CCLVI.—*The Rotatory Dispersion of the Esters of Lactic Acid. Part II. The Isomeric Butyl Esters.*

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Part I of this investigation (J., 1923, **123**, 600) described the rotatory dispersion of the normal esters of lactic acid and was undertaken as a preliminary step to afford a standard of reference for the work now described, *viz.*, the study of the isomeric butyl lactates with special reference to the effect of two simple asymmetric carbon atoms in the molecule.

Specific Rotations.

Considering the first two esters in the following tables, it is clear that the primary branching of the normal carbon chain results in an increase of rotatory power; further branching, as shown in the tertiary ester, brings about a considerable decrease.

Temp. 20°.	λ 6708.	λ 5893.	λ 5461.	λ 5086.	λ 4359.
n-Butyl *l*-lactate	+10·41°	+13·45°	+15·50°	+17·62°	+22·40
*iso*Butyl *l*-lactate	+11·72	+15·18	+17·55	+20·08	+25·97
tert.-Butyl *l*-lactate	+ 7·76	+ 9·45	+10·93	+12·44	+15·90
dl-sec.-Butyl *l*-lactate	+ 7·50	+ 9·44	+10·74	+12·03	+14·80
d-sec.-Butyl *l*-lactate	+16·02	+20·67	+23·91	+27·42	+35·37
d-sec.-Butyl *d*-lactate	− 1·53	− 1·83	− 1·83	− 1·54	+ 0·75
Temp. 110°.					
n-Butyl *l*-lactate	+11·53	+15·10	+17·68	+20·14	+26·56
*iso*Butyl *l*-lactate	+12·54	+16·48	+19·22	+22·13	+29·32
tert.-Butyl *l*-lactate	+ 8·35	+11·00	+13·00	+14·95	+19·37
dl-sec.-Butyl *l*-lactate	+ 9·86	+12·79	+14·73	+16·60	+20·74
d-sec.-Butyl *l*-lactate	+17·03	+21·90	+25·39	+28·95	+37·13
d-sec.-Butyl *d*-lactate	− 4·52*	− 6·03*	− 6·65*	− 7·05*	− 7·52*

* Temperature 100°.

The inactive secondary ester also shows a decrease of rotatory power to approximately the same extent as the tertiary ester.

Where there are two asymmetric centres of the same sign in the molecule, as in *d-sec.*-butyl *l*-lactate,† the rotation is considerably increased, whilst two asymmetric centres of opposite sign in the molecule, as in *d-sec.*-butyl *d*-lactate, result in a very pronounced decrease in the specific rotation. In each case, the effect is more pronounced for rotations in the violet end of the spectrum.

It is to be noted that the last member of the series is an ester of *dextro-* and not *lævo*-lactic acid, so that the numerical values, and not the sign of rotation (except the value for $[\alpha]^{20°}_{4359}$), can be compared with the values for the other esters.

It has been suggested (Hilditch, *Z. physikal. Chem.*, 1911, **77**, 482) that accumulation of identical radicals upon one carbon atom near the asymmetric centre produces a kind of symmetry resulting in a diminution of rotation. Our results support this idea. Rupe, however (*Trans. Faraday Soc.*, 1914, **10**, 5), cites the case of the molecular rotations of the menthyl esters of monomethyl-, dimethyl-, and trimethyl-acetic acids, where the symmetry of the last has no marked influence on the asymmetric system.

Dispersion Ratios and Dispersion.

The following table shows that the dispersion ratios for the temperatures 20° and 110° (except those for *d-sec.*-butyl *d*-lactate, which exhibits anomalous rotatory dispersion) are sensibly constant.

Temp. 20°.	λ 6708.	λ 5893.	λ 5461.	λ 5086.	λ 4359.
n-Butyl *l*-lactate	0·67	0·87	1	1·14	1·45
*iso*Butyl *l*-lactate	0·67	0·87	1	1·14	1·43
tert.-Butyl *l*-lactate	0·71	0·86	1	1·14	1·45
dl-sec.-Butyl *l*-lactate	0·70	0·88	1	1·12	1·38
d-sec.-Butyl *l*-lactate	0·67	0·87	1	1·15	1·48
d-sec.-Butyl *d*-lactate	0·84	1·00	1	0·84	−4·10

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† The esters of *l*-lactic acid are *dextro* rotatory.

Temp. 110°.	λ 6708.	λ 5893.	λ 5461.	λ 5086.	λ 4359.
n-Butyl *l*-lactate	0·66	0·86	1	1·14	1·50
*iso*Butyl *l*-lactate	0·65	0·86	1	1·14	1·51
tert.-Butyl *l*-lactate	0·64	0·85	1	1·15	1·49
dl-*sec.*-Butyl *l*-lactate	0·67	0·87	1	1·13	1·41
d-*sec.*-Butyl *l*-lactate	0·67	0·86	1	1·14	1·47
d-*sec.*-Butyl *d*-lactate	0·68*	0·91*	1*	1·06*	1·13*

* Temperature 100°.

A slight irregularity is observed for the *dl*-*sec.*-butyl ester, particularly in the region of shorter wave-length. The ratios differ only slightly from the values calculated for the normal alkyl lactates (*loc. cit.*). The ratios $[\alpha]^{t°}_{4359}/[\alpha]^{t°}_{5461}$ (except for *d*-*sec.*-butyl *d*-lactate) lie below the value 1·57, thus indicating complexity of the dispersion curves. The curves obtained by plotting $1/\alpha$ against λ^2 for all these esters show marked curvature. The irregularities noted for *d*-*sec.*-butyl *d*-lactate are due to the anomalous rotatory dispersion of this ester, by reason of which the ratios may vary considerably.

All the dispersion curves (except those for *d*-*sec.*-butyl *d*-lactate) are convex towards the axis of zero-rotation. The curves obtained for the *iso*-, *tert.*- and *dl*-*sec.*-esters are exactly similar in type to those obtained for the *n*-butyl ester, *i.e.*, similar in type to those of the *n*-alkyl lactates. They neither intersect nor show minima; further, each ester exhibits a distinct and similar spreading of the curves on passing to shorter wave-lengths; this holds even in the case of the *dl*-*sec.*-butyl *l*-ester, which shows that the dextro- and lævo-centres in the inactive secondary radical have no abnormal effect.

The curves for *d*-*sec.*-butyl *l*-lactate are remarkable for the absence of spreading, being almost parallel lines of convex curvature crossing the diagram, the rotation being considerably increased owing to the molecule containing two optically active centres of the same sign.

The curves for *d*-*sec.*-butyl *d*-lactate lie almost wholly in the negative region and are concave to the axis of zero-rotation except for light of short wave-length; those for the *l*-*sec.*-butyl *l*-ester, however, would lie almost wholly in the positive region and would be concave to the axis. Therefore the curvature has been reversed owing to the molecule containing two optically active centres of opposite sign and unequal rotation.

The dispersion of the *n*-alkyl lactates is in agreement with the conditions of Case III (Hunter, J., 1924, **125**, 1198) involving a two-term Drude equation in which $k_0 > k_1$ when $\lambda_0 > \lambda_1$. In this class may be included all the isomeric butyl lactates with the exception of *d*-*sec.*-butyl *d*-lactate. The type of dispersion is not changed in either the *dl-sec.*- or the *d-sec.*-butyl *l*-lactates, where there is more than one asymmetric centre in the molecule.

A different type of dispersion is exhibited by *d-sec.*-butyl *d*-lactate which is in accordance with Case IV (Hunter, *loc. cit.*), in which $k_0 < k_1$ when $\lambda_0 > \lambda_1$. The dispersion here is similar in every respect to the anomaly shown by the tartrates, crossing of the axis and minima occurring in certain of the rotation–dispersion curves. The minima move in the usual manner towards the violet end of the spectrum with increase of temperature and ultimately disappear.

According to Tschugaev, one of the factors giving rise to anomalous rotatory dispersion is "the superposition of the partial rotations produced by two asymmetric complexes within the molecule of an active body, the necessary condition being that these partial rotations should be of opposite sign and should possess different dispersion ratios." Up to the present the only substances exhibiting phenomena of this kind which have been carefully studied have contained two fairly complicated centres of activity (Tschugaev, *Ber.*, 1911, **44**, 2023; *Z. physikal. Chem.*, 1913, **85**, 481).

Two of the esters included in this paper, *d-sec.*-butyl *l*-lactate and *d-sec.*-butyl *d*-lactate, afford the simplest examples of compounds containing two asymmetric centres in the molecule, and where the rotations of the asymmetric complexes are of the same sign the rotatory dispersion remains complex in character in common with that of the other isomeric butyl lactates and the *n*-alkyl lactates (except, of course, *d-sec.*-butyl *d*-lactate); when, however, the rotations of the two asymmetric centres are of opposite sign, anomalous dispersion results.

Effect of Change of Temperature.—The temperature effect is small, as is the case with the *n*-alkyl lactates, lines of slight curvature concave to the axis (with the exception of those for *d-sec.*-butyl *l*-lactate) being obtained. Increase of temperature results in an increase in rotation (except in the case of *d-sec.*-butyl *d*-lactate at low temperatures and for short wave-lengths), the increase becoming more pronounced with decrease in wave-length.

Maxima occur in the temperature–rotation curves for *iso*butyl *l*-lactate. A similar observation was made with regard to *n*-butyl *l*-lactate, in which case, however, the maxima persisted farther into the blue end of the spectrum.

Curves for the *d-sec.*-butyl *l*-lactate are of the same general nature, except that they exhibit no maxima and are convex towards the axis of zero-rotation. In the latter respect they differ from all other temperature–rotation curves obtained for the lactates hitherto examined.

The temperature–rotation curves for different wave-lengths for the *d-sec.*butyl *d*-lactate show only an approach to maxima (for there is no intersection of the rotation dispersion curves), but intersection of these curves takes place in a manner precisely the same as in the cases of methyl and ethyl tartrates. The rotation in the red end of the spectrum for a lower temperature is less than for a higher temperature, but, as the wave-length decreases, the rotation increases more rapidly with temperature and intersection takes place; in addition, the maxima are apparently moving to a higher temperature with decrease of wave-length. Phenomena of the same kind are encountered in certain esters of tartaric acid which are anomalous.

Optical Superposition.

A point of interest with respect to optical superposition arises from the data given in the table on p. 1929. The three esters *d*-butyl *l*-lactate (having two rotations of the same sign, giving a large rotation), *d*-butyl *d*-lactate (having two rotations of opposite sign, giving a small rotation), and *dl*-butyl *l*-lactate (a solution of *d*-butyl *l*-lactate in *l*-butyl *l*-lactate) have a bearing on the validity of van 't Hoff's assumption.

sec.-Butyl *l*-lactates.	λ 6708.	λ 5893.	λ 5461.	λ 5086.	λ 4359.	
½ (*d*- + *l*-)	8·78°	11·25°	12·87°	14·48°	17·31°	Temp. 20°.
dl-	7·50	9·44	10·74	12·03	14·80	
Diff.	1·28	1·81	2·13	2·45	2·51	
½ (*d*- + *l*-)	10·68	13·87	15·91	17·88	22·20	Temp. 100°.
dl-	9·80	12·53	14·38	16·17	20·26	
Diff.	0·88	1·34	1·53	1·71	1·94	

It will be noted that the rotations for the ester (*dl*-alcohol *l*-acid) differ from the mean for the two esters (*d*-alcohol *l*-acid and *l*-alcohol *l*-acid *). The difference is beyond the experimental limits and increases on passing into the blue end of the spectrum. The differences from the mean given by Patterson and Buchanan (J., 1924, **125**, 2579) in the case of the methyl *n*-hexylcarbinyl dimethoxysuccinates also increase on passing from the red to the blue end of the spectrum. These examples indicate that measurements should be taken over as wide a range of wave-lengths as possible.

At the higher temperature, 100°, the differences are somewhat smaller. Our case is open to an objection, since the *dl-sec.*-butyl *l*-lactate is a solution of equal parts of the *d*- and *l*-butyl esters, a disadvantage which has been overcome in the examples selected by Patterson. These lactic esters afford no quantitative vindication of the rule and the values of the rotations calculated for wave-lengths in the neighbourhood of sodium light are outside the limits of experimental error.

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* Experimentally the ester *d*-alcohol *d*-acid was obtained.

Hudson (*J. Amer. Chem. Soc.*, 1925, **47**, 265, 543, 873) states that van 't Hoff's principle of optical superposition holds closely for the methylglucosides, galactosides, etc., the maximum deviation being about 4%, but his calculations are based on rotations for sodium light.

EXPERIMENTAL.

iso*Butyl* l-*Lactate*.—25 G. of dry zinc ammonium *l*-lactate, 80 c.c. of *iso*butyl alcohol (b. p. 109°/748 mm.), and 10·8 c.c. of concentrated sulphuric acid were heated together on a water-bath for 6 hours. The reaction mixture was treated similarly to *n*-hexyl *l*-lactate (Wood, Scarf, and Such, *loc. cit.*). After four fractional distillations the ester had b. p. 73·1°/13 mm. Yield 11 g. (38% of the theoretical).

The ester had a penetrating fragrant odour. In the following table its physical constants as found by the authors (W. S. and S.) are compared with those (G. and W.) found by Guye and Wassmer (*J. Chim. phys.*, 1903, **1**, 257).

	B. p. /13 mm.	$d_{4^\circ}^{18^\circ}$.	$d_{4^\circ}^{55^\circ}$.	$[\alpha]_D^{18^\circ}$.	$[\alpha]_D^{18^\circ}$ (calc.).	$[M]_D^{18^\circ}$.
(G. & W.)	72—75°	0·9760	0·9390	13·03°	15·4°	22·5°
(W. S. & S.)	73·1	0·9755	0·9378	15·13	—	22·18

Densities determined :

t°	8·3°	29·9°	57·1°	91·5°	120·5°	139·9°
$d_{4^\circ}^{t^\circ}$	0·9849	0·9636	0·9356	0·9015	0·8717	0·8523

The ester shows maxima in the temperature–rotation curves for longer wave-lengths and exhibits complex rotatory dispersion.

The following *specific rotations*—and all others recorded in this paper—were determined in a 1 dcm. tube.

	$[\alpha]_{\lambda}^{t^\circ}$.						
λ.	14·1°.	22·1°.	48·2°.	77·6°.	97·7°.	121·6°.	138·0°.
6708	+11·64°	+11·74°	+12·02°	+12·26°	+12·49°	+12·59°	+12·47°
6563	12·15	12·26	12·29	12·92	13·11	13·22	13·15
6438	12·67	12·77	13·10	13·47	13·67	13·80	13·74
6152	13·85	13·98	14·37	14·78	15·02	15·20	15·19
5893	15·08	15·21	15·65	16·09	16·37	16·60	16·64
5590	16·70	16·86	17·39	17·89	18·21	18·51	18·61
5324	18·28	18·46	19·11	19·67	20·04	20·40	20·53
5086	19·93	20·13	20·84	21·46	21·91	22·33	22·53
4861	21·54	21·76	22·52	23·29	23·79	24·33	24·60
4678	22·97	23·20	24·06	24·92	25·48	26·05	26·44
4455	24·89	25·16	26·13	27·12	27·77	28·53	28·90
4359	25·75	26·04	27·03	28·10	28·89	29·71	30·24
$d_{4^\circ}^{t^\circ}$	0·9791	0·9711	0·9445	0·9155	0·8950	0·8706	0·8541

tert.-*Butyl* l-*Lactate*.—*tert*.-Butyl alcohol, m. p. 25°, b. p. 82°/760 mm., was prepared in 78% yield by the Grignard reaction from magnesium methyl iodide and methyl acetate (Grignard, *Compt.*

rend., 1901, **132**, 336), with certain modifications in apparatus (see *J. Soc. Chem. Ind.*, 1923, **42**, 13T). Considerable difficulty was experienced in the preparation of this ester. The following methods were tried with the results indicated :

(1) Similar to the preparation of the *n*-alkyl lactates. Yield small owing to the decomposition of the alcohol by the acid.

(2) Esterification by hydrochloric acid under various conditions. Scarcely any ester was formed. The alcohol was attacked and a chloro-compound produced.

(3) A cyclic method (Frankland and Aston, J., 1901, **79**, 511) in which free *l*-lactic acid was employed. The yield was poor.

(4) A modification of the sulphuric acid method was adopted which gave better but by no means good yields. Three specimens of the ester were prepared in this way, the rotations of which, after vacuum distillation, were identical.

27 G. of dry zinc ammonium *l*-lactate were mixed with 25 g. of *tert.*-butyl alcohol, and 17 g. of concentrated sulphuric acid were slowly added with shaking. The mixture was heated at 60—70° for 7 hours. During the esterification a further 10 g. of the alcohol were added in small portions. The subsequent treatment was similar to that described for the *iso*butyl ester. After four fractional distillations 7 g. (22% of theoretical) of the ester were obtained, which had b. p. 46—47°/9 mm., $[\alpha]_D^{20^\circ}$ + 9·48°, $[M]_D^{20^\circ}$ + 13·84°, $d_{4^\circ}^{20^\circ}$ 0·9139. No comparative data are available (equivalent weight by saponification, 146·4. Calc. : 146·1).

Densities determined :

t°	0°	16·1°	48·8°	80·8°	112·7°
$d_{4^\circ}^{t^\circ}$	0·9328	0·9170	0·8865	0·8553	0·8242

The ester exhibits complex rotatory dispersion.

	$[\alpha]_\lambda^{t^\circ}$					
λ.	3°.	25°.	45°.	67·7°.	88·1°.	111·1°.
6708	+ 7·50°	+ 7·82°	+ 8·03°	+ 8·20°	+ 8·27°	+ 8·37°
6563	7·71	8·05	8·34	8·48	8·59	8·74
6438	7·93	8·27	8·63	8·82	8·95	9·10
6152	8·52	8·85	9·25	9·61	9·88	10·06
5893	9·16	9·55	9·95	10·37	10·68	11·04
5590	10·09	10·56	11·03	11·57	12·04	12·45
5461	10·48	11·02	11·60	12·10	12·61	13·07
5324	10·99	11·61	12·20	12·76	13·27	13·80
5086	11·92	12·59	13·19	13·85	14·42	15·01
4861	12·87	13·66	14·38	15·00	15·67	16·37
4678	13·66	14·54	15·26	15·99	16·64	17·41
4455	14·65	15·60	16·43	17·21	17·95	18·75
4359	15·10	16·08	17·00	17·91	18·68	19·41
$d_{4^\circ}^{t^\circ}$	0·9298	0·9090	0·8899	0·8681	0·8485	0·8260

d-sec.-*Butyl* l-*Lactate*.—The racemic *sec.*-butyl alcohol was obtained by the interaction of acetaldehyde and magnesium ethyl bromide. Resolution of the alcohol was effected by the method described by Pickard and Kenyon (J., 1912, **101**, 620) with slight modifications. The final product of *d-sec.*-butyl brucine phthalate had m. p. 159° (Pickard and Kenyon give 155°). The *d-sec.*-butyl hydrogen phthalate obtained from this salt had m. p. 48° and $[\alpha]_D^{20^\circ} + 39{\cdot}5^\circ$ (alcoholic solution). Pickard and Kenyon give m. p. 46—47° and $[\alpha]_D^{20^\circ} + 38{\cdot}9^\circ$. On hydrolysis 7·5 g. of *d-sec.*-butyl alcohol were obtained of b. p. 99°/760 mm. and $[\alpha]_D^{20^\circ} + 13{\cdot}89^\circ$.

Preliminary investigations showed that the best method for preparing higher lactic esters when only a small quantity of the alcohol was available was by intermolecular change from ethyl *l*-lactate. 17 G. of ethyl *l*-lactate, 7·5 g. of *sec.*-butyl alcohol, and 0·1 c.c. of concentrated sulphuric acid were maintained at 90—100° for 6 hours. The mixture was then treated as in the preparation of the other butyl esters, and yielded, after four fractional distillations, 7 g. of *d-sec.*-butyl *l*-lactate, b. p. 59°/7 mm. (oil-bath temperature, 90°): $[\alpha]_D^{20^\circ} + 20{\cdot}67^\circ$, $[M]_D^{20^\circ} + 30{\cdot}18^\circ$, $d_{4^\circ}^{20^\circ}$ 1·0041 (Found: C, 57·6; H, 9·6; *M*, by saponification, 145·6. $C_7H_{14}O_3$ requires C, 57·5; H, 9·6%; *M*, 146·1).

After hydrolysis of the ester the alcohol isolated had a rotation identical with that of the original.

Densities determined:

t°	0°	18·03°	49·5°	82·3°	140·0°
$d_{4^\circ}^{t^\circ}$	1·0247	1·0063	0·9732	0·9377	0·8789

The ester exhibits complex rotatory dispersion.

	$[\alpha]_\lambda^{t^\circ}$.					
λ.	2·1°.	23·9°.	51·0°.	74·1°.	110·8°.	137·8°.
6708	+15·99°	+16·03°	+16·23°	+16·45°	+17·08°	+17·58°
6563	16·70	16·73	16·93	17·15	17·83	18·32
6438	17·31	17·37	17·59	17·78	18·44	18·96
6152	18·98	19·03	19·21	19·47	20·11	20·66
5893	20·61	20·69	20·92	21·24	21·92	22·48
5590	22·85	22·94	23·20	23·49	24·30	24·92
5461	23·81	23·96	24·19	24·63	25·42	26·05
5324	25·00	25·14	25·42	25·79	26·66	27·28
5086	27·32	27·46	27·79	28·13	28·96	29·62
4861	29·65	29·81	30·13	30·51	31·33	32·03
4678	31·69	31·83	32·14	32·51	33·41	34·14
4455	34·07	34·25	34·57	35·05	36·01	36·84
4359	35·22	35·43	35·76	36·25	37·18	37·98
$d_{4^\circ}^{t^\circ}$	1·0227	1·0000	0·9717	0·9476	0·9094	0·8813

d-sec.-*Butyl* d-*Lactate*.—Attempts to obtain zinc ammonium *d*-lactate by the use of the alkaloids strychnine, brucine, codeine, narcotine, quinine and cinchonine gave negative results. The following method, an adaptation of that used to obtain the lævo-variety, was finally adopted.

One equivalent of morphine was added to slightly less (2%) than two equivalents of *N*-lactic acid, and the less soluble morphine *l*-lactate was removed by alternate evaporation and crystallisation. The resulting solution contained *d*-lactic acid and a little morphine *d*-lactate, all the *l*-lactic acid having been removed as the morphine salt. Ammonia was added, and the solution was filtered, boiled with zinc oxide, filtered again, and crystallised. Recrystallisation from dilute ammonia yielded pure zinc ammonium *d*-lactate, $[\alpha]_D^{17^\circ}$ − 10·05° (2·5 g. of salt in 50 c.c. of dilute ammonia).

d-*sec*.-Butyl *d*-lactate was obtained by intermolecular change from ethyl *d*-lactate, the latter ester being obtained from the zinc ammonium *d*-lactate. 8 G. of ethyl *d*-lactate ($[\alpha]_D^{19^\circ}$ − 11·26°, b. p. 53°/15 mm.), 8 g. of *d*-*sec*.-butyl alcohol, and 0·1 c.c. of concentrated sulphuric acid were heated on a water-bath for 12 hours. The mixture was then treated as in previous esterifications. Yield 5 g. of ester, b. p. 69—70°/16 mm. (oil-bath temperature, 100°), which gave constant rotation after four fractionations.

The ester had $[\alpha]_D^{20^\circ}$ − 1·83°, $[M]_D^{20^\circ}$ − 2·67°, $d_{4^\circ}^{20^\circ}$ 1·0047 (Found : C, 57·5; H, 9·7%; *M*, by saponification, 146·5).

After hydrolysis of the ester, the alcohol isolated had a rotation identical with that of the original.

Densities determined :

t°	0°	15·2°	39·2°	70·5°	98·0°
$d_{4^\circ}^{t^\circ}$	1·0255	1·0095	0·9847	0·9528	0·9243

The ester exhibits anomalous rotatory dispersion.

	$[\alpha]_\lambda^{t^\circ}$.				
λ.	2·5°.	17·0°.	44·5°.	76·5°.	100·0°.
6708	−0·42°	−1·34°	−2·84°	−4·01°	−4·52°
6563	−0·51	−1·45	3·00	4·25	4·83
6438	−0·58	−1·51	3·13	4·53	5·10
6152	−0·57	−1·60	3·37	4·95	5·60
5893	−0·50	−1·59	3·60	5·35	6·03
5590	−0·26	−1·55	3·78	5·67	6·46
5461	−0·12	−1·51	3·87	5·80	6·65
5324	+0·06	−1·39	3·90	5·88	6·81
5086	+0·50	−1·17	3·96	6·05	7·05
4861	+1·00	−0·84	3·92	6·13	7·22
4678	+1·65	−0·56	3·98	6·18	7·36
4455	+2·24	−0·06	3·51	6·18	7·50
4359	+2·60	+0·17	3·37	6·17	7·52
$d_{4^\circ}^{t^\circ}$	1·0230	1·0079	0·9797	0·9469	0·9225 (extrapolated)

At 120° the rotatory power of the ester indicated decomposition or racemisation.

dl-sec.-*Butyl* l-*Lactate.*—The ester was obtained by intermolecular change from active ethyl *l*-lactate by the method described under *d-sec.*-butyl *l*-lactate. 17 G. of ethyl *l*-lactate, 15 g. of *dl-sec.*-butyl alcohol, and 0·2 c.c. of concentrated sulphuric acid were heated at 95° for 5 hours, the mixture being subsequently treated as in the case of the other butyl esters. A 50% yield of *dl-sec.*-butyl *l*-lactate was obtained, which after four fractional distillations had b. p. 65—67°/12 mm. (oil-bath temperature, 100°), $[\alpha]_D^{20°}$ +9·45°, $[M]_D^{20°}$ + 13·80°, $d_4^{20°}$ 0·9968 (Found: C, 57·5; H, 9·7%; *M*, by saponification, 145·8).

The alcohol obtained after hydrolysis of the ester proved to be inactive.

Densities determined :

$t°$	−13°	1°	15·4°	53°	74·2°	88·5°	132°
$d_4^{t°}$	1·0313	1·0170	1·0015	0·9617	0·9395	0·9241	0·8780

The ester exhibits complex rotatory dispersion.

	$[\alpha]_\lambda^{t°}$.					
λ.	−10·8°.	0°.	21·9°.	56·5°.	86·6°.	125·8°.
6708	+ 6·35°	+ 6·79°	+ 7·57°	+ 8·69°	+ 9·56°	+10·00°
6563	6·62	7·11	7·87	9·02	9·93	10·42
6438	6·87	7·28	8·15	9·41	10·29	10·87
6152	7·37	7·83	8·81	10·19	11·18	11·96
5993	7·94	8·47	9·51	11·05	12·12	13·11
5590	8·61	9·20	10·42	12·16	13·35	14·50
5461	8·95	9·60	10·84	12·66	13·90	15·19
5324	9·31	9·99	11·31	13·27	14·57	16·63
5086	9·92	10·69	12·12	14·31	15·69	17·08
4861	10·50	11·34	13·01	15·36	16·88	18·35
4678	10·99	11·90	13·73	16·25	17·82	19·47
4455	11·62	12·58	14·59	17·27	19·00	20·73
4359	11·92	12·90	15·01	17·80	19·56	21·42
$d_4^{t°}$	1·0296	1·0180	0·9948	0·9579	0·9272	0·8847

Summary.

1. In the isomeric butyl lactates, the *iso*butyl ester shows an increase whilst the tertiary and inactive secondary butyl esters show a considerable decrease in rotation. Enhanced rotation results when there are two asymmetric centres of the same sign in the molecule (*d-sec.*-butyl *l*-lactate). Pronounced decrease in rotation occurs when there are two asymmetric centres of opposite sign in the molecule (*d-sec.*-butyl *d*-lactate).

2. All the esters examined are normal and complex with the exception of *d-sec.*-butyl *d*-lactate, which shows anomalous rotatory dispersion.

3. The effect of temperature on the rotation is in all cases small. Maxima occur in the rotation–temperature curves for the *iso*butyl

ester and intersections (similar in type to those found in several alkyl tartrates) take place in those for the anomalous ester, *d-sec.*-butyl *d*-lactate.

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