LXVI.—*Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part VI. Rotatory Powers of Phenyl,* o, m, p-*Tolyl and β-Naphthyl Derivatives of* d-*Camphorimide and* d-*Camphoramic Acid.*

By BAWA KARTAR SINGH and AMAR NATH PURI.

THE rotatory powers of a number of aryl derivatives of *d*-camphorimide and *d*-camphoramic acid in three solvents at different concentrations have been studied with the object of finding some relation between their optical activity and chemical constitution, and the following conclusions drawn :

1. Substitution of an aryl group for the imido-hydrogen atom increases the rotatory power, and more so than does substitution of the benzyl group (Singh and Biswas, J., 1924, **125**, 1895).

2. The influence of the solvent on the rotatory power is considerable in the case of derivatives of *d*-camphoramic acid, but it is small in the case of those of *d*-camphorimide.

The order of the dielectric constants of the solvents employed is methyl alcohol (32·5) > ethyl alcohol (26·0) > acetone (21·2). In most cases (see Tables I and II), the order of the rotatory powers in these solvents is methyl alcohol > ethyl alcohol > acetone. It thus appears that in the case of these solvents the order of the rotatory powers generally runs parallel to their dielectric constants, although there is no direct proportionality between them.

3. The relative magnitude of the rotatory powers of phenyl and tolyl derivatives of *d*-camphorimide and *d*-camphoramic acid varies with the nature of the solvent and the concentration of the solution, as is seen in Tables I and II.

TABLE I.

	$[M]_D$.					
Derivatives of *d*-camphoramic acid.	2% Solution.			1% Solution.		
	EtOH.	MeOH.	Me_2CO.	EtOH.	MeOH.	Me_2CO.
Phenyl	+131°	+150°	+101°	+133°	+152°	+101°
o-Tolyl	144	146	98	158	151	91
m-Tolyl	118	140	89	122	147	92
p-Tolyl	144	167	120	146	170	122

o= *p*>un.>*m*; *p*>un.>*o*>*m*; *p*>un.>*o*>*m*; *o*>*p*>un.>*m*; *p*>un., *o* and *m*; *p*>un.>*m* and *o*.

For none of these derivatives do Frankland's and Cohen's rules hold.

TABLE II.

	$[M]_D$.					
	1·5% Solution.			0·75% Solution.		
Derivatives of *d*-camphorimide.	EtOH.	MeOH.	Me$_2$CO.	EtOH.	MeOH.	Me$_2$CO.
Phenyl	+48°	+49°	+44°	+48°	+52°	+48°
o-Tolyl	45	46	36	53	56	43
m-Tolyl	48	48	50	55	53	37
p-Tolyl	46	52	54	42	48	49

In the case of the derivatives of *d*-camphorimide, the differences in the rotatory powers of the position isomerides are in many cases so small, and within the limits of experimental error, that it is not permissible to draw any general conclusions.

The variation of the optical rotatory power with concentration was more fully investigated in the case of *d*-camphor-*p*-tolylamic acid in ethyl and methyl alcohols for concentrations varying from 1 to 10%. In both solvents the rotatory power decreases as the concentration increases. This may be due to the decrease in the number of optically active molecules in more concentrated solutions owing to molecular association.

4. The rotatory power of a cyclic compound is usually considerably greater than that of the corresponding open-chain derivative. Thus the rotatory powers of esters of 1-methyl-3-*cyclo*pentanone-4-carboxylic acid are about thirty times as great as those of the corresponding esters of methyladipic acid (Haller, *Compt. rend.*, 1905, **140**, 1205), and the hexahydrophthalic acids have much lower rotatory powers than their anhydrides (Werner, *Ber.*, 1899, **32**, 3046). This rule is more strikingly borne out in the case of derivatives of monosaccharides. The rotatory power of *d*-mannitol is $[\alpha]_D^{20^\circ} = -0{\cdot}2^\circ$ (Fischer, *Ber.*, 1890, **23**, 3684), whereas that of *d*-mannonolactone is +53·8° (Fischer, *Ber.*, 1889, **22**, 3219). The high rotatory power of most of the sugars as compared with the corresponding polyhydric alcohols is a proof of the ring structure of the former. The increase which is brought about in the rotatory power of sugar alcohols by boric acid is attributed to the formation of ring complexes. Camphoramic acids and their anhydrides form an exception to the rule, the acids having $[M]_D$ 89·45° (α), 119·4° (β) in ethyl alcohol, whilst the anhydride has $[M]_D$ 10·99°. It was pointed out (J., 1924, **125**, 1895) that opening the rings of *d*-camphorimide and its derivatives increases the rotation considerably; *e.g.* the following are values of $[M]_D$ in ethyl alcohol: camphorbenzylimide 30·19°, camphorbenzylamic acid 99·88°, camphor-*m*-nitrobenzylimide 31·92°, camphor-3-nitrobenzylamic acid 106·7°. The differences in the molecular rotatory powers of the aryl derivatives

of *d*-camphorimide and *d*-camphoramic acid are of the same order as of the foregoing substances, except in the case of β-naphthyl derivatives, for which the difference is much greater; *e.g.*, the following are values of $[M]_D$ in ethyl alcohol: camphor-β-naphthylimide 60°, *d*-camphor-β-naphthylamic acid 229°. From the foregoing instances it may be concluded that when an open-chain, optically active compound is transformed into a ring compound, there is a marked change (not necessarily an increase) in the rotatory power.

EXPERIMENTAL.

Aryl Derivatives of d-*Camphoramic Acid.*—d-*Camphorphenylamic acid*, $CO_2H{\cdot}C_8H_{14}{\cdot}CO{\cdot}NHPh$, was prepared by heating camphoric anhydride and aniline in molecular proportions in chloroform on the water-bath for 4—5 hours. The solid obtained on cooling crystallised from aqueous alcohol in needles, m. p. 209—210°. Auwers and Schleicher (*Annalen*, 1899, **309**, 341) give m. p. 203—204°.

d-*Camphor*-p-*tolylamic acid*, $CO_2H{\cdot}C_8H_{14}{\cdot}CO{\cdot}NH{\cdot}C_7H_7$, was prepared like the foregoing substance as leaflets, m. p. 214—215°. Wootton (J., 1910, **97**, 405), who obtained it by heating an intimate mixture of camphoric anhydride and the substituted amine for a few minutes at 150—180°, gives the melting point 212—214°, whereas Abati and Notaris (*Gazzetta*, 1909, **39**, ii, 219) give 201—209°.

d-*Camphor*-m-*tolylamic acid* was prepared by Wootton's method (*loc. cit.*) and purified by dissolving it in alcohol and adding animal charcoal. It was recrystallised as needles, m. p. 208—209°.

d-*Camphor*-o-*tolylamic acid*, prepared in the foregoing way, melted at 196—197°.

d-*Camphor*-β-*naphthylamic acid*, $CO_2H{\cdot}C_8H_{14}{\cdot}CO{\cdot}NH{\cdot}C_{10}H_7$, was prepared by both methods as white leaflets, m. p. 212—213°. The yield was, however, better when the condensation was carried out without any solvent.

N-*Aryl Derivatives of* d-*Camphorimide.*—These compounds were prepared by heating camphoric anhydride and the substituted amines in molecular proportions with the addition of a little anhydrous sodium sulphate in an oil-bath (215—230°) for 2 to 3 hours. The products of condensation were extracted with alcohol, decolorised by animal charcoal, and precipitated by adding water. They were twice recrystallised from aqueous alcohol, and gave the following melting points: phenyl, 117—118°; *o*-tolyl, 105—106°; *m*-tolyl, 121—122°; *p*-tolyl, 127—128°; β-naphthyl, 171—172°.

The tolyl and β-naphthyl derivatives of camphorimide were prepared by Wootton (*loc. cit.*) by boiling a solution of the corresponding *N*-substituted *d*-camphoramic acid in glacial acetic acid with acetyl chloride for 2 hours. Wootton gives the melting point

TABLE III.

Solvent.	Conc. (g./100 c.c.).	Temp.	α_D.	$[M]_D$.	Conc. (g./100 c.c.).	Temp.	α_D.	$[M]_D$.
	d-Camphorphenylamic acid.				*d*-Camphorphenylimide.			
EtOH	0·5265	26°	+0·51°	+133°	0·7693	18°	+0·29°	+48°
,,	1·0516	27	1·00	131	1·4950	19	0·56	48
MeOH	1·0025	22	1·11	152	0·7447	18	0·30	52
,,	2·0030	22	2·19	150	1·4765	17	0·56	49
Me_2CO	0·9775	23	0·72	101	0·7457	17	0·28	48
,,	2·0230	24	1·47	100	1·4755	18	0·50	44
	d-Camphor-*o*-tolylamic acid.				*d*-Camphor-*o*-tolylimide.			
EtOH	1·0155	26	1·11	158	0·7618	18	0·30	53
,,	2·0345	24	2·03	144	1·4925	19	0·49	45
MeOH	1·0140	22	1·06	151	0·6807	17	0·28	56
,,	1·9995	22	2·02	146	1·1772	18	0·40	46
Me_2CO	0·9099	22	0·57	91	0·6607	17	0·21	43
,,	2·0701	23	1·40	98	1·4585	17	0·39	36
	d-Camphor-*m*-tolylamic acid.				*d*-Camphor-*m*-tolylimide.			
EtOH	1·0210	23	0·86	122	0·7678	18	0·31	55
,,	1·9710	25	1·61	118	1·5135	19	0·53	48
MeOH	1·0130	22	1·03	147	0·7187	17	0·28	53
,,	1·7292	22	1·68	140	1·4374	18	0·51	48
Me_2CO	1·0325	22	0·66	92	0·5906	17	0·16	37
,,	2·0340	23	1·25	89	1·4565	18	0·54	50
	d-Camphor-*p*-tolylamic acid.				*d*-Camphor-*p*-tolylimide.			
EtOH	0·9970	27	1·01	146	1·0030	23	0·31	42
,,	1·9965	27	1·99	144	2·0070	24	0·68	46
,,	2·8994	17	2·91	145				
,,	4·0040	17	3·92	142				
,,	5·0140	17	4·86	140				
,,	5·9710	18	5·70	138				
,,	7·0395	18	6·58	135				
,,	8·0981	17	7·50	134				
,,	9·0550	18	8·16	130				
,,	10·0560	18	8·95	129				
MeOH	1·0035	22	1·18	170	0·7673	18	0·27	48
,,	2·0070	22	2·32	167	1·4580	17	0·56	52
,,	3·0130	18	3·40	163				
,,	4·0100	19	4·49	162				
,,	5·0671	17	5·26	150				
,,	10·0360	17	10·10	145				
Me_2CO	0·9510	24	0·80	122	0·7708	18	0·28	49
,,	2·0250	22	1·68	120	1·4700	18	0·59	54
	d-Camphor-β-naphthylamic acid.				*d*-Camphor-β-naphthylimide.			
EtOH	1·1505	14	1·62	229	0·9130	13	0·37	60
MeOH	1·0180	14	1·54	246	0·5100	15	0·21	61
Me_2CO	1·0530	15	1·38	213	0·8520	15	0·32	56

for the *o*-tolyl derivative 195—196°, which is obviously wrong. We also prepared this substance by his method and found the melting point 105—106°.

Before their rotatory powers were determined, the compounds were recrystallised three times in order to ensure their "optical" purity. Wootton has recorded the rotatory powers of these substances in acetone; his exact concentrations are not stated. In the case of derivatives of camphoramic acid, his values agree with ours, except in the case of the *p*-tolyl derivative, his value (107°) being lower than ours (120° to 122°, according to concentration). In the case of the *p*-tolyl derivative of *d*-camphorimide, his value ($[\alpha]_D$ 34°) is again lower than ours (49° to 54°, according to concentration).

The rotatory powers recorded in Table III were determined by dissolving a given weight of the substance in a solvent, and making up the solution to a definite volume. The readings were taken in a 2-dcm. tube within 45 minutes of making up the solution. There was no mutarotation.

The rotatory powers and dispersion ratios of *d*-camphorbenzylamic acid and *d*-camphor-*m*-nitrobenzylamic acid (higher-melting form) were omitted from Part V of this series (*loc. cit.*). They are given below for the sake of completeness.

Solvent.	Conc. (g./100 c.c.).	Temp.	Molecular rotatory powers.			Dispersion ratios.
			$[M]_{5893}$.	$[M]_{5780}$.	$[M]_{5461}$.	$\alpha_{5461}/\alpha_{5893}$.
			d-Camphorbenzylamic acid.			
Chloroform	1·6193	23°	+92°	+95°	+108°	1·18
Acetone..............	1·9143	25	97	98	111	1·15
Ether.................	1·1590	21	89	92	107	1·21
Ethyl alcohol	3·3400	22	100	107	120	1·25
Methyl alcohol ...	1·2249	23	93	98	115	1·23
		d-Camphor-*m*-nitrobenzylamic acid, m. p. 179°.				
Chloroform	2·0485	23	80	83	94	1·18
Acetone..............	2·0676	25	95	97	111	1·13
Ethyl alcohol	2·8900	22	107	116	140	1·29
Methyl alcohol ...	1·5784	23	109	112	127	1·16

We wish to thank Mr. Sher Singh, B.Sc., for determining the rotatory powers of the β-naphthyl derivatives.

RAVENSHAW COLLEGE, CUTTACK,
BIHAR AND ORISSA, INDIA.

[*Received, October* 24*th*, 1925.]