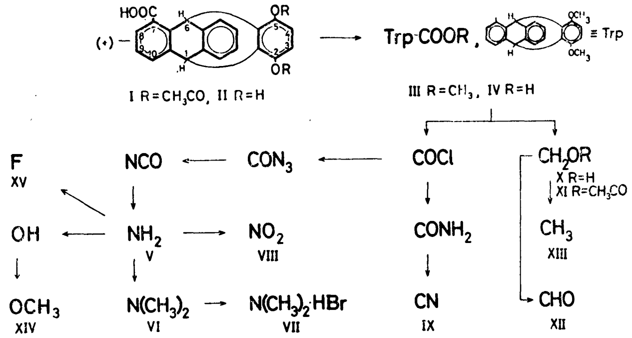

Fig. 1. General scheme of preparation of optically active triptycenes.

Treatment of IV in tetrahydrofuran with thionyl chloride yielded acid chloride, which was subjected to the Curtius reaction *via* acid azide and isocyanate to give 2,5-dimethoxy-7-aminotriptycene (V).

Methylation of V with trimethyl phosphate yielded 2,5-dimethoxy-7-dimethylaminotriptycene (VI).9)

Amine (V) was oxidized to 2,5-dimethoxy-7-nitrotriptycene (VIII) by peracetic acid in chloroform.10)

The above-mentioned acid chloride was treated with ammonia in tetrahydrofuran to yield acid amide. Dehydration of the amide by thionyl chloride in dimethylformamide afforded 2,5-dimethoxy-7-cyanotriptycene (IX).

Reduction of the ester (III) with lithium aluminum hydride in tetrahydrofuran gave 2,5-dimethoxy-7-hydroxymethyltriptycene (X), which was converted into 2,5-dimethoxy-7-acetoxymethyltriptycene (XI) on treatment with acetic anhydride.

Oxidation of carbinol (X) with chromium trioxide-pyridine complex in pyridine yielded 2,5-dimethoxy-7-formyltriptycene (XII).11)

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5) N. Sakabe, K. Sakabe, K. Ozeki-Minakata, C. Katayama, and J. Tanaka. Presented at The Ninth International Congress of Crystallography, Kyoto (1972). *Acta Crystallogr.*, in press.

6) K. J. Palmer and D. H. Templeton, *ibid.*, **B24**, 1048 (1968).

7) The phenolic hydroxyl group in II could not be methylated even by an excess of diazomethane, probably owing to their low acidity.

8) Hydrogen bromide could not be used as partial demethylation occurred.

9) J. H. Billman, A. Radike, and B. W. Mundy, *J. Amer. Chem. Soc.*, **64**, 2977 (1942); D. G. Thomas, J. H. Billman, and C. E. Davis, *ibid.*, **68**, 895 (1946).

10) W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 5528 (1958); *idem*, *ibid.*, **76**, 3470 (1954).

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Chloromethyl derivative obtained by the reaction of X with thionyl chloride was reduced to 2,5-dimethoxy-7-methyltriptycene (XIII) with lithium aluminum hydride in refluxing tetrahydrofuran.[12]

Amine (V) was diazotized with sodium nitrite in acetic acid. Diazonium compound thus obtained was hydrolyzed in dilute boiling sulfuric acid to afford phenol derivative.[13] The crude phenol was methylated with dimethyl sulfate in acetone in the presence of anhydrous potassium carbonate to yield methyl ether (XIV).

Fluoro derivative (XV) was obtained from amine (V) by the Schiemann reaction.

All the new compounds described above gave satisfactory data of elemental analyses and their structures were confirmed by means of IR, UV, and NMR spectra.

X-Ray crystallographic analysis performed on the single crystal of (+)-2,5-dimethoxy-7-dimethylaminotriptycene hydrobromide (VII) demonstrated that the absolute configuration of VII was 1*R*,6*S* as shown in Fig. 2.[5] Consequently, all the compounds shown in Fig. 1 were proved to have the same 1*R*,6*S* configuration. All the compounds of this series showed dextro optical rotation regardless of the change of nature of substituent group at 7-position.

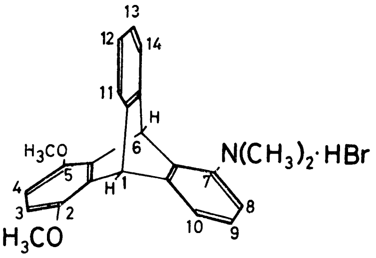

Fig. 2. The absolute configuration of (+)-2,5-dimethoxy-7-dimethylaminotriptycene hydrobromide.

Experimental

All the melting points were not corrected. The experimental procedures refer to the optically active substances, and purified anhydrous solvents were used throughout the experiments unless otherwise stated. Ligroin boiling at 60—80°C was used. The IR spectra were measured with a Hitachi EPI-2 and a JASCO DS-301 spectrophotometer. The NMR spectra in deuteriochloroform solution were obtained with a Varian A-60 spectrometer using TMS as an internal standard. Chemical shifts are recorded in δ unit. The electronic spectra were obtained with a Hitachi EPS-3T and a Zeiss PMQIIM4QIIId spectrometer. The optical rotations were measured with a Rudolf Model 200S-80 and a Yanagimoto ORD-185 spectropolarimeter. The circular dichroism spectra were measured with a Roussel-Jouan dichrograph B, II-CD-185 and JASCO J-20 spectropolarimeter with CD attachments. The inflections and shoulders are indicated with an asterisk. The optical rotations were measured at 20°C throughout the present research unless otherwise stated. Ethanol (99%) containing 0.1 N aqueous hydrochloric acid (2 m*l* of the hydrochloric acid was made up to 20 m*l* solution with the ethanol) was used as a solvent of measurement and abbreviated as 99% EtOH-HCl.

2,5-Dihydroxy-7-carboxytriptycene(II). To a hot solution of (+)-2,5-diacetoxy-7-carboxytriptycene (I, 1.436 g) was added hydrobromic acid (47%, 3.3 m*l*). The mixture was refluxed for 6 hr and allowed to cool to room temperature to precipitate fairly pure II (light brown leaflets, sintered at *ca.* 220°C and melted at *ca.* 300°C, 0.999 g, 94.5%) which could be used directly for the preparation of derivatives. Recrystallization of this material from acetic acid-water gave pure II, mp 332—335°C (decomp.). Elemental analyses of this substance gave no satisfactory results presumably owing to its nature of incomplete combustibility. IR (Nujol mull): 3700—2500 (ν_{O-H}, -COOH, -OH), 1689 (ν_{C-O}, -COOH) cm^{-1}. UV: $\lambda_{max}^{99\%EtOH}$ (ε) 261 (4160) 269 (4200), 294 (8330) nm. ORD: $[M]_{5791}^{18°C}+189.4°$, $[M]_{5461}^{18°C}+215.9°$, $[M]_{4358}^{18°C}+412.2°$, $[M]_{4047}^{18°C}+535.5°$, $[M]_{3650}^{18°C}+849.0°$ (*c*, 0.4356, dioxane).

Hydrolysis of *dl*-I was carried out under somewhat different conditions. Racemic I (20 g) was dissolved in hot acetic acid (20 m*l*). A mixture of water (30 m*l*) and hydrobromic acid (47%, 4 m*l*) was added to the solution and refluxed for 7 hr. Racemic II was obtained as faint pink plates (1.3 g, 84.5%) on cooling the reaction mixture, mp 325°C (decomp.). Racemate exhibited a slightly different IR spectrum.

2,5-Dimethoxy-7-methoxycarbonyltriptycene (III). A mixture of II (0.60 g), dimethyl sulfate (1.1 g), anhydrous potassium carbonate (3.0 g), and acetone (40 m*l*) was refluxed for 8 hr under stirring. After cooling, the reaction mixture was poured onto water (*ca.* 300 m*l*) and extracted 3 times with benzene. The crude crystalline product obtained from the extract was dissolved in benzene and purified by passing through a short column of alumina (25 g). Colorless crystals (0.6 g) were obtained on evaporating the first 500 m*l* fraction. Recrystallization from a small amount of benzene gave pure III, mp 261.5—262.5°C (racemate, mp 227—228.5°C). IR (KBr-disk): 2830 (ν_{C-H}, $-OCH_3$), 1715 ($\nu_{C=O}$, $-COOCH_3$) cm^{-1}. NMR: 3.83 (6H, s, $-OCH_3$), 4.02 (3H, s, $-COOCH_3$), 5.95 (1H, s, C_1-H), 6.56 (2H, aromatic at C_{3-4}), 6.97—7.71 (8H, m, aromatic at C_{8-14} and C_6-H).[14] UV: $\lambda_{max}^{99\%EtOH}$ (ε) 294 (8220), 270 (3450), 262 (2790), 208 (63600), 195 (52500) nm. $\lambda_{max}^{dioxane}$ (ε) 295 (8200), 270 (3230), 262 (2500) nm. ORD: $[M]_{5791}^{25°C}+91.6°$, $[M]_{5461}^{25°C}+104.6°$, $[M]_{4358}^{25°C}+195.9°$, $[M]_{4047}^{25°C}+248.8°$, $[M]_{3650}^{25°C}+386.2°$ (*c*, 0.7475, dioxane). CD: $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 302 (+1.35), 279 (+0.43), 268.5 (−3.83), 262 (−2.87), 249 (+1.82), 244 (−1.25), 232 (+5.14), 219 (−10.42), 207 (+37.64) nm. $\lambda_{max}^{dioxane}$ ($\Delta\varepsilon$) 303 (+1.61), 280 (+0.57), 267 (−3.06), 262 (−2.66) nm.

Found: C, 77.19; H, 5.48%. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41%.

2,5-Dimethoxy-7-carboxytriptycene (IV). Methyl ester (III, 0.30 g) in acetic acid (20 m*l*) was mixed with 6 N sulsulfuric acid (5 m*l*) and the mixture was refluxed for 12 hr. Crystals obtained on cooling the reaction mixture were recrystallized from acetic acid to give pure IV, mp 320—321°C (racemate, mp 305—306°C (decomp.)). IR (KBr disk): 3400—2200 (ν_{O-H}, -COOH), 2835 (ν_{C-H}, $-OCH_3$), 1683 ($\nu_{C=O}$, -COOH) cm^{-1}. UV: $\lambda_{max}^{99\%EtOH}$ (ε) 293 (6800),

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12) Racemic XIII was obtained by lithium aluminum hydride reduction of tosylate of *rac*-X which was prepared by the reaction of sodium salt of *rac*-X with tosyl chloride (see Experimental).

13) Diazotization of amine (V) with nitrosyl sulfate in sulfuric acid resulted in the formation of a nitrosophenol derivative.

14) The signal of the bridgehead proton bonded to C_6 was shifted to down-field by the effect of anisotropy of the methoxycarbonyl group.

268.5 (3340), 261 (2780), 209 (59300) nm. $\lambda_{\max}^{\text{dioxane}}$ (ε) 295 (8330), 270 (3660), 263 (2910), 220 (38300) nm. ORD: $[\mathrm{M}]_{5893}$+144.2°, $[\mathrm{M}]_{5461}$+167.3°, $[\mathrm{M}]_{4358}$+301.4°, $[\mathrm{M}]_{4047}$+398.0°, $[\mathrm{M}]_{3650}$+588.4° (*c*, 0.0497, dioxane). CD: $\lambda_{\max}^{\text{dioxane}}$ ($\Delta\varepsilon$) 303.5 (+1.28), 279 (+0.49), 267.5 (−2.50), 263 (−2.23), 250 (+0.93) nm.

Found: C, 77.22; H, 5.19%. Calcd for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06%.

2,5-Dimethoxy-7-aminotriptycene (V). Carboxylic acid (IV, 0.410 g) was dissolved in tetrahydrofuran (25 m*l*) and treated with thionyl chloride (2 m*l*) under reflux for 3 hr. The solvent was removed under reduced pressure to give colorless crystals. The acid chloride obtained was fairly pure and could be used directly in the following reaction [IR (Nujol mull): 1755 $\nu_{\text{C=O}}$, –COCl) cm⁻¹]. A solution of sodium azide (0.140 g) in water (3 m*l*) was added to an ice-cooled solution of the acid chloride (0.458 g) in tetrahydrofuran (35 m*l*). The reaction mixture was stirred for 2 hr and poured onto 300 m*l* of cold water. Colorless precipitate was collected by filtration and washed with water and dried. The acid azide is fairly stable and can be handled safely at room temperature, though spontaneous rearrangement to isocyanate occurred in part even under room temperature [IR (Nujol mull): 2150 ($\nu_{\text{N=N=N}}$, $-CON_3$), 1695 ($\nu_{\text{C=O}}$, $-CON_3$) cm⁻¹. Weak absorption band at 2270 cm⁻¹ indicated the presence of a minor amount of isocyanate]. The well-dried acid azide (0.429 g) was spread over the bottom of a 300 m*l* Erlenmeyer flask and heated slowly up to 130°C and maintained at this temperature for 3 hr yielding light brown crystalline powder (0.385 g) with evolution of nitrogen [IR (Nujol mull): 2270 ($\nu_{\text{N=C=O}}$) cm⁻¹]. A mixture of the isocyanate (0.249 g), 99% ethanol (40 m*l*) and water (10 m*l*) was refluxed for 8 hr. Crystals deposited were collected by filtration and washed with 50% ethanol and water, successively, to give V as faintly pink leaflets (0.191 g). The filtrate and washings were combined and poured water(300 m*l*) and extracted 4 times with benzene. The combined extracts were washed with water and dried (sodium sulfate). Evaporation of the solvent afforded further 0.036 g of the amine (total yield 93% based on IV). Colorless pure crystals of V [mp 259—261°C (decomp.) in a sealed tube] were obtained by repeated sublimation under reduced pressure (bath temp. 200—220°C/3 mmHg). IR (KBr disk): 3495, 3470 ($\nu_{\text{N-H}}$, $-NH_2$), 1623 ($\delta_{\text{N-H}}$, $-NH_2$), 2845 ($\nu_{\text{C-H}}$, $-OCH_3$) cm⁻¹. UV: $\lambda_{\max}^{\text{99\%EtOH}}$ (ε) 296 (5540), 275 (3630), 269 (3840), 260 (3200), 217 (53500), 195 (50800) nm. $\lambda_{\max}^{\text{dioxane}}$ (ε) 302 (6500), 275 (4040), 269.6 (4100), 219.5 (52600) nm. $\lambda_{\max}^{\text{99\%EtOH-HCl}}$ (ε) 296 (4090), 277.5 (3820), 271· (2750), 262.5 (2560), 212 (61700), 194 (55400) nm. CD: $\lambda_{\max}^{\text{99\%EtOH}}$ ($\Delta\varepsilon$) 303 (+6.37), 270 (−9.11), 244 (−7.50), 225 (+26.5), 204 (−6.38), 197 (−7.46) nm. $\lambda_{\max}^{\text{dioxane}}$ ($\Delta\varepsilon$) 303 (+6.77), 268 (−9.83), 245 (−5.53), 225 (+27.7) nm. $\lambda_{\max}^{\text{99\%EtOH-HCl}}$ ($\Delta\varepsilon$) 297 (+1.77), 277.5 (+4.30), 273.5 (−0.70), 262 (−9.08), 239 (+2.86), 219 (−5.14) nm. ORD: $[\mathrm{M}]_{5893}$ +62.44°, $[\mathrm{M}]_{5461}$+66.60°, $[\mathrm{M}]_{4358}$+149.9°, $[\mathrm{M}]_{4047}$+233.1°, $[\mathrm{M}]_{3650}$+562.0° (*c*, 0.3165, dioxane).

Found: C, 79.84; H, 5.84%. Calcd for $C_{22}H_{19}O_2N$: C, 80.22; H, 5.81%.

Racemate was recrystallized from methanol and showed no tendency to sublime, mp 267—268°C.

2,5 - Dimethoxy - 7 - dimethylaminotriptycene (VI). The amine (V, 0.080 g) was mixed with trimethyl phosphate (0.60 g) and heated to reflux for 3 hr. After cooling, a mixture of water (1.3 m*l*) and sodium hydroxide (1.7 g) was added to the reaction mixture and refluxed for 30 min. Colorless crystals deposited were collected by filtration and washed with water. Sublimation under reduced pressure (bath temp. 220—230°C/3 mmHg) afforded pure VI, mp 246—248°C. IR (KBr disk): 2970 ($\nu_{\text{C-H}}$, $-N-CH_3$), 2840 ($\nu_{\text{C-H}}$, $-OCH_3$) cm⁻¹. UV: $\lambda_{\max}^{\text{99\%EtOH}}$ (ε) 294 (4770), 275* (4510), 268* (5900), 261* (6760), 230* (*ca.* 25000, broad), 211 (45100), 195 (55500) nm. $\lambda_{\max}^{\text{dioxane}}$ (ε) 295 (4820), 275* (4970), 268* (6560), 256* (8000, broad), 230* (24700, broad), 216 (41300) nm. $\lambda_{\max}^{\text{99\%EtOH-HCl}}$ (ε) 297.5 (4300), 279 (4730), 272.5 (3520), 263 (3320), 255 (2920), 208 (60200), 197 (54200) nm. CD: $\lambda_{\max}^{\text{99\%EtOH}}$ ($\Delta\varepsilon$) 304 (+1.82), 275.5 (−4.72), 271 (−5.17), 261.5 (+1.40), 244 (−9.65), 228 (+27.9), 214 (−17.8), 204 (+3.80), 199 (−6.33) nm. $\lambda_{\max}^{\text{dioxane}}$ ($\Delta\varepsilon$) 298 (+2.60), 272.5 (−6.11), 260.5 (+3.20), 243 (−10.0), 228 (+31.8) nm. $\lambda_{\max}^{\text{99\%EtOH-HCl}}$ ($\Delta\varepsilon$) 297 (+1.26), 279 (+2.45), 273.5 (−1.03), 264.5 (−8.61), 247 (+5.47), 213 (−9.45) nm. ORD: $[\mathrm{M}]_{4047}$ +5.40°, $[\mathrm{M}]_{3650}$+34.10° (*c*, 0.2788, dioxane).

Found: C, 80.45; H, 6.57%. Calcd for $C_{24}H_{23}O_2N$: C, 80.64; H, 6.49%.

2,5-Dimethoxy-7-dimethylaminotriptycene Hydrobromide (VII). The dimethylamine (VI, 0.038 g) dissolved in 99% ethanol (22 m*l*) was mixed with 47% aqueous hydrobromic acid (3 m*l*) and water (3 m*l*). Clear and homogeneous solution obtained on warming and filtration was placed in a loosely stoppered ground joint vessel and kept in the dark. Beautiful rhomboidal single crystals of VII developed gradually on storing the solution over a period of two or three months. Sometimes VII crystallized in needles. In such cases the solution had to be warmed to dissolve the needles and filtered again to get rhomboidal crystals. The crystals began to sublime at *ca.* 240°C and partly melted at the same time. It crystallized again in needles and perfectly decomposed to red oil at 250°C, IR (KBr disk): 2845 ($\nu_{\text{C-H}}$, $-OCH_3$), 2785 ($\nu_{\text{C-H}}$, $-N-CH_3$), 2700—2000 ($\nu_{\text{N-H}}$, $-\overset{+}{N}H(CH_3)_2$) cm⁻¹. UV: $\lambda_{\max}^{\text{99\%EtOH}}$ (ε) 297 (4490), 278.5 (4320), 269.5 (4460), 262 (4870), 255* (5100), 210 (55900), 196.5 (68700) nm. CD: $\lambda_{\max}^{\text{99\%EtOH}}$ ($\Delta\varepsilon$) 299.5 (+1.52), 279.5 (+0.88), 273.5 (−2.33), 264 (−5.84), 256 (−1.17), 248.5 (−0.53), 230 (+9.21), 214.5 (−14.3) nm.

Found: C, 65.70; H, 5.48; Br, 18.33%. Calcd for $C_{24}H_{24}O_2NBr$: C, 65.75; H, 5.52; Br, 18.23%.

2,5-Dimethoxy-7-nitrotriptycene (VIII). Ninety percent hydrogen peroxide (0.083 m*l*) and a small drop of concentrated sulfuric acid were added to ice-cooled chloroform (0.36 m*l*). Acetic anhydride (0.4 g) was then added to the mixture. The cooling bath was removed and the mixture was stirred for 15 min. After further addition of chloroform (0.24 m*l*) the mixture was heated to reflux under stirring. The heating bath was removed and a solution of V (0.196 g) in chloroform (20 m*l*) was added dropwise to the hot oxidizing mixture. Deposition of pale yellow crystals from the yellow reaction mixture was observed. The reaction mixture was refluxed under stirring. The resulting brown reaction mixture was poured onto water (100 m*l*) and extracted 3 times with chloroform. The combined extracts were washed successively with 10% aqueous potassium hydroxide, 10% aqueous hydrochloric acid and water, and dried (sodium sulfate). Brown yellow solid (0.203 g) obtained on evaporating the solvent under reduced pressure was dissolved in benzene and passed through a short column alumina (15 g). Yellow crystals (0.135 g) were obtained on concentrating the first 300 m*l* fraction eluted. The crude material was recrystallized 3 times from a mixture of ethyl acetate and ethanol, and then sublimed under reduced pressure (bath temp. 250°C/3 mmHg) to afford faintly yellow crystals. This material did not melt up to 300°C. IR (KBr disk): 2840 ($\nu_{\text{C-H}}$, $-OCH_3$), 1525 ($\nu_{\text{N-O asym}}$, $-NO_2$), 1350

($\nu_{\mathrm{N-O\,sym}}$, $-NO_2$) cm^{-1}. NMR: 3.83 (6H, s, $-OCH_3$) 5.98 (1H, s, bridgehead proton at C_1), 6.55 (2H, s, aromatic at C_{3-4}), 6.97—7.70 (8H, m, aromatic st C_{8-14} and C_6-H). The signal of bridgehead proton at C_6 is shifted to down-field owing to the anisotropic effect of the nitro group. UV: $\lambda_{\max}^{99\%\mathrm{EtOH}}$ (ε) 330* (2700, broad), 294.5 (7030), 273 (6670), 267 (6940), 261 (6730), 207 (62200), 194 (48500) nm. $\lambda_{\max}^{\mathrm{dioxane}}$ (ε) 330* (2770, broad), 296 (6780), 273.5 (6810), 267 (7120), 262 (7060), 220 (27700) nm. CD: $\lambda_{\max}^{\mathrm{dioxane}}$ ($\Delta\varepsilon$) 350 (+1.45), 301.5 (+3.78), 265 (−7.90), 238 (+3.52), 225 (+5.42), 209 (+28.48), 195 (−12.03) nm. $\lambda_{\max}^{\mathrm{dioxane}}$ ($\Delta\varepsilon$) 350 (+0.69), 302 (+3.28), 264 (−6.76), 236 (+4.14) nm. ORD: $[M]_{4358}+117.3°$, $[M]_{4047}+207.7°$, $[M]_{3730}+334.7°$ (peak), $[M]_{3650}+260.0°$ (*c*, 0.006785, EtOH). $[M]_{4358}+51.9°$, $[M]_{4047}+111.0°$, $[M]_{3770}+161.0°$ (peak), $[M]_{3650}+110.0°$ (*c*, 0.00706, dioxane).

Found: C, 73.87; H, 4.80%. Calcd for $C_{22}H_{17}O_4N$: C, 73.53; H, 4.77%.

Careful combustion of a mixture of VIII (2.019 mg) and sucrose (1.295 mg) gave the above results.

Racemate was recrystallized from benzene-ligroin, mp 270—274°C (decomp.). It showed no tendency to sublime.

2,5-Dimetoxy-7-cyanotriptycene (IX). Acid chloride (0.680 g) obtained by the reaction of IV with thionyl chloride according to the above procedure was dissolved in tetrahydrofuran (40 m*l*). Aqueous ammonia (28%, 5 m*l*) was added to the solution and the resulting clear two-layer mixture was allowed to stand overnight at room temperature. Colorless crystals of amide (0.353 g) deposited were filtered and washed with tetrahydrofuran. The combined filtrate and washings were concentrated under reduced pressure, yielding a second crop of the amide (0.257 g). The combined crystals were recrystallized from methyl acetate-methanol to yield pure amide, mp 305—320°C (decomp.). IR (Nujol mull): 3400, 3300, 3250, 3140 ($\nu_{\mathrm{N-H}}$, $-CONH_2$), 1680 ($\nu_{\mathrm{C=O}}$, $-CONH_2$) cm^{-1}.

The amide (0.454 g) was dissolved in warm dimethylformamide (15 m*l*) and mixed with thionyl chloride (9 m*l*). Immediate development of red color and generation of heat were observed. As soon as the mixture was heated on a water-bath (80—90°C), deposition of a considerable amount of colorless solid was observed. Most of the solid again dissolved in the solution in a period of 10 min with evolution of sulfur dioxide and hydrogen chloride. The reaction mixture was kept at 80—90°C for 20 hr and then chilled in an ice-bath. Crystals of sulfur (0.125 g) deposited were removed by filtration and washed with dimethylformamide. The combined filtrate and washings were poured into water (300 m*l*). Red brown oil separated under evolution of gas was extracted 3 times with ether and once with benzene. The combined extracts were washed with water and dried over sodium sulfate. Yellow solid (0.554 g) obtained on evaporating the solvent under reduced pressure was dissolved in benzene and passed through a short column of alumina (25 g). IX was obtained as colorless crystals (0.270 g) on drying up the first 500 m*l* fraction eluted. It crystallized in fine needles from 99% ethanol. IX sublimed on heating *ca.* 200°C, mp 263—265°C. IR (KBr disk): 2840 ($\nu_{\mathrm{C-H}}$, $-OCH_3$), 2225 ($\nu_{\mathrm{C\equiv N}}$) cm^{-1}. UV: $\lambda_{\max}^{99\%\mathrm{EtOH}}$ (ε) 296.5 (8880), 268.5 (3180), 262 (2190), 206 (73000), 194* (46500) nm. $\lambda_{\max}^{\mathrm{dioxane}}$ (ε) 297 (9200), 268.5 (3190), 261 (2180), 215.5 (45900) nm. ORD: $[M]_{5893}+71.4°$, $[M]_{5461}+95.6°$, $[M]_{4358}+178.8°$, $[M]_{4047}+248.1°$, $[M]_{3650}+432.3°$ (*c*, 0.1264, dioxane). CD: $\lambda_{\max}^{99\%\mathrm{EtOH}}$ ($\Delta\varepsilon$) 305 (+1.86), 279 (+0.60), 268.5 (−2.55), 261.5 (−1.53), 246 (+1.45), 235.5 (−1.24), 221 (−5.62), 206 (+11.81) nm. $\lambda_{\max}^{\mathrm{dioxane}}$ ($\Delta\varepsilon$) 303 (+2.18), 293 (+1.20), 268 (−2.66), 260* (−1.7) nm.

Found: C, 81.19; H, 5.07%. Calcd for $C_{23}H_{17}O_2N$: C, 81.39; H, 5.05%.

2,5-Dimethoxy-7-hydroxymethyltriptycene (X). A solution of III (0.438 g) in tetrahydrofuran (10 m*l*) was added dropwise to a stirred suspension of lithium aluminum hydride (0.438 g) in the same solvent (10 m*l*). After stirring for 6 hr at room temperature, ethyl acetate, wet ether, water, and 6 N sulfuric acid were added successively to the reaction mixture under ice-cooling. The acidified mixture was poured onto water (200 m*l*) and extracted with ether. The combined extracts were washed with a saturated aqueous solution of sodium chloride and dried (sodium sulfate). Colorless crystals obtained on evaporating the solvent under reduced pressure were recrystallized from 99% ethanol to yield pure X, mp 224°C. IR (KBr disk): 3600—3100 ($\nu_{\mathrm{O-H}}$), 2840 ($\nu_{\mathrm{C-H}}$, $-OCH_3$) cm^{-1}. UV: $\lambda_{\max}^{99\%\mathrm{EtOH}}$ (ε) 293.5 (3910), 280.5 (4100), 264.5 (2640), 216 (66900), 194 (57200) nm. $\lambda_{\max}^{\mathrm{dioxane}}$ (ε) 294 (4280), 280 (4200), 264 (2620), 219 (59800) nm. ORD: $[M]_{5893}+93.2°$, $[M]_{5461}+118.0°$, $[M]_{4358}+247.6°$, $[M]_{4047}+313.4°$, $[M]_{3650}+507.5°$ (*c*, 0.5285, dioxane). CD: $\lambda_{\max}^{99\%\mathrm{EtOH}}$ ($\Delta\varepsilon$) 297 (+0.60), 279.5 (+2.31), 263 (−5.44), 238 (−2.97), 224 (+5.95), 205 (+17.1) nm. $\lambda_{\max}^{\mathrm{dioxane}}$ ($\Delta\varepsilon$) 295 (+0.96), 279 (+2.24), 263.5 (−3.99) nm.

Found: C, 80.47; H, 5.77%. Calcd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85%.

Racemate was recrystallized from methanol, mp 235—236°C.

2,5-Dimethoxy-7-acetoxymethyltriptycene (XI). A mixture of carbinol (X, 0.100 g) and acetic anhydride (3 m*l*) was heated on a boiling water-bath for 6 hr. The excess of anhydride was decomposed by water to yield crude yellow crystals. The crystals were recrystallized twice from 99% ethanol, yielding XI, mp 177—178°C. IR (KBr disk): 2840 ($\nu_{\mathrm{C-H}}$, $-OCH_3$), 1740 ($\nu_{\mathrm{C=O}}$, $CH_3CO_2CH_2-$) cm^{-1}. UV: $\lambda_{\max}^{\mathrm{dioxane}}$ (ε) 294.5 (3940), 281 (4470), 264 (2650), 221.5 (37400) nm. ORD: $[M]_{5893}+64.0°$, $[M]_{5461}+72.8°$, $[M]_{4358}+128.1°$, $[M]_{4047}+168.5°$, $[M]_{3650}+281.0°$ (*c*, 0.6215, dioxane). CD: $\lambda_{\max}^{\mathrm{dioxane}}$ ($\Delta\varepsilon$) 295 (+1.56), 281 (+1.89), 263.5 (−5.18) nm. $\lambda_{\max}^{99\%\mathrm{EtOH}}$ ($\Delta\varepsilon$) 297 (+0.60), 279.5 (+2.31), 263 (−5.44), 238 (−2.97), 223 (+5.95), 205 (+17.1) nm.

Found: C, 77.45; H, 5.72%. Calcd for $C_{25}H_{22}O_4$: C, 77.70; H, 5.74%.

2,5-Dimethoxy-7-formyltriptycene (XII). To a slurry of pyridine-chromium trioxide complex prepared from pyridine (4 m*l*) and chromium trioxide (0.2 g) was added a solution of X (0.202 g) in pyridine (4 m*l*) under ice-cooling. After 30 min ice-bath was removed and the reaction mixture was stirred for 5 hr at room temperature. After being put to stand overnight in a refrigerator, the mixture was poured onto cold water and extracted with ether. The combined extracts were worked up in the usual way,[15] yielding colorless crystals (0.165 g, 82.2%). This material was recrystallized from 99% ethanol to result in pure XII, mp 258—259°C. IR (KBr disk): 2830 ($\nu_{\mathrm{C-H}}$, $-OCH_3$), 2720 ($\nu_{\mathrm{C-H}}$, $-CHO$), 1694 ($\nu_{\mathrm{C=O}}$, $-CHO$) cm^{-1}. NMR: 3.81 (6H, s, $-OCH_3$), 5.96 (1H, s, bridgehead proton at C_1), 6.53 (2H, s, aromatic at C_{3-4}), 7.13—7.70 (8H, m, bridgehead proton at C_6 and aromatic at C_{8-14}), 10.51 (1H, s, $-CHO$). The down-field shift of the signal of bridgehead proton at C_6 can be attributed to the anisotropic effect of the formyl group. UV: $\lambda_{\max}^{99\%\mathrm{EtOH}}$ (ε) 317* (3780), 302 (6430), 272* (4210), 258* (11600), 252* (12900), 230—236* (15300), 212.5 (56300), 194 (53800) nm. $\lambda_{\max}^{\mathrm{dioxane}}$ (ε) 315* (4440), 302 (7130), 272.5 (3120), 261* (11200), 252* (15400), 237* (19800), 215 (56300) nm.

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15) A small amount of IV (0.012 g, 5.7%) was obtained from 10% aqueous potassium carbonate washings on acidification.

ORD: $[M]_{5893}+70.2°$, $[M]_{5461}+71.4°$, $[M]_{4358}+154.9°$, $[M]_{4047}+210.1°$, $[M]_{3750}+405.0°$ (peak), $[M]_{3650}+354.0°$, $[M]_{3600}+400.9°$ (peak), (*c*, 0.295, dioxane). CD: $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 354 (+0.13), 334 (−0.23), 324 (−0.29), 297 (+1.78), 280* (+0.80), 271* (−1.78), 263* (−3.83), 256* (−4.97), 250 (−5.33), 238 (+6.02), 223 (−4.24), 211 (+27.7) nm. $\lambda_{max}^{dioxane}$ ($\Delta\varepsilon$) 295 (+1.49), 280* (+0.94), 272* (−2.60), 263* (−3.70), 248 (−5.82), 232.5 (+5.75) nm.

Found: C, 80.64; H, 5.36%. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30%.

Racemate was recrystallized from *n*-propyl alcohol and purified on sublimation at *ca.* 220°C, mp 246—248°C.

2,5-Dimethoxy-7-methyltriptycene (XIII). A solution of carbinol (X, 0.195 g) in benzene (25 m*l*) was mixed with thionyl chloride (2 m*l*). The mixture was stirred for 4 hr at room temperature and then refluxed for 30 min. Light brown solid [mp 160—180°C (decomp.)] obtained by evaporating the solvent and volatile material under reduced pressure gave no absorption of hydroxyl group in its IR spectrum. Owing to the unstable nature of the halide, the crude material was used directly in the following reaction. A solution of the crude chloride (0.213 g) in tetrahydrofuran (25 m*l*) was added dropwise to a mixture of lithium aluminum hydride (0.4 g) in the same solvent (20 m*l*) which had been stirred previously for 30 min at room temperature. After the mixture had been refluxed under stirring for 4 hr, it was cooled on an ice-bath and treated with methyl acetate, water and 6 N sulfuric acid, successively. The acidified mixture was poured onto water (200 m*l*) and extracted with ether. The combined extracts were washed with 5% aqueous sodium hydroxide and water, successively, and dried (sodium sulfate). Colorless solid obtained on evaporating the solvent under reduced pressure was dissolved in benzene and passed through a short column of alumina (20 g). Colorless crystals were obtained from the first fraction (300 m*l*). The crystals were recrystallized from methanol–methyl acetate to afford pure XIII, mp 207—209°C. IR (KBr disk): 2845 (ν_{C-H}, $-OCH_3$) cm^{-1}. NMR: 2.52 (3H, s, $-CH_3$), 3.81 (6H, s, $-OCH_3$), 5.58 (1H, s, bridgehead proton at C_6), 6.18 (1H, s, bridgehead proton at C_1) 6.51 (2H, s, aromatic at C_{3-4}) 6.81—7.52 (7H, m, aromatic at C_{8-14}). UV: $\lambda_{max}^{99\%EtOH}$ (ε) 293.5 (3780), 279 (3170), 276* (2770), 272 (2370), 264 (2360), 258* (1820), 216 (67500), 195.5 (53000) nm. $\lambda_{max}^{dioxane}$ (ε) 294 (4130), 279 (3110), 273* (2310), 264 (2330) 219.5 (49800) nm. ORD: $[M]_{5893}+99.4°$, $[M]_{4358}+136.6°$, $[M]_{4047}+161.5°$, $[M]_{3650}+335.4°$ (*c*, 0.02115, dioxane). CD: $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 301 (+0.91), 290 (+1.17), 278.5 (+2.76), 274 (−0.20), 263 (−4.48), 240.5 (−2.44), 228 (+1.47), 221 (−2.23), 215 (+5.83), 206 (−13.0). $\lambda_{max}^{dioxane}$ ($\Delta\varepsilon$) 300* (+0.90), 279 (+2.24), 263 (−3.54).

Found: C, 84.08; H, 6.05%. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14%.

The racemate was prepared as follows. Racemate of X (1.310 g) dissolved in a mixture of ether (50 m*l*) and tetrahydrofuran (25 m*l*) was mixed with a sodium hydride suspension (content 50%, 0.229 g). The mixture was refluxed for 2 hr under vigorous agitation and allowed to stand overnight at room temperature. An additional sodium hydride suspension (0.236 g) was added and the mixture was refluxed for further 2 hr under vigorous agitation. *p*-Toluenesulfonyl chloride (0.728 g) in tetrahydrofuran (15 m*l*) was added under ice-cooling and the mixture was stirred for 48 hr. The mixture was filtered under careful protection from moisture. The filtrate was concentrated under reduced pressure to give crude tosylate as a solid.[16] The presence of unreacted X was clearly indicated by its IR spectrum. As the purification by recrystallization or by chromatography on alumina was not feasible owing to its unstable nature, the crude tosylate was subjected directly to the following reaction. A solution of the crude tosylate in tetrahydrofuran was added to a mixture of lithium aluminum hydride (0.250 g) in the same solvent (15 m*l*) which had been stirred for 30 min at room temperature. The mixture was refluxed for 7 hr. After being put to stand overnight at room temperature, methyl acetate, water, and 6 N sulfuric acid were successively added to the reaction mixture. The mixture was poured onto a saturated aqueous sodium chloride solution and extracted with ether. The combined ethereal extracts were washed with water and dried (sodium sulfate). Colorless solid obtained on evaporating the solvent was dissolved in benzene and passed through a short column of alumina (25 g). From the first fraction (300 m*l*), colorless crystals contaminated with mineral oil were obtained. It was digested with boiling ligroin for a short period and recrystallized from methanol–methyl acetate (2 : 3), mp 228—230°C.

Found: C, 83.90; H, 6.08%. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14%.

2,5,7-Trimethoxytriptycene (XIV). The amine (V, 6.953 g) was dissolved in acetic acid (307 m*l*) on warming and the resulting clear pink solution was cooled to 12—14°C. Sodium nitrite (1.468 g) in water (41.6 m*l*) was added dropwise to the solution under stirring in a period of 1.5 hr. To the resulting red brown solution was added acetic acid (100 m*l*) and stirring was continued for further 30 min at 12—14°C. Strongly cooled red brown solution of the diazonium compound was added dropwise to refluxing 6 N sulfuric acid (918 m*l*) to yield phenolic derivative. The resulting light brown solution containing brown precipitate was extracted 3 times with benzene. The combined extracts were washed with water and dried over sodium sulfate. Crude phenol derivative (6.440 g, 92.4%) was obtained as light brown solid on evaporating the solvent. A solution of the phenol (100.0 mg) in acetone (15 m*l*) was refluxed with dimethyl sulfate (0.1 g) in the presence of anhydrous potassium carbonate (1 g) for 2 hr. After being put to stand overnight at room temperature, the reaction mixture was poured onto cold water (150 m*l*) and extracted 3 times with benzene. The combined extracts were washed with water and dried over sodium sulfate. Light brown solid obtained on evaporating the solvent was dissolved in benzene and passed through a short column of alumina (30 g) and eluted with the same solvent. Light yellow crystals obtained from the first eluate (300 m*l*) were dissolved in carbon tetrachloride and passed again through a short column of alumina (30 g). Colorless crystals obtained in a quantitative yield on evaporating the first eluate (300 m*l*) were recrystallized twice from a mixture of methanol and methyl acetate to give pure XIV, mp 273—275°C. IR (KBr disk): 2840 (ν_{C-H}, $-OCH_3$), 1265 (ν_{C-O}, $Ar-O-CH_3$) cm^{-1}. UV: $\lambda_{max}^{99\%EtOH}$ (ε) 293 (4360), 276 (3440), 267.5 (3750), 216 (63900), 195 (46400) nm. ORD: $[M]_{5893}+22.4°$, $[M]_{5461}+32.6°$, $[M]_{4358}+65.2°$, $[M]_{4047}+94.6°$, $[M]_{3650}+180.8°$ (*c*, 0.2695, dioxane). CD: $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 290 (+2.11), 279 (+1.87), 269 (+0.87), 241.5 (−9.91), 218.5 (+17.38), 212 (+21.36), 199 (−14.80) nm.

Found: C, 80.29; H, 5.92%. Calcd for $C_{23}H_{20}O_3$: C 80.21; H, 5.85%.

2,5-Dimethoxy-7-fluorotriptycene (XV). To a red brown solution of diazonium compound, prepared from V (0.187 g) according to the procedure used in the case of XIV, was

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[16] Tosylate of *d*-X could not be obtained by the reaction of *d*-X with *p*-toluenesulfonyl chloride in the presence of pyridine. In this case an unidentified solid bearing carbonyl group was obtained.

added a solution of sodium fluoroborate (0.1 g) in water (2 m*l*). The resulting reaction mixture was poured into a nearly saturated aqueous solution of sodium fluoroborate (15 g in 30 m*l* of water) to obtain the diazonium fluoroborate as red brown precipitate. The precipitate was collected by filtration and washed throughly with a small amount of cold water and dried exhaustively under reduced pressure. The dried fluoroborate (0.201 g) was spread over the bottom of a 300 m*l* Erlenmeyer flask and heated slowly up to 150 °C. The temperature of the flask was maintained at 150—160°C for 1.5 hr. The fluoroborate decomposed under evolution of nitrogen, yielding purple red crystalline powder. The reaction mixture was mixed with water (150 m*l*) and extracted with benzene. The combined extracts were washed with water and dried over sodium sulfate. The crude fluoro derivative obtained on evaporating the solvent was dissolved in benzene and passed through a short column of alumina (30 g). Concentration of the first benzene eluate (300 m*l*) gave the fluoro derivative as faintly yellow crystals (0.0816 g, 43.3%). The crystals were further purified by passing through a short column of alumina using carbon tetrachloride as a solvent. Colorless crystals (0.076 g) obtained from the first eluate (300 m*l*) were recrystallized twice from methanol give pure XV, mp 253.5—256.5°C (racemate, mp 248—249.5°C). UV: $\lambda_{\text{max}}^{\text{99\%EtOH}}$ (ε) 294 (4290), 276 (2570), 269 (1980), 261 (2010), 212.5 (70900), 195 (51800) nm. ORD: $[M]_{5893}+16.6°$, $[M]_{5461}+23.3°$; $[M]_{4358}+56.5°$, $[M]_{4047}+70.5°$, $[M]_{3650}+126.3°$ (*c*, 0.250, dioxane). CD: $\lambda_{\text{max}}^{\text{99\%EtOH}}$ ($\Delta\varepsilon$) 290 (+0.68), 276 (+3.50), (+0.84), 260 (−2.65), 228 (+1.60), 215.5 (−8.11), 202 (+9.05) nm.

Found: C, 79.46; H, 5.16%. Calcd for $C_{22}H_{17}O_2F$: C, 79.50; H, 5.16%.