Optically Active Triptycenes. VI.[1] Optical Resolution of 2,5-Dihydroxy-8-methoxycarbonyltriptycene and Absolute Configuration of 2,5-Dimethoxy-8-methoxycarbonyltriptycene

Yasumi SHIMIZU, Taketoshi NAITO, Fumio OGURA, and Masazumi NAKAGAWA
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

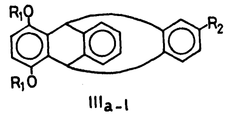
(Received December 1, 1972)

After several unsuccessful attempts, optical resolution of 2,5-dihydroxy-8-methoxycarbonyltriptycene could be attained by means of bis-camphanate derivative. The absolute configuration of (+)-2,5-dimethoxy-8-methoxycarbonyltriptycene derived from (+)-2,5-dihydroxy-8-methoxycarbonyltriptycene was determined as 1*R*,6*S* by chemical correlation with (+)-2,5-dimethoxy-7-dimethylaminotriptycene hydrobromide whose absolute configuration had been proved to be 1*R*,6*S* by the X-ray structure analysis using the Bijvoet method.

Optically active triptycene derivatives can be regarded as ideally suited model compounds for the study of rotatory properties in view of their rigid and definite molecular structure. As reported in previous papers, 2,5,7- and 2,5,8-trisubstituted triptycene derivatives have been synthesized and one of the former compounds has been resolved into enantiomers[2] which could be transformed in a number of optically active 2,5,7-trisubstituted triptycenes bearing various kinds of substituent groups.[3] We have also reported the synthesis and absolute configuration of optically active 2,7-disubstituted triptycenes[4] and the analysis of their CD spectra.[5]

The direction of long-axis polarized transition moment in 7-substituted benzene ring in 2,5,7-trisubstituted triptycenes is parallel to the three-fold symmetry axis of triptycene skeleton, whereas the direction of the transition moment in 8-substituted nucleus in 2,5,8-trisubstituted derivatives should deviate from the parallel direction.[6] Therefore, it seemed to be of considerable interest to compare the optical rotatory properties of 2,5,8-trisubstituted triptycenes with those of 2,5,7-trisubstituted analogues. The present paper deals with the optical resolution of 2,5-dihydroxy-8-methoxycarbonyltriptycene and determination of the absolute configuration of its dimethyl ether derivative by chemical means.

Optical Resolution. The optical resolution of 2,5-disubstituted-8-carboxytriptycenes using the carboxyl group (R_2) as a handle was encountered by serious difficulty. Since the difficulty seemed to be ascribable to the remote position of R_2 from the asymmetric center, 2,5-dihydroxy-8-carboxytriptycene was converted into 2,5-diacyloxy-8-carboxytriptycenes (IIIa–d) bearing various acyl groups with increasing steric requirement to increase the interaction with resolving agent attached to carboxyl group at 8-position. All attempts to resolve IIIa–b with optically active amines and alkaloids gave fruitless results. Partial resolution was observed in the case of IIId. However, complete resolution could not be achieved owing to a gradual decomposition of IIId during the course of fractional recrystallization. Considering the presence of carboxyl groups in acyloxy substituents in IIId, the introduction of acid phthalate groups into 2- and 5-positions was attempted. But bis-acid phthalate derivative could not be obtained in pure form. The attempts of resolution *via* menthoxyacetate (IIIe) or urethane (IIIf) gave unsatisfactory results. The alkaloid salts of IIIj and cholesteryl derivatives (IIIk and IIIl) could be obtained in good crystalline states. However, no optical resolution could be attained with these derivatives.



IIIa-l

a : $R_1=COCH_3$, $R_2=COOH$;
b : $R_1=COCH(CH_3)_2$, $R_2=COOH$
c : $R_1=COC(CH_3)_3$, $R_2=COOH$
d : $R_1=CO(CH_2)_2COOH$, $R_2=COOH$
e : $R_1=COCH_2$–M, $R_2=COOCH_3$
f : $R_1=CONHCH(\alpha\text{-Naph})CH_3$, $R_2=COOCH_3$
g : $R_1=$Camph, $R_2=COOCH_3$
h : $R_1=H$, $R_2=COOCH_3$
i : $R_1=CH_3$, $R_2=COOCH_3$
j : $R_1=CH_3$, $R_2=COOH$
k : $R_1=COCH_3$ $R_2=$COO–Chol
l : $R_1=COCH(CH_3)_2$, $R_2=$COO–Chol

M = *l*-menthoxy, α-Naph = α-naphthyl, Chol = cholesteryl, Camph = (−)-camphanoyl

Considering these fruitless results, we decided to use camphanic acid as resolving agent[7] which has a reacting site at a proximity of its own asymmetric center. The synthesis of 2,5-dihydroxy-8-methoxycarbonyltriptycene (IIIh) was performed by the reported method[2] with modification. The Diels-Alder reaction of *p*-benzoquinone with 2-methoxycarbonylanthracene was carried out in dioxane in place of benzene resulting in a much higher yield of the adduct (II, 65%). The adduct (II) could be separated in a high melting and low melting stereoisomers by recrystal-

---

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

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

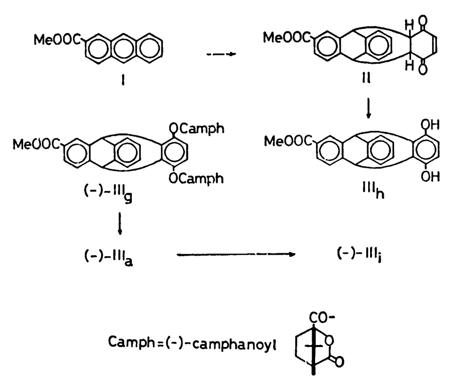
[3] a) F. Ogura and M. Nakagawa, *ibid.*, **38**, 155 (1965); b) F. Ogura, Y. Sakata, and M. Nakagawa, *ibid.*, **45**, 3646 (1972); c) F. Ogura and M. Nakagaws, *ibid.*, **46**, 651 (1973).

[4] a) M. Kuritani, Y. Sakata, F. Ogura, and M. Nakagawa, *Chimia*, **26**, 470 (1972); b) M. Kuritani, Y. Sakata, F. Ogura, and M. Nakagawa, This Bulletin, **46**, 605 (1973).

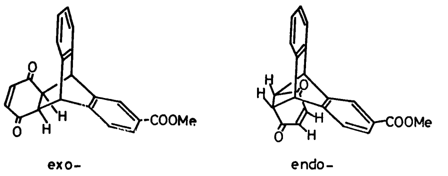
[5] J. Tanaka, F. Ogura, M. Kuritani, and M. Nakagawa, *Chimia*, **26**, 471 (1972).

[6] J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951); J. Petruska, *ibid.*, **34**, 1111 (1961).

[7] *Cf.*, H. Gerlach, *Helv. Chim. Acta*, **51**, 1587 (1968).



Scheme 1. Optical resolution of 2,5-dihydroxy-8-methoxycarbonyltriptycene (IIIh).



lization from methanol which could be assigned to *exo*- and *endo*-isomers, respectively, on the basis of NMR spectral evidence. As illustrated in Fig. 1, *endo*-isomer exhibits poorly resolved signal of olefinic protons at τ 3.62, whereas the olefinic protons of *exo*-isomer gave a sharp singlet at τ 3.63. The splitting of signal of *endo*-isomer can be reasonably attributed to the anisotropy of methoxycarbonyl group situated in a relatively proximate position. Treatment of a mixture of *endo*- and *exo*-isomers (II) in benzene with hydrogen chloride yielded 2,5-dihydroxy-8-methoxycarbonyltriptycene (IIIh).

(—)-Camphanic acid chloride was prepared from (+)-camphor *via* (+)-camphoric acid, (—)-camphoric anhydride and (—)-monobromocamphoric anhydride.[8]

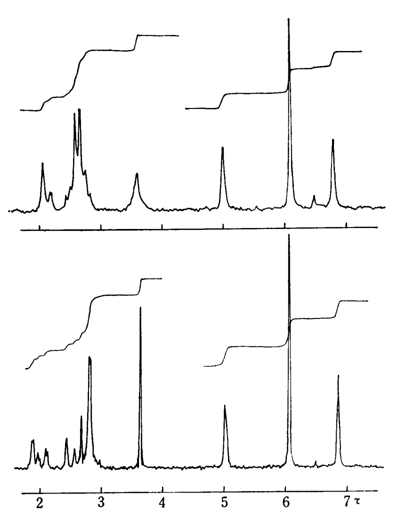
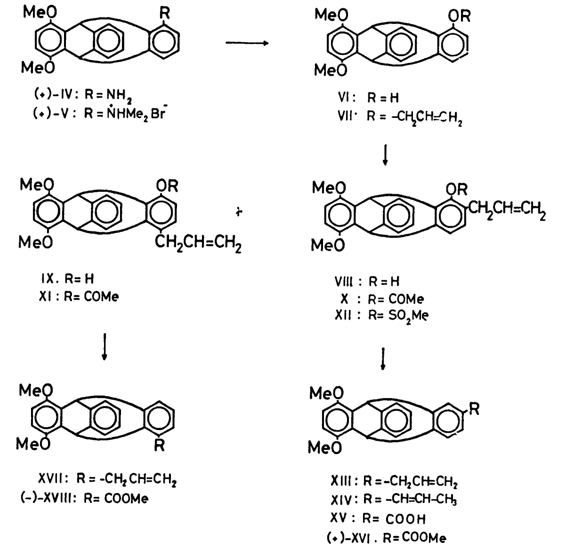


Fig. 1. NMR spectra of *endo*- (top) and *exo*-adducts (bottom) (II).

The reaction of acid chloride with IIIh in pyridine afforded bis-camphanate (IIIg) in a high yield (82—97%). Bis-camphanate (IIIg) was repeatedly recrystallized from methanol (4—7 times) to give crystals with a constant specific rotation. The resolved bis-camphanate (IIIg) was dissolved in methanol saturated with hydrogen chloride and the mixture was refluxed to convert IIIg into (—)-IIIh and methyl camphanate. Chromatography of the reaction product on silica gel afforded (—)-IIIh in a quantitative yield. (—)-2,5-Dimethoxy-8-methoxycarbonyltriptycene (IIIi) was obtained from (—)-IIIh on treatment with dimethyl sulfate.

Absolute Configuration. The reaction of allyl chloride with crude phenol (VI) obtained by hydrolysis of the diazonium salt of (+)-2,5-dimethoxy-7-aminotriptycene (IV)[3b] afforded (+)-allyl ether (VII).



Scheme 2. Chemical correlation of 2,5,7-trisubstituted triptycene with 2,5,8-trisubstituted triptycene.

The Claisen rearrangement of (+)-VII in boiling diethylaniline gave rearranged products (VIII and IX) in an almost quantitative yield. Separation of VIII and IX could be attained by chromatography on silica gel. Although the purification of the allylic phenols (VIII and IX) were found to be difficult, the IR spectrum of IX in Nujol exhibits a sharp absorption at 3400 cm^{-1} due to stretching vibration of OH group, on the other hand, the spectrum of VIII shows a broad absorption at 3300—3350 cm^{-1}. Broadening of the band to higher wave number can be presumably attributed to an increased crowding by the presence of vicinal allyl group. Acetylation of VIII and IX yielded pure X and XI, respectively. The NMR spectra of X and XI provide further support for the assigned structures. The bridgehead protons of XI exhibit signals at τ 4.10 and 3.88. On the other hand, those of X give signals at τ 4.20 and 4.15. The signal at τ 3.88 in XI can be assigned to bridgehead proton at C-6 which suffers the deshielding effect of acetoxyl group at C-7. The fact that the bridgehead protons of X resonate at nearly the same field (τ 4.20

---

[8] O. Aschan, *Acta Soc. Sci. fenn.*, **21**, 1 (1895); *Chem. Zentr.*, **1895II**, 967.

and 4.15) indicates a decrease of deshielding effect of acetoxyl group due to a twisting by a steric interference with the vicinal allyl substituent.

Crude methanesulfonate (XII) obtained from VIII and methanesulfonyl chloride was treated with sodium in liquid ammonia⁹⁾ to give XIII. Allylic rearrangement of XIII with potassium hydroxide in diethylene glycol yielded propenyl derivative (XIV). 2,5-Dimethoxy-8-carboxytriptycene (XV) obtained by permanganate oxidation of XIV was converted into (+)-methyl ester (XVI). The NMR spectrum of XVI was found to be identical with that of (−)-IIIi obtained by the optical resolution of (±)-IIIh. The melting points [(+)-XVI: mp 255.8—256.1 °C; (−)-IIIi: mp 256.1—256.8 °C] and optical rotations [(+)-XVI: $[\alpha]^{16}_{D}+11.3°$, $[\alpha]^{16}_{500}+19.7°$ (*c* 0.531, dioxane); (−)-IIIi: $[\alpha]^{20}_{D}-10.3°$, $[\alpha]^{16}_{500}-20.5°$ (*c* 0.291, dioxane)] indicate clearly that (+)-XVI is the antipode of (−)-IIIi. Because the absolute configuration of (+)-V derived from (+)-IV has been determined as 1*R*, 6*S* by the Bijvoet method of X-ray structure analysis,[10] the chemical correlation of (+)-XVI with (+)-IV clearly demonstrates 1*R*,6*S* absolute configuration of (+)-XVI, *i.e.*, 1*R*,6*S* absolute configuration of (−)-IIIi.

A mixture of VIII and IX obtained by the Claisen rearrangement of (+)-VII was converted into a mixture of propenyl derivatives (XIV and XVII) according to the method used for VIII. Permanganate oxidation of the mixture XIV and XVII followed by esterification afforded (+)-XVI and (−)-XVIII. The NMR spectrum of (−)-XVIII is identical with that of (+)-2,5-dimethoxy-7-methoxycarbonyltriptycene (XIX).[3b)]. The specific rotations of (−)-XVIII and (+)-XIX indicate that the former is the enantiomer of the latter [(−)-XVIII: $[\alpha]^{20}_{D}-23.2°$; (+)-XIX: $[\alpha]^{25}_{D}+25.5°$ (*c* 0.7475, dioxane)]. Because it is evident that (−)-XVIII is derived from *para*-Claisen rearrangement product (IX), and (+)-IV, the parent compound of (+)-XVI and (−)-XVIII, has been prepared from (+)-XVIII,[3b)] the formation of (−)-XVIII from (+)-IV provides an interesting instance of conversion of absolute configuration of triptycene derivative by the transfer of a substituent group from 7- to 10-position.

Experimental

The melting points were measured on Mettler FP2 apparatus and Shimadzu Kohfler micro hot stage, and uncorrected. Purified and anhydrous solvents were used, unless otherwise stated. The IR spectra were obtained on Hitachi EPI-2 or JACSO DS-301 spectrometer. The electronic spectra were measured with Hitachi EPS-3T spectrophotometer. The NMR spectra in deuteriochloroform were taken with Varian A-60 spectrometer using TMS as an internal standard and given in τ-values. The rotations and CD spectra were obtained on Yanagimoto ORD-185 and JASCO J-20 spectropolarimeters, respectively. The shoulder and inflection are denoted with an asterisk. Only the main peaks of IR and NMR spectra were recorded.

Preparation of Adduct (II). To a hot solution of 2-methoxycarbonylanthracene (I, 10.0 g, 0.042 mol) in dioxane (120 ml) was added in one portion a solution of *p*-benzoquinone (10.0 g, 0.093 mol) in the same solvent (50 ml). After being stirred for 7 hr, the mixture was concentrated under reduced pressure and the quinone remained was removed by steam distillation. The residue was extracted with benzene and crystalline solid (13.7 g) obtained by working up the benzene extract was recrystallized twice from methanol to give a mixture of *endo*- and *exo*-II as yellow crystals (9.5 g, 65%). Repeated recrystallization of the mixture from methanol afforded *exo*-II (less soluble) and *endo*-II (more soluble).

exo-II, mp 188—189 °C (sintered at 170 °C), IR (KBr disk): $\nu_{C=O}$ 1717, 1677 cm^{-1}, NMR: 6.87 (s, 2H, bridge), 6.07 (s, 3H, $-CO_2CH_3$), 5.02 (s, 2H, bridgehead), 3.63 (s, 2H, olefinic), 1.88—2.81 (m, 7H, aromatic), UV: $\lambda^{\text{dioxane}}_{\text{max}}$ (ε) 240* (15,600), 247* (13,600), 251* (12,300), 257* (9,010), 262* (6,490), 269* (3,110), 275* (2,180), 284* (1,390), 360* (71.5), 378 (76.3), 400* (55.7), 420* (22.5) nm.

Found: C, 76.30; H, 4.73%. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68%.

endo-II, mp 149—157 °C (sintered at 148 °C), IR (KBr disk): $\nu_{C=O}$ 1725, 1675 cm^{-1}, NMR: 6.81 (s, 2H, bridge), 6.11 (s, 3H, $-CO_2CH_3$), 5.01 (s, 2H, bridgehead), 3.62 (broad s, 2H, olefinic), 2.07—2.83 (m, 7H, aromatic), UV: $\lambda^{\text{dioxane}}_{\text{max}}$ (ε) 238.5 (16,200), 243.5 (15,500), 249 (16,000), 255 (15,100), 261 (9.170), 271* (2,710), 284* (1,380), 360* (69.1), 377 (78.8), 395* (63.8), 410* (18.0) nm.

Found: C, 76.18; H, 4.76%. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68%.

2,5-Dihydroxy-8-methoxycarbonyltriptycene (IIIh). Hydrogen chloride was introduced to a solution of a mixture of *endo*- and *exo*-II (20.0 g, 0.058 mol) in benzene (400 ml). After the mixture was allowed to stand for 4 hr at room temperature, the reaction mixture containing colorless fine crystals was concentrated under reduced pressure. The residue was recrystallized from benzene to yield IIIh, colorless crystals, mp 159—162 °C, 17.1 g (85%), IR (Nujol mull): ν_{OH} 3270, $\nu_{C=O}$ 1690 cm^{-1}.

Found: C, 76.56; H, 5.06%. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68%.

IIIh was also obtained in a 60.8% yield by refluxing a mixture of 2,5-dihydroxy-8-carboxytriptycene[2)] (14.5 g), methanol (73 ml) and sulfuric acid (4.4 ml) for 8 hr.

2,5-Bis(camphanoyl)-8-methoxycarbonyltriptycene (IIIg).
A solution of IIIh (15.0 g, 0.0436 mol), camphanoyl chloride[8)] (20.8 g, 0.0960 mol) in pyridine (330 ml) was allowed to stand overnight at room temperature. The mixture was poured onto ice-water (2 l) and extracted with benzene. The extract was washed successively with 1 M hydrochloric acid, water, 1% aqueous sodium hydrogen carbonate and water, and dried. Concentration of the extract afforded colorless crystals, mp 141—188°C, 21.1 g (81.8%), IR (Nujol mull): 1795, 1730 cm^{-1}.

The crystals decomposed on an attempted chromatography on silica gel.

A portion of the bis-camphanate (2.7 g) was repeatedly recrystallized from methanol (4—7 times) to obtain bis-camphanate with constant specific rotation, mp 195.9—198.2 °C (the mp gradually increased to 240 °C and again decreased to the constant value during the course of recrystallization), IR (Nujol mull) 1800, 1730 cm^{-1}, $[\alpha]^{15}_{390}$

---

9) H. W. Thompson, *J. Org. Chem.*, **33**, 621 (1968).

10) N. Sakabe, K. Sakabe, K. Ozeki-Minakata, and J. Tanaka, presented at the 9th International Congress of Crystallography (1972); *Acta Crystallogr.*, **B28**, 3441 (1972).

$-20.4°$ (c 0.588, dioxane).

Found: C, 71.25; H, 5.73%. Calcd for $C_{42}H_{40}O_{10}$: C, 71.58; H, 5.72%.

Optically pure bis-camphanate was also obtained when a solution of the crude bis-camphanate (2.7 g) in dichloromethane (10 ml) was mixed with hot methanol (500 ml) and the mixture was concentrated to one-half of its original volume.

(−)-2,5-Dihydroxy-8-methoxycarbonyltriptycene (IIIh). To a mixture of optically pure bis-camphanate (IIIg, 2.05 g) in methanol (140 ml) was introduced hydrogen chloride for 40 min under ice-cooling, and the mixture was refluxed for 5 hr to give a colorless homogeneous solution. After one-half of the methanol had been removed under reduced pressure at room temperature, the reaction mixture was poured into a saturated sodium chloride solution (300 ml) and extracted with ether. The extract, after being washed with a saturated aqueous sodium chloride, was concentrated under reduced pressure. Crude crystals (1.96 g) thus obtained were chromatographed on silica gel (Merck, 250 g). Elution with benzene–ether (9 : 1) afforded methyl camphanate (1.04 g). Crude (−)-IIIh (1.13 g) obtained by elution with benzene–ether (7.5 : 2.5) was recrystallized from a small amount of benzene to give pure (−)-IIIh, colorless crystals, 0.90 g (90%), $[\alpha]^{20}_{589}$ $-9.71°$ (c 0.258, ethanol).

(−)-2,5-Dimethoxy-8-methoxycarbonyltriptycene (IIIi). A solution of (−)-IIIh (37.0 mg, 0.107 mmol) in acetone (30 ml) was refluxed for 6 hr under stirring with dimethyl sulfate (112 mg) in the presence of anhydrous potassium carbonate (200 mg). The reaction mixture was worked up by the usual way to give crude (−)-IIIi which was dissolved in benzene and passed through a short column of alumina. Crystals obtained from the filtrate were recrystallized from methanol to give pure (−)-IIIi, mp 256.1—256.8 °C (racemate, mp 248—249 °C), $[\alpha]^{20}_{D}$ $-10.3°$ (c 0.291, dioxane), UV: λ^{EtOH}_{max} (ε) 303* (4.030), 292 (6,480), 285* (5,830), 267 (7,870), 226 (35,700), 203.5 (52,800) nm, CD: λ^{EtOH}_{max} ($\Delta\varepsilon$) 320 (+0.3), 299.2 (−3.11), 289.8 (+1.80), 280.5 (−0.29), 268.0 (+9.41), 261.5 (+4.99), 243.5 (+20.9), 229.0 (−44.9), 218.6 (+31.9), 208.4 (−35.5) nm.

Found: C, 77.35; H, 5.49%. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41%.

2,5-Dimethoxy-7-allyloxytriptycene (VII). (+)-2,5-dimethoxy-7-aminotriptycene[3b] (IV, 6.95 g, 21.1 mmol) was dissolved in hot acetic acid (307 ml) and a solution of sodium nitrite (0.49 g, 21.3 mmol) in water (42 ml) and acetic acid (100 ml) were added at 12—14 °C over a period of 1 hr. After the mixture being stirred for 30 min at the same temperature, the solution of diazonium salt was added dropwise over a 40-min period to boiling 3 M sulfuric acid under vigorous stirring, and stirring was continued for further 30 min under reflux. Precipitate obtained on cooling the reaction mixture was washed with water to give crude (+)-VI, 6.44 g (92%). A mixture of the crude (+)-VI (6.34 g, 19.2 mmol), acetone (340 ml), potassium carbonate (8.4 g), allyl chloride (4.0 g) and a small amount of sodium iodide was refluxed for 19 hr under stirring. Further amount of allyl chloride (2.0 g) was added during the period of reflux. Insoluble material was removed by filtration and the filtrate was concentrated under reduced pressure. The residue was extracted with benzene. The extract, after washing and drying, was evaporated under reduced pressure to give crude (+)-VII (7.3 g). The crude (+)-VII was chromatographed on alumina. Crystals obtained from benzene-eluate were recrystallized from the same solvent to yield pure (+)-VII, mp 255.0—256.0 °C, 4.57 g (59.3% based on (+)-IV), (racemate, mp 229.5—231.0 °C).

Found: C, 80.94, H, 6.07%. Calcd for $C_{25}H_{22}O_3$: C, 81.05; H, 5.99%.

(+)-2,5-Dimethoxy-7-hydroxy-8-allyltriptycene (VIII) and (−)-2,5-Dimethoxy-7-hydroxy-10-allyltriptycene (IX). A solution of (+)-VII (4.25 g, 11.5 mmol) in diethylaniline (450 ml) was refluxed for 6 hr under nitrogen atmosphere. The reaction mixture was acidified with 8 M hydrochloric acid under ice-cooling and then mixed with water (2.5 l), and extracted with benzene. The extract, after being washed and dried, was evaporated to give an amorphous solid (4.27 g). The solid dissolved in benzene was chromatographed on silica gel (Merck). Elution with benzene afforded (+)-VIII 3.37 g (79.3%), IR (Nujol mull): 3300—3550 (broad), 715 cm^{-1}, and (−)-IX, 0.82 g (19.3%), IR (Nujol mull): 3400 (sharp), 735, 725 cm^{-1} was obtained from benzene–ether eluate (8 : 2).

(+)-2,5-Dimethoxy-7-acetoxy-8-allyltriptycene (X). The product obtained by the acetylation of (+)-VIII (223 mg, 0.602 mmol) with acetic anhydride (7 ml) and sodium acetate (0.1 g) by the usual way was dissolved in benzene and chromatographed on silica gel. The crystals obtained from benzene-eluate were recrystallized twice from ethanol, mp 166.8—169.0 °C, 137.0 mg (55%) (racemate, mp 167.0—168.0°C), IR (Nujol mull): $\nu_{C=O}$, 1770, 1760*, $\nu_{C=C(allyl)}$, 1645 cm^{-1}, $[\alpha]^{20}_{D}$ $+13.0°$ (c 0.276, dioxane), NMR: 7.57 (s, CH_3CO–), 6.25 (s, CH_3O–), 4.20, 4.15 (bridgehead), 3.57 (aromatic H(3), H(4)).

Found: C, 78.18; H, 5.95%. Calcd for $C_{27}H_{24}O_4$: C, 78.62; H, 5.86%.

(−)-2,5-Dimethoxy-7-acetoxy-10-allyltriptycene (XI). According to the procedure for (+)-X, (−)-IX was converted into (−)-XI, mp 223.0—223.7 °C (from ethanol), 0.58 g (61%), IR (Nujol mull): $\nu_{C=O}$, 1770, $\nu_{C=C(allyl)}$, 1645 cm^{-1}, $[\alpha]^{20}_{D}$ $-5.6°$ (c 0.252, dioxane),, NMR: 7.60 (CH_3-CO–), 6.25 (CH_3O–), 4.10, 3.88 (bridgehead), 3.55 (aromatic, H(3), H(4)), 3.28 (aromatic, H(8), H(9), AB-quartet, J_{AB}= 8 Hz).

Found: C, 78.25; H, 5.77%. Calcd for $C_{27}H_{24}O_4$: C, 78.62; H, 5.86%.

(+)-2,5-Dimethoxy-8-allyltriptycene (XIII). Methanesulfonyl chloride (2.0 g) was added to a solution of (+)-VIII (3.37 g, 9.09 mmol) in pyridine (30 ml). After being kept at room temperature overnight, the reaction mixture was poured onto ice-water, acidified with 3 M hydrochloric acid and extracted with benzene. After being washed and dried, the solvent was removed under reduced pressure, yielding crude (+)-XII, 3.95 g (97%) as an amorphous solid, IR (Nujol mull): 1360 cm^{-1} (racemate, 1350 cm^{-1}). A solution of crude (+)-XII, 3.89 g (8.67 mmol) in tetrahydrofuran (150 ml) was added to liquid ammonia. Sodium, 0.51 g (22.3 mg-atom) was added to the stirred solution. After being stirred for 10 min, ammonium chloride (5 g) was added to the reaction mixture, and allowed to stand overnight at room temperature. Volatile material was removed under reduced pressure and the residue was extracted with benzene. The extract, after washing and drying, was concentrated to give crude amorphous (+)-XIII, 3.17 g which was chromatographed on silica gel (Merck). Elution with carbon tetrachloride–benzene (3 : 7) afforded crude (+)-XIII, 1.40 g (48%). Recovered (+)-VIII, 1.40 g (42%) was obtained from ether–benzene (1 : 9) eluate which was converted into (+)-XII and reduced with sodium in liquid ammonia. This procedure was repeated twice to give (+)-XIII (total 2.66 g, 83.9%) and recovered (+)-VIII (0.18 g, 5.4%).

(+)-2,5-Dimethoxy-8-propenyltriptycene (XIV). A mixture of (+)-XIII (2.68 g, 7.57 mmol), diethylene glycol (27 ml) and finely powdered potassium hydroxide (3.0 g) was heated to 190—220 °C for 1.5 hr. Crystals deposited were washed successively with a small amount of diethylene glycol and water to yield (+)-XIV, colorless needles, 2.45 g (91.5%). Second crop of crystals obtained from the mother liquor were recrystallized from ethanol, yielding pure (+)-XIV, 0.16 g (total yield 2.61 g, 97.6%), mp 226.2—231.0 °C, NMR: 8.21 (d, J=5 Hz, CH_3 of propenyl), 4.17 (s, bridgehead).

Found: C, 84.63; H, 6.25%. Calcd for $C_{25}H_{22}O_2$: C, 84.71; H, 6.26%.

(+)-2,5-Dimethoxy-8-methoxycarbonyltriptycene (XVI). Potassium permanganate (5.24 g) was added to a solution of (+)-XIV (2.20 g, 6.21 mmol) in acetone (920 ml) and the mixture was stirred at room temperature overnight. Excess permanganate was reduced by sodium hydrogen sulfite and manganese dioxide was removed by filtration. The residue obtained by evaporation of the solvent was mixed with 3M hydrochloric acid and extracted with benzene. The extract, after being washed and dried, was concentrated to yield crude (+)-XV (2.44 g). A mixture of the crude (+)-XV, (2.41 g), methanol (150 ml) and concentrated sulfuric acid (5 ml) was refluxed for 8 hr and the reaction mixture was worked up by the usual way to yield crude amorphous (+)-XVI (2.66 g) which was chromatographed on alumina. Crystals obtained from benzene-eluate were recrystallized from methanol, yielding pure (+)-XVI, mp 255.8—256.1 °C, 0.803 g (34.8% based on XIV), $[\alpha]^{16}_{D}$ +11.7° (c 0.531, dioxane). (racemate, mp 248—249 °C, sintered at 237 °C).

The NMR spectrum of (+)-XVI was found to be identical with that of (—)-2,5-dimethoxy-8-methoxycarbonyltriptycene (IIIi).

Found: C, 77.39; H, 5.37%. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41%.

(—)-2,5-Dimethoxy-7-methoxycarbonyltriptycene (XVIII). A mixture of VIII and IX, product of the Claisen rearrangement of (+)-VII, was converted into a mixture of propenyl derivatives (XIV and XVII) according to the procedure used in the transformation of (+)-VIII into (+)-XIV. Permanganate oxidation followed by esterification of the mixture of XIV and XVII afforded a mixture of (+)-XVI and (—)-XVIII which was repeatedly chromatographed on alumina using carbon tetrachloride–benzene (1 : 4) as an eluant. Crystals obtained from initial eluate were recrystallized from methanol to give (—)-XVIII, mp 267.4—268.0 °C $[\alpha]^{20}_{D}$ —23.2° (c 0.198, dioxane). (—)-XVIII gave an identical NMR spectrum with that of (+)-2,5-dimethoxy-7-methoxycarbonyltriptycene prepared by a different route.[3b)]

Found: C, 76.80; H, 5.33%. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41%.

Preparation of 2,5-Diacyloxy-8-carboxytriptycenes (IIIa—d). Crude 2,5-dihydroxy-8-carboxytriptycene[2)] was heated with a large excess of corresponding acid anhydride or acid chloride in the absence or presence of solvent. The reaction mixture was treated with water and the acid formed from excess of reagent was removed. Crude materials were purified by recrystallization. The structures were confirmed by elemental analyses, IR and NMR spectroscopy. Reaction conditions, melting points, solvent of recrystallization and yields are summarized in Table 1.

2,5-Bis(1-menthoxyacetoxy)-8-methoxycarbonyltriptycene (IIIe). To an ice-cooled solution of IIIh (2.10 g, 6.10 mmol) in pyridine (10 ml) was added l-menthoxyacetyl chloride (3.12 g, 13.4 mmol) over a 10-min period under nitrogen atmosphere. The mixture was stirred for 80 min under ice-cooling and then for 17 hr at 33 °C. The neutral portion of the reaction product dissolved in benzene was passed through a column of silica gel (30 g) and eluted successively with benzene–ligroin and benzene. Crude IIIe (2.25 g, 50.6%) obtained from the eluates was recrystallized 3 times from methanol–methyl acetate to give pure IIIe, mp 177.5—181 °C, $[\alpha]^{25}_{D}$ —53.1° (methanol). IIIe gave unsatisfactory result of hydrogen analysis.

Found: C, 74.96; H, 6.87%. Calcd for $C_{46}H_{56}O_8$: C, 74.97; H, 7.66%.

2,5-Dimethoxy-8-carboxytriptycene (IIIj). A mixture of IIIi (0.67 g), acetic acid (44 ml) and 3M sulfuric acid (11 ml) was refluxed for 12 hr. Colorless crystals (0.575 g, 88.7%) deposited on cooling the reaction mixture, after being washed with water and dried, were recrystallized from methanol and then sublimed *in vacuo* to give pure IIIj. IIIj showed double melting points, mp 140—150 °C, mp 280.2—283.5 °C.

Found: C, 76.86; H. 5.03%. Calcd for $C_{23}H_{18}O_7$: C, 77.08; H, 5.06%.

Preparation of 8-Cholesteryloxycarbonyltriptycene Derivatives (IIIk and IIIl). IIIa and IIIb in tetrahydrofuran were converted into corresponding acid chloride by the reaction with thionyl chloride according to the usual way. A mixture of the acid chloride, cholesterol and pyridine was heated. The reaction product dissolved in benzene was chromatographed on alumina. IIIk and IIIl were obtained from benzene eluate. Their IR and NMR spectra were found to be consistent with the assigned structures. They gave satisfactory data of elemental analyses. Reaction conditions and physical properties are summarized in Table 2.

Table 1. 2,5-Diacyloxy-8-carboxytriptycene (IIIa—d)

Product	Dihydroxy compound (g)	Acylating agent (g)	Solvent (ml)	Reaction time (hr)	Reaction temp. (°C)	Yield (g)	Yield (%)	Mp (°C)	Solvent of recryst.
IIIa[2)]	2.1	acetic anhydride (40 ml) + sodium acetate	none	4	100	1.9	49.5	235—237	acetic acid
IIIb	0.92	isobutyric anhydride 9	none	1.5	100	0.95	72.2	137—145	benzene
IIIc	3.49	trimethylacetyl chloride 16.3	pyridine 6	3.0	reflux	1.26	23.7	253—255	methanol
IIId	4.0	succinic anhydride 7.2	pyridine 100	7.5	75	5.25	81.5	167—172.5	ethyl acetate

TABLE 2. 8-CHOLESTERYLOXYCARBONYLTRIPTYCENE DERIVATIVES (IIIk AND IIIl)

Product	Triptycene (g)	Cholesterol (g)	Solvent (ml)	Reaction temp. (°C)	Reaction time (hr)	Mp (°C)	$[\alpha]_D$ in dioxane	Solvent of recryst.
IIIk	1.00	1.10	20	85	3.5	212—216	+6.18° (*c* 0.648)	ethanol
IIIl	1.10	0.92	5	75	5.0	196—201	+11.2° (*c* 0.807)	methanol–methyl acetate

(+)-2,5-Bis(1-α-naphthylethylcarbamoyl)-8-methoxycarbonyltriptycene (IIIf). To a boiling solution of IIIh (1.00 g, 2.91 mmol) in toluene (80 ml) was added a solution (−)-1-α-naphthylethyl isocyanate (1.20 g, 6.11 mmol) in the same solvent (20 ml). After several drops of triethylamine had been added, the mixture was refluxed for 5 hr under stirring. Crude IIIf (2.13 g, IR: ν_{NH} 3300, $\nu_{C=O}$ 1720 cm^{-1}) obtained by evaporating the solvent under reduced pressure was recrystallized 6 times from carbon tetrachloride to give pure IIIf, 39.7 mg, mp 140—144 °C, $[\alpha]_D^{24}$ +12.9° (*c* 1.07, benzene). IIIf (25 mg) thus obtained was dissolved in a mixture of acetic acid (10 ml) and concentrated hydrochloric acid (10 ml) and the mixture was refluxed for 4 hr. 2,5-Dihydroxy-8-carboxytriptycene formed showed no optical activity.