543. *The Optical Resolution of* (±)-trans-9 : 10-*Dihydroxy*-9 : 10-*dihydrophenanthrene.*

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trans-9 : 10-Dihydroxy-9 : 10-dihydrophenanthrene has been obtained in (+)- and (−)-forms by resolution of the diastereoisomeric di-(−)-menthoxyacetates. This completes the proof that the biologically produced diol has the *trans*-configuration.

The partial resolution of 9 : 10-dihydroxy-9 : 10-dihydrophenanthrene, announced in a recent communication (*J.*, 1950, 1188), has now been completed, so that the proof that the biologically produced diol (cf. Boyland and Wolf, *Biochem. J.*, 1950, **47**, 64) has the *trans*-configuration is fully confirmed.

The diol, obtained by reduction of phenanthraquinone with ethereal lithium aluminium hydride, was converted into the di-(−)-menthoxyacetates. Crystallisation of the diastereoisomeric mixture from ethyl alcohol gave erratic and unpredictable results, but crystallisation from light petroleum readily gave the optically pure (dextrorotatory) di-(−)-menthoxyacetate of the (−)-diol. This, on hydrolysis with methyl-alcoholic potassium hydroxide, gave the (−)-diol, but hydrogenolysis of the ester with ethereal lithium aluminium hydride was experimentally easier and gave a purer product. Although one of the characteristics of the (±)-diol is its readiness to crystallise well from solvents such as benzene, solutions of the (−)-diol in most organic solvents set to a jelly when cooled. From *iso*octane some indications of partial crystallisation were observed, but for analytical purposes purification by vacuum-sublimation proved the only satisfactory expedient.

The mother-liquors of the light petroleum crystallisations were, after considerable trouble, made to give the di-(−)-menthoxyacetate of the (+)-diol and from this ester the (+)-diol was obtained. It naturally formed jellies similar to those formed by the (−)-diol; when equal quantities of jellies containing the (+)- and (−)-diols, each in benzene, were mixed, the jellies liquefied and the benzene was filled with the voluminous mass of long needles of the (±)-diol.

Diacetylation of the active diols was accompanied by a change of sign of rotation. The main optical data are set out below. Where (see Experimental section) rotation varied with concentration, the highest figures observed are given here:

			Di-(−)-menthoxyacetate of		Diacetate of	
	(−)-Diol.	(+)-Diol.	(−)-diol.	(+)-diol.	(−)-diol.	(+)-diol.
$[\alpha]_{5790}^{20}$	−143°	+137°	+137°	−302°	+363°	−349°
$[\alpha]_{5460}^{20}$	−165	+155	+161	−349	+422	−403
	(chloroform solution)		(ethyl-alcoholic solution)		(acetone solution)	

The rotation of the (−)-diol was lower in acetone than in chloroform and still lower in ethyl alcohol. The polarity of the solvent thus has much less effect than in the case of *trans*-acenaphthylene glycol (Jack and Rule, *J.*, 1938, 188).

The optical rotations of the (−)-phenanthrenediol and related compounds in different solvents are shown in the following table ($[\alpha]_D^{21}$ with c, 0·25 for the first three compounds, $[\alpha]_{5461}^{20}$ for the acenaphthylene glycol).

	Dioxan.	Chloroform.	Ethyl alcohol.	Acetone.	Nitrobenzene.
(−)-9 : 10-Dihydroxy-9 : 10-dihydrophenanthrene (sublimed specimen: see Experimental)	−130°	−128°	−76°	−110°	−132°
(+)-1 : 2-Dihydroxy-1 : 2-dihydroanthracene (from rabbit urine; cf. Booth and Boyland, *Biochem. J.*, 1949, **44**, 361)	+154	+150	+125	+173	+161
(+)-1 : 2-Diacetoxy-1 : 2-dihydroanthracene	+347	+345	+351	+316	+324
trans-Acenaphthylene glycol (values from Jack and Rule, *loc. cit.*)	—	+52	0	−25	−76

EXPERIMENTAL.

Resolution of the Di-(−)*-menthoxyacetates of* (±)-trans-9 : 10-*Dihydroxy*-9 : 10-*dihydrophenanthrene*.—To a solution of 6·55 g. (1 mol.) of the diol in 20 c.c. of pyridine were gradually added, with cooling, 2 mol. proportions of (−)-menthoxyacetyl chloride. The mixture was kept overnight and then poured into dilute hydrochloric acid. The precipitate was filtered off, washed, dried, and then crystallised 5 times from light petroleum (b. p. 40—60°). The *di*-(−)-*menthoxyacetate* of (−)-9 : 10-dihydroxy-9 : 10-dihydrophenanthrene was so obtained as slightly distorted hexagonal plates (1·85 g.), m. p. 110° (corr.), $[\alpha]^{20}_{5790}$ +137°, $[\alpha]^{20}_{5461}$ +161° (*c*, 0·3395 in absolute ethyl alcohol) (Found : C, 75·3; H, 8·4. $C_{38}H_{52}O_6$ requires C, 75·5; H, 8·7%). The mother-liquors from the above crystallisations, when evaporated, gave various crops of fluctuating rotation, but after elaborate fractionation from light petroleum (b. p. 40—60°) 0·9 g. of the *di*-(−)-*menthoxyacetate* of (+)-*trans*-9 : 10-dihydroxy-9 : 10-dihydrophenanthrene was isolated as long fine needles (frequently in the form of brushes), m. p. 117° (corr.), $[\alpha]^{20}_{5790}$ −302°, $[\alpha]^{20}_{5461}$ −349° (*c*, 0·4476 in absolute ethyl alcohol) (Found : C, 75·6; H, 8·9%).

In another series of resolution experiments, in which the dimenthoxyacetates derived from 4·6 g. of (±)-diol were crystallised once from ethyl alcohol and then 3 times from light petroleum (b. p. 60—80°), 1·35 g. of the pure di-(−)-menthoxyacetate of the (−)-diol was obtained, with $[\alpha]^{20}_{5790}$ +137° and $[\alpha]^{20}_{5461}$ +161° (*c*, 0·3965 in ethyl alcohol).

Crystallisation of the di-(−)-menthoxyacetates of the (±)-diol from ethyl alcohol gave erratic results, successive crystallisations giving crops having $[\alpha]^{20}_{5790}$ −73°, −74°, +24°, −25°, and −42° (in ethyl alcohol). The last crop, when crystallised, first gave a product with $[\alpha]^{20}_{5790}$ +120°, the mother-liquor rapidly depositing crystals having $[\alpha]^{20}_{5790}$ −282°. Presumably the partial racemate has, in ethyl alcohol, a solubility very similar to that of one of the two diastereoisomerides.

(−)-9 : 10-*Dihydroxy*-9 : 10-*dihydrophenanthrene*.—(*a*) A specimen (0·3 g.) of the dimenthoxyacetate having $[\alpha]^{20}_{5790}$ +137° in ethyl alcohol was dissolved in 15 c.c. of methyl-alcoholic potassium hydroxide (potassium hydroxide 10 g., water 10 c.c., and methyl alcohol 240 c.c.), and the solution boiled under reflux for 30 minutes and then poured into water. The solution, in which a very small amount of yellowish crystalline matter was suspended, was extracted 4 times with ether. The combined ethereal extracts were washed twice with dilute sodium carbonate solution and then 3 times with brine. Evaporation of the ethereal layer gave 0·1 g. of an orange-coloured solid, readily dissolving in benzene to give a solution which set to a gel on cooling. Removal of most of the benzene, followed by addition of light petroleum (b. p. 40—60°) gave the crude diol as a pale yellow solid having $[\alpha]^{20}_{5790}$ −129° and $[\alpha]^{20}_{5461}$ −148° (*c*, 0·1550 in chloroform).

(*b*) A second portion (0·3 g.) of the foregoing dimenthoxyacetate was dissolved in 50 c.c. of anhydrous ether, and 0·5 g. of lithium aluminium hydride added. The mixture was boiled under reflux for an hour, cooled, and treated with water and then with dilute sulphuric acid until two clear layers were obtained. The aqueous layer was extracted 3 times with ether, and the combined ethereal extracts were washed twice with brine, once with dilute sodium carbonate, and again with brine. Evaporation of the ethereal solution gave a jelly which became solid when ground with light petroleum (b. p. 40—60°), which removed ethylene glycol (−)-menthyl ether. The crude diol had $[\alpha]^{20}_{5790}$ −141° and $[\alpha]^{20}_{5461}$ −164° (*c*, 0·4400 in chloroform).

Reduction as under (*b*) of a different specimen of dimenthoxyacetate having $[\alpha]^{20}_{5790}$ +137° gave a crude diol, m. p. 162°, having (i) $[\alpha]^{20}_{5790}$ −143° and $[\alpha]^{20}_{5461}$ −165° (*c*, 0·2975 in chloroform), (ii) $[\alpha]^{20}_{5790}$ −81° and $[\alpha]^{20}_{5461}$ −91° (*c*, 0·2580 in absolute ethyl alcohol), and (iii) $[\alpha]^{20}_{5790}$ −119° and $[\alpha]^{20}_{5461}$ −135·5° (*c*, 0·1845 in acetone).

All attempts to crystallise the active diol from a solvent were unsuccessful owing to the formation of jellies. (A very concentrated solution in ethyl alcohol set to a mass of fine needles when the last traces of solvent were removed and a solution in boiling *iso*octane set on cooling to a jelly in which minute hair-like crystals were suspended.) The crude diol sublimed at 100—110°/10^{-2} mm. as a white micro-crystalline solid, m. p. 162° (Found : C, 79·4; H, 5·5; $C_{14}H_{12}O_2$ requires C, 79·3; H, 5·7%). It had $[\alpha]^{21}_{D}$ −135° (*c*, 1·0), −132° (*c*, 0·5), and −128° (*c*, 0·25) in chloroform; $[\alpha]^{21}_{D}$ −88° (*c*, 1·0), −78° (*c*, 0·5), and −76° (*c*, 0·25), $[\alpha]^{21}_{5790}$ −77°, and $[\alpha]^{21}_{5461}$ −90° (*c*, 0·3490) in absolute ethyl alcohol.

(+)-9 : 10-*Diacetoxy*-9 : 10-*dihydrophenanthrene*.—A solution of the crude (−)-diol in pyridine was treated with acetic anhydride and kept overnight. Addition of water and dilute hydrochloric acid precipitated the crude diacetate, which was washed with water. It crystallised from diluted ethyl alcohol in orthorhombic prisms, m. p. 121—122° (Found : C, 72·7; H, 5·8. $C_{18}H_{16}O_2$ requires C, 73·0; H, 5·4). It had $[\alpha]^{20}_{5790}$ +363° and $[\alpha]^{20}_{5461}$ +422° (*c*, 0·3510 in acetone).

(+)-9 : 10-*Dihydroxy*-9 : 10-*dihydrophenanthrene*.—A specimen of (−)-dimenthoxyacetate having $[\alpha]^{20}_{5790}$ −302° in ethyl alcohol was reduced in ethereal solution with lithium aluminium hydride, 0·18 g. of white solid crude diol, m. p. 162°, being obtained. It had $[\alpha]^{20}_{5790}$ +137° and $[\alpha]^{20}_{5461}$ +155° (*c*, 0·4830 in chloroform). It gave only jellies when attempts were made to crystallise it from solvents. After sublimation at 100—110°/10^{-2} mm., it was obtained as a white micro-crystalline solid, m. p. 158° (Found : C, 79·5; H, 6·3. $C_{14}H_{12}O_2$ requires C, 79·3; H, 5·7). The sublimed material had $[\alpha]^{21}_{D}$ +128° (*c*, 1·0), +122° (*c*, 0·5) in chloroform.

(−)-9 : 10-*Diacetoxy*-9 : 10-*dihydrophenanthrene* was obtained from the crude (+)-diol by acetylation in pyridine solution. After being crystallised from diluted alcohol, it had the same m. p. and crystalline form as the (+)-diacetate (Found : C, 72·9; H, 5·8%). In acetone solution (*c*, 0·2695) it had $[\alpha]^{20}_{5790}$ −349° and $[\alpha]^{20}_{5461}$ −403°.

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