

LXXX.—*The Optical Activity of Salts and Derivatives of d-Camphor- $\beta$ -sulphonic Acid.*

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IN view of the extended use now made of the methods of resolving externally compensated bases by Pope and his pupils, it is highly desirable that accurate measurements should be made of the rotatory powers exhibited by salts and derivatives of the optically active acids concerned. The author has therefore, at the suggestion of Professor Pope, prepared and determined the rotation constants of a number of salts of *d*-camphor- $\beta$ -sulphonic acid for mercury-green, mercury-yellow, and sodium lights, using water as the solvent, for the purpose of ascertaining to what extent the molecular rotatory powers are dependent on the concentration of the solution.

Amongst the salts used in the present work, some, those, namely, of zinc, calcium, barium, and ammonium, have been described by previous workers (Pope and Gibson, *Trans.*, 1910, **97**, 2211); the author has checked their compositions by determinations of the water of crystallisation. The new salts, namely, those of magnesium, cadmium, copper, and piperidine, have been completely analysed.

The aqueous solutions of the salts were examined in 4-dcm. tubes at concentrations of 2, 4, 8, and, if solubility permitted, 16 per cent. (in the case of the ammonium salt, from 1 to 16 per cent.). All the measurements were made at 20°, duplicate series of readings being taken in every case for the same concentration.

The results obtained show that, in the case of the zinc, magnesium, and cadmium salts, no change in rotatory power for either mercury green, mercury yellow, or sodium lights, except within the limits of

experimental error, takes place in solutions varying in concentration from 2 to 8 per cent. in the case of the zinc and magnesium salts, and from 2 to 16 per cent. in the case of the cadmium salt.

With solutions of the calcium and barium salts, however, increase of concentration is accompanied by slight diminution in rotatory power, the rotatory dispersion, however, remaining constant; thus for the calcium salt,  $[M]_D^{20^\circ}$  at 2 per cent. =  $98.9^\circ$ ; 4 per cent.,  $98.5^\circ$ ; 8 per cent.,  $97.1^\circ$ ; and 16 per cent.,  $95.6^\circ$ . A similar change is observed in the case of the barium salt,  $[M]_D^{20^\circ}$  varying from  $98.6^\circ$  at 2 per cent. to  $95^\circ$  at 16 per cent. concentration.

With the ammonium and piperidine salts, on the other hand, increase of concentration produces a slight but unmistakable increase in the rotatory power; thus for the former salt,  $[M]_D^{20^\circ}$  for 1 per cent. is  $50.38^\circ$ ; 2 per cent.,  $50.45^\circ$ ; 4 per cent.,  $51.0^\circ$ ; 8 per cent.,  $51.0^\circ$ ; and 16 per cent.,  $51.85^\circ$ , corresponding increases being observed for the mercury green and yellow rays respectively.

Only a limited number of observations could be made with solutions of the copper salt, owing to the strong absorptive power of the solution for all light except the bluish-green; thus it was only possible to examine solutions of this salt with the mercury green ray, and owing to the general weakening of the light by passing through 4-dcm. thickness of solution, it was not practicable to examine a greater concentration than 4 per cent. The examination of 2, 3, and 4 per cent. solutions gave evidence of a slight diminution of  $[M]_{H\gamma}^{20^\circ}$  with increasing concentration.

It was found inadvisable to examine solutions of smaller concentration than 2 per cent., as the angle of rotation was then too small for the result to be of value for this investigation.

From the results thus briefly summarised it is evident that increase of concentration of the salts of *d*-camphor- $\beta$ -sulphonic acid in aqueous solution produces:

(1) in the case of some salts, *no appreciable change* in rotatory power;

(2) in the case of some *a diminution* in rotatory power;

(3) in the case of other salts *an increase* in rotatory power.

It will thus appear evident that these observed changes cannot be dependent on the change of degree of electrolytic dissociation alone, but depend principally on the character of the metallic atom or electropositive grouping, since the above results show that similar effects are produced by members of the same group in the periodic classification. It also appears evident that the atomic weight of the metal in combination cannot be an important factor in this question of change of rotatory power.

## EXPERIMENTAL.

*d*-Camphor- $\beta$ -sulphonic acid was prepared by Reychler's method (*Bull. Soc. chim.*, 1898, [iii], 19, 120). The crude acid was recrystallised several times from glacial acetic acid, and finally from ethyl acetate. This acid was kept over solid potassium hydroxide and sulphuric acid in an exhausted desiccator for several days to free the acid from traces of acetic acid.

The metallic salts were prepared from this purified acid and the carbonates of the metals, being purified by recrystallisation (at least three times), from aqueous solution.

The ammonium and piperidine salts were prepared from the acid and aqueous solutions of the base, the latter being added in slight excess, and the excess then removed by evaporation.

These two salts were purified by repeated recrystallisation—the ammonium salt from aqueous solution, but in the case of the piperidine salt purification was effected by repeated crystallisation from acetone, the salt being exceedingly soluble in water.

In the examination of the rotatory powers of the salts at different concentrations, all the solutions were made up at 20°, "conductivity" distilled water being employed as solvent.

For the same solution (that is, the same concentration) the polarimetric readings were always made in duplicate, the two series of readings in practically all cases not differing by more than 0.01°.

All the solutions were examined in 4-dcm. tubes at 20°, the temperature being kept constant by means of a brass jacket, through which water at 20° was circulated from a thermostat, the tubes being kept at 20° for at least three-quarters of an hour before examination.

*Magnesium Salt*,  $(C_{10}H_{15}O_4S)_2Mg \cdot 6H_2O$ .—This salt crystallises beautifully from water, a solution saturated at 20° containing about 10 per cent. of the hexahydrate:

0.5921 gave 0.1127  $Mg_2P_2O_7$ .  $Mg = 4.16$ .

1.3356 lost 0.2422 at 195°.  $H_2O = 18.14$ .

$(C_{10}H_{15}O_4S)_2Mg \cdot 6H_2O$  requires  $Mg = 4.09$ ;  $H_2O = 18.18$  per cent.

*Cadmium Salt*,  $(C_{10}H_{15}O_4S)_2Cd \cdot 6H_2O$ .—This salt is more soluble than the magnesium one; it loses all water of crystallisation below 200°:

1.0070 gave 0.2124 CdS.  $Cd = 16.41$ .

0.5121 lost 0.0809 below 200°.  $H_2O = 15.80$ .

$(C_{10}H_{15}O_4S)_2 \cdot 6H_2O$  requires  $Cd = 16.46$ ;  $H_2O = 15.83$  per cent.

*Copper Salt*,  $(C_{10}H_{15}O_4S)_2Cu, 6H_2O$  :

0.9991 gave 0.1257 CuO. Cu = 10.05.

1.0802 „ 0.1356 CuO. Cu = 10.03.

1.1788 „ 0.1485 CuO. Cu = 10.07.

$(C_{10}H_{15}O_4S)_2Cu, 6H_2O$  requires Cu = 10.03 per cent.

$(C_{10}H_{15}O_4S)_2Cu, 5\frac{1}{2}H_2O$  „ Cu = 10.18 „ „

It would therefore appear that the hexahydrate formula represents the constitution of the copper salt more nearly than  $(C_{10}H_{15}O_4S)_2Cu, 5\frac{1}{2}H_2O$  (Pope and Gibson, *Trans.*, 1910, **97**, 2216). On heating to 100° for several hours, loss of weight corresponding with 4H<sub>2</sub>O is produced, the salt then being of a pale blue colour.

The following determinations were made in aqueous solutions at 20° for the mercury green line:

Approximate concentration, per cent.	Grams in 29.979 c.c. at 20°.	$\alpha$ .	[ $\alpha$ ].	[M].
2	0.6073	1.714°	21.15°	134.1°
3	0.9025	2.528	21.00	133.15
4	1.2063	3.369	20.94	132.8

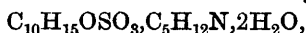
Estimations of the amount of water of crystallisation in the zinc, calcium, and barium salts were found to agree with the figures calculated from the established formulæ of these salts.

*Piperidine Salt*,  $C_{10}H_{15}O_4S, C_5H_{12}N$ .—This salt was purified by repeated crystallisation from acetone, the melting point of the pure salt being 140°. As is described more fully later on, this salt was found to be identical with the so-called piperido-lactone of *d*-camphor- $\beta$ -sulphonic acid (Armstrong and Lowry, *Trans.*, 1902, **81**, 1449; Lowry and Magson, *Trans.*, 1906, **89**, 1050), being produced in small quantities during the preparation of the piperidide of this acid. The salt is extremely soluble in water and most organic solvents; it crystallises in stellate groups of needles from a warm solution of acetone, being much more soluble in the hot than in the cold solvent. If, however, in recrystallisation the acetone solution is evaporated too far, the resulting crystals of piperidine salt are found to melt at quite a low temperature, varying from 50° to 100°, and the salt has evidently become decomposed or altered in constitution. If these crystals are heated in a water-oven for some days, the melting point is found to have become raised again to about 134° (m. p. of pure salt = 140°).

A sample of the salt, the melting point of which had become lowered to approximately 50° in the above manner, gave [ $\alpha$ ]<sub>D</sub><sup>20</sup> 29.3°, whence [M]<sub>D</sub><sup>20</sup> 93.2°, in chloroform solution, whereas [M]<sub>D</sub><sup>20</sup> = 102.3° for the pure piperidine salt (m. p. 140°). The two

results practically agree if we assume that in the compound of low melting point two molecules of water are present;  $[M]_D^{20^\circ}$  for the latter being then  $103.7^\circ$ . The rotatory dispersion,  $Hg_{\text{green}}/Na_{\text{yellow}}$ , is practically the same as that for the pure piperidine salt in chloroform solution.

On heating at  $110-130^\circ$  for fourteen hours, 0.2527 gram of the sample melting about  $50^\circ$  lost 0.018, the melting point of the residue being  $90-100^\circ$ . It seems probable, therefore, that the piperidine salt also exists in the form of a dihydrate,



the melting point of which lies about  $50^\circ$ .

*Piperidine Salt*, m. p.  $140^\circ$ :

0.1182 gave 0.2440  $CO_2$  and 0.0880  $H_2O$ . C=56.30; H=8.35.

0.1484 ,, 0.3060  $CO_2$  ,, 0.1122  $H_2O$ . C=56.24; H=8.47.

$C_{10}H_{15}O_4S, C_5H_{12}N$  requires C=56.71; H=8.59 per cent.,

whereas a *piperidide* or *piperido-lactone*:

$C_{10}H_{15}O_3S, C_5H_{10}N$  requires C=60.13; H=8.43 per cent.

No loss in weight was produced by heating the salt at  $95-100^\circ$  for seven and a-half hours.

*Rotatory Powers and Rotatory Dispersions at Different Concentrations.*—The following figures represent the mean values of the two series of measurements made for each concentration:

*Zinc Salt*,  $(C_{10}H_{15}O_4S)_2Zn, 6H_2O$ .

Approximate concentration, per cent.	Mercury.								
	Sodium yellow.			Yellow.			Green.		
	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .
2	1.281°	15.83°	100.7°	1.362°	16.84°	107.1°	1.678°	20.75°	131.95°
4	2.531	15.79	100.5	2.706	16.89	107.4	3.349	20.90	133.0
8	5.086	15.80	100.55	5.392	16.75	106.55	6.675	20.74	131.95

Concentrations: approximately 2 per cent. : 0.6069 gram in 30.006 c.c. at  $20^\circ$ .  
 ,, 4 ,, 1.2005 ,, 29.979 ,, ,,  
 ,, 8 ,, 2.4150 ,, 30.006 ,, ,,

*Rotatory dispersions:*

Approximate concentration, per cent.	$Hg_{\text{yellow}}/Na_{\text{yellow}}$ .	$Hg_{\text{green}}/Na_{\text{yellow}}$ .
2	1.063	1.310
4	1.069	1.323
8	1.060	1.312
Mean .....	1.064	1.315

*Magnesium Salt*,  $(C_{10}H_{15}O_4S)_2Mg \cdot 6H_2O$ .

Approximate concentration, per cent.	Sodium yellow.			Yellow.			Green.		
	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .
	2	1·366°	16·88°	100·4°	1·449°	17·92°	106·6°	1·797°	22·22°
4	2·762	16·92	100·7	2·942	18·02	107·1	3·612	22·12	131·6
8	5·416	16·82	100·1	5·770	17·92	106·6	7·149	22·20	132·0

Concentrations : approximately 2 per cent. : 0·6068 gram in 30·006 c.c. at 20°.

		4	1·2248		
		8	2·4154		

*Rotatory dispersions :*

Approximate concentration, per cent.	Hg <sub>yellow</sub> /Na <sub>yellow</sub> .	Hg <sub>green</sub> /Na <sub>yellow</sub> .
2	1·061	1·316
4	1·065	1·308
8	1·065	1·320
Mean	1·064	1·315

*Cadmium Salt*,  $(C_{10}H_{15}O_4S)_2Cd \cdot 6H_2O$ .

Approximate concentration, per cent.	Sodium yellow.			Yellow.			Green.		
	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .
	2	1·210°	14·74°	100·7°	1·290°	15·72°	107·3°	1·589°	19·37°
4	2·421	14·80	101·0	2·560	15·65	106·8	3·171	19·38	132·4
8	4·712	14·66	100·1	5·024	15·63	106·7	6·225	19·37	132·2
16	9·487	14·70	100·4	10·073	15·60	106·6	12·483	19·34	132·1

Concentrations : approximately 2 per cent. : 0·6157 gram in 30·006 c.c. at 20°.

		4	1·2275		
		8	2·4117		
		16	4·8426		

*Rotatory dispersions :*

Approximate concentration, per cent.	Hg <sub>yellow</sub> /Na <sub>yellow</sub> .	Hg <sub>green</sub> /Na <sub>yellow</sub> .
2	1·066	1·313
4	1·057	1·310
8	1·066	1·321
16	1·062	1·316
Mean	1·063	1·315

*Calcium Salt*,  $(C_{10}H_{15}O_4S)_2Ca \cdot 4H_2O$ .

Approximate concentration, per cent.	Sodium yellow.			Yellow.			Green.		
	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .
	2	1·410°	17·22°	98·94°	1·512°	18·47°	106·1°	1·863°	22·76°
4	2·773	17·15	98·50	2·964	18·32	105·26	3·667	22·67	130·2
8	5·423	16·91	97·15	5·774	18·00	103·4	7·166	22·35	128·4
16	10·657	16·65	95·67	11·378	17·77	102·12	14·123	22·06	126·75

Concentrations : approximately 2 per cent. : 0·6142 gram in 30·006 c.c. at 20°.

		4	1·2137		
		8	2·4058		
		16	4·8023		

*Rotatory dispersions :*

Approximate concentration, per cent.	Hg <sub>yellow</sub> /Na <sub>yellow</sub> .	Hg <sub>green</sub> /Na <sub>yellow</sub> .
2	1·072	1·321
4	1·068	1·322
8	1·065	1·321
16	1·068	1·325
Mean .....	1·068	1·322

*Barium Salt, (C<sub>10</sub>H<sub>15</sub>O<sub>4</sub>S)<sub>2</sub>Ba, 3H<sub>2</sub>O.*

Approximate concentration, per cent.	Mercury.									
	Sodium yellow.			Yellow.			Green.			
	α <sup>20°</sup> .	[α] <sup>20°</sup> .	[M] <sup>20°</sup> .	α <sup>20°</sup> .	[α] <sup>20°</sup> .	[M] <sup>20°</sup> .	α <sup>20°</sup> .	[α] <sup>20°</sup> .	[M] <sup>20°</sup> .	
2	1·209°	15·08°	98·58°	1·310°	16·34°	106·9°	1·603°	20·00°	130·8°	
4	2·424	14·98	98·00	2·606	16·11	105·3	3·220	19·89	130·1	
8	4·767	14·77	96·64	5·086	15·77	103·1	6·313	19·57	127·9	
16	9·114	14·53	95·04	9·710	15·49	101·3	12·064	19·23	125·8	
Concentrations : approximately 2 per cent. : 0·6007 gram in 29·979 c.c. at 20°.										
			4	4	1·2141		30·006			
			8	8	2·4203		30·006			
			16	16	4·7040		30·006			

*Rotatory dispersions :*

Approximate concentration, per cent.	Hg <sub>yellow</sub> /Na <sub>yellow</sub> .	Hg <sub>green</sub> /Na <sub>yellow</sub> .
2	1·083	1·326
4	1·075	1·328
8	1·067	1·324
16	1·065	1·323
Mean .....	1·072	1·325

*Ammonium Salt, C<sub>10</sub>H<sub>15</sub>O<sub>4</sub>S·NH<sub>4</sub>.*

Approximate concentration, per cent.	Mercury.									
	Sodium yellow.			Yellow.			Green.			
	α <sup>20°</sup> .	[α] <sup>20°</sup> .	[M] <sup>20°</sup> .	α <sup>20°</sup> .	[α] <sup>20°</sup> .	[M] <sup>20°</sup> .	α <sup>20°</sup> .	[α] <sup>20°</sup> .	[M] <sup>20°</sup> .	
1	0·813°	20·21°	50·38°	0·873°	21·70°	54·09°	1·073°	26·68°	66·50°	
2	1·661	20·24	50·45	1·732	21·71	54·12	2·191	26·70	66·55	
4	3·297	20·46	51·00	3·512	21·79	54·31	4·354	27·01	67·35	
8	6·544	20·46	51·00	6·977	21·81	54·37	8·634	26·99	67·29	
16	13·294	20·79	51·85	14·188	22·20	55·34	17·538	27·43	68·39	
Concentrations : approximately 1 per cent. : 0·3018 gram in 30·006 c.c. at 20°.										
			2	2	0·6129					
			4	4	1·2095					
			8	8	2·3998					
			16	16	4·7953					

SALTS AND DERIVATIVES OF *d*-CAMPHOR- $\beta$ -SULPHONIC ACID. 753*Rotatory dispersions :*

Approximate concentration, per cent.	Hg <sub>yellow</sub> /Na <sub>yellow</sub> .	Hg <sub>green</sub> /Na <sub>yellow</sub> .
1	1·074	1·320
2	1·073	1·319
4	1·065	1·320
8	1·066	1·319
16	1·067	1·319
Mean .....	1·069	1·319

*Piperidine Salt*, C<sub>10</sub>H<sub>15</sub>O<sub>4</sub>S·C<sub>5</sub>H<sub>12</sub>N.

Approximate concentration, per cent.	Mercury.								
	Sodium yellow.			Yellow.			Green.		
	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .
2	1·303°	15·97°	50·70°	1·390°	17·04°	54·09°	1·699°	20·83°	66·12°
4	(1) 2·423	16·07	51·00	2·619	17·36	55·11	3·229	21·41	67·96
	(2) 2·320	16·18	51·36	2·472	17·24	54·72	3·061	21·34	67·74
		16·12	51·18		17·30	54·91		21·37	67·85
8	5·431	16·50	52·38	5·779	17·56	55·72	7·121	21·63	68·66
16	Solution too concentrated to read for "Na" light			11·061	18·07	57·35	13·645	22·29	70·77

Concentrations : approximately 2 per cent. : 0·6115 gram in 29·979 c.c. at 20°.

" 4 " (1) 1·1805 " " "

" 8 " (2) 1·0747 " " "

" 16 " 2·4680 " " "

" " 4·5871 " " "

*Rotatory dispersions :*

Approximate concentration, per cent.	Hg <sub>yellow</sub> /Na <sub>yellow</sub> .	Hg <sub>green</sub> /Na <sub>yellow</sub> .
2	1·067	1·304
4	1·073	1·325
8	1·064	1·311
Mean .....	1·068	1·313

*Summary of Rotatory Dispersions (mean values) of the Salts of d-Camphor- $\beta$ -sulphonic Acid.*

	Hg <sub>yellow</sub> /Na <sub>yellow</sub> .	Hg <sub>green</sub> /Na <sub>yellow</sub> .
Zinc .....	1·064	1·315
Magnesium .....	1·064	1·315
Cadmium .....	1·063	1·315
Calcium .....	1·068	1·322
Barium .....	1·072	1·325
Ammonium .....	1·069	1·319
Piperidine .....	1·068	1·313

From these results it is evident that there is practically no change in rotatory dispersion with change of concentration, and



that the mean rotatory dispersions for the different salts are practically identical.

*Lead Salt.*—This salt was also prepared, but as it decomposed rather readily in aqueous solution into a white, insoluble compound, presumably a basic salt, its rotatory power was not examined.

*Rotatory Powers and Rotatory Dispersions of other derivatives of d-Camphor-β-sulphonic Acid, with Chloroform as Solvent.*

The chloride, amide, and anhydramide of this acid were prepared in the manner described by Reychler (*Bull. Soc. chim.*, 1898, [iii], 19, 120) and Armstrong and Lowry (*Trans.*, 1902, 81, 1448), except that in the preparation of the chloride the ammonium salt was employed instead of the free acid. The piperidide was obtained from the chloride and piperidine by the Schotten-Baumann reaction.

*d-Camphor-β-sulphonyl Chloride.*—This compound was in the first place recrystallised from dry ether, but as the purified substance after a short time showed signs of decomposition, dry benzene was subsequently employed as solvent, on crystallisation from which the chloride appeared to decompose less easily.

Two solutions were made up with purified chloroform, the strength of the solutions being approximately 4 per cent. The polarimetric results were as follows:

	Mercury.								
	Sodium.			Yellow.			Green.		
	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .	$\alpha^{20^\circ}$ .	$[\alpha]^{20^\circ}$ .	$[M]^{20^\circ}$ .
I .....	4·516°	32·14°	80·54°	4·740°	33·73°	84·51°	5·598°	39·83°	99·83°
II .....	4·892	32·21	80·71	5·178	34·09	85·43	6·125	40·34	101·10
Mean .....		32·17	80·62		33·91	84·97		40·08	100·46
I.	1·0533 gram of chloride in 29·979 c.c. of chloroform at 20°.								
II.	1·1385     "     "     "     "     "     "     "     "								

*Mean rotatory dispersions:*

$$H_{g\text{yellow}}/N_{a\text{yellow}} = 1\cdot054; \quad H_{g\text{green}}/N_{a\text{yellow}} = 1\cdot245.$$

*d-Camphor-β-sulphonamide*,  $C_{10}H_{15}O\cdot SO_2\cdot NH_2$ .—This compound was purified by repeated crystallisation from hot water, and finally twice from alcohol. The amide was thus obtained in a state of purity, but when polarimetric readings were made with material preserved in a stoppered bottle for four or five weeks, the substance had decomposed largely into the anhydramide.

As only a small amount of the pure amide had been obtained, owing to its ready conversion into the anhydramide, this compound was not examined polarimetrically.

As an instance of the ease with which the amide is transformed

into the anhydramide, it may be remarked that, on boiling an aqueous solution of the former, a deposit of the nearly insoluble anhydramide is formed. On keeping over anhydrous calcium chloride in a desiccator for a few days, the amide is converted practically completely into the anhydramide.

*d*-Camphor- $\beta$ -sulphonanhydramide,  $C_{10}H_{15}O_2NS$ .—This compound was purified by repeated crystallisation from boiling alcohol, when it melted at  $223^\circ$ . Two approximately 2 per cent. solutions, with chloroform as solvent, were examined, with the following results:

	Sodium.			Mercury.					
	$\alpha^{20^\circ}$	$[\alpha]^{20^\circ}$	$[M]^{20^\circ}$	Yellow.			Green.		
	$\alpha^{20^\circ}$	$[\alpha]^{20^\circ}$	$[M]^{20^\circ}$	$\alpha^{20^\circ}$	$[\alpha]^{20^\circ}$	$[M]^{20^\circ}$	$\alpha^{20^\circ}$	$[\alpha]^{20^\circ}$	$[M]^{20^\circ}$
I.	-3.048°	-33.83°	-72.15°	-3.073°	-34.10°	-72.74°	-3.450°	-38.29°	-81.66°
II.	3.080	33.76	71.99	3.162	34.65	73.90	3.543	38.83	82.80
Mean ...	-33.79	-72.07		-34.37	-73.32		-38.56	-82.23	
		I.	0.6753 gram in 29.979 c.c. of chloroform at $20^\circ$						
		II.	0.6840 " " " " " "						

*Mean rotatory dispersions:*

$$H_{\text{gyellow}}/N_{\text{ayellow}} = 1.017; \quad H_{\text{green}}/N_{\text{ayellow}} = 1.141.$$

*Piperidide.*—The two compounds formulated by Armstrong and Lowry (Trans., 1902, **81**, 1449) as piperidides, and later by Lowry and Magson (Trans., 1906, **89**, 1050) as normal piperidide and piperido-lactone respectively, were prepared by the Schotten-Baumann reaction. The compound of low melting point was obtained as an oil, and was separated from the other substances present in the mixture by repeated extraction with water, the piperidide being insoluble. This oil is exceedingly difficult to crystallise, and success in this respect was only attained by cooling it in liquid air. The oil solidified, but on attaining the temperature of the laboratory again, appeared to revert to the original condition of an oil. However, on keeping overnight, it was found that the supercooled oil had crystallised out as a solid mass of crystals. These were collected and washed with light petroleum (b. p.  $30$ — $40^\circ$ ), and then dried on a porous plate. This compound is not very soluble in light petroleum, but crystallisation takes place more easily from this solvent than from any other. In the case of almost any other solvent the impure piperidide is left as a gummy mass, which crystallises only after a considerable time.

The piperidide of low melting point was thus purified by repeated crystallisation from light petroleum, the crystals being powdered and washed with light petroleum after each crystallisation. They were dried on a porous plate, and again crystallised from light petroleum. As the melting point during the last couple of crystal-

lisations remained practically constant (and sharp) at 46—47°, this purified sample was examined polarimetrically, with the following results:

*Solvent: Chloroform.*

	Mercury.								
	Sodium.			Yellow.			Green.		
	$\alpha^{20^\circ}$	$[\alpha]^{20^\circ}$	$[M]^{20^\circ}$	$\alpha^{20^\circ}$	$[\alpha]^{20^\circ}$	$[M]^{20^\circ}$	$\alpha^{20^\circ}$	$[\alpha]^{20^\circ}$	$[M]^{20^\circ}$
I .....	0.762°	33.45°	100.15°	0.818°	35.91°	107.5°	0.970°	42.58°	127.5°
II .....	1.292	33.38	99.90	1.389	35.88	107.4	1.644	42.46	127.1
Mean .....		33.41	100.02		35.89	107.4		42.52	127.3

Concentrations: I. 0.1708 gram in 29.979 c.c. of chloroform at 20°.

II. 0.2903

(Armstrong and Lowry give  $[\alpha]_{D}^{10} = 33.6^\circ$ , for a concentration of 10 grams in 100 c.c. of chloroform.)

*Mean rotatory dispersions:*

$$H_{g_{\text{yellow}}}/N_{a_{\text{yellow}}} = 1.074; \quad H_{g_{\text{green}}}/N_{a_{\text{yellow}}} = 1.272.$$

The second compound produced in the reaction between the acid chloride and piperidine, melting at 140° and formulated by Lowry and Magson as the piperido-lactone, was isolated from the aqueous solution by evaporation to dryness, extracting the residue with chloroform, evaporating again to dryness, and extracting with acetone. The latter solution on evaporation leaves a brown, oily mass, which on cooling and stirring with a little light petroleum suddenly becomes solid. On recrystallising twice from acetone, a sample melting at 136—137° was obtained.

In the meantime the piperidine salt of *d*-camphor- $\beta$ -sulphonic acid described above had been prepared and purified by recrystallisation from acetone. This compound melted at 140°, and appeared to be identical in properties with the so-called piperido-lactone isolated from the piperidide preparation. The identity was confirmed by the value obtained for the specific rotation in chloroform solution, this value being practically identical with that obtained by Armstrong and Lowry. That this compound, prepared as the piperidine salt, was really such was proved by the following facts:

(1) Sodium hydroxide in the cold liberates piperidine from an aqueous solution of the compound.

(2) Combustion results, given above, agree with the formula for the piperidine salt, no water of crystallisation being present, and not with the figures required for a piperidide or piperido-lactone.

(3) The molecular rotatory powers and rotatory dispersions of the compound in aqueous solution correspond in value with the figures obtained for the ammonium salt.

It is therefore evident that the compound melting at 140° isolated

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in the preparation of the piperidide is in reality the piperidine salt of *d*-camphor- $\beta$ -sulphonic acid, and not a piperido-lactone of this acid.

As the compound described as  $\alpha$ -bromocamphor- $\beta$ -sulphopiperido-lactone (m. p. 123°) (Armstrong and Lowry, *Trans.*, 1902, **81**, 1452; Lowry and Magson, *Trans.*, 1906, **89**, 1051) yields the above compound, namely, the piperidine salt of *d*-camphor- $\beta$ -sulphonic acid, on reduction, it is intended to examine it and the piperidine salt of  $\alpha$ -bromocamphor- $\beta$ -sulphonic acid.

*Rotatory Power of Piperidine d-Camphor- $\beta$ -sulphonate in Chloroform.*

	Mercury.								
	Sodium.			Yellow.			Green.		
	$\alpha^{20^\circ}$ .	[ $\alpha$ ] $^{20^\circ}$ .	[M] $^{20^\circ}$ .	$\alpha^{20^\circ}$ .	[ $\alpha$ ] $^{20^\circ}$ .	[M] $^{20^\circ}$ .	$\alpha^{20^\circ}$ .	[ $\alpha$ ] $^{20^\circ}$ .	[M] $^{20^\circ}$ .
I .....	2·027°	32·37°	102·8°	2·188°	34·94°	110·9°	2·593°	41·40°	131·4°
II .....	1·175	32·08	101·9	1·248	34·06	108·2	1·485	40·54	128·7
Mean .....		32·22	102·3		34·50	109·6		40·97	130·0
	I. 0·4694 gram in 29·979 c.c. of chloroform at 20°.								
	II. 0·2747 ,, ,, 30·0 ,, ,, ,,								

*Mean rotatory dispersions:*

$$H_{\text{gyellow}}/N_{\alpha\text{yellow}} = 1·071; \quad H_{\text{ggreen}}/N_{\alpha\text{yellow}} = 1·271.$$

A sample of the pure acid was obtained from the purified ammonium salt by preparing the barium salt, and exactly precipitating the barium as sulphate; the filtered solution was evaporated to dryness, and the acid then crystallised three times from dry acetone. The resulting product was found to lose an amount in weight at 100° corresponding with 1H<sub>2</sub>O. A titration of the solution of a weighed amount of acid also pointed to the formula C<sub>10</sub>H<sub>15</sub>O·SO<sub>3</sub>H<sub>2</sub>O. When, however, these crystals were examined polarimetrically, the different results obtained for the specific and molecular rotations from two samples showed that the acid had absorbed varying amounts of water. As, however, the rotatory dispersions are independent of the weight of active substance, the figures for these are given. The solutions were approximately 1 per cent. in chloroform at 20°.

A comparison of the rotatory dispersions of the derivatives of *d*-camphor- $\beta$ -sulphonic acid is made in the following table:

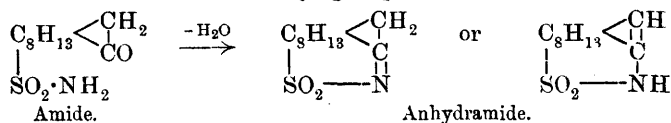
*Rotatory Dispersions in Chloroform at 20°.*

	H <sub>gyellow</sub> /N <sub>αyellow</sub> .	H <sub>ggreen</sub> /N <sub>αyellow</sub> .
<i>d</i> -Camphor- $\beta$ -sulphonic acid.....	1·056	1·274
(Mean of two determinations)		
<i>d</i> -Camphor- $\beta$ -sulphonyl chloride ...	1·054	1·245
piperidide.	1·074	1·272
Piperidine <i>d</i> -camphor- $\beta$ -sulphonate	1·071	1·271
<i>d</i> -Camphor- $\beta$ -sulphonanhydramide	1·017	1·141

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These figures indicate that there is comparatively little difference in rotatory dispersions between the acid, its chloride, piperidide, and piperidine salt; it will be noted that the figures for the piperidide and piperidine salt are practically identical, and from this it may be deduced that the configuration, formulated by Lowry and Magson for the former compound as the true piperidide, is the correct one.

Again, it will be noticed that the anhydramide differs considerably in rotatory dispersions from the other derivatives of camphorsulphonic acid; this is as might be expected from the change of configuration produced by the linking up of the nitrogen atom with the carbon atom of the carbonyl group, thus:



The residual solution obtained from the preparation of the crystalline "Reychler" camphorsulphonic acid, and described by Reychler (*Bull. Soc. chim.*, 1898, [iii], 19, 127) as containing an amorphous acid, is at present the subject of further investigation. Evidence has, however, been obtained, showing that there are at least two other compounds present, one of which has been isolated, besides a certain amount of *d*-camphor- $\beta$ -sulphonic acid, which remains in solution, and which thus renders the isolation of a second acid from the residual solution more difficult.

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