CLXXVI.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXII. Some Compounds containing the Secondary Octyl Radical Linked to Oxygen.*

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WHATEVER may be the significance ultimately attached to natural rotatory dispersion, it is now an established experimental fact that optically active organic compounds may be divided into two classes : those of which the rotatory dispersion in the limited range of the spectrum available to measurement may be expressed by one term of Drude's dispersion equation, $\alpha = \Sigma k_n/(\lambda^2 - \lambda_n^2)$; and those which require more than one such term. The latter type of dispersion—" complex," as it is usually termed—has hitherto been associated almost entirely with acids and esters; the carboxyl group or one of its equivalents, the carboalkyloxyl group or the xanthogenic ester group, nearly always appears in the formula of a compound which exhibits complex rotatory dispersion. The simpler alcohols, on the other hand, so far as available measurements go, rarely require more than a one-term Drude equation : the rotatory dispersions of these are said to be " simple."

In view of the considerations brought forward in Part XXI (this vol., p. 1198), it seems undesirable to insist on a distinction between simple and complex rotatory dispersion as far as theories are concerned, and therefore it is proposed, in this paper at least, to restrict the discussion to a classification of the observed facts of rotatory dispersion. The following table contains those so far observed : R represents the β-octyl group, and R′ a *n*-alkyl group.

Compounds of which the observed rotatory dispersion is :

Apparently Simple.	*Obviously* Complex.
R·OH secondary alcohol.	$R'\cdot C\diagup^{O}_{\diagdown OR}$ carboxylic ester
R·O·R′ ethers.	
$CH_2(OR)_2$ formal.	
$CH(OR)_3$ orthoformate.	
RO·CO·OR symmetrical carbonate.	R·O·N:O nitrite.*
RO·CO·OR′ unsymmetrical carbonate.	
RO·SO·OR sulphite.	
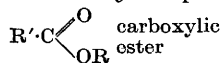
* The author is indebted to Prof. H. E. Merwin, of the Geophysical Laboratory, Washington, D.C., U.S.A., for pointing out an arithmetical mistake in Part XIX (J., 1923, **123**, 434), where the refractive index of *d*-γ-nonyl nitrite is given as 1·4384 for $\lambda = 4358$. This figure should read $n^{20°}_{4358} = 1·4284$. The refractive dispersion of this compound now shows a proper relation to those of *iso*butyl and *iso*amyl nitrites as observed by Brühl.

It must be clearly understood that this classification is provisional only, and may be considerably modified if measurements in other parts of the spectrum become available. It has already broken down in some cases; thus there are some secondary alcohols which show complex rotatory dispersion. These, however, generally contain an aromatic nucleus, at present an unknown factor as far as rotatory dispersion is concerned. Further, in the next paper there is described a series of ethers exhibiting complex rotatory dispersion, whilst, on the other hand, there are two series of esters (see Parts XI and XVIII, J., 1915, **107**, 35; 1923, **123**, 105), both apparently exhibiting simple rotatory dispersion. Broadly, however, this classification represents the behaviour of β-octyl compounds when observations are confined to the visible, and in some cases even when they are extended to the near ultra-violet, region of the spectrum. In view of the considerations discussed in Part XXI (*loc. cit.*), however, it would be rash to ignore the possibility that observations pushed farther into the ultra-violet, that is to say nearer to the absorption band or bands dominating the rotatory dispersion of the compound under consideration, may modify this provisional classification.

As far as these observations go, however, it may be said that the complex rotatory dispersion associated with the carboxyl group or its equivalents is due to the presence, in one molecule, of both a singly and a doubly linked oxygen atom, arranged unsymmetrically. It will be seen that β-octyl compounds containing only saturated oxygen atoms, such as the alcohol, the formal, the orthoformate, and the ethers, exhibit rotatory dispersions which are apparently simple, whilst those containing a doubly bound oxygen atom—the esters—show rotatory dispersions which are obviously complex. The exceptions to this statement are the carbonates and the sulphite. In these cases, it is suggested that the saturated oxygen atoms are distributed symmetrically about the unsaturated one, and that this arrangement is sufficient to suppress any obvious complexity of rotatory dispersion.

Some of the experimental figures are noteworthy. Di-*d*-β-octyl-formal has a very high rotatory power which decreases rapidly with rise of temperature. This compound shows apparently simple

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Furthermore, the Sellmeier equation for this compound now contains two terms, thus :

$$n^2 = 2 \cdot 0266 + \frac{0 \cdot 00127}{\lambda^2 - 0 \cdot 14} - 0 \cdot 0626 \ \lambda^2$$

and is at once comparable with the Drude equation for the same substance. With the above equation, the observed and calculated values for its refractive index agree within $\pm \ 0 \cdot 0001$ for each wave-length employed.

rotatory dispersion and yet possesses a rotatory power which is exceedingly sensitive to change in external conditions, a sensitivity which has been associated since the time of Biot with anomalous, and hence complex, dispersion. The Drude equation for the formal at 20° is quoted in the experimental part. On account of the difficulty of obtaining measurements of sufficient precision at higher temperatures no attempt has been made to fit Drude equations to these figures, but the dispersion remains apparently simple throughout the experimental range of temperature, and, as indicated by the constancy of the dispersion ratio $(\alpha_{4358}/\alpha_{5461})$, the dispersion constant, λ_0^2, is apparently independent of temperature. Tri-l-β-octyl orthoformate, although similar in constitution to the formal in that it is the next higher homologue, containing one more optically active β-octyloxyl group, yet exhibits a lower rotatory power, both specific and molecular, than the formal. This is entirely different from the case of ethyl d-β-octyl and di-d-β-octyl carbonates, of which the latter has a specific rotatory power practically double that of the former. Finally, it should be noted that the rotatory power of di-d-β-octyl sulphite is negative, its optical behaviour in this respect being analogous to that of the lævorotatory d-β-octyl formate (Part XIII, J., 1923, **123**, 1).

Experimental.

All the compounds described herein were prepared from optically pure β-octanol, $[\alpha]_{5461}^{16°} \pm 11\cdot72°$, and were distilled under diminished pressure until the refractive index and rotatory power were constant.

Di-d-β-*octylformal*, $CH_2(O\cdot C_8H_{17})_2$, was prepared by Trillat and Gambier's method (*Bull. Soc. chim.*, 1889, [iii], **2**, 817) by heating together at 100° for 4 hours, β-octanol (12 grams), trioxymethylene (5 grams), and anhydrous ferric chloride (0·4 gram). After the action, the mixture was diluted with ether, washed repeatedly with water, dried over anhydrous potassium carbonate, and distilled, a clear, colourless, mobile liquid with a faint, fragrant odour, b. p. 175—177°/16 mm., being obtained.

d-β-*Octyl chlorocarbonate*, $C_8H_{17}\cdot O\cdot COCl$, prepared by dropping slowly a solution of 100 grams of carbonyl chloride in a litre of toluene into a solution of 149 grams of d-β-octanol in 90 grams of pyridine, cooled in a mixture of ice and salt, had the following physical constants : b. p. 92°/13 mm., $d_4^{19°}$ 0·9748, $n_D^{20°}$ 1·4282, $\alpha_{100\,mm.}^{19°}$ λ 5893, + 23·78°; λ 5780, + 24·78°; λ 5461, + 28·06°; λ 4358, + 46·33°; whence $\alpha_{4358}/\alpha_{5461} = 1\cdot651$.

Ethyl d-β-*Octyl Carbonate*, $EtO\cdot CO\cdot O\cdot C_8H_{17}$.—$d$-β-Octyl chlorocarbonate (8·8 grams) was slowly dropped into a well-cooled solution of ethyl alcohol (2·3 grams) in 30 grams of pyridine. The mixture

was washed, dried, and distilled in the usual way. A second preparation from ethyl chlorocarbonate and d-β-octanol had exactly the same rotatory power. The ester is a fragrant, limpid liquid, b. p. 110°/14 mm.

Di-d-β-$octyl$ $carbonate$, $(C_8H_{17}\cdot O)_2CO$, b. p. 168°/13 mm., was prepared from d-β-octanol and d-β-octyl chlorocarbonate exactly as before.

Tri-l-β-$octyl$ $Orthoformate$, $(C_8H_{17}\cdot O)_3CH$.—Five grams of ethyl orthoformate were heated for 30 hours at 140° $\pm$ 5° with 15 grams of l-β-octanol, a volatile liquid (mainly ethyl alcohol) distilling in considerable quantity at first. The fraction, b. p. 195—205°/ca. 1 mm., was redistilled. Some decomposition was noticed during the distillation and the rotatory power (α_{5461} 25 mm.) varied from $- 6\cdot25°$ to $- 6\cdot20°$. The orthoformate is a nearly odourless liquid, b. p. 202—203°/ca. 1 mm., $d_4^{15°}$ 0·8592, $n_D^{15°}$ 1·4376, whence $[R_L]_{5896}^{15°} = 122\cdot38$ [Calc. for $(C_8H_{17}\cdot O)_3CH$, 122·58 ; the corresponding figures for $(C_8H_{17}\cdot O)_2CH\cdot OEt$ are, calc. 94·87, obs. 96·52].

Di-d-β-$octyl$ $Sulphite$, $(C_8H_{17}\cdot O)_2SO$.—To 26 grams of d-β-octanol in 200 c.c. of dry light petroleum a solution of thionyl chloride (12 grams) in 200 c.c. of the same solvent was added very slowly at $- 10°$ to $- 5°$ with vigorous shaking. Much hydrogen chloride and very little sulphur dioxide were evolved. After 12 hours, the petroleum was removed on the water-bath and the ester distilled. It is a mobile, practically colourless and odourless liquid, b. p. 133—134°/1 mm. After hydrolysis for 1 hour with alcoholic caustic soda, the sulphite was estimated by means of iodine absorption in acid solution [Found : S = 10·61. $(C_8H_{17}\cdot O)_2SO$ requires S = 10·46 per cent.].

Physical Measurements.

Densities were determined in a pyknometer holding about 1·5 c.c., and are referred to water at 4°.

Refractive indices were determined in a jacketed Pulfrich refractometer with water circulation from a thermostat. The sodium and lithium flames, the enclosed mercury and cadmium arcs, the open copper arc, and the neon * lamp were used as light sources. For use with the copper and neon lines the refractometer prism was calibrated with quartz.

Polarimetric measurements were made visually and photographically, the sodium and lithium flames, the enclosed mercury

* The author is indebted to the Director of the Research Laboratories of the General Electric Co., Wembley, for the loan of a new type of neon glow lamp working on 220 volts D.C. This lamp is exceedingly convenient for refractometric work, as the glow is concentrated on a very small cathode.

and cadmium arcs, and the open iron arc being used as light sources. Jacketed tubes were employed with water circulation for the photographic and visual readings at 20°, and hot-oil circulation for the visual readings at higher temperatures. All values were observed in a 50 mm. tube.

Di-d-β-octylformal.

$t°$.	17·0	46·5	75·5	97·5	128·0	157·5
d.	0·8523	0·8307	0·8071	0·7883	0·7658	0·7427

λ	6438	5896	5461	5086	4800	4678	4358
$n_\lambda^{20·6°}$	1·4295	1·4314	1·4334	1·4352	1·4371	1·4379	1·4409

Rotatory power.

α_{6438} $+ 12·89°$ at $13·5°$; $12·35°$ at $17·5°$; $11·13°$ at $30°$; $10·96°$ at $31·5°$; $9·54°$ at $45°$; $7·35°$ at $72°$; $5·71°$ at $97°$; $5·51°$ at $103°$; $4·56°$ at $119·5°$; $4·13°$ at $132°$; $3·57°$ at $148°$; $2·77°$ at $172°$.

α_{5893} $+ 15·69°$ at $14°$; $15·01°$ at $19·3°$; $14·35°$ at $24·5°$; $13·13°$ at $33°$; $12·08°$ at $40·5°$; $8·68°$ at $72°$; $7·02°$ at $96°$; $6·55°$ at $106°$; $5·80°$ at $119·5°$; $4·60°$ at $145°$.

α_{5461} $+ 18·51°$ at $13°$; $17·77°$ at $18·5°$; $16·82°$ at $26°$; $15·46°$ at $33·5°$; $14·14°$ at $42·5°$; $10·97°$ at $67°$; $8·30°$ at $95°$; $7·48°$ at $107°$; $6·69°$ at $121°$; $5·30°$ at $146°$.

α_{5086} $+ 21·64°$ at $13·5°$; $20·76°$ at $17·5°$; $18·93°$ at $29°$; $18·25°$ at $32°$; $15·82°$ at $45·5°$; $12·01°$ at $72°$; $9·42°$ at $97°$; $9·15°$ at $103°$; $7·95°$ at $117°$; $6·13°$ at $144°$; $4·50°$ at $171°$.

α_{4800} $+ 24·75°$ at $13·5°$; $23·83°$ at $18°$; $21·72°$ at $28°$; $20·78°$ at $31°$; $18·42°$ at $44°$; $13·84°$ at $72°$; $10·99°$ at $96°$; $10·56°$ at $103°$; $9·38°$ at $117°$; $8·33°$ at $131°$; $7·27°$ at $147°$.

α_{4678} $+ 26·32°$ at $13·5°$; $25·54°$ at $17°$; $23·36°$ at $27°$; $22·25°$ at $31°$; $19·69°$ at $43·5°$; $14·33°$ at $72°$; $9·96°$ at $115°$; $8·73°$ at $131°$; $7·71°$ at $145°$.

α_{4358} $+ 30·64°$ at $17°$; $29·68°$ at $18°$; $27·89°$ at $25°$; $25·49°$ at $33·5°$; $23·55°$ at $42°$; $16·88°$ at $71°$; $16·14°$ at $75°$; $13·78°$ at $94°$; $12·55°$ at $105°$; $11·17°$ at $120°$; $8·65°$ at $146°$.

The following figures have been obtained from the smoothed curves drawn through the above values.

Specific rotatory power of di-d-β-octylformal.

$t°$.	$d_{4°}^{t°}$.	$[\alpha]_\lambda^{t°}$.							$\dfrac{[\alpha]_{4358}}{[\alpha]_{5461}}$.
		λ_{6438}.	λ_{5893}.	λ_{5461}.	λ_{5086}.	λ_{4800}.	λ_{4678}.	λ_{4583}.	
20	0·8499	$+28·56°$	35·14°	41·28°	48·00°	54·99°	58·61°	68·20°	1·65
40	0·8342	24·16	29·10	34·89	40·40	46·17	49·05	57·53	1·65
60	0·8158	20·20	23·96	28·93	33·58	37·72	39·75	47·56	1·65
80	0·8028	16·89	20·13	23·92	27·65	31·81	33·36	39·24	1·64
100	0·7871	14·22	17·43	20·20	23·37	27·45	28·59	33·40	1·65
120	0·7714	11·80	14·98	17·37	19·97	23·71	24·89	28·52	1·64
140	0·7557	10·19	12·71	14·82	16·94	20·43	21·44	24·48	1·65

The rotatory dispersion of the formal may be represented at 20° by the equation $[\alpha]_\lambda^{20°} = 10·83/(\lambda^2 - 0·033)$.

Ethyl d-β-octyl carbonate.

$t°$.	18	40	74	77	129	
$d_{4°}^{t°}$.	0·9136	0·8892	0·8586	0·8543	0·8052	

λ	6708	6402	6096	5896	5882	5790	5782	5700
$n_\lambda^{20°}$	1·4150	1·4159	1·4168	1·4175	1·4176	1·4180	1·4181	1·4189

λ	5461	5218	5153	5105	4358
$n_\lambda^{20°}$	1·4194	1·4214	1·4208	1·4209	1·4264

Rotatory power.

a_{5893} + 3·39° at 19°; 2·75° at 48°; 2·04° at 78°; 1·65° at 108°; 1·32° at 136°; 1·13° at 160°; 0·97° at 180°.

a_{5461} + 3·99° at 19°; 3·37° at 43°; 2·41° at 78°; 1·95° at 108°; 1·58° at 134°; 1·26° at 162°; 1·12° at 180°.

a_{4358} + 6·58° at 19°; 5·50° at 43°; 3·98° at 78°; 3·24° at 108°; 2·64° at 134°; 2·10° at 161°; 1·80° at 180°.

Values obtained from the smoothed curves.

$t°$.	20.	40.	60.	80.	100.	120.	140.	160.	180.
$d_{4°}^{t°}$.	0·9110	0·8913	0·8717	0·8521	0·8325	0·8130	0·7935	0·7740	0·7542
$[a]_{5893}^{t°}$	+7·37°	6·56°	5·74°	4·95°	4·28°	3·69°	3·28°	2·90°	2·57°
$[a]_{5461}^{t°}$	8·74	7·75	6·75	5·83	5·05	4·34	3·78	3·31	2·97
$[a]_{4358}^{t°}$	14·37	12·59	10·90	9·49	8·29	7·25	6·31	5·48	4·78

Di-d-β-octyl carbonate.

$d_{4°}^{t°}$ 0·8828 at 19°; 0·8608 at 45°; 0·8349 at 79°; 0·7843 at 138°.

λ	6708	6402	6096	5896	5882	5790	5782
$n_\lambda^{20°}$	1·4280	1·4288	1·4298	1·4305	1·4306	1·4309	1·4309

λ	5700	5461	5218	5153	5105	4675	4358
$n_\lambda^{20°}$	1·4313	1·4325	1·4335	1·4341	1·4343	1·4373	1·4399

Rotatory power.

a_{5893} + 6·82° at 13·5°; 5·63° at 49·5°; 5·21° at 60·5°; 4·60° at 90°; 4·11° at 114°; 3·90° at 138°.

a_{5461} + 8·02° at 13·5°; 6·57° at 49°; 6·04° at 61·5°; 5·33° at 86°; 4·74° at 117·5°; 4·34° at 133°; 4·26° at 148°; 4·12° at 156°.

a_{4358} + 13·26° at 13·5°; 10·72° at 50°; 10·04° at 62°; 8·90° at 86·5°; 7·71° at 116·5°; 7·20° at 136°; 7·00° at 151°; 6·83° at 155°.

Values obtained from the smoothed curves.

$t°$.	20.	40.	60.	80.	100.	120.	140.
$d_{4°}^{t°}$.	0·8820	0·8653	0·8488	0·8323	0·8158	0·7992	0·7829
$[a]_{5893}$	+15·00°	13·76°	12·50°	11·50°	10·73°	10·10°	9·71°
$[a]_{5461}$	17·60	15·96	14·43	13·28	12·39	11·65	11·00
$[a]_{4358}$	29·93	26·33	23·91	22·11	20·38	19·04	18·20

Tri-l-β-octyl orthoformate.

$d_{4°}^{t°}$ 0·8592 at 15°; 0·8140 at 56·5°; 0·7485 at 116·5°.
$n_D^{15°} = 1·4376$.

Rotatory power.

a_{5893} − 8·72° at 14·5°; 7·40° at 37°; 6·18° at 67°; 5·19° at 101°; 5·02° at 112·5°; 4·80° at 130°.

a_{5461} − 10·19° at 14·5°; 8·89° at 37°; 7·35° at 69°; 6·25° at 103°; 5·98° at 112°; 5·57° at 130°.

a_{4358} − 16·94° at 14·5°; 14·47° at 37°; 12·13° at 72°; 10·33° at 103°; 9·88° at 113·5°; 9·30° at 128°.

Values obtained from the smoothed curves.

$t°$.	20.	40.	60.	80.	100.	120.
$d_{4°}^{t°}$.	0·8535	0·8319	0·8100	0·7881	0·7665	0·7448
$[a]_{5893}$	$-19·58°$	$17·50°$	$15·84°$	$14·47°$	$13·60°$	$13·22°$
$[a]_{5161}$	23·09	20·98	19·30	17·52	16·31	15·57
$[a]_{4358}$	38·13	34·38	31·80	29·42	27·40	25·79

Di-d-β-*octyl sulphite.*

$d_4^{17°} = 0·9264$

λ	6708	6402	6096	5896	5882	5790	5782
$n_\lambda^{20°}$	1·4401	1·4412	1·4422	1·4429	1·4430	1·4435	1·4436
λ	5700	5461	5218	5153	5105	4358	
$n_\lambda^{20°}$	1·4438	1·4449	1·4462	1·4467	1·4469	1·4530	

Rotatory power.

λ	6708	5893	5461	4555 *	4481 *	4358	4144 *
$[a]_\lambda^{17°}$	$-14·09°$	$18·43°$	$21·98°$	$32·4°$	$35·1°$	$37·80°$	$40·5°$
λ	4085 *	3998 *	3912 *	3830 *			
$[a]_\lambda^{17°}$	$43·2°$	$45·8°$	$48·5°$	$51·3°$			

* Photographic measurements.