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Optically Active Triptycenes. III.* Synthesis of Optically Active 2-Methoxy-5-acyloxy- and 2-Acyloxy-5-methoxy-7-methoxycarbonyltriptycenes

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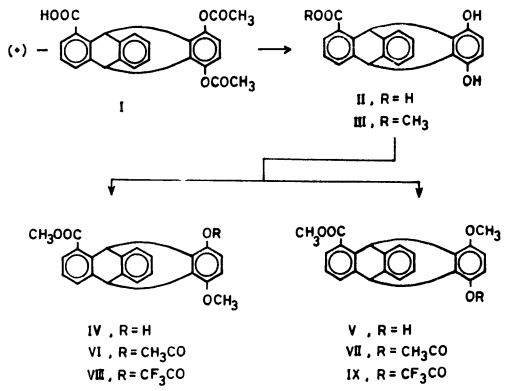
A report was given on the synthesis and optical resolution of 2,5-diacetoxy-7-carboxytriptycene (I).[1] The present paper deals with the transformation of (+)-I into the title compounds. As outlined in Scheme 1, (+)-2,5-dihydroxy-7-carboxytriptycene (II) obtained by the hydrolysis of (+)-I was converted into (+)-methyl ester (III). Monomethylation of (+)-III by the Robinson method[2] with some modification afforded (+)-2-methoxy-5-hydroxy-7-methoxycarbonyltriptycene (IV) and 2-hydroxy-5-methoxy-7-methoxycarbonyltriptycene (V) together with a small amount of 2,5-dimethoxy-7-methoxycarbonyltriptycene and 7-methoxycarbonyltriptycene-2,5-quinone. Formation of the quinone seems to be attributable to the presence of a small amount of peroxide in tetrahydrofuran used as a solvent. The isomeric (+)-IV and (+)-V could be separated on column chromatography on alumina. Treatment of (+)-IV and (+)-V with dimethyl sulfate afforded an identical dimethyl ether, 2,5-dimethoxy-7-methoxycarbonyltriptycene. The structures of IV and V could be confirmed by IR spectroscopy, *i.e.*, the IR spectrum in chloroform of



Scheme 1.

* For a preliminary report, see Ref. 6. For part II of this series, see Ref. 7.

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

2) R. Robinson and J. C. Smith, *J. Chem. Soc.*, **1926**, 393.

IV exhibits a broad absorption due to hydrogen bonded hydroxyl group even in a dilute solution indicating the proximate spatial positions of hydroxyl and methoxycarbonyl groups. On the other hand, the absorption of associated hydroxyl group observed in the spectrum of V disappeared on dilution indicating the absence of intramolecular hydrogen bonding. The fact that the carbonyl stretching vibration ($\nu_{C=O}$) of IV in chloroform is observed at a lower wave number (1710 cm^{-1}) than that of V (1720 cm^{-1}) is also consistent with the assigned structures.

Acylation of (+)-IV and (+)-V with acetic and trifluoroacetic anhydrides gave two sets of optically active isomers, VI, VII and VIII, IX. The structures of VI and VII were also supported by the measurement of dipole moment using 2-acetoxy-5-methoxytriptycene as a reference substance[3] which was prepared by a similar procedure from 2,5-dihydroxytriptycene.[4]

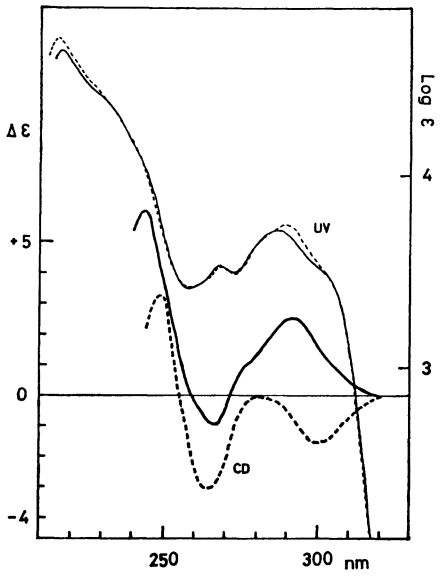


Fig. 1. UV and CD spectra of VI (——) and VII (----) in dioxane.

The absolute configurations of optically active triptycenes described above are evident in relation to I, *i.e.*, all of them have 1*R*,6*S* configuration since the absolute configuration of (+)-2,5-dimethoxy-7-methoxycarbonyltriptycene derived from (+)-I was proved to be 1*R*,6*S* on the basis of X-ray structure analysis by the Bijvoet method.[5] The UV and CD spectra of (+)-VI and (+)-VII are shown in Fig. 1. The sign of the longest wavelength Cotton effect is reversed as suggested by the ORD data.[6] This indicates that the center of transition dipole of $^1B_{2u}$ state in the hydroquinone ring is displaced in opposite direction according to the inversion of the position of electron attractive substituent. However, the CD spectral pattern at shorter wavelength region suggests that the effect is restricted to the $^1B_{2u}$ state.

Experimental

The experimental procedures refer to optically active substances unless otherwise stated. The IR and UV spectra were obtained on Hitachi EPI-2 and Hitachi EPS-2 spectrophotometers, respectively. The optical rotations and CD spectra were measured with a Rudolf Model 200S-80 spectropolarimeter and a Roussel-Jouan Dichrograph B, respectively. The inflections and shoulders are indicated by an asterisk.

2,5-Dihydroxy-7-methoxycarbonyltriptycene (III). A mixture of II[6] (1.0 g), methanol (5 ml) and concentrated sulfuric acid (0.3 ml) was refluxed for 8 hr. After being left standing overnight, the crystals deposited were washed successively with methanol and water to yield pure III, mp 294—297°C [racemate, mp 285—290°C].

Found: C, 76.59; H, 4.74%. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68%.

IR (KBr-disk): 3600—3100 (ν_{O-H}), 1680 ($\nu_{C=O}$) [racemate, 1683] cm^{-1}. UV: $\lambda_{max}^{dioxane}$ (ε) 298 (8610), 269.5 (2940), 261.5 (2370), 214.5 (45400) nm. ORD (15°C): $[M]_{5791}$ +95.0°, $[M]_{5461}$ +115.7°, $[M]_{4358}$ +230.4°, $[M]_{4047}$ +318.9°, $[M]_{3650}$ +547.5° (*c* 0.420, dioxane).

2-Methoxy-5-hydroxy-7-methoxycarbonyltriptycene (IV), 2-Hydroxy-5-methoxy-7-methoxycarbonyltriptycene (V), 2-Methoxy-5-acetoxy-7-methoxycarbonyltriptycene (VI), and 2-Acetoxy-5-methoxy-7-methoxycarbonyltriptycene (VII). A solution of III (4.50 g) in tetrahydrofuran (90 ml) was mixed with sodium methoxide in methanol (from sodium, 0.6 g and methanol, 75 ml). To the resulting suspension of sodium salt was added a solution of dimethyl sulfate (1.6 g) in tetrahydrofuran (15 ml) in an atmosphere of nitrogen. After being stirred overnight and left to stand overnight, the product dissolved in benzene–tetrahydrofuran (5: 1) was chromatographed on alumina (130 g) and eluted successively with benzene–tetrahydrofuran (5: 1 and 1: 1), tetrahydrofuran, and tetrahydrofuran–methanol (100: 1 and 10: 1). Dimethyl ether and quinone derivatives were obtained from benzene–tetrahydrofuran eluate and could be separated on re-chromatography on alumina. Tetrahydrofuran and tetrahydrofuran–methanol (100: 1) eluates afforded a mixture of IV and V, the former in abundance. A mixture of the same isomers rich in V was obtained from tetrahydrofuran–methanol (10: 1) eluate.

Acetylation: A mixture containing a larger amount of IV (0.5 g) in tetrahydrofuran (10 ml) was refluxed with acetic anhydride (1.5 g) for 1.5 hr to yield VI, mp 270—271°C (from methyl acetate) [racemate, mp 279—280°C], IR (KBr-disk): 2855 (ν_{C-H}, $-OCH_3$), 1765 ($\nu_{C=O}$, CH_3COO-), 1716 ($\nu_{C=O}$, $-COOCH_3$) cm^{-1}.

Similarly, a mixture rich in V afforded VII, mp 278—279°C (from methanol–methyl acetate) [racemate, mp 269—270°C, from methyl acetate], IR (KBr-disk): 2845 (ν_{C-H}, $-OCH_3$), 1750 ($\nu_{C=O}$, CH_3COO-), 1722 ($\nu_{C=O}$, $-COOCH_3$) cm^{-1}.

Found: VI, C, 74.48; H, 5.01%. VII, C, 74.69; H, 5.06%. Calcd for $C_{25}H_{20}O_5$: C, 74.99; H, 5.03%.

UV: $\lambda_{max}^{dioxane}$ (ε) VI, 217 (45700), 268 (3470), 288 (5290); VII, 216 (52700), 268.5 (3410), 290 (5660) nm. ORD: VI (15°C), $[M]_{5791}$ +402.4°, $[M]_{5461}$ +466.5°, $[M]_{5000}$ +583.0°, $[M]_{4358}$ +873.5°, $[M]_{4047}$ +1104°, $[M]_{3650}$ +1312° (*c* 0.8975, dioxane); VII (16.5°C), $[M]_{5791}$ +3.0°, $[M]_{5000}$ +3.0°, $[M]_{4358}$ −23.6°, $[M]_{4047}$ −51.3°, $[M]_{3650}$ −152.2°

3) F. Ogura, Y. Toshiyasu, K. Kimura, R. Fujishiro, and M. Nakagawa, This Bulletin, **37**, 757 (1964).

4) P. D. Bartlett, M. J. Ryan, and S. G. Cohen, *J. Amer. Chem. Soc.*, **62**, 2649 (1942).

5) N. Sakabe, K. Sakabe, K. Ozeki-Minakata, and J. Tanaka, presented at the 9th International Congress of Crystallography (1972), *Acta Crystallogr.*, **B24**, 3441 (1972).

6) F. Ogura and M. Nakagawa, This Bulletin, **38**, 155 (1965).

(*c* 0.7990, dioxane). CD: $\lambda_{max}^{dioxane}$ ($\Delta\varepsilon$) VI, 291 (+2.6), 266.5 (−1.07), 244 (+6.12); VII, 300 (−1.51), 266 (−3.07), 262.5 (−2.92), 249 (+3.31) nm.

Hydrolysis and Esterification: A mixture of *dl*-VI (0.50 g), acetic acid (35 ml) and 3N sulfuric acid (15 ml) was refluxed for 8 hr to yield 2-methoxy-5-hydroxy-7-carboxytriptycene (0.4 g, mp 280—287°C). The crude material in acetone–methanol was treated with an ethereal solution of diazomethane to afford *dl*-IV, mp 279—280°C (from benzene).[7] The same treatment of *dl*-VII gave 2-hydroxy-5-methoxy-7-carboxytriptycene, mp 290—302°C which gave *dl*-V, mp 255—258°C (from benzene) on treatment with diazomethane. Optically active VI and VII were converted into IV, mp 249—251°C and V, mp 256—258°C by the same method.

Found: IV, C, 76.91; H, 5.01%. V, C, 77.73; H, 5.06%. Calcd for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06%.

IR (KBr-disk): IV, 3700—3200 (ν_{O-H}), 2840 (ν_{C-H}, $-OCH_3$), 1707 ($\nu_{C=O}$, $-CO_2CH_3$); V, 3700—3100 (ν_{O-H}), 2840 (ν_{C-H}, $-OCH_3$), 1715, 1695 ($\nu_{C=O}$, $-CO_2CH_3$) cm^{-1}. ORD: IV (14—16°C), $[M]_{5791}$ −120.4°, $[M]_{5461}$ −121.5°, $[M]_{5000}$ −144.1°, $[M]_{4358}$ −210.4°, $[M]_{4047}$ −273.1°, $[M]_{3650}$ −482.4° (*c* 0.286, dioxane); V (12.5—16°C), $[M]_{5791}$ −76.7°, $[M]_{5461}$ −85.7°, $[M]_{5000}$ −113.2°, $[M]_{4358}$ −179.2°, $[M]_{4047}$ −236.9°, $[M]_{3650}$ −382.0° (*c* 0.472, dioxane).

2-Methoxy-5-trifluoroacetoxy-7-methoxycarbonyltriptycene (VIII) and 2-Trifluoroacetoxy-5-methoxy-7-methoxycarbonyltriptycene (IX). Trifluoroacetylation of mixtures of IV and V followed by chromatography on silica gel according to the method used for VI and VII afforded VIII, mp 262—263°C (from benzene–benzine) and IX, mp 241—243°C (from benzene–benzine).

Found: VIII, C, 66.30; H, 4.10%. IX, C, 66.50; H, 3.87%. Calcd for $C_{25}H_{17}O_5F_3$: C, 66.08; H, 3.77%.

IR (Nujol mull): VIII, 1805 ($\nu_{C=O}$, CF_3CO_2-), 1722 ($\nu_{C=O}$, $-CO_2CH_3$); IX, 1802 ($\nu_{C=O}$, CF_3CO_2-), 1716 ($\nu_{C=O}$, $-CO_2CH_3$) cm^{-1}. UV: $\lambda_{max}^{dioxane}$ (ε) VIII, 215.5 (48500), 267 (3910), 285 (4910); IX, 215 (49300), 261 (3580), 267.5 (4010), 288 (5420) nm. ORD: VIII (12—14°C), $[M]_{5791}$ +379.1°, $[M]_{5461}$ +441.2°, $[M]_{5000}$ +565.7°, $[M]_{4358}$ +842.0°, $[M]_{4047}$ +1059°, $[M]_{3650}$ +1558° (*c* 0.2780, dioxane); IX (11—14°C), $[M]_{5791}$ −3.8°, $[M]_{5461}$ −9.1°, $[M]_{4358}$ −42.3°, $[M]_{4047}$ −85.4°, $[M]_{3650}$ −191.3° (*c* 0.3990, dioxane).

2-Acetoxy-5-methoxytriptycene and 2,5-Dimethoxytriptycene. According to a previously described method, 2,5-dihydroxytriptycene[4] was methylated and the product was chromatographed on alumina. The benzene–tetrahydrofuran (10: 1) eluate afforded the dimethyl derivative, mp 241—243°C (from acetic acid).

Found: C, 84.21; H, 5.80%. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77%.

IR (KBr-disk): 2850 (ν_{C-H}, $-OCH_3$) cm^{-1}. UV: $\lambda_{max}^{dioxane}$ (ε) 217 (57300), 262 (2720), 271 (3030), 277.5 (4430), 294 (4,050) nm.

Acetylation of the monomethylated product obtained from the tetrahydrofuran–methanol (100: 1) eluate yielded 2-acetoxy-5-methoxytriptycene, mp 274—275.5°C (from acetic acid).

Found: C, 80.77; H, 5.29%. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30%.

IR (KBr-disk): 2850 (ν_{C-H}, $-OCH_3$), 1745 ($\nu_{C=O}$, CH_3CO_2-) cm^{-1}. UV: $\lambda_{max}^{dioxane}$ (ε) 217 (58500), 261 (2990), 270 (3140), 277.5 (3880), 288 (2040) nm.

7) F. Ogura, Y. Sakata, and M. Nakagawa, This Bulletin, **45**, 3646 (1972).