CLXV.—*The Action of Substituted Aromatic Amines on Camphoric Anhydride. Hydroxy-, Methoxy-, and Ethoxy-camphoranilic Acids and Camphoro-methoxy- and -ethoxy-phenylimides.*

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THE work on the effect of the substituents on the rotatory powers of substituted camphoranilic acids and camphorophenylimides (J., 1925, **127**, 1966; 1927, 1944; 1928, 2410) has been extended to include 2′- and 4′-hydroxy-, -methoxy-, and -ethoxy-camphoranilic acids and the corresponding phenylimides.

Table I records the values of $[M]_D$ for the 2′- and the 4′- substituted camphoranilic acids in the four solvents formulated. In every case the 4′-substituted compound exceeds the 2′- in molecular rotatory power. The relative influence of the substituents on the rotatory power is in the order OEt > OH > OMe for the 2′- and OH > OEt > OMe for the 4′-substituted acids. Methoxyl, which in the

TABLE I.

2′-Substituent.	MeOH.	EtOH.	Me_2CO.	MeEtCO.
OH	−37°	−47°	−45°	−53°
OMe	+30	+28	−16	−10
OEt	−50	−62	−90	−89
4′-Substituent.				
OH	+246°	+266°	+154°	+203°
OMe	+163	+152	+122	+ 99
OEt	+180	+154	+116	+104

2′-position produces an exceptionally large depression (compare Bretscher, Rule, and Spence, J., 1928, 1493), stands at one end of the polar series, carboxyl being at the other. Ethoxyl, instead of occupying a position near methoxyl, follows iodine in the polar series: this position is also indicated by the values of the acid/imide ratio (see J., 1928, 2411) for the phenetidines (see below).

The rotatory powers of cyclic compounds are generally greater than those of the corresponding open-chain derivatives, but the camphoranilic acids and the camphorophenylimides are exceptions to the rule (Wootton, J., 1910, **97**, 405; see also Singh and Puri, J., 1926, 504). Wootton has cited the cases of α-naphthyl and *o*-bromophenyl derivatives of camphoranilic acid, where the molecular rotatory powers of the imides are greater than those of the corresponding acids. It has, however, been shown (Singh, Ahuja, and Lal, J., 1928, 2410) that the *o*-bromo-acid prepared by Wootton was impure and that the pure acid has $[M]_D = -61°$ (in acetone) and not $-41°$. Examples are now given in camphoro-*o*-methoxyphenylimide and camphoro-*o*-ethoxyphenylimide (in methyl alcohol and in ethyl alcohol) which have greater rotatory powers than the corresponding acids.

EXPERIMENTAL.

Camphoric anhydride was condensed with the hydroxy-, methoxy-, and ethoxy-anilines by the general method (J., 1928, 2410). The condensations were carried out at different temperatures to ascertain the effect of temperature on the acid/imide ratio.

2′-Hydroxycamphoranilic Acid.—The condensation product, which had a repulsive odour, was dissolved in alcohol, water was added, and the precipitated oil was removed and extracted with dilute sodium bicarbonate solution. The reddish-brown extract on acidification with dilute acetic acid gave the camphoranilic acid as a gummy mass. A solution of this in aqueous ammonia was boiled with animal charcoal and filtered, and the acid reprecipitated. *2′-Hydroxycamphoranilic acid* finally separated from an alcoholic solution (charcoal), after addition of a little water, in minute prisms, m. p. 183° after shrinking at 159° (Found : N, 4·9. $C_{16}H_{21}O_4N$ requires N, 4·8%).

4′-Hydroxycamphoranilic acid crystallised from dilute alcohol in deep violet prisms, which gave a light grey mass when powdered; m. p. 241—242° (Wootton, *loc. cit.*, gives m. p. 239°) (Found : N, 4·9. Calc. : N, 4·8%).

*2′-Methoxycamphoranilic Acid and Camphoro-*o*-methoxyphenylimide.*—The condensation was carried out at 125°, at 140°, and at 150° : the yield of imide was 38—40% at 150°.

The *acid* crystallised from dilute alcohol in small plates, m. p. 152° after shrinking at 141° (Found: N, 4·8; equiv., 309. $C_{17}H_{23}O_4N$ requires N, 4·6%; equiv., 305). The *imide* crystallised in needles, m. p. 136° (Found: N, 4·9. $C_{17}H_{21}O_3N$ requires N, 4·9%). The acid is more soluble than the imide in the usual organic solvents.

4'-Methoxycamphoranilic acid formed colourless prismatic needles, m. p. 204° (Found: N, 4·7%; equiv., 303).

*Camphoro-*p*-methoxyphenylimide* separated from alcohol in needles, m. p. 122—123° (Found: N, 5·0%). The following yields were obtained: at 120°, 0; at 140°, trace; at 150°, 33—34%; above 200°, 100%.

*2'-Ethoxycamphoranilic Acid and Camphoro-*o*-ethoxyphenylimide*.—The *acid* crystallised in short prismatic needles, m. p. 146—147° (Found: N, 4·5; equiv., 319. $C_{18}H_{25}O_4N$ requires N, 4·4%; equiv., 319).

The *imide*, obtained by heating the condensation mixture at 220° for 1½ hours or by Wootton's method (*loc. cit.*), melted at 138° (Found: N, 4·7. $C_{18}H_{25}O_3N$ requires N, 4·65%). The yield of the imide was: at 125°, 0; at 140°, 0; at 150°, very small; above 200°, 100%.

*4'-Ethoxycamphoranilic Acid and Camphoro-*p*-ethoxyphenylimide*.—The *acid* crystallised in small thick prisms, m. p. 202—203° (Found: N, 4·5%; equiv., 316).

The *imide* crystallised from alcohol in thin needles, m. p. 122° (Found: N, 4·7%). The yield was negligible at 125° and at 140° and 27% at 150°.

If anisidine and phenetidine compounds are heated too rapidly in the combustion tube during analysis, methane is evolved (compare Forster, J., 1909, **95**, 952).

TABLE II.

Rotatory Powers of Hydroxy-, Methoxy-, and Ethoxy-camphoranilic Acids and of the Corresponding Imides ($l = 2$).

Camphoranilic Acids.

Solvent.	Conc. (g./25 c.c.).	$[\alpha]_D$.	Conc. (g./25 c.c.).	$[\alpha]_D$.	Conc. (g./25 c.c.).	$[\alpha]_D$.
	2'-Hydroxy-.		4'-Hydroxy-.		2'-Methoxy-.	
MeOH	0·1385	−12·6°	0·1242	+84·5°	0·2183	+9·7°
EtOH	0·1450	−16·2	0·1200	+91·6	0·2201	+9·0
Me_2CO	0·1427	−15·4	0·1251	+52·9	0·3268	−5·3
MeEtCO	0·1564	−18·5	0·1290	+69·8	0·4390	−3·1
	4'-Methoxy-.		2'-Ethoxy-.		4'-Ethoxy-.	
MeOH	0·2671	+53·3	0·4161	−15·6	0·2465	+56·3
EtOH	0·2570	+49·9	0·4220	−19·5	0·2504	+48·3
Me_2CO	0·2491	+40·1	0·4498	−28·3	0·2559	+36·4
MeEtCO	0·2757	+32·7	0·4144	−28·0	0·2459	+32·6

Camphorophenylimides.

	Conc. (g./25 c.c.).	$[\alpha]_D$.	$[M]_D$.	Conc. (g./25 c.c.).	$[\alpha]_D$.	$[M]_D$.
		o-Methoxy-.			*p*-Methoxy-.	
MeOH ...	0·2638	+17·1°	49°	0·2515	+29·3°	84°
EtOH	0·2427	+14·9	43	0·3437	+21·8	63
Me_2CO ...	0·2657	+14·1	40	0·2561	+17·0	49
MeEtCO ...	0·2628	+15·3	44	0·2724	+11·9	34
		o-Ethoxy-.			*p*-Ethoxy-.	
MeOH ...	0·1205	+38·1	115	0·2461	+28·4	86
EtOH	0·1257	+32·6	98	0·3429	+15·6	47
Me_2CO ...	0·1201	+26·6	80	0·2461	+17·7	53
MeEtCO ...	0·1256	+25·4	77	0·2553	+13·0	39

The readings were taken in a 2-dcm. tube at 23° within 30 minutes of making up the solution. There was no mutarotation.

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