301.—*Studies in Stereochemical Structure. Part IV. Esters of (—)Menthol and the (—), (+), and* r-*Mandelic Acids.*

By Robert Roger.

The esters of (—)menthol and the three mandelic acids [(—), (+), and *r*-] have long been known and are well-defined crystalline solids (McKenzie, J., 1904, **85**, 378, 1254; McKenzie and Thompson, J., 1905, **87**, 1021; Findlay and Hickmans, J., 1907, **91**, 910; J., 1909, **95**, 1386; McKenzie and Müller, J., 1907, **91**, 1817; McKenzie and Wren, J., 1920, **117**, 680; McKenzie and Smith, J., 1923, **123**, 1962). McKenzie (*loc. cit.*) was unable to separate the *r*-mandelic ester into diastereoisomerides by intensive crystallisation, but found it to be a well-defined, homogeneous compound and not a simple mixture.

With a view to study the physical nature of this ester and the relationships of the asymmetric centres in the three esters, an investigation was made of the rotatory dispersions of the following compounds: *d*(—)-mandelic acid,* ethyl *d*(—)-mandelate, and the (—)menthyl esters of the three mandelic acids. The rotatory powers were determined for 5—8 wave-lengths between λ6708 and 4358 in various solvents, and within a temperature range of 40°. Rupe's criteria were applied in all cases, and showed that the dispersion of menthyl *r*-mandelate differs from those of the *d*- and *l*-esters.

Dispersion of d(—)-*Mandelic Acid.*—This acid was examined in acetone, ethyl alcohol, water, and chloroform, and the rotatory powers were very similar except in the last :

	CMe_2O.	EtOH.	H_2O.	$CHCl_3$.
$[\alpha]_{5893}$	− 158°	−154·5°	− 157·5°	− 188°

Lewkowitsch (*Ber.*, 1883, **16**, 1567) found $[\alpha]_{5893}$ −187·44° ($p = 17·5$) for this acid in acetic acid, a value very close to that in chloroform. The rotatory power increases with decreasing temperature; for instance, in chloroform :

t	2°	20°	39°
$[\alpha]_{5893}$	− 205°	−187·9°	− 177·8°

The values from λ6563 to λ4861 could be expressed by one-term

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* The terminology *d*(—)-mandelic acid is used to designate lævorotatory mandelic acid in accordance with the views of Freudenberg and Markert and of Clough. This terminology was also adopted formerly (Roger, *Helv. Chim. Acta*, 1929, **12**, 1060; *Biochem. Z.*, 1931, **230**, 320; Roger and McKay, J., **1931**, 2229).

Drude equations, but in certain solvents divergency was apparent for λ4358. Thus, in chloroform :

$$[\alpha] = 55{\cdot}24/(\lambda_2 - 0{\cdot}05319).$$

λ	6563	5893	5461	5109	4861	4358
[α], obs.	− 146·6°	− 187·9°	− 224·6°	− 265·5°	− 303·7°	− 409·5°
[α], calc.	− 146·3	− 188·2	− 225·4	− 266·1	− 301·6	− 403·7

The Rupe criteria (see Hagenbach, *Z. physikal. Chem.*, 1915, **89**, 570; Rupe, *Annalen*, 1915, **409**, 327; Rupe and Akermann, *ibid.*, 1920, **420**, 1; Rupe, *ibid.*, 1922, **428**, 188; Roger and McKay, J., 1931, 2229) were calculated on the data between λ6563 and λ4861 :

Solvent.	λ_0^2 (D.A.).	λ_0.	λ_α.	P.R.D.	q ($[\alpha]_{4861}/[\alpha]_{6563}$).
CMe_2O	0·05746	0·2397	634	152	2·082
$CHCl_3$	0·05319	0·2307	636	147	2·072
EtOH	0·05379	0·2320	639	148	2·063
H_2O	0·04764	0·2183	646	141	2·045

These figures are very consistent except that there is a slight lowering of the P.R.D. and a corresponding increase in the λ_α for the aqueous solution. From consideration of the various facts, the dispersion of *d*(−)-mandelic acid *is not simple but normal and complex*; the differentiation between simple and complex dispersion, however, is sometimes difficult (compare Lowry and Richards, J., 1924, **125**, 1593; Lowry and Lloyd, J., 1929, 1771).

Simple Esters of d(−)-*Mandelic Acid.*—Wood, Chrisman, and Nicholas (J., 1928, 2180) have described the dispersions of the isomeric butyl mandelates in the homogeneous states at various temperatures as " normal and complex." From their figures, the various dispersion criteria have been calculated from the standpoint of Rupe's views :

Ester.	λ_0^2 (D.A.).	λ_0.	λ_α.	P.R.D.	$[\alpha]_{4861}/[\alpha]_{6563}$.
n-Butyl	0·06498	0·2549	625	159	2·123
*iso*Butyl	0·06680	0·2584	623	161	2·144
tert.-Butyl	0·06494	0·2549	625	159	2·133
d-sec.-Butyl ...	0·07216	0·2689	613	165	2·182

Clearly the substitution of the various butyl radicals causes little change in the dispersions. Of especial interest is the *d-sec.*-butyl ester, in which two centres of asymmetry appear. The P.R.D. for this compound is increased, whilst λ_α is depressed, when compared with the other butyl esters. This depression is, however, hardly sufficient to warrant the application of the term " relative anomaly " originated by Rupe.*

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* Rupe and Kägi (*Annalen*, 1920, **420**, 33) define this term as follows: " Anscheinend normaler Verlauf der Kurve $1/[\alpha]$ über λ^2 gibt gerade Linien, aber λ_α und λ_0^2 weichen stark (ersteres wenigstens um ±15 $\mu\mu$) von den für die betreffende Körperklasse geltende Normalzahlen ab."

The dispersion of ethyl *d*(—)-mandelate has now been measured at 40° and 25° :

	Homog.	CMe_2O.	$CHCl_3$.	EtOH.
$[\alpha]_{5893}$	— 115°	— 86·2°	— 126°	— 104°

In chloroform the value of $[\alpha]_{5893}$ at 25° was —126° and at 2° it was —138°. The dispersion criteria were as follows :

	λ_0^2 (D.A.).	λ_0.	λ_α.	P.R.D.	*q*.
Homog.	0·05840	0·2417	632	153	2·086
CMe_2O	0·06154	0·2480	625	155	2·132
$CHCl_3$	0·06109	0·2472	630	156	2·104
EtOH	0·04497	0·2121	649	138	2·023

The value for λ_α in ethyl alcohol is much higher than the average (629) for the other solvents, and the P.R.D. is correspondingly lower. The constants for the homogeneous state and for acetone and chloroform solutions are in close agreement with those calculated from Wood, Chrisman, and Nicholas's figures for the isomeric butyl esters in the homogeneous states. *The dispersion of ethyl* d(—)-*mandelate is normal and complex,* as in the case of the butyl esters.

Wood, Such, and Scarf (J., 1926, 1928) have described the dispersions of certain esters of the optically active lactic acids as normal and complex. *Calculation of the dispersion criteria from their figures shows that in this case the complexity of dispersion is of a different nature from that displayed by the esters of* d(—)-*mandelic acid.* (Moreover, the effect of temperature on the rotations of the two classes of ester is also different.)

	λ_0^2 (D.A.).	λ_0.	λ_α.	P.R.D.	*q*.
n-Propyl lactate	— 0·01818	—	735	—	1·773
n-Butyl lactate	— 0·02412	—	766	—	1·747

Here the need for a two-term Drude equation for the expression of the dispersions is obvious. The dispersion coefficient (*q*) is below the value for simplicity (1·87) in each case. The negative values for the dispersion parameters are interesting (see Lowry and Owen, *Trans. Faraday Soc.*, 1930, **31**, 374). Rupe has given a few examples of negative λ_0^2 (compare Freudenberg and Rhino, *Ber.*, 1924, **57**, 1547). These negative values seem to arise only in certain types of complex dispersion.

This more marked complexity of dispersion in the lactates may be the result of substitution of the unsaturated phenyl group for the methyl group in glycollic acid. It is also of interest that mandelic acid does not obey the " amide rule " of Hudson. Kuhn (*Ber.*, 1930, **63**, 191) and Kuhn and Freudenberg (*Ber.*, 1931, **64**, 703) have shown that mandelic acid has a strong absorption band in the near ultra-violet due to the phenyl group. This group is highly anisotropic, and thus the rotation of derivatives of mandelic acid is not controlled by the anisotropy of the carboxyl group as in the case of derivatives of sugar acids. Possibly this explanation also accounts for the different results which are discussed later in connexion with superposition with the lactates and the mandelates.

Mandelates of (—)*Menthol.*—The dispersions of the (—)menthyl esters of *d*(—)-, *l*(+)-, and *r*-mandelic acid were measured in various solvents.

(—)*Menthyl* d(—)-*mandelate.* In the solvents used this ester was lævorotatory, and the rotations were affected by solvent and temperature :

	CMe_2O.	C_6H_6.	$CHCl_3$.	CS_2.	EtOH.
$[\alpha]_{5893}$ ...	− 114·3°	− 135·7°	− 140·3°	− 166°	− 138·3°

In carbon disulphide, $[\alpha]^{20°}_{5893}$ was —166° but it increased to —176° at 2°.

In acetone and benzene one-term Drude equations served to express the dispersions between the wave-lengths λ6563 and λ4358; in other solvents, however, a small divergency appeared, *e.g.*, for carbon disulphide :

λ	6563	5893	5461	5106	4861	4358
[α], obs.	− 130·9°	− 166°	− 199·5°	− 236·5°	− 267·3°	− 360·2°
[α], calc.	− 128·9	− 166·5	− 199·5	− 235·6	− 266·9	− 356·7

The dispersion criteria were :

	λ_0^2 (D.A.).	λ_0.	λ_a.	P.R.D.	*q*.
CMe_2O	0·04969	0·2230	646	144	2·031
C_6H_6	0·05613	0·2369	637	151	2·071
$CHCl_3$	0·05224	0·2285	639	146	2·066
CS_2	0·05225	0·2286	642	147	2·043
EtOH	0·04146	0·2036	666	136	1·988

Once again, in ethyl alcohol, there is a marked departure from the average of the P.R.D. in the other solvents. It is interesting to compare the Rupe criteria for this ester with those of (—)menthol and *d*(—)-mandelic acid. The average P.R.D. and λ_a for the acid are respectively 150 and 635, and for (—)menthol 104 and 683. From this it seems that it is the *d*(—)-mandelyl complex of the (—)menthyl *d*(—)-mandelate which is the dominant factor in the rotatory power of the ester. *The dispersion is normal and complex.*

(—)*Menthyl* l(+)-*mandelate.* This ester was lævorotatory in acetone and ethyl alcohol, but dextrorotatory in benzene and carbon disulphide. In chloroform at 25° it was lævorotatory for λ6563, the rotatory power was practically zero at λ6162, and for shorter wave-lengths it was dextrorotatory; with increase of temperature the point of zero rotation was displaced towards the violet region :

t.	λ = 6708	6563	6162	5893	5461	5106	4861	4358
− 14°	+ 2·3°	+ 3·0°		+ 5·2°	+ 8·8°	+ 13°	+ 17·8°	
+ 2		+ 1·7		+ 4	+ 7	+ 10·5		
25	− 1·4	− 0·9	− 0·06°	+ 0·7	+ 2·8	+ 5·9	+ 9·4	+ 21·2°
34	− 1·7	− 1·4		0	+ 1·8			
52		− 2·7		− 1·93	0		+ 3·3	

Similar results have been obtained by other authors (Pope and Winmill, J., 1912, **101**, 2309; Frankland, *Trans. Faraday Soc.*, 1914, **10**, 143; Wood and Nicholas, J., 1928, 1671; Lowry, J., 1929, 2858; Freudenberg and Rhino, *loc. cit.*).

In ethyl alcohol (—)menthyl *l*(+)-mandelate is lævorotatory, but a maximum is reached at λ5106 and thereafter the rotatory power decreases with decreasing wave-length :

λ	6563	5893	5461	5106	4861	4358
[α]	− 9·12°	− 10·5°	− 11·13°	− 11·2°	− 10·26°	− 6·1°

Tschugaev (*Ber.*, 1911, **44**, 2023) gives rotation curves of an exactly similar type for (—)menthyl (+)-β-camphorsulphonate, which is the classical example of the so-called " intramolekulare Anomalie."

In carbon disulphide, (—)menthyl *l*(+)-mandelate manifests its largest rotatory power and is normal and complex in dispersion as far as examined. Application of the equation $[\alpha] = 6{\cdot}901/(\lambda^2 - 0{\cdot}1307)$ showed that the observed and calculated values for the rotatory power agreed between λ6563 and λ5106, but thereafter diverged rapidly :

λ	6563	5893	5461	5106	4861	4358
[α], obs.	+ 23°	+ 31·8°	+ 41·6°	+ 52·9°	+ 63·9°	+ 97·3°
[α], calc.	+ 23	+ 31·9	+ 41·2	+ 53·1	+ 65·4	+116·5

In all other solvents there was no agreement between observed and calculated values for the rotatory powers on the basis of a one-term equation. The Rupe criteria emphasise the anomalous behaviour of this ester :

	λ_0^2 (D.A.).	λ_0.	λ_a.	P.R.D.	q.	*$\Delta \times 10^3$.
CMe_2O ...	− 0·07858	—	993	—	1·604	7·08
C_6H_6	0·1683	0·4103	530	218	4·905	18·2
$CHCl_3$	0·2412	0·4911	520	256	− 11·3	43·9
CS_2	0·1307	0·3615	547	198	3·502	27·9
EtOH	− 0·7700	—	2088	—	1·125	549

* See Rupe, Héritier, and Schaefer, *Annalen*, 1927, **459**, 324.

The dispersion coefficient, P.R.D., and λ_a show a very wide range. *The dispersion of the ester is complex and in certain solvents anomalous.*

(—)*Menthyl* r-*mandelate.* Temperature and solvent had little effect on the rotatory powers :

	CMe_2O.	C_6H_6.	$CHCl_3$.	CS_2.	EtOH.
$[\alpha]_{5893}$ =	− 70°	− 65·3°	− 70·2°	− 64·2°	− 73·2°

In ethyl alcohol, $[\alpha]_{5893}$ = − 74·1°, −73·2°, and − 72·6° for t = 3°, 25°, and 33°, respectively.

One-term Drude equations sufficed to express the dispersions in all solvents; *e.g.*, for carbon disulphide:

λ	6564	6162	5893	5461	5106	4861	4358
[α], obs.	− 51·3°	− 58·4°	− 64·2°	− 75·6°	− 87·8°	− 97·6°	− 124·7°
[α], calc.	− 51·3	− 58·5	− 64·3	− 75·8	− 87·7	− 97·7	− 124·7

The Rupe criteria indicate that there is a definite difference between the dispersion of this ester and those of the other two menthyl mandelates:

	λ_0^2 (D.A.).	λ_0.	λ_a.	P.R.D.	q.
CMe_2O	0·02583	0·1608	680	109	1·930
C_6H_6	0·02223	0·1491	682	102	1·927
$CHCl_3$	0·01835	0·1578	682	107	1·922
CS_2	0·02249	0·1499	688	103	1·904
EtOH	0·02949	0·1717	670	115	1·962

Here again the solution in ethyl alcohol shows a displacement of the P.R.D. and λ_a from the average in the other four solvents. The value of q is very close to that corresponding to simplicity, and the small variation of the rotatory power of this ester with temperature and solvent * and other facts all point to *its dispersion being simple.* The dispersion of (—)menthol and of (—)menthyl benzoate has been described by Rupe and Akermann (*loc. cit.*) and Lowry and Abram (J., 1919, **115**, 305) as simple; the ester was therefore prepared and the Rupe criteria calculated for it in order to make a direct comparison with (—)menthyl *r*-mandelate: the figures for the two esters are very close.

(—)*Menthyl benzoate.*

	λ_0^2 (D.A.).	λ_0.	λ_a.	P.R.D.	q.
CMe_2O	0·0255	0·1597	682	109	1·922
C_6H_6	0·0285	0·1687	678	114	1·933
EtOH	0·0333	0·1825	673	123	1·945

Once again, ethyl alcohol is exceptional as a solvent.

It will be seen that the dispersions of the three methyl mandelates vary considerably. That of the *r*-mandelate is simple, whilst that of the *d*(—)-mandelate is normal and complex; the dispersion of the *l*(+)-mandelate is complex but to a much greater extent than

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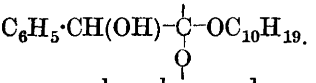
* Frankland and Garner (J., 1919, **115**, 636) summarise the position as regards these factors as follows: " In cases of normal dispersion the rotation value is little influenced by solution, change of temperature, and substitution. On the other hand, in cases of anomalous dispersion, the rotation is markedly affected by solution, change of temperature, and substitution. Between these two classes of substance, there are, of course, intermediate types." These authors found in the case of certain esters of tartaric acid that anomaly of dispersion could be made to disappear by alteration of temperature conditions (see also Wedekind and Maiser, *Z. Elektrochem.*, 1929, **35**, 438).

that of the *d*(—)-mandelate, and in certain solvents is definitely anomalous. This difference is not unexpected, for Tschugaev (*loc. cit.*) has shown that the (—)menthyl ester of (+)-β-camphorsulphonic acid displays a " totale intramolekular Anomalie " arising from the presence within the molecule of two asymmetric centres of different dispersive powers and of opposite influence. The dispersion, however, of the (—)menthyl ester of (—)-β-camphorsulphonic acid is normal. Rupe and Kägi (*loc. cit.*) found that, of the (—)menthyl esters of (—), (+), and *dl*-(diphenylmethyl)acetoacetic acids, only the ester of the (+) acid showed a " relative oder komplexe Anomalie." The dispersions of the other esters were normal :

(—)Menthyl ester of	λ_0^2 (D.A.).	λ_0.	λ_α.	P.R.D.	*q*.
(—)Acid	0·04875	0·2209	653	144	2·01
(+)Acid	— 0·01787	—	738	—	1·77
dl-Acid	0·02772	0·1665	679	113	1·93

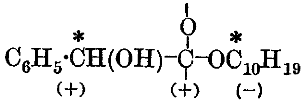
These results are very similar to those now obtained for the menthyl mandelates. The values for the P.R.D. and λ_α of the ester of the *dl*-acid are very similar to those of (—)menthol. With regard to the ester of the (+)acid, Rupe and Kägi have not realised the true " intramolekulare Anomalie " of Tschugaev, but they only carried out their measurements in benzene solution. Measurements in other solvents, such as have now been used with the menthyl mandelates, might also have revealed a true anomaly of dispersion in the case of (—)menthyl *d*-(diphenylmethyl)acetoacetate.

The complex and anomalous dispersion of (—)menthyl *l*(+)-mandelate may, therefore, be due to the presence of oppositely active centres of asymmetry in the one molecule (see Lowry and Cutter, J., 1925, **127**, 604) and constitutes another example of the " intramolekulare Anomalie " of Tschugaev. The dispersion of (—)menthol is simple and that of *l*(+)-mandelic acid almost simple, but the dispersive powers of these two parts of the ester molecule are different and opposite in influence. The two centres of asymmetry, however, are linked together by a carboxyl group, and it is possible that the dispersion of the menthyl mandelates is complicated by an induced asymmetry arising in the carbonyl constituent of the carboxyl group, thus,  $C_6H_5\cdot CH(OH)-\underset{O}{\overset{|}{\underset{|}{C}}}-OC_{10}H_{19}$. Induced asymmetry of the α-ketonic group has been advanced as an explanation of mutarotation phenomena observed with the (—)menthyl and other esters of α-ketonic acids by McKenzie and his co-workers (McKenzie and Mitchell, *Biochem. Z.*, 1929, **208**, 456, 471 ; 1930, **224**, 242 ; McKenzie and Ritchie, *ibid.*, 1931, **231**, 412 ;

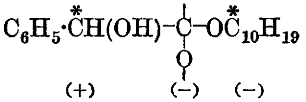
237, 11; compare Lowry and Cutter, J., 1925, **127**, 604). Richards and Lowry (J., 1925, **127**, 1503) have shown that elimination of the ketonic group in derivatives of camphor may lead to such a modification in the complexity of dispersion that it becomes almost simple.

It is therefore possible that in (—)menthyl *l*(+)-mandelate or (—)menthyl *d*(—)-mandelate there are three centres of asymmetry, two fixed and one induced. In the latter ester this induced centre of asymmetry is probably of the same influence as the two centres of fixed asymmetry (*viz.*, lævo-). In the former, however, this centre of induced asymmetry is under the influence of two antagonistic centres and may be controlled by the fixed centre of most dominant character. The Rupe criteria show that the rotatory power of the (—)menthyl *d*(—)-mandelate is dominated by the *d*(—)-mandelyl complex, the (—)menthyl part of the molecule exercising no important effect. (—)Menthyl *l*(+)-mandelate may therefore have one of the two configurations (I) and (II), the superposition of the

(I.)



$$C_6H_5\cdot\underset{(+)}{\overset{*}{C}}H(OH)-\underset{(+)}{\overset{\overset{|}{O}}{\underset{|}{C}}}-O\underset{(-)}{\overset{*}{C}}_{10}H_{19}$$



$$C_6H_5\cdot\underset{(+)}{\overset{*}{C}}H(OH)-\underset{\underset{(-)}{\underset{|}{O}}}{\overset{\overset{|}{*}}{C}}-O\underset{(-)}{\overset{*}{C}}_{10}H_{19}$$

(II.)

three partial rotations leading to anomalous dispersion. Solvates may be formed through this centre of induced asymmetry (see McKenzie and Mitchell, *loc. cit.*), and the exceptional dispersion criteria for ethyl-alcoholic solutions might be explained on such grounds. Hall (J., 1923, **123**, 32) has also shown that the dispersion of *d*-β-octyl succinate is complex in carbon disulphide but definitely anomalous in ethyl alcohol. Also, the observed rotatory power of a solution of (—)menthyl *l*(+)-mandelate may be the resultant of superposition of the rotations of two different forms of the ester, *viz.*, (I) and (II). The proportions of these esters and their rotatory powers would depend largely on the solvent and other physical conditions.

The simple dispersion of (—)menthyl *r*-mandelate and the close relationship of its dispersion to those of esters of simple acids and (—)menthol might be regarded as evidence of the existence of a true racemic compound in solution. From the evidence given by McKenzie it would seem that this ester is a true compound. It is sharp-melting, and crystallisation does not effect separation into the diastereoisomeric esters (compare, Findlay and Hickmans, *loc. cit.*). If a solution of (—)menthyl *r*-mandelate consists of the two diastereoisomerides (in equal amounts), what will the superposition of a complex and anomalous dispersion on a slightly complex dispersion give? First, the rotatory powers of the two diastereoisomeric esters were used to calculate the rotatory powers of the racemic ester; quite good agreement was obtained between the observed and calculated values on the basis of optical superposition. The agreement was good in ethyl-alcoholic solution, the maximum value of Δ being 2·9°, but still better in chloroform solution :

λ	6563	6162	5893	5461	5106	4861	4358
[α], obs. ...	− 55·6°	− 63·5°	− 70°	− 82·3°	− 95·6°	− 106·9°	− 137·1°
[α], calc. ...	− 56	− 63·9	− 70·2	− 82	− 96	− 106·1	− 137
Δ	0·4	0·4	0·2	0·3	0·4	0·8	0·1

In both these cases, the difference between the observed and calculated values is less than 4%, the maximum deviation allowed by Hudson (*J. Amer. Chem. Soc.*, 1925, **47**, 265). A similar agreement was found when equal amounts of (—)menthyl *d*(—)- and *l*(+)-mandelates were dissolved in chloroform ($c = 2{\cdot}703$, $l = 2$, $t = 20°$) :

[α], obs. ...	− 55·5°	− 63·5°	− 70·5°	− 82·9°	− 96·4°	− 106·9°	− 138·8°
Δ	0·5	0·4	0·3	0·9	0·4	0·8	1·8

Furthermore, solutions of equal concentration of the two diastereoisomeric esters were made in chloroform, placed in tubes of 1 dm., and the polarised light sent through the tubes successively; agreement was again found ($c = 2{\cdot}718$, $l = 1$, $t = 20°$) :

λ	6563	5893	5461	4861	4358
[α], obs.	− 55·2°	− 70·5°	− 82·6°	− 106·7°	− 138·6°
Δ	0·8	0·3	0·6	0·6	1·6

Biot (*Compt. rend.*, 1836, **2**, 543) produced anomalous dispersion by passing polarised light through successive tubes containing oil of lemon (dextrorotatory) and oil of turpentine (lævorotatory), both these substances being simple in dispersion. He obtained a similar result when he dissolved (+)camphor in (—)turpentine, although in this case the dispersion of (+)camphor is complex. Tschugaev (*Z. physikal. Chem.*, 1911, **76**, 469) also produced anomalous dispersion by using unequal mixtures of (—)menthone and (+)*iso*menthone. In all these cases, however, an anomalous dispersion has been created out of two simple ones, or from a simple and a complex dispersion. In the menthyl mandelates a simple dispersion is produced by the superposition of a complex on an anomalous dispersion. It is, of course, questionable how much stress can be laid on these " synthetic " dispersions, but one point emerges : the synthesis of a simple dispersion from the superposition of two separate solutions of (—)menthyl *d*(—)-mandelate and *l*(+)-mandelate shows that the simple dispersion of homogeneous (—)-menthyl *r*-mandelate cannot be accepted as evidence of the existence of a true racemic compound in solution.

Optical superposition has been previously noted in derivatives of the mandelic acids. Walden (*Z. physikal. Chem.*, 1895, **17**, 705 found that the law of optical superposition was obeyed by *dl*-amyl *d*(−)-mandelate, (−)amyl *r*-mandelate, and (−)amyl *d*(−)-mandelate, but since he did not use pure amyl alcohol (Marckwald and McKenzie, *Ber.*, 1901, **34**, 489), his data are vitiated. McKenzie and Smith (*loc. cit.*) also found agreement in the isomeric (−)-menthyl phenylchloroacetates (compare Wren and Wright, J., 1921, **119**, 798; Patterson and Buchanan, J., 1924, **125**, 2579; Patterson, Fulton, and Semple, J., 1926, 3226).

An interesting contrast to the (−)menthyl mandelates has been described by Wood, Such, and Scarf (*loc. cit.*), who investigated the question of superposition with certain lactates and found that the principle did not operate. They used *dl*- and *d*-*sec*.-butyl *l*-lactates and *d*-*sec*.-butyl *d*-lactate, and they give the following values for the observed and calculated rotations of the first :

λ	6708	5893	5461	5086	4359
$[\alpha]$, calc.	8·78°	11·3°	12·9°	14·5°	17·3°
$[\alpha]$, obs.	7·5	9·44	10·7	12·0	14·8
Δ	1·28	1·86	2·2	2·5	2·5

The difference exceeds 10% and increases towards the violet end of the spectrum. This difference between the lactates and mandelates may again be a consequence of the substitution of the methyl group by the unsaturated phenyl group in glycollic acid (see p. 2170).

EXPERIMENTAL.

d(−)-*Mandelic Acid.* (All rotations are negative.)

λ ...	6708	6563	6162	5893	5461	5106	4861	4358
(1) In water ($c = 2·1875$, $l = 2$, $t = 20·4°$).								
$[\alpha]$	—	121·6°	141·3°	157·5°	187·0°	220·1°	248·6°	334·3°
As above, but $t = 2°$.								
$[\alpha]$	—	128·7	—	165·0	196·3	—	261·9	—
As above, but $t = 39°$.								
$[\alpha]$	—	115·9	—	148·8	178·8	—	237	—
(2) In acetone ($c = 5·046$, $l = 1$, $t = 20°$).								
$[\alpha]$	115·9	122·9	141·3	158	189·9	224·9	255·9	—
(3) In chloroform ($c = 1·2825$, $l = 2$, $t = 38°$).								
$[\alpha]$	—	138·4	—	177·8	213·5	—	285	—
As above, but $t = 25°$.								
$[\alpha]$	138·4	146·6	168·8	187·9	224·6	265·5	303·7	409·4
As above, but $t = 2°$.								
$[\alpha]$	—	159·8	—	205·1	248	—	326·3	—
(4) In ethyl alcohol ($c = 2·8280$, $l = 2$, $t = 38°$).								
$[\alpha]$	—	111·9	—	143·0	171·9	—	230·2	—
As above, but $t = 21°$.								
$[\alpha]$	114·0	119·9	137·7	154·5	184·6	218·2	247·4	333·9
As above, but $t = 2°$.								
$[\alpha]$	—	134·1	—	167·6	202·0	—	271·6	—

The following (negative) values, amongst others, have been quoted for the rotatory power of *d*(—)-mandelic acid.

t.	*p*.	*c*.	*l*.	$[\alpha]_{5893}$.	Solvent.	Observer.
20°	8·62	—	1	159·73°	H_2O	Lewkowitsch, *Ber.*, 1883, **16**, 1567.
20	2·925	—	1	156·44	H_2O	
20	17·5	—	1	187·44	HOAc	
22	—	2·45	2	153·06	H_2O	Walden, *loc. cit.*
22	—	2·50	2	148*	CMe_2O	
20	—	4·69	1	158·2	H_2O	McKenzie, J., 1899, **75**, 753.
14	—	1·59	2	158	H_2O	Clough, J., 1925, **127**, 2808.
20	—	2·01	2	157·2	H_2O	Wood, Chrisman, and Nicholas, *loc. cit.*
—		2·32	—	154·4	H_2O	McKenzie and Wren, J., 1919, **115**, 602.

* Repeated determinations have failed to confirm this value, those obtained being always about — 158°.

Ethyl d(—)-*Mandelate*. (All rotations are negative.)

λ	6563	5893	5461	4861	4358
(1) Homogeneous ($D^{40°}$ = 1·1106, *t* = 39°).					
[α]	90·30°	114·7°	138·2°	188·4°	253·1°
(2) In acetone (*c* = 3·851, *l* = 2, *t* = 25°).					
[α]	66·86	86·21	104·3	143·3	189·7
(3) In chloroform (*c* = 2·012, *l* = 2, *t* = 25°).					
[α]	98·16	126·2	152·8	206·5	279·6
As above, but *t* = 2°.					
[α]	109·8	138·2	165·8	225·6	—
(4) In ethyl alcohol (*c* = 3·294, *l* = 2, *t* = 24·6°).					
[α]	82·62	104·4	124·2	167·1	224·4

Walden (*loc. cit.*) gives the following (negative) values for this ester : homog., $[\alpha]_{5893}$ 123·12°; in CMe_2O, $[\alpha]_{5893}$ 90·62° ($c = 5·81$, $l = 2$); in $CHCl_3$, $[\alpha]_{5893}$ 128·4° ($c = 6·67$, $l = 2$). Walker (*J. Physical Chem.*, 1909, **13**, 574) gives $[\alpha]^{70°}_{5893}$ 109·5°, $[\alpha]^{20°}_{5893}$ 125·4°. Clough (*loc. cit.*) gives $[\alpha]^{15°}_{5893}$ 129·4° for the homogeneous ester. It is questionable how much reliance can be placed on observations of the rotatory power in the liquid state when taken below the point of solidification.

(—)*Menthyl* d(—)-*Mandelate*. (All rotations are negative.)

λ ...	6708	6563	6162	5893	5461	5106	4861	4358
(1) In acetone (*c* = 2·8705, *l* = 2, *t* = 25°).								
[α]	86·5°	90·2°	—	114·3°	137·6°	—	183·2°	244·2°
(2) In benzene (*c* = 2·4130, *l* = 2, *t* = 25°).								
[α]	101·8	105·3	121·3°	135·7	162·9	192·9°	218·0	294·7
(3) In chloroform (*c* = 1·7715, *l* = 2, *t* = 21°).								
[α]	103·6	108·6	125·3	140·3	167·4	197·3	224·4	295·2
(4) In carbon disulphide (*c* = 2·8195, *l* = 2, *t* = 20°).								
[α]	123·6	130·9	149·6	166	199·5	236·5	267·3	360·2
As above, but *t* = 3°.								
[α]	—	137·3	—	175·9	209·3	—	283·7	—
(5) In ethyl alcohol (*c* = 3·863, *l* = 2, *t* = 20°).								
[α]	105·4	109·9	—	138·3	165·5	—	218·5	284·1

McKenzie and Findlay and Hickmans (*loc. cit.*) give $[\alpha]_{5893}$ 138·6° (c = 4·3732) and 140·9° respectively for the solution of this ester in EtOH.

(−)*Menthyl* l(+)-*Mandelate.*

λ ...	6708	6563	6162	5893	5461	5106	4861	4358
(1) In acetone (c = 6·7455, l = 2, t = 24°).								
$[\alpha]$	—	−18·17°	−20·39°	−21·9°	−24·8°	−27·7°	−29·1°	−30·8°
(2) In benzene (c = 7·4595, l = 2, t = 25°).								
$[\alpha]$	+3·75°	+ 4·16	+ 6·37	+ 7·44	+11·13	+15·81	+20·38	+37·4
(3) In chloroform (c = 13·487, l = 1, t = − 14°).								
$[\alpha]$	+2·3	+ 3·0	—	+ 5·2	+ 8·8	+13·3	+17·8	—
In chloroform (c = 8·7525, l = 2, t = 23°).								
$[\alpha]$	—	− 0·9	− 0·06	+ 0·74	+ 2·8	+ 5·94	+ 9·37	+21·2
In chloroform (c = 13·487, l = 1, t = 52°).								
$[\alpha]$	—	− 2·7	—	− 1·93	0·0	—	+ 3·26	—
(4) In carbon disulphide (c = 5·9055, l = 2, t = 24·5°).								
$[\alpha]$	+21·6	+22·95	+27·86	+31·76	+41·58	+52·91	+63·85	+97·3
(5) In ethyl alcohol (c = 7·454, l = 2, t = 34°).								
$[\alpha]$	−10·4	−11·0	—	−12·1	−12·7	—	−13·0	—
As above, but t = 24·5°.								
$[\alpha]$	− 9·26	− 9·12	− 9·73	−10·5	−11·13	−11·2	−10·26	− 6·1
As above, but t = 2°.								
$[\alpha]$	—	− 6·57	—	−6·24	− 6·44	—	− 3·09	—

Values in ethyl alcohol quoted for this ester are: $[\alpha]_{5893}$ = − 7·6° (c = 3·5956, McKenzie, *loc. cit.*); $[\alpha]_{5893}$ = − 9·45° (Findlay and Hickmans, *loc. cit.*).

(−)*Menthyl* r-*Mandelate.*

λ ...	6708	6563	6162	5893	5461	5106	4861	4358
(1) In acetone (c = 4·004, l = 2, t = 25°).								
$[\alpha]$	—	55·2°	63·1°	69·9°	82·1°	95·3°	106·5°	137·6°
(2) In benzene (c = 4·7905, l = 2, t = 24·8°).								
$[\alpha]$	49·5°	51·6	59·3	65·3	76·0	88·9	99·4	127·2
(3) In chloroform (c = 4·4660, l = 2, t = 20·8°).								
$[\alpha]$	—	55·6	63·5	70·0	82·3	95·6	106·8	137·1
(4) In carbon disulphide (c = 5·951, l = 2, t = 24·6°).								
$[\alpha]$	48·9	51·3	58·4	64·2	75·6	87·8	97·6	124·7
As above, but t = 2°.								
$[\alpha]$	—	51·7	—	65	76·3	—	98·6	—
(5) In ethyl alcohol (c = 4·2560, l = 2, t = 33°).								
$[\alpha]$	—	57·6	—	72·6	85·6	—	112·1	—
As above, but t = 25°.								
$[\alpha]$	55·8	57·3	66·3	73·2	86·2	100	112·5	144
As above, but t = 3°.								
$[\alpha]$	—	59·1	—	74·1	87·6	—	114·1	—

Values in ethyl alcohol quoted for this ester are: $[\alpha]^{18^\circ}_{5893}$ = − 74·2° (c = 10·89, l = 2, McKenzie, *loc. cit.*); $[\alpha]^{11\cdot3^\circ}_{5893}$ = − 75·03° (Findlay and Hickmans *loc. cit.*).

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