26. *The Resolution of Phenyl-n-propylcarbinol.*

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By fractional crystallisation of the strychnine salt of phenyl-*n*-propylcarbinyl hydrogen phthalate until the liberated hydrogen phthalic ester had reached a constant rotatory power ($[\alpha]_{5893}$ — 7·0° in ether) Levene and Marker (*J. Biol. Chem.*, 1932, **97**, 386) obtained *l*-phenyl-*n*-propylcarbinol with $[\alpha]_{5893}$ —35·8° (in benzene). For reasons which we hope to discuss in a forthcoming communication, we considered—in opposition to the view of Levene and Marker—that optical purity had not been reached. Accordingly we have re-examined the method of resolution.

By fractional crystallisation of its quinidine salt, phenyl-*n*-propylcarbinyl hydrogen phthalate was readily obtained with $[\alpha]_{5893}$ + 9·8° (in ether). When the highly lævorotatory hydrogen phthalic ester obtained from the more soluble fractions of the quinidine salt was converted into its strychnine salt, and this submitted to fractional crystallisation, the corresponding *l*-phenyl-*n*-propylcarbinyl hydrogen phthalate was obtained with $[\alpha]_{5893}$ — 10·0° (in ether).

Saponification of the *d*-acid ester yielded *d*-phenyl-*n*-propylcarbinol, m. p. 49°, b. p. 115°/14 mm., the rotatory powers of which are recorded in Table I. The rotatory powers of the various derivatives are given in Table II.

Table I.

Rotatory Power (l, 0·5) *and Refractive Index of* (+) *Phenyl-n-propylcarbinol.*

Temp.	43°	47·5°	50°	54°	56°	57°	60°	65°
α_{5780}	+ 15·86°	—	+ 16·42°	—	+ 16·75°	+ 16·75°	—	+ 17·11°
α_{5461}	+ 17·84°	—	+ 18·75°	—	+ 18·98°	+ 19·03°	—	+ 19·02°
α_{4358}	+ 30·52°	—	+ 31·66°	—	+ 32·40°	+ 32·51°	—	+ 33·06°
n_D°	—	1·5005	—	1·4989	—	—	1·4969	1·4945

Table II.

	Solvent.	*c.*	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
1. *d*-Phenyl-*n*-propylcarbinol	C_6H_6	4·791	+ 43·6°	+ 46·2°	+ 52·2°	+ 87·3°
,, ,, ...	CS_2	4·415	—	+ 55·72	+ 63·42	+ 108·7
2. *l*-Phenyl-*n*-propylcarbinol	C_6H_6	5·150	— 45·9	— 47·2	— 53·5	— 90·0
3. *d*-Phenyl-*n*-propylcarbinyl hydrogen phthalate	Et_2O	3·467	+ 9·8	+ 11·2	+ 11·5	+ 13·2
4. *l*-Phenyl-*n*-propylcarbinyl hydrogen phthalate	Et_2O	4·721	— 10·0	— 10·9	— 11·0	— 13·5
5. Quinidine salt of (3)	$CHCl_3$	2·08	—	+ 140·0	+ 181·0	+ 322
6. Strychnine salt of (4)	$CHCl_3$	0·538	— 37·2	—	— 40·9	— 112·4

Experimental.

Phenyl-*n*-propylcarbinol, b. p. 117—118°/18 mm., m. p. 16°, $d_4^{16\cdot2^\circ}$ 0·9822, $d_4^{26\cdot3^\circ}$ 0·9739, $d_4^{37\cdot0^\circ}$ 0·9654, $d_4^{46\cdot7^\circ}$ 0·9582, $n_D^{22^\circ}$ 1·5166 (Grignard, *Ann. Chim. Phys.*, 1901, **24**, 466, gives b. p. 113°/10 mm., $d_4^{13\cdot7^\circ}$ 0·9861, $n_D^{13\cdot7^\circ}$ 1·51914), obtained in 69% yield by the Grignard reaction, was smoothly converted into its hydrogen phthalic ester, which formed clusters of small needles, m. p. 90—91°, from carbon disulphide and light petroleum (Found, by titration with sodium hydroxide: *M*, 297·6. $C_{18}H_{18}O_4$ requires *M*, 298).

Quinidine (200 g.) was dissolved in a solution of the hydrogen phthalic ester (171 g.) in acetone (1000 c.c.). The salt, which separated at once, was only sparingly soluble in hot acetone and was recrystallised from ethyl acetate (9 l.), forming rosettes of woolly needles (132 g.), m. p. 168—169°; a further crop (30 g.) of the optically pure salt was obtained by concentration of the second mother-liquor.

The more soluble fractions of the quinidine salt yielded a somewhat pasty *l* + *dl*-hydrogen phthalic ester (35 g.), which was combined with strychnine (38 g.) in methyl-alcoholic solution (180 c.c.). The strychnine salt, after two recrystallisations from methyl alcohol, was obtained in rosettes of needles (40 g.), m. p. 184—185° (decomp.). *d*-Phenyl-*n*-propylcarbinyl hydrogen phthalate, from the less soluble quinidine salt, separated from carbon disulphide–light petroleum

in long needles, m. p. 53—54°; the corresponding *l*-phenyl-*n*-propylcarbinyl hydrogen phthalate, m. p. 52—53°, was obtained from the less soluble strychnine salt.

d-Phenyl-*n*-propylcarbinol, obtained by saponification of the *d*-hydrogen phthalic ester by aqueous-alcoholic sodium hydroxide, solidified with remarkable readiness to a mass of long needles, m. p. 49°, b. p. 115°/14 mm. The corresponding *l*-alcohol had m. p. 48—49°.

d-Phenyl-*n*-propylcarbinyl acetate, b. p. 125°/16 mm., obtained by heating the *d*-alcohol with acetic anhydride in pyridine solution, had $n_D^{20\cdot5°}$ 1·4889 and $\alpha_{5780}^{20°}$ + 26·96°, $\alpha_{5461}^{20°}$ + 30·85°, $\alpha_{4358}^{20°}$ + 55·35° (*l*, 0·25) (Grignard, *loc. cit.*, gives b. p. 117—118°/8 mm.).

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