CCLXXXV.—*The Rotatory Dispersion of Certain Isomeric Butyl Esters of* l-*Mandelic Acid.*

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The interesting points associated with these esters are that mandelic acid is the simplest hydroxy-acid in the aromatic series and is analogous to lactic acid in the aliphatic series; both *l*-mandelic and *l*-lactic acid are configuratively related to *d*-tartaric acid, but the esters of the first exhibit rotatory dispersion entirely in the negative region, whereas the esters of the second in the homogeneous condition exhibit rotatory dispersion which is situated in general in the positive region (Wood, Such, and Scarf, J., 1923, **123**, 600; 1926, 1928).

Rotatory Power.

The following table indicates that the primary branching of the *n*-butyl chain enhances very considerably the high negative rotation of the *n*-ester; further branching of the chain to the *tert*.-ester brings about a diminution of negative rotation.

Specific rotations $[\alpha]_{\lambda}^{t^{\circ}}$ of *l*-mandelates at 45° and 75°.

Ester.	λ 6708.	λ 5893.	λ 5461.	λ 5086.	λ 4359.
			Temp. 45°.		
n-Butyl	−66·3°	−91·1°	−111·0°	−133·6°	−189·0°
*iso*Butyl	73·7	101·9	123·5	148·8	214·3
tert.-Butyl	56·4	78·0	94·5	114·1	162·6
d-*sec*.-Butyl	48·2	67·5	82·0	99·2	151·1
			Temp. 75°.		
n-Butyl	−61·3°	−84·3°	−102·1°	−122·4°	−174·0°
*iso*Butyl	68·0	93·1	113·0	134·8	192·0
tert.-Butyl	52·8	72·9	88·2	106·5	152·8
d-*sec*.-Butyl	44·3	61·5	75·0	90·75	140·1

These results are analogous with respect to the zero axis to those obtained for the alkyl *l*-lactates situated in the positive region, and it appears, therefore, that in both cases the esters, of relative configuration " *d*," formed from a primary *iso*-alcohol have greater rotatory power than the esters of the corresponding normal alcohol, and that further branching of the chain, resulting in the tertiary esters, effects a diminution in rotatory power. The changing alkyl group is contrasted with the strongly negative phenyl group in the mandelates and compared with the positive methyl group in the lactates, and the progressive change of the alkyl grouping leads to a regularity in rotatory effect in the positive and the negative region respectively. The mere comparison of the position of the dispersion curves with respect to the zero axis does not infer a relative configuration relationship. The types of symmetry (Wood, Such, and Scarf, *loc. cit.*) and of asymmetry produced with the accumulation of identical radicals near the asymmetric carbon atom result in a similar relative position of the dispersion curves of the normal, *iso*-, and *tert.*-esters for "*d*"-mandelic and "*l*"-lactic acids.

d-*sec.*-Butyl *l*-mandelate, containing two centres of optical asymmetry of opposite rotatory power and of the same relative configuration, exhibits a marked decrease in specific rotation which is very pronounced in the violet end of the spectrum. The effect of the active mandelic acid radical, however, dominates the rotatory power, which in all cases is high.

Rotational Displacements in Related Series.

Consideration of Table I shows that (1) the molecular rotatory power is displaced to the right as the normal series of esters is ascended, particularly in passing from the methyl to the ethyl ester; (2) the molecular rotations of the *iso*-esters of lactic, tartaric, glyceric (*iso*butyl), and malic (*iso*butyl) acids are greater than those of the corresponding normal esters, these being situated in the positive region; (3) the molecular rotations of the *iso*-esters of mandelic, α-hydroxybutyric, and glyceric (*iso*propyl) acids exhibit a reverse behaviour, being displaced towards the left; (4) both the tertiary esters of lactic and mandelic acids are displaced towards the zero axis.

The above compounds are of relative configuration "*d*," and although observation (1) may serve in general (Clough, J., 1918, **113**, 526) as a criterion for configuration, no such rule can be applied to the relationship between the *n*-, *iso*-, and *tert.*-esters.

The *n*-esters of tartaric, lactic, hexahydromandelic (Wood and Comley, J., 1924, **125**, 2630), and mandelic acids form an interesting group; for the group, as well as each series, shows a displacement towards the right, the mandelic acid series being situated far down in the negative region, the hexahydromandelic acid series almost on the zero axis, and the tartrates and lactates in the positive region.

In the acetyl and benzoyl derivatives of mandelic acid, acetylation causes a similar displacement of the rotations of both the methyl and the ethyl esters, without change of order, further into the negative region (Freudenberg and Markert, *Ber.*, 1925, **58**, 1753). Similar displacements occur for the diacetyl- and dibenzoyl-*d*-tartrates, as indicated by Table II. (The temperatures 30°, 90°, and 110° have been taken to avoid extrapolation.) When the lactates are considered, however, acetylation causes a *right* displacement without change of order (Freudenberg and Markert, *Ber.*,

TABLE I.

Molecular rotations $[M]_D^{t^\circ}$ of esters.

	CH_3.	C_2H_5.	C_3H_7.	C_4H_9.	C_8H_{17}.	Temp.
l-Mandelic acid.						
n-Esters	−255·5[1]	−210·3[1]	−191·3[1]	−189·6		45°
iso-Esters				−212·1		
tert.-Esters				−162·4		
l-Lactic acid.						
n-Esters	+8·59	+13·37	+17·44	+19·58	+19·85[2]	20
iso-Esters				+22·16		
tert.-Esters				+13·8		
d-Tartaric acid.						
n-Esters			+29·34[3]	+26·75[4] (21·5°)	+31·87 (45°)	20
iso-Esters			+48·91[3]	+46·50[3]		
d-Malic acid.						
n-Esters	+11·10[5]	+19·34[5]	+25·33[5]	+26·37[6]		20
iso-Esters			+22·69[5]	+27·40[5]		
d-α-Hydroxy-butyric acid.						
n-Esters		+2·51[7]		+15·5[7]	+11·45[7] (18°)	15
iso-Esters				+12·32[7]		
l-Glyceric acid.						
n-Esters	+5·76[8]	+12·30[8]	+19·15[8] (17°)	+21·37[8] (17°)	+22·28[8] (19°)	15
iso-Esters			+17·5[8]	+23·05[8] (18—19·5°)		

[1] Deduced from values obtained by Walker, *J. Physical Chem.*, 1909, **13**, 574.

[2] Nonyl ester.

[3] Patterson, J., 1913, **103**, 145.

[4] Frankland and Garner, J., 1919, **115**, 636.

[5] Walden, *Z. physikal. Chem.*, 1895, **17**, 248.

[6] Anschütz and Reitter, *ibid.*, 1895, **16**, 493.

[7] Guye, *Bull. Soc. chim.*, 1896, **15**, 477.

[8] Frankland and MacGregor, J., 1893, **63**, 1415.

TABLE II.

	Temp.	$[M]_\lambda^{t^\circ}$. 6708.	5893.	4678.	Type of dispersion.
Methyl tartrate	20°	+ 4·47°	+ 3·67°	− 6·74°	Anom.
Ethyl ,, ...	20	+14·50	+16·14	+11·54	,,
Methyl ,, ...	100	+10·06	+11·28	+ 7·33	,,
Ethyl ,, ...	100	+23·11	+27·89	+33·62	,,
Methyl ,, ...	150	+11·4	+13·53	+11·53	,,
Ethyl ,, ...	150	+24·89	+30·62	+39·51	,,
Methyl acetyltartrate	90	+ 5·13	+ 4·71	− 1·34	,,
Ethyl ,, ...	90	+28·36	+35·13	+42·68	,,
Methyl diacetyltartrate ...	110	−13·27	−20·03	−46·76	,,
Ethyl ,, ...	110	+17·41	+20·33	+18·82	,,
Methyl ,, ...	150	− 5·82	− 9·91	−27·66	,,
Ethyl ,, ...	150	+23·29	+28·4	+33·56	,,
Methyl benzoyltartrate ...	30	+11·91	+11·43	− 2·06	,,
Ethyl ,, ...	30	+48·07	+59·17	+72·56	,,
Methyl ,, ...	150	+13·82	+15·32	+ 8·58	,,
Ethyl ,, ...	150	+40·46	+50·29	+65·43	,,
Methyl dibenzoyltartrate ...	150	−167·8	−236·1	−460·2	Complex
Ethyl ,, ...	150	−157·1	−221·5	−437·4	,,

1927, **60**, 2447), and it is noteworthy that the temperature–rotation curves are at maxima. On benzoylation a change of order occurs with displacement into the negative region (Freudenberg and Rhino, *Ber.*, 1924, **57**, 1547).

The *d*-malates afford an almost exact parallel, except that the benzoyl derivatives are in the positive region (Walden, *Z. physikal. Chem.*, 1895, **17**, 245; Frankland, J., 1899, **75**, 337).

The peculiar displacement of the methyl with respect to the ethyl ester was first noted by Frankland (*loc. cit.*; compare also the *o*-, *m*-, and *p*-toluoyl derivatives, in which this order persists).

The rule that a hydroxy-acid of " *d* " configuration shows a right displacement in passing from the methyl to the ethyl ester is broken by the benzoyl-lactates, the rotational values of which are far removed from the region of anomaly and in the negative region; it is also broken by the *d*-benzoylmalates and they are situated in the region of anomaly and exhibit positive rotation (Freudenberg and Noë, *Ber.*, 1925, **58**, 2404).

l-Glyceric acid (" *d* ") obeys the rule for the esters of its acetyl derivative, but is exceptional with respect to those of its benzoyl derivative (Frankland and Price, J., 1897, **71**, 253). The di-*o*-, -*m*-, and -*p*-toluoyl derivatives are similar to the dibenzoyl esters in behaviour.

It is thus seen to be difficult to draw up a general rule connecting displacement and configuration for *iso*-esters, and esters of acetyl and benzoyl derivatives. A certain generality holds, however: when acetylation of the esters causes a displacement to the left, the order of the rotations is maintained in the benzoyl derivatives (*e.g.*, the mandelates and tartrates), and when it causes a displacement to the right, the order of the rotations is reversed in the benzoyl derivatives (*e.g.*, lactates and malates). In general, benzoylation of the esters causes a left displacement into the negative region, but the benzoylmalates are situated in the positive region, the methyl ester having suffered a right and the ethyl ester a left displacement.

In the case of the methyl and ethyl acetyltartrates, although the displacements are respectively left and right, yet a study of the dispersion and temperature–rotation diagrams shows that in both cases the rotational displacement has resulted in a more extended field of anomaly, the effect in both cases being similar. The corresponding benzoyl derivatives show rotationally right displacements (without change in order). The dispersion and temperature–rotation diagrams indicate that the methyl monobenzoyl ester has attained maxima for certain wave-lengths, whilst the ethyl ester has just passed maxima; here again the effects of benzoylation are similar. Owing to the detailed data available with respect to these esters a deeper interpretation of rotational values has been possible, resulting in exact comparison in particular regions of anomaly.

Although similar displacements occur in certain derivatives of mandelic and tartaric acids, yet it should be noted that, in the former, increase of the acyl chain of both the methyl and ethyl esters produces displacements to the right (from the data given by Walden, *Z. physikal. Chem.*, 1895, **17**, 706), whereas in the latter, displacements to the left occur (from data given by Frankland and Wharton, J., 1899, **75**, 337), resulting in the methyl esters being carried progressively further into the negative region and the ethyl ester from the positive to the negative region. The mandelates are allied in this respect to the malates which are situated in the positive region, the molecular rotational displacements moving only slowly further into the positive region with increase of the acyl chain.

Comparative data for lactic acid are afforded by the *iso*butyl ester and its derivatives (Wassmer and Guye, *J. Chim. phys.*, 1903–4, **1**, 257), in which the molecular rotation passes through a maximum at the propionyl derivative :

$[M]_D$	+22·5	+91·2	+95·8	+82·7	
t	18°	20°	18·5°	19°	
	Ester.	Acetyl-	Propionyl-	Butyryl-	derivative.

The observations of Freudenberg and his collaborators with respect to certain derivatives of the amino-acids are of importance. The following data indicate a *right* rotational displacement on passage from the methyl to the ethyl ester, both compounds being of configuration denoted by "*l*" :

Methyl acetyl-*l*-aspartate	$[M]^{20^\circ}_{5780}$	−31°;	$[M]^{100^\circ}_{5780}$	−25°
Ethyl ,, ,,	,,	−21°;	,,	−18° *
Methyl benzoyl-*l*-alanine	$[M]^{19^\circ}_{5780}$	+13·7°		
Ethyl ,, ,,	$[M]^{20^\circ}_{5780}$	+98·6° †		

* Freudenberg and Noë, *Ber.*, 1925, **58**, 2399.
† Freudenberg and Rhino, *Ber.*, 1924, **57**, 1547.

Thus this empirical method breaks down when applied to the naturally occurring amino-acids. Anomaly, however, is a true criterion for their configuration.

Rotatory Dispersion.

The dispersion ratios for the *n*-, *iso*-, and *tert.*-esters are sensibly constant as indicated in the table below.

Ester.	λ 6708.	λ 5893.	λ 5461.	λ 5086.	λ 4359.
		Dispersion ratios at 45°.			
n-Butyl	0·602	0·821	1	1·207	1·703
*iso*Butyl	0·598	0·820	1	1·203	1·715
tert.-Butyl	0·601	0·823	1	1·204	1·720
d-*sec*.-Butyl	0·588	0·823	1	1·210	1·843
		Dispersion ratios at 75°.			
n-Butyl	0·603	0·828	1	1·203	1·705
*iso*Butyl	0·602	0·821	1	1·195	1·708
tert.-Butyl	0·600	0·829	1	1·208	1·730
d-*sec*.-Butyl	0·590	0·820	1	1·210	1·868

The slight irregularity for the tertiary ester, particularly for 75° and λ 4359, was confirmed on a new preparation of the ester. The dispersion curves tend to diverge from the corresponding curves of the *n*- and *iso*-esters and to become steeper on proceeding into the violet end of the spectrum. Thus the substitution of branched chains for the normal chain has apparently little effect on the value of the dispersion ratios, as in the results obtained for the corresponding esters of lactic acid. The magnitudes of the ratios vary considerably on proceeding from the lactates to the mandelates.

The ratios for *d*-*sec*.-butyl *l*-mandelate show greatest divergence from an average value for light of short wave-length.

It is to be noted that the ratio $[\alpha]^{t°}_{4359}/[\alpha]^{t°}_{5461}$ lies above the minimum value 1·57 for cases of simple rotatory dispersion. All the esters exhibit normal and complex rotatory dispersion. The chief points of interest with regard to the dispersion diagrams are: (1) The curves obtained by plotting $1/\alpha$ against λ^2 show curvature; (2) increase of temperature decreases the rotation; (3) the dispersion curves are very nearly parallel, only slight convergency and divergency occurring at the red and blue ends of the spectrum, respectively; (4) no intersections take place in either the α–λ or $[\alpha]$–λ curves; (5) the dispersion is allied to that of the lower normal esters of *l*-hexahydromandelic acid (Wood and Comley, J., 1924, **125**, 2630), *i.e.*, it is similar in general character to that exhibited by certain of the *n*-alkyl *l*-lactates in the positive region. From a consideration of (3), (4), and (5), it is inferred that the esters are not in proximity to the region of anomaly.

The rotatory dispersion exhibited by *d*-*sec*. butyl *l*-mandelate is a simple example of the superposition of the partial rotations of two asymmetric centres in a single molecule (the centres possessing rotations of opposite sign and different dispersion ratios). The esterification of mandelic acid, which has a high negative rotation ($[\alpha]^{20°}_{D}$, in water, 156·8°), with *sec*.-butyl alcohol, which has a low positive rotation ($[\alpha]^{27°}_{D}$ 13·56°), results in the formation of an ester showing a decrease of rotation compared with the other isomeric esters investigated, the effect not being marked enough to cause the appearance of visual anomaly, and the dispersion data indicate the dominant centre to be the asymmetric mandelyl group. It follows, therefore, that the partial rotations of the two asymmetric centres should be of comparable magnitude for visual anomaly. This case is different from that of *d-sec.*-butyl *d*-lactate, in which the rotatory powers of the two centres are comparable and favourable for anomaly in the visible region.

Effect of Change of Temperature.

The esters are sensitive to temperature change, the change in rotatory power being more pronounced in the blue region of the spectrum; an increase in temperature causes a decrease in rotation. The temperature–rotation curves for the longer wave-lengths are nearly linear, but as the wave-length decreases the curvature increases uniformly. They form a series of curves converging to a small extent in the direction of increase of temperature; they are slightly convex and inclined to the axis of zero rotation. Curvature is most apparent in the *d-sec.*-butyl ester. Unsuccessful attempts were made with certain of these esters to see whether at higher temperatures a more definite change in curvature could be realised.

The temperature range over which the esters were investigated was comparatively small owing to the low decomposition and racemisation temperature, which occurred at 105—110°, for the *n*-, *iso*-, and *d-sec.*-esters, and at 95—100° for the tertiary ester.

EXPERIMENTAL.

Resolution of Mandelic Acid.—Mandelic acid was resolved by the precipitation and fractional crystallisation of its morphine salt (McKenzie, J., 1899, **75**, 966) with the following modification. 50 G. of mandelic acid (1 mol.) were neutralised with 95 g. of morphine (1 mol.) in 400 c.c. of water and evaporated on a water-bath to a gum; while this was still warm, 400 c.c. of alcohol were added and the mixture was allowed to cool; addition of a nucleus of the pure active salt and vigorous stirring and scratching then precipitated the impure morphine *l*-mandelate, m. p. 185°, rising to 223—224° after two recrystallisations from absolute alcohol; $[\alpha]_D^{18^\circ}$ — 110·5° in water ($c = 0{\cdot}9499$; $l = 2$). Yield, 47 g. The alkaloid was precipitated from an aqueous solution of the salt with ammonia and filtered off, the acidified solution extracted with ether, the extract dried, the solvent distilled, and the acid recrystallised from benzene; m. p. 133·5°; $[\alpha]_D^{20^\circ}$, in water, —157·2° ($c = 2{\cdot}01$; $l = 2$). This was the highest rotation observed in a large number of resolutions.

Resolution by means of quinine was best effected from dilute alcohol. Mandelic acid (7·6 g.; 1 mol.) and quinine (8·1 g.; ½ mol.) dissolved in 200 c.c. of 40% alcohol were gradually cooled to 0°. Crystallisation proceeded slowly, and the salt recrystallised from absolute alcohol had m. p. 180—181° (decomp.) and $[\alpha]_D^{21°}$, in alcohol, $-143·3°$ ($c = 0·579$; α $-1·66°$; $l = 2$). McKenzie (*loc. cit.*) gives 202° for the *l*-salt and 180° for the *d*-salt. The *l*-mandelic acid obtained after decomposition of the salt and recrystallisation from water had $[\alpha]_D^{20°}$ − 156·6° (c = approx. 2% in water); yield, 55%.

n-*Butyl* l-*Mandelate*.—Concentrated sulphuric acid (2·6 g.) was added carefully to a mixture of 8·7 g. of *l*-mandelic acid and 13 g. of *n*-butyl alcohol (b. p. 117°); the mixture was refluxed for 8 hours on a water-bath, diluted with dry ether, neutralised with potassium carbonate, filtered, dried over anhydrous sodium sulphate, and the ether evaporated. Excess of alcohol was removed at a low temperature in a vacuum. The *ester* was dissolved in light petroleum (b. p. 40—60°) and cooled in a freezing mixture; the resulting crystals were recrystallised eight times and obtained in long, colourless needles, m. p. 38·5° (corr.). Yield, 7·8 g. (62%) (Found: C, 69·05; H, 7·7; equiv. by saponification, 207·8. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%; equiv., 208·2).

Comparative data available for this ester are as follows:

	Smiles and Walker (*J. Physical Chem.*, 1909, **13**, 580).	Present authors.
M. p.	31°	38·5°
$d_{4°}^{50°}$	1·0460	1·0443
$d_{4°}^{60°}$	1·0370	1·0355
$[M]_D^{50°}$	−192·2°	−186·99°
$[M]_D^{60°}$	−187·4°	−181·79°

Rotations were taken with a 1 dcm. tube. The rotatory dispersion is complex.

The ester decomposed at about 110°. Densities determined:

Temp.	39·1°	61·1°	80·0°	102·7°
$d_{4°}^{t°}$	1·0536	1·0346	1·0182	0·9983

	$d_{4°}^{43·2°} = 1·0504$.	$d_{4°}^{61·5°} = 1·0345$.	$d_{4°}^{81°} = 1·0174$.	$d_{4°}^{102·1°} = 0·9988$.
λ.	$[\alpha]_\lambda^{43·2°}$.	$[\alpha]_\lambda^{61·5°}$.	$[\alpha]_\lambda^{81°}$.	$[\alpha]_\lambda^{102·1°}$.
6708	−67·02°	−63·61°	−60·00°	−56·67°
6563	70·62	67·07	63·26	59·61
6438	73·88	70·29	66·49	62·40
6152	82·35	78·55	74·35	70·09
5893	91·77	87·37	82·90	78·92
5589	105·80	100·05	95·00	90·03
5461	111·71	105·79	100·10	95·31
5324	119·19	113·27	107·05	102·28
5086	134·32	127·38	120·50	115·04
4861	149·94	142·02	135·15	128·55
4678	164·03	155·73	148·22	141·25
4455	181·83	172·32	164·15	157·29
4359	190·21	180·03	171·62	164·90

iso*Butyl* l-*Mandelate*.—The preparation was similar to that of the normal ester [10 g. of *l*-acid, 15 g. of *iso*butyl alcohol (b. p. 106·5°), and 3 g. of sulphuric acid], and the crude ester purified as follows. A regulated current of dry air was drawn through a dilute solution of the ester in light petroleum (b. p. 40—60°), which was cooled in a freezing mixture. The gradual removal of the solvent caused crystallisation of the ester; eight to ten recrystallisations were necessary to give material of constant rotation and of m. p. 35·5° (corr.). Yield, 8·5 g. (60%) (Found: C, 69·1; H, 7·65; equiv., 208·4. Calc. for $C_{12}H_{16}O_3$: C, 69·2; H, 7·7%; equiv., 208·2). Walden (*Z. physikal. Chem.*, 1895, **17**, 706) gives $[M]_D^{20°}$ − 209°; $[\alpha]_D^{20°}$ −100·73°.

A 1 dcm. tube was employed for the measurements. The ester exhibits complex rotatory dispersion.

Above 105° decomposition of the ester was noted. Densities determined:

Temp.	38·5°	61·2°	80·1°	102·3°
$d_{4°}^{t°}$	1·0536	1·0337	1·0173	0·9977

	$d_{4°}^{42°}$ = 1·0506.	$d_{4°}^{59°}$ = 1·0357.	$d_{4°}^{81°}$ = 1·0165.	$d_{4°}^{99°}$ = 1·0007.
λ.	$[\alpha]_\lambda^{42°}$.	$[\alpha]_\lambda^{59°}$.	$[\alpha]_\lambda^{81°}$.	$[\alpha]_\lambda^{99°}$.
6708	−74·30°	−70·90°	−66·94°	−63·56°
6563	78·20	74·92	70·18	66·67
6438	81·97	78·53	73·58	69·82
6152	91·90	87·75	82·01	77·31
5893	102·65	97·68	91·34	86·01
5589	117·76	111·87	104·40	98·57
5461	124·58	118·32	110·78	104·23
5324	134·02	126·77	118·32	111·54
5086	150·35	142·03	132·54	125·65
4861	167·72	157·86	147·66	140·90
4678	184·27	172·98	161·45	153·99
4455	206·52	193·31	180·03	170·95
4359	217·01	202·97	188·65	179·03

tert.-*Butyl* l-*Mandelate*.—To a mixture of *tert.*-butyl alcohol (10 g.; b. p. 83°/760 mm.), *l*-mandelic acid (10 g.), and 10 c.c. of light petroleum (b. p. 75—80°), sulphuric acid (3 g.) was added in the cold and the mixture refluxed on a water-bath for 4 hours; 4—5 volumes of dry, light petroleum (b. p. 40—60°) were then shaken with the reaction mixture, and the upper layer was neutralised with potassium carbonate, filtered, dried over anhydrous sodium sulphate, and the ether evaporated. The excess of alcohol was removed in a vacuum, and the *ester* recrystallised 8 times, as for the preceding ester, to a constant rotation and m. p. 65°. Yield 6·8 g. (45%) (Found: C, 69·4; H, 7·8%; equiv., 208·6). A peculiarity was noted in the behaviour of samples of the esters when kept in a vacuum desiccator: the rotation increased and a compound of low m. p. was formed which rendered crystallisation of the ester difficult; this was most pronounced in the tertiary ester and may be due to the formation of a lactide or ether.

Rotations were taken in a 1 dcm. tube. The ester exhibits complex rotatory dispersion.

Decomposition was noted above 95°. Densities determined:

Temp.	19·0°	37·5°	59·6°	79·6°
$d^{t°}_{4°}$	1·0682	1·0520	1·0325	1·0146

	$d^{21°}_{4°}$ = 1·0665.	$d^{38·7°}_{4°}$ = 1·0507.	$d^{58·3°}_{4°}$ = 1·0335.	$d^{78·5°}_{4°}$ = 1·0157.
λ.	$[\alpha]^{21°}_{\lambda}$.	$[\alpha]^{38·7°}_{\lambda}$.	$[\alpha]^{58·3°}_{\lambda}$.	$[\alpha]^{78·5°}_{\lambda}$.
6708	−59·73°	−57·64°	−54·80°	−52·54°
6563	62·82	60·66	57·63	55·21
6438	65·86	63·63	60·47	58·08
6152	74·06	71·44	67·83	65·01
5893	82·70	79·53	75·55	72·32
5589	94·54	90·66	86·16	82·52
5461	100·20	96·03	91·48	87·46
5324	107·04	102·52	97·72	93·60
5086	121·11	116·02	110·20	105·63
4861	134·03	129·04	123·12	118·05
4678	146·65	141·20	135·02	129·98
4455	164·83	158·30	151·33	145·30
4359	172·40	165·75	157·85	151·64

d-sec.-*Butyl* l-*Mandelate.*—To a mixture of 8 g. of *d-sec.*-butyl alcohol (b. p. 99°/757 mm.; $[\alpha]^{27°}_{D}$ + 13·56°) and 10 c.c. of light petroleum (b. p. 75—80°), cooled in ice and salt, sulphuric acid (2·6 g.) was added, followed by 8 g. of *l*-mandelic acid. The mixture was refluxed on a water-bath for 6 hours and the *ester* isolated in a similar way to the tertiary ester; after 2 fractionations it had b. p. 88°/0·05 mm. and $\alpha^{20°}_{D}$ 77·50°. A further preparation gave the same result, and a third fractionation was unnecessary. Yield, approx. 6 g. (50%) (Found: C, 69·2; H, 7·6%; equiv., 208·4).

Hydrolysis of the ester. 4 G. of the ester were treated with caustic potash and steam-distilled; the recovered alcohol was converted into the hydrogen phthalate of m. p. 46—47°, $[\alpha]^{20°}_{D}$ + 38·9° (m. p. of original hydrogen phthalate 48°, and $[\alpha]^{20°}_{D}$ + 39·5° in alcohol). Acid hydrolysis and extraction with ether gave a specimen of acid which on recrystallisation once from benzene had m. p. 133°, $[\alpha]^{20°}_{D}$ −156·3° (m. p. of original acid 133·5°, and $[\alpha]^{20°}_{D}$ −156·8°).

A 0·5-dcm. polarimeter tube was employed, and the ester was found to exhibit complex rotatory dispersion. Decomposition was noted at 105—110°. Densities determined:

Temp.	3·0°	18·0°	43·5°	68·5°	93·0°
$d_{4^\circ}^{t^\circ}$	1·0746	1·0623	1·0410	1·0209	0·9992

	$d_{4^\circ}^{4^\circ}$ = 1·0742.	$d_{4^\circ}^{19 \cdot 8^\circ}$ = 1·0607.	$d_{4^\circ}^{49 \cdot 8^\circ}$ = 1·0360.	$d_{4^\circ}^{68 \cdot 2^\circ}$ = 1·0207.	$d_{4^\circ}^{91 \cdot 4^\circ}$ = 1·0014.
λ.	$[\alpha]_\lambda^{4^\circ}$.	$[\alpha]_\lambda^{19 \cdot 8^\circ}$.	$[\alpha]_\lambda^{49 \cdot 8^\circ}$.	$[\alpha]_\lambda^{68 \cdot 2^\circ}$.	$[\alpha]_\lambda^{91 \cdot 4^\circ}$.
6708	−56·34°	−52·89°	−47·90°	−45·63°	−42·86°
6563	59·43	55·76	50·04	47·73	44·99
6438	62·30	58·49	52·94	50·29	47·35
6152	69·88	65·63	59·50	56·32	53·04
5893	77·85	73·12	66·51	62·96	59·11
5589	89·51	84·07	76·14	72·18	67·84
5461	94·75	89·06	80·93	76·55	71·98
5324	101·32	95·18	86·58	82·14	76·95
5086	114·58	107·74	97·88	92·62	87·03
4861	128·99	121·71	110·56	105·09	98·66
4678	143·79	135·92	123·51	117·15	110·20
4455	163·30	154·25	140·33	133·57	126·48
4359	173·02	163·21	149·03	141·78	135·06

Summary.

1. In the isomeric butyl mandelates, the *iso*butyl ester shows an increase and the *tert.*-ester a decrease of negative rotation when compared with the *n*-ester. Pronounced decrease in rotation takes place when there are two asymmetric centres of opposite sign in the molecule, but without visual anomaly. For visual anomaly the partial rotations of the two asymmetric centres should be of comparable magnitude.

2. All the esters exhibit normal and complex rotatory dispersion.

3. Increase of temperature causes a decrease in rotation of the esters. No maxima or minima occur in the temperature–rotation diagrams.

4. Comparison of the rotation data of the *n*-, *iso*-, and *tert.*-esters affords no generalisation for relative configuration purposes.

5. Rotational displacements in related series are discussed as a guide to configuration.

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