XIV.—*Rotation of Optically Active Compounds in Organic Solvents.*

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IN pursuing the study of the connection between optical activity and chemical composition, the investigation is frequently hampered by the circumstances that the active compounds under examination are solid at those temperatures at which polarimetric observations can be conveniently made, and that the optical activity displayed by the substance in solution is liable to enormous variations according to the particular solvent employed. Great importance, therefore, attaches to the discovery of any relationship between the real optical

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* The sign ± is employed, as it has not yet been determined whether dextro-ethoxysuccinic acid is derived from dextro- or from lævo-malic acid; in either case, however, our statement above is strongly supported by the facts.

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activity of a particular substance and the variable activity which it exhibits in different solvents.

This problem has been attacked in a very suggestive way by Freundler (*Thèses présentés à la Faculté des Sciences de Paris*, 1894) in connection with his interesting researches on the derivatives of tartaric acid, and his conclusions are summarised in the two following statements.

" When a solvent gives normal figures for the molecular weight of the dissolved active compound, it does not alter its rotatory power for any concentration.

" On the contrary, if the solvent gives abnormal figures for the rotatory power, it causes the compound to undergo some change, and yields also abnormal cryoscopic and ebullioscopic figures. In this case, the concentration influences $[\alpha]_D$, which departs from the normal value in proportion as the solution is more dilute."

The latter mode of behaviour is ascribed by Freundler to the operation of a dissociation process in neutral organic solvents analogous to that which takes place in saline solutions.

The double importance of this subject, from the point of view of optical activity on the one hand, and from that of the dissociation theory on the other, appeared to render it highly desirable that the validity of these conclusions should be tested by further experiments, and for which some of the optically active compounds prepared by one of us were particularly well adapted.

The experiments which we have carried out with this object consist, firstly, in the determination of the optical activity of a pure substance in the liquid state, secondly in the determination of its activity at different dilutions in solidifiable solvents, and, thirdly, in the cryoscopic determination of the molecular weight of the active substance in the same solvents at similar dilutions.

The optically active substance which served for the greater number of our experiments was methylic dibenzoylglycerate, which crystallises in beautiful, slender needles melting at 58—59°, and often upwards of an inch in length.

The optical activity and molecular weight of methylic dibenzoylglycerate were determined in the following solvents:—Benzene, acetic acid, ethylene dibromide, and nitrobenzene.

Experiments with Benzene as Solvent.

In order to test the cryoscopic apparatus employed, which was of the ordinary Beckmann type with a thermometer graduated in hundredths of a degree Cent., the following determinations were made with naphthalene.

Cryoscopic Determinations with Naphthalene in Benzene.

Molecular weight of Naphthalene = 128.

Molecular depression for Benzene = 49 (Raoult, *Annales d. Chim. et Phys.*, [6] **2**, 1884).

Weight of benzene in grams.	Weight of naphthalene in grams.	Grams of naphthalene in 100 grams of solution.*	Depression of freezing-point in °C.	Molecular weight deduced.
37·4965	0·6345	1·6	0·685	121·1
,,	0·7555	1·9	0·810	121·8
,,	1·1842	3·0	1·285	120·4
,,	1·6545	4·2	1·745	123·9
37·2020	1·6800	4·3	1·770	125·0
37·4965	2·5320	6·3	2·660	124·4
37·2020	3·2540	8·0	3·395	126·3
37·4965	3·3070	8·1	3·440	125·6

The above figures, which approximate to the theoretical molecular weight of naphthalene, show that the arrangement employed was capable of yielding accurate results.

In the next instance, a similar series of cryoscopic determinations was made with active methylic dibenzoylglycerate (derived from dextrorotatory glyceric acid).

Cryoscopic Determinations with Active Methylic Dibenzoylglycerate in Benzene.

Molecular weight of Methylic Dibenzoylglycerate = 328.

Weight of benzene in grams.	Weight of methylic dibenzoylglycerate in grams.	Grams of substance in 100 grams of solution.	Depression of freezing-point in °C.	Indicated molecular weight.
6·5776	0·1567	2·3	0·370	315·5
,,	0·3489	5·0	0·865	300·5
,,	0·3787	5·4	0·945	298·6
,,	0·5554	7·8	1·360	304·2
,,	0·7144	9·8	1·710	311·2
,,	0·8863	11·9	2·100	314·4
,,	1·1010	14·3	2·595	316·0
,,	1·2920	16·4	3·010	319·8
,,	1·4439	18·0	3·380	318·2
,,	1·8644	22·0	4·320	321·5

* The percentage of substance employed is, throughout the paper, given in terms of 100 parts of the *solution* and not of the *solvent*, as is usually done. The

In this series it will be seen that the indicated molecular weights of the ethereal salt are in all cases decidedly below the theoretical, the values being, on the whole, smallest for the most dilute solutions, and rising with increased concentration.

The molecular weight of an optically active compound at once raises the question as to what is the molecular weight of the corresponding inactive "racemate." This question was discussed many years ago by Perkin (Trans., 1867, **20**, 149), who was, however, unable to obtain the molecular weights of the ethereal salts of tartaric and racemic acids by vapour density determination, but came to the conclusion that their molecular weights must be identical in consequence of the identity of the boiling points of the corresponding ethereal salts of the tartaric and racemic acids. As far as we are aware, however, this point has not yet been investigated by means of cryoscopic and ebullioscopic methods for racemates dissolved in organic liquids.* We proceeded, therefore, to make a similar series

object of this is to render the percentage composition of the solutions submitted to cryoscopic examination directly comparable with that of the solutions examined in the polarimeter.

* Since making these experiments, we find that K. Auwers (*Zeit. physikal. Chem.*, 1894, **15**, 51) has cryoscopically examined methylic and ethylic lactates (inactive of course) in benzene solution, with the following results.

Methylic lactate (inactive), $C_4H_8O_3 = 104.$

Grams of solvent (benzene).	Grams of substance.	Grams of substance to 100 grams solvent.	Observed depression.	Molecular weight deduced.
15·00	0·1050	0·70	0·347	98·9
,,	0 2220	1·48	0·662	110·0
,,	0·5555	3·70	1·430	127·0
,,	1·0205	6·80	2·271	147·0
,,	1·3920	9·28	2·801	162·0
		Ethylic lactate (inactive).	$C_5H_{10}O_3 = 118.$	
,,	0·0600	0·40	0·183	107·0
,,	0·1090	0·73	0·302	118·0
,,	0·3258	2·17	0·831	128·0
,,	0·6225	4·15	1·463	139·0
,,	0·9862	6·57	2·101	153·0
,,	1·3265	8·84	2·535	171·0
,,	1·5350	10·23	2·945	170·0
,,	1·7725	11·82	3·294	176·0

There is no reference made to the possibility of the lactates being present as racemised molecules, and the very high values obtained for the molecular weights are attributed exclusively to the abnormal behaviour which is exhibited by hydroxy-compounds in general. This conclusion can, however, obviously be only provisionally drawn in the absence of any information as to the cryoscopic behaviour of the corresponding active compounds.

of cryoscopic determinations with inactive methylic dibenzoylglycerate, a substance which also crystallises in long, slender needles melting at 44—46°, whilst the active body melts at 58—59°.

The solubility of the active and inactive compounds in alcohol was also found to be very different; thus at 12·8°, 100 parts by weight of methylated spirit dissolves 1·96 part of active, and 5·33 parts of inactive methylic dibenzoylglycerate.

Cryoscopic Determinations with Inactive Methylic Dibenzoylglycerate in Benzene Solution.

Molecular weight of inactive methylic dibenzoylglycerate (calculated as a racemate) = 328 × 2 = 656.

Weight of benzene in grams.	Weight of methylic diben-zoylglycerate in grams.	Grams of substance in 100 grams of solution.	Depression of freezing point in °C.	Indicated molecular weight.
5·8980	0·2281	3·7	0·600	308·7
8·2791	0·3350	3·8	0·640	309·8
,,	0·4602	5·2	0·915	297·7
5·8980	0·4559	7·1	1·240	305·4
8·2791	0·6542	7·3	1·285	301·3
,,	0·8111	8·9	1·570	305·7
,,	1·0280	11·0	1·980	307·3
,,	1·3430	13·9	2·560	310·5
,,	1·5917	16·1	3·015	312·4
,,	1·8346	18·2	3·445	315·2

The above figures for the molecular weight are obviously substantially the same as those obtained with active methylic dibenzoylglycerate, and clearly indicate that *in the benzene solution the molecules of the oppositely active ethereal salts, which give rise to the inactive compound, are not in combination.* The figures afford, moreover, in their divergence from the calculated weight of the single molecule, a confirmation of the results recorded above for active methylic dibenzoylglycerate.

It will be interesting now to compare with these cryoscopic measurements the polarimetric determinations made with similar solutions of active methylic dibenzoylglycerate in benzene. The results are recorded in the following table (p. 128).

These figures show that the rotation $[\alpha]_D$ of the ethereal salt in benzene solution is greatly in excess of its rotation in the pure state, and, further, that the rotation increases slowly, but unmistakably, with the dilution of the solution. From the diagram given on p. 140, it will be seen that the rate of increase in rotation proceeds very steadily with the dilution until the highest dilution is reached, when

an abrupt rise in the rotation was observed.   But, on extrapolation, it is found that, even with infinite concentration, the rotation is considerably in excess of that experimentally obtained with the pure substance in a state of fusion.   Thus, on producing the straight line beyond the diagram to 100 per cent. concentration, the value $[\alpha_D] = +33 \cdot 3°$ is obtained, whilst the rotation of the pure substance at 15° is $[\alpha]_D = +26 \cdot 89°$.

Rotation of Benzene Solutions of Active Methylic Dibenzoylglycerate.

$[\alpha]_D$ for methylic dibenzoylglycerate in the pure state at 15° C. $= + 26 \cdot 89°$.

Weight of benzene solution in grams.	Weight of substance in grams.	Grams of substance in 100 grams of solution.	Observed rotation, α_D, in 100·47 mm. tube.	Density of solution at temperature of observation compared with water at 4°.	Temperature at which rotation and density were determined.	Specific rotation, $[\alpha]_D$.
4·7633	0·1435	3·0	+ 1·23°	0·8929	14·5°	+ 45·70°
3·4963	0·1641	4·7	1·86	0·8962	16·5	44·01*
3·3259	0·2414	7·2	2·87	0·9017	16·5	43·66
6·2430	1·2191	19·5	7·80	0·9411	15·0	42·26
4·9486	1·6916	34·1	13·76	0·9847	14·5	40·72

EXPERIMENTS WITH ETHYLENE DIBROMIDE AS SOLVENT.

A similar series of experiments was made both with the active and inactive methylic dibenzoylglycerates in ethylene dibromide solution (see next page). The ethylene dibromide employed, both in the cryoscopic and polarimetric determinations, was dried with calcium chloride and redistilled (b. p. 129°).   The melting point was 10°.

Thus, in the case of the ethylene dibromide solution there is little or no evidence of dissociation, even with the highest dilutions employed, whilst in the more concentrated solutions the indicated values for the molecular weight are distinctly excessive.   The values obtained in the case of the inactive compound are substantially the same as those for the active.

* In order to ascertain whether the rotation is affected by the solution being kept, this particular solution was preserved 18 hours before examination, whilst the other solutions were examined at once.   The result shows that no change appears to take place, as the figure obtained falls into line with the others.

Cryoscopic Determinations with Active and Inactive Methylic Dibenzoyl-glycerates in Ethylene Dibromide Solution.

Molecular weight of methylic dibenzoylglycerate = 328.
Molecular depression for ethylene dibromide = 118.

Weight of ethylene dibromide in grams.	Weight of methylic diben-zoylglycerate in grams.	Grams of substance in 100 grams of solution.	Depression of the freezing-point in °C.	Indicated molecular weight.
(a). *Active Compound.*				
9·7573	0·2078	2·0	0·780	322·2
25·2479	0·6784	2·6	0·985	321·9
,,	0·9805	3·7	1·415	323·8
,,	1·2457	4·7	1·755	331·7
,,	1·4982	5·6	2·090	335·0
9·7573	0·6807	6·5	2·470	333·3
,,	0·7809	7·4	2·740	344·7
,,	0·9238	8·6	3·240	344·8
,,	1·0589	9·8	3·695	346·6
25·2479	2·7747	9·9	3·725	348·1
,,	2·9323	10·4	3·885	352·7
,,	3·1297	11·0	4·155	352·1
,,	3·3903	11·9	4·525	350·1
9·7573	1·3553	12·2	4·630	354·0
,,	1·7050	14·9	5·745	358·8
(b). *Inactive Compound.*				
15·7778	0·2125	1·3	0·475	334·6
5·5932	0·0963	1·7	0·580	350·3
15·7778	0·4595	2·8	1·040	330·5
5·5932	0·3107	5·3	1·900	345·0
,,	0·4031	6·7	2·450	347·1
,,	0·4643	7·6	2·870	341·3
,,	0·5596	9·0	3·460	341·2
,,	0·7146	11·3	4·290	351·4
,,	0·9003	13·8	5·290	359·0

The results given in the table on p. 130 were obtained on examining similar solutions in the polarimeter.

Thus, the rotation for all concentrations is greatly inferior to that exhibited by the pure substance in a state of fusion; there is, more-over, very little variation with the concentration, but such as there is leads to the stronger solutions having a distinctly higher rotation than the weaker ones. This slightly greater rotation is thus obtained in the case of those solutions which yield the markedly high values for the molecular weight as determined by the cryoscopic method.

The relationship between the rotation and concentration is best seen by reference to the diagram on p. 140. By producing the straight line beyond the diagram until a concentration of 100 per cent. is reached, the value $[\alpha]_D = +32°$ is obtained, and which is con-siderably in excess of that actually yielded by the pure substance.

Rotation of Ethylene Dibromide Solutions of Active Methylic Dibenzoylglcerate.

$[\alpha]_D$ for methylic dibenzoylglycerate in the pure state at $15° = +26\cdot89°$.

Weight of ethylene dibromide solution, in grams.	Weight of substance, in grams.	Grams of substance in 100 grams solution.	Observed rotation, α_D, in $100\cdot47$ mm. tube.	Density of solution at temperature of observation compared with water at 4°.	Temperature at which rotation was observed.	$[\alpha]_D$.
10·9492	0·3695	3·3	+1·38°	2·1286	17·5°	+19·18°*
13·5373	0·8982	6·6	2·78	2·0749	17·5	20·09*
10·1979	1·1146	10·9	4·36	2·0103	17·0	19·77
16·8104	2·5857	15·4	6·33	1·9494	15·0	21·02
13·8365	3·0936	22·3	9·03	1·8538	17·5	21·69

EXPERIMENTS WITH NITROBENZENE AS SOLVENT.

A similar series of cryoscopic determinations was made both with active and inactive methylic dibenzoylglycerate in nitrobenzene solution. The nitrobenzene employed both in these and in the subsequent polarimetric measurements had a constant boiling point of 207° and melted at 5·4°. The cryoscopic determinations gave very irregular results ; we have, however, recorded them in the following table.

The figures from the cryoscopic determinations (next page), although disappointingly irregular, show that the indicated molecular weight is distinctly greater in nitrobenzene than in benzene, many of the values found approximating closely to the theoretical, irrespectively of the concentration. In spite of their irregularity, the general tendency of the figures is to show that with the greatest dilution the molecular weight is lower than the theoretical, and with the highest concentration that it rises above the theoretical.

As regards the indicated molecular weight of the inactive compound, all the values obtained very closely approximate to the theoretical weight of a single molecule, and thus confirm the conclusion arrived at in the case of the benzene and ethylene dibromide solutions, that the oppositely active molecules of which the inactive compound consists are not in combination in the solution.

On now turning to the polarimetric determinations made with the nitrobenzene solution of the active compound, the following results were obtained (see second table on next page).

* These solutions were made up 18 hours before examination with the polarimeter.

Cryoscopic Determinations with Active and Inactive Methylic Dibenzoyl-glycerate in Nitrobenzene Solution.

(a). *Active Compound.*

Molecular weight of methylic dibenzoylglycerate = **328**.
Molecular depression for nitrobenzene = 72.

Weight of nitrobenzene in grams.	Weight of substance in grams.	Grams of substance in 100 grams of solution.	Depression of freezing point in °C.	Indicated molecular weight.
5·2072	0·0925	1·7	0·420	304·5
5·4957	0·2247	3·9	0·900	327·1
5·2072	0·2919	5·3	1·270	317·8
,,	0·3780	6·7	1·655	315·8
5·4957	0·4702	7·8	1·910	322·5
5·2072	0·4681	8·3	2·050	315·7
5·4957	0·6501	10·5	2·500	340·7
5·0482	0·6333	11·1	2·665	338·9
5·2072	0·6580	11·2	2·810	323·8
5·4957	0·7367	11·8	2·885	334·4
,,	0·8782	13·7	3·495	329·2
5·2072	0·9519	15·4	4·015	327·8
5·0482	0·9642	16·0	4·030	341·2
5·2072	1·0019	16·1	4·200	329·8
5·4957	1·1507	17·3	4·475	336·9

(b). *Inactive Compound.*

5·0764	0·2336	4·4	1·000	331·3
,,	0·3536	6·5	1·545	324·6
,,	0·4064	7·4	1·760	327·5
,,	0·4936	8·8	2·160	324·1
,,	0·5452	9·7	2·390	323·6
,,	0·6623	11·5	2·860	328·4
,,	0·8919	14·9	3·785	334·2
,,	1·0563	17·2	4·500	332·9

Rotation of Nitrobenzene Solutions of Active Methylic Dibenzoylglycerate.
$[a]_D$ from ethylic dibenzoylglycerate in the pure state at 15° C. = +26·89°.

Weight of nitrobenzene solution in grams.	Weight of substance in grams.	Grams of substance in 100 grams solution.	Observed rotation a_D in 100·47 mm. tube.	Density of solution at temperature of observation compared with water at 4°.	Tempera-ture at which rotation was observed.	$[a]_D$.
6·9157	0·1668	2·4	+0·58	1·2079	15·0	+19·83
4·7130	0·2632	5·5	1·40	1·2082	15·9	20·62
5·9898	0·6795	11·3	2·94	1·2082	16·3	21·33*
5·7157	0·9950	17·4	4·60	1·2096	16·6	21·75
6·6643	1·8694	28·1	7·54	1·2164	15·5	21·99

* This solution was made up 18 hours before polarimetric examination.

From these figures it will be seen that, although the observations were made over a very wide range of concentration, the specific rotation only suffered comparatively slight change. The specific rotation was only about one-half of that exhibited in benzene solution, and was markedly inferior to that possessed by the pure substance in a state of fusion. Moreover, whilst in benzene the rotation increases with the dilution, in nitrobenzene it diminishes. The relationship is best seen from the diagram on p. 140, from which it may also be shown that, by extrapolating, the value for infinite concentration closely approaches, although it is slightly below, the experimental value for $[\alpha]_D$ obtained with the pure substance in a state of fusion. Thus, by producing the straight line beyond the diagram until it reaches a concentration of 100 per cent., the value obtained for $[\alpha]_D$ is $+ 25°$, whilst the pure substance actually gives $[\alpha]_D = +26\cdot89°$.

EXPERIMENTS WITH ACETIC ACID AS SOLVENT.

The acetic acid employed boiled at 118°, and had a melting point of 10·4°, a specimen with higher melting point not being available at the time.

Cryoscopic Determinations with Active and Inactive Methylic Dibenzoylglycerate in Acetic acid Solution.

Molecular weight of methylic dibenzoylglycerate = 328.
Molecular depression for acetic acid = 39.

Weight of acetic acid in grams.	Weight of substance in grams.	Grams of substance in 100 grams of solution.	Depression of freezing point in °C.	Indicated molecular weight.
(a). *Active Compound.*				
3 ·7355	0 ·0785	2 ·0	0 ·250	327 ·9
5 ·0224	0 ·1806	3 ·4	0 ·460	304 ·9
3 ·7500	0 ·1636	4 ·1	0 ·495	343 ·7*
3 ·8540	0 ·2089	5 ·1	0 ·690	306 ·4
5 ·0565	0 ·3016	5 ·6	0 ·710	327 ·6
3 ·7500	0 ·3197	7 ·8	0 ·970	342 ·9*
4 ·3326	0 ·3609	7 ·7	1 ·000	324 ·9
5 ·0224	0 ·4212	7 ·7	1 ·045	313 ·0
3 ·9021	0 ·3645	8 ·5	1 ·080	337 ·3
3 ·7500	0 ·4362	10 ·4	1 ·330	341 ·1*
5 ·0224	0 ·6145	10 ·9	1 ·515	315 ·0
3 ·8540	0 ·5733	12 ·9	1 ·840	315 ·3
3 ·9021	0 ·6024	13 ·3	1 ·830	329 ·0
4 ·3326	0 ·6998	13 ·9	1 ·850	340 ·5
5 ·0224	0 ·9775	16 ·2	2 ·345	323 ·7

* It will be observed that these figures, which are the most erratic, were all

(b). *Inactive Compound.*

4·4101	0·1145	2·5	0·300	337·5
,,	0·2725	5·8	0·770	312·9
,,	0·3947	8·2	1·095	318·8
,,	0·5317	10·7	1·385	339·5
,,	0·6862	13·4	1·750	346·8

From the above figures, it will be seen that the results were of a more erratic character than with the other solvents, the values for the molecular weight being sometimes above and sometimes below the theoretical. This is doubtless to be accounted for partly by the molecular depression possessed by acetic acid being smaller than that of the other solvents, and partly to the very hygroscopic character of the glacial acid, both circumstances which would tend to diminish the accuracy of the determinations. Another circumstance which must have interfered with the accuracy of the results was that the quantities of both solvent and substance employed were exceptionally small.

In the case of the inactive compound, again, the cryoscopic determinations negative the existence of a double molecule racemate in the solution, the values obtained for the molecular weight being essentially similar to those obtained for the active compound.

Solutions of active methylic dibenzoylglycerate were also examined polarimetrically, with the following results.

Rotation of Acetic acid Solutions of Active Methylic Dibenzoylglycerate.

$[\alpha]_D$ for methylic dibenzoylglycerate in state of fusion at 15° C. $= +26·89°$.

Weight of acetic acid solution in grams.	Weight of substance in grams.	Grams of substance in 100 grams of solution.	Observed rotation, α_D, in 100·47 mm. tube.	Density of solution at temperature of observation compared with water at 4°.	Temperature at which rotation was observed.	$[\alpha]_D$.
7·6560	0·1313	1·7	$+0·63°$	1·0561	16·2°	34·34°
5·0756	0·2430	4·7	1·71	1·0694	16·7	32·27
5·8478	0·5548	9·5	3·31	1·0699	15·6	32·45*
7·6152	1·0356	13·6	4·79	1·0750	16·8	32·61
6·0307	1·1219	18·6	6·55	1·0820	16·3	32·38*

obtained in a single series of experiments in which successive additions of the substance were made to *one and the same quantity* (viz., 3·75 grams) of the solvent.

* These solutions were prepared 18 hours before polarimetric examination.

The figures obtained for $[\alpha]_D$ are all in excess of that obtained for the pure substance in a state of fusion at 15°, but they change comparatively little on varying the degree of concentration; the highest dilutions, however, exhibit the greatest rotation, and by reference to the diagram on p. 140 it willbe seen that the acetic acid solution gives values for $[\alpha]_D$, which approximate more closely than in the case of the other solvents to the value obtained for the pure substance. On extrapolation for infinite concentration, moreover, it is found that the value for $[\alpha]_D$ almost exactly coincides with the value obtained for the pure substance.   Thus on producing the acetic acid straight line beyond the diagram, the value $[\alpha]_D = +27 \cdot 2°$ is obtained for 100 per cent. concentration, the pure substance giving $[\alpha]_D = +26 \cdot 89°$ at 15°.

EXPERIMENTS MADE WITH SOLUTIONS OF ACTIVE ETHYLIC DIACETYL-GLYCERATE.

The striking contrasts between the results, both cryoscopic and polarimetric, obtained with benzene and acetic acid solutions of active methylic dibenzoylglycerate, rendered it desirable to ascertain whether similar results would be yielded in the case of other active substances.   To this end, cryoscopic and polarimetric determinations were made with benzene and acetic acid solutions of active ethylic diacetylglycerate.   The preparation and properties of this compound have already been described by one of us (Percy Frankland and Macgregor, Trans., 1893, **63**, 1422), and the following results were now obtained with its solutions in benzene and acetic acid respectively.

Cryoscopic Determinations with Benzene Solutions of Active Ethylic Diacetylglycerate.

Molecular weight of ethylic diacetylglycerate $= 218.$
Molecular depression for benzene $= 49.$

Weight of benzene in grams.	Weight of ethylic diacetyl-glycerate in grams.	Grams of substance in 100 grams of solution.	Depression of freezing-point in °C.	Indicated molecular weight.
3·5666	0·1261	3·4	0·830°	208·7
,,	0·3709	9·4	2·380	214·1
,,	0·5208	12·7	3·320	215·5
,,	0·6451	15·2	4·050	218·8
,,	0·7223	16·8	4·410	225·0
,,	0·7988	18·3	4·855	226·1

The above figures show that the solutions of ethylic diacetyl-glycerate in benzene give nearly true cryoscopic values for the molecular weight. The values for the higher dilutions are somewhat below the theoretical, whilst with increasing concentration they rise somewhat above it. The rotation of these benzene solutions was now investigated.

Rotation of Benzene Solutions of Active Ethylic Diacetylglycerate.

$[\alpha]_D$ for pure ethylic diacetylglycerate at $15° = -16.31$.

Weight of benzene solution, in grams.	Weight of ethylic diacetyl-glycerate, in grams.	Grams of substance in 100 grams of solution.	Observed rotation, a_D, in 100.47 mm. tube.	Density at temperature of observation compared with water at $4°$.	Temperature at which rotation was observed.	$[\alpha]_D$.
4·0621	0·2153	5·3	$-0.82°$	0·8948	15.3°	$-17.20°$
7·4943	2·2290	29·8	-4.24	0·9580	15·0	-14.83*

Thus with a low concentration the value for $[\alpha]_D$ is somewhat greater than that exhibited by the pure substance, whilst with a high concentration it is somewhat below the latter.

Similar experiments were then made with solutions of ethylic diacetylglycerate in acetic acid.

Cryoscopic Determinations with Acetic acid Solutions of Active Ethylic Diacetylglycerate.

Molecular weight of ethylic diacetylglycerate $= 218$.
Molecular depression of acetic acid $= 39$.

Weight of acetic acid, in grams.	Weight of ethylic diacetyl-glycerate, in grams.	Grams of substance in 100 grams of solution.	Depression of freezing point, in $°C$.	Indicated molecular weight.
4·8301	0·0521	1·0	0·310	135·7
,,	0·1208	2·4	0·705	138·3
,,	0·2337	4·5	1·270	148·6
,,	0·4678	8·8	2·040	185·2
,,	0·7709	13·7	3·250	191·6
,,	0·9257	16·1	3·860	193·6

The results present a striking contrast to those obtained in the case of benzene, for with all the concentrations investigated the values

* This solution stood for 18 hours before it was examined.

for the molecular weight were greatly below the theoretical, the values rising with the concentration. Thus whilst with benzene for a concentration of 15·2 per cent. the cryoscopic value for the molecular weight was normal, with acetic acid for a concentration of 16·1 per cent. the value for the molecular weight was much lower than with a concentration of only 3·4 per cent. in the case of the benzene.

Rotation of Acetic acid Solutions of Active Ethylic Diacetylglycerate.

$[\alpha]_D$ for pure ethylic diacetylglycerate at $15° = -16·31$.

Weight of acetic acid solution, in grams.	Weight of ethylic diacetyl-glycerate, in grams.	Grams of substance in 100 grams solution.	Observed rotation, α_D, in 100·47 mm. tube.	Density at temperature of observation compared with water at 4°.	Temperature of observation of rotation.	$[\alpha]_D$.
4·8922	0·1651	3·4	$-1·03°$	1·0599	15·1°	$-28·74°$
9·4825	2·3775	25·0	$-5·28$	1·0783	15·4	$-19·44*$

Thus, with a concentration of 3·4 per cent., the value for $[\alpha]_D$ is much greater, and, even with a concentration of 25 per cent., considerably greater than that exhibited by the pure substance.

These results are of particular interest, as showing that even in the case of two compounds so closely allied as methylic dibenzoylglycerate and ethylic diacetylglycerate, there may be this great divergence in the optical and cryoscopic properties, according to the solvent employed.

The experimental results recorded in the previous pages may be thus summarised:—

1. Cryoscopic determinations show that inactive methylic dibenzoylglycerate does not exist as a racemised molecule when dissolved in benzene, ethylene dibromide, nitrobenzene, or acetic acid respectively. The values for the molecular weight are in all cases similar to those obtained under the same conditions for that of active methylic dibenzoylglycerate.

2. The cryoscopic values for the molecular weight of methylic dibenzoylglycerate vary according to the solvent and the concentration employed. With benzene, all the values are below the theoretical. With ethylene dibromide and with nitrobenzene, the values are with low concentration below, and with high concentration above the theoretical. In the case of acetic acid, the values are, with all concentrations, sometimes above and sometimes below the theoretical.

3. In all cases, the specific rotation $[\alpha]_D$ of active methylic di-

* This solution stood for 18 hours before examination.

benzoylglycerate is more or less affected by the solvent.   In the case of benzene, the values of $[\alpha]_D$ are much in excess, and in that of ethylene dibromide and nitrobenzene they are much below the value of $[\alpha]_D$ for the pure substance.   In the case of acetic acid, the values for $[\alpha]_D$ most closely approximate to that of the pure substance.

4. Low cryoscopic values for the molecular weight of methylic dibenzoylglycerate are accompanied by high values for the specific rotation, and *vice versâ*.

5. This relationship between specific rotation and indicated molecular weight is borne out by the behaviour of ethylic diacetylglycerate in benzene and acetic acid respectively, but in this case the low molecular weights and high rotations are obtained in acetic acid, the high molecular weight and low rotations in benzene.

6. The real rotation of the active compound cannot be directly calculated from the rotation of its solution, even when the cryoscopic examination of that solution shows the molecular weight to be normal. Thus for methylic dibenzoylglycerate in acetic acid solutions giving normal molecular weights, $[\alpha]_D$ was too high, whilst conversely in nitrobenzene and ethylene dibromide solutions, giving normal molecular weights, the values of $[\alpha]_D$ were too low.   By graphic extrapolation for infinite concentration, as in the diagram on p. 140, however, all three solvents give values at any rate approximating to the actual specific rotation obtained with the pure substance.   In the case of benzene, on the other hand, all the solutions examined gave molecular weights below the theoretical, and the produced rotation curve gives a value for $[\alpha]_D$ at infinite concentration which departs more widely from the real value than do the produced curves for nitrobenzene, ethylene dibromide, and acetic acid.   It would appear, therefore, that even a moderately accurate estimate of the real rotation can only be arrived at by the study of solutions giving normal molecular weights, and extrapolating for infinite concentration on their rotation curves.

Thus the real specific rotation of methylic dibenzoylglycerate is

$$[\alpha]_D = +26 \cdot 89° \text{ at } 15° \text{ C.,}$$

whilst

$[\alpha]_D$ calculated by extrapolation from benzene solu-
tion values.. $= +33 \cdot 3°$
  ,, calculated by extrapolation from acetic acid
solution values..................................... $= +27 \cdot 2$
  ,, calculated by extrapolation from nitrobenzene
solution values .... $= +25 \cdot 0$
  ,, calculated by extrapolation from ethylene di-
bromide solution values.......................... $= +32 \cdot 0$
  ,, calculated from mean of the above extrapola-
tion values... $= +29 \cdot 4$

7. Our experiments show that the rotation of an active substance may be either raised or depressed by solvents; similarly, the molecular weight, cryoscopically measured, may be either raised or depressed by solvents, the variations in the rotation being doubtless dependent on the variations in molecular weight. Now, the variations in molecular weight can be most consistently explained on the assumption of dissociation and association processes taking place, both of which may go on concurrently.

The phenomenon of dissociation is most conspicuously exhibited in the case of the benzene solution of methylic dibenzoylglycerate and in that of the acetic acid solution of ethylic diacetylglycerate. In both cases, the cryoscopic values for the molecular weight are markedly below the theoretical figures. The effect of this assumed dissociation is in both cases to greatly increase the rotation. The active ion must, however, be different in the two cases, as the dibenzoyl-glycerate is dextrorotatory, whilst the diacetylglycerate is lævo-rotatory, although both are derived from one and the same active glyceric acid (dextro-). By dissociation of the dibenzoylglycerate, the rotation becomes more dextrorotatory, whilst by dissociation of the diacetylglycerate the rotation becomes more lævorotatory.

It must not be supposed, however, that the effect of dissociation is invariably to increase the rotation; thus, in Freundler's experiments on the tetra-substituted tartrates, the dissociation was accompanied by diminution in the value of $[\alpha]_D$, thus

	Molecular weight (theoretical).	Molecular weight (cryoscopic).	$[\alpha]$ from benzene solution.	$[\alpha]_D$ real.
Propylic diacetyl-tartrate	318	277	$+1\cdot2°$.	$+13\cdot4°$

(*Loc. cit.*, p. 114).

If, in the case of methylic dibenzoylglycerate, high values for specific rotation are shown by cryoscopic measurement to be accompanied by dissociation, we should naturally infer that low values for $[\alpha]_D$ must be due to the opposing influence of association.*

Such low values for $[\alpha]_D$ we find in the case of the ethylene dibromide and nitrobenzene solutions of methylic dibenzoylglycerate. The variation in $[\alpha]_D$ for differences of concentration is comparatively small in the case of these two solvents, but such as it is, this

* Just as there is at present no *à priori* means of ascertaining whether dissociation will be attended by increase or by decrease in the value of $[\alpha]_D$, so there is none for predicting the effect on $[\alpha]_D$ of association.

variation takes place in the opposite sense to that which goes on in the dissociating benzene solution, for with high dilution in the case of ethylene dibromide and nitrobenzene there is a diminution in the values for $[\alpha]_D$ (see the diagram on p. 140). These low values for the specific rotation would thus find the readiest explanation on the hypothesis of association becoming more pronounced the greater the dilution of the solution.

Of such association at high dilutions there is, however, no direct evidence from the cryoscopic determinations, the indicated molecular weights in the case of ethylene dibromide, and still more so in the case of nitrobenzene being somewhat below the theoretical value. On the other hand, with these two solvents at high concentrations, the indicated values for molecular weight are considerably in excess of the theoretical. But if these high indicated molecular weights were the result of association we ought to find the values for $[\alpha]_D$ simultaneously falling, whilst, as a matter of fact, they rise with the concentration.

The only polarimetric confirmation of this cryoscopic evidence of association which we can find in our experiments is in the case of the benzene solutions of ethylic diacetylglycerate. Here the most concentrated solutions give indicated molecular weights in excess of the theoretical, the value of $[\alpha]_D$ calculated from such solutions being less than the value of $[\alpha]_D$ for the pure substance, and since the dilute solutions give cryoscopic evidence of dissociation accompanied by excessive values for $[\alpha]_D$, we can conclude that association and deficient values for $[\alpha]_D$ are connected, and that the deficient value for $[\alpha]_D$ with high concentration is confirmation of the association cryoscopically indicated.

Amongst the experimental material furnished by Freundler (*loc. cit.*, p. 117) there are the following cases exhibiting cryoscopic evidence of association.

Benzene Solutions.

Active compound.	Molecular weight (theoretical).	Molecular weight (found).	$[\alpha]_D$ measured on the solution.	$[\alpha]_D$ obtained with the pure substance.
Methylic tartrate...	178	411	$-8 \cdot 8°$	$+2 \cdot 14°$
Propylic ,, ...	234	306	$+20 \cdot 1$	$+12 \cdot 44$

Ethylene Dibromide Solution.

| Propylic tartrate...	234	326	$-0 \cdot 6°$	$+12 \cdot 44°$

Thus, in all the above cases, the cryoscopic determinations afford

strong evidence of association, and yet the effect on the rotation is quite irregular, for in the benzene solution the effect on the rotation of methylic tartrate is negative, whilst in that of propylic tartrate it is positive. There is of course nothing surprising in these results, as association with the molecules of the same solvent may produce opposite rotatory effects in the case of two different active compounds, and association with the molecules of two different solvents may produce opposite rotatory effects in the case of one aad the same active compound.

In his experiments on the tetra-substituted tartrates, Freundler finds evidence, in several cases, of dissociation in organic solvents, and is of opinion that the dissociation consists in the splitting off of the two acid radicles* substituting the two alcoholic hydrogen atoms of the tartaric acid. Our experiments, however, clearly show that the molecules of the fully substituted glycerates dissociate otherwise. Thus, as already pointed out, methylic dibenzoyl-glycerate dissociates in benzene, and the active ion is more dextro-rotatory than the undissociated molecule. Ethylic diacetylglycerate, on the other hand, dissociates in acetic acid, and the active ion is more powerfully lævorotatory than the undissociated compound. Thus, the two active ions differ not only in sign but enormously in degree, whilst, if the acid radicles were split off, the only difference in their constitution would be the presence of methyl in the one and of ethyl in the other, thus

$$CH_2 \cdot O | C_7H_5O$$
$$CH \cdot O | C_7H_5O$$
$$COOCH_3$$

Methylic dibenzoylglycerate
(dextrorotatory).

$$CH_2 \cdot O | C_2H_3O$$
$$CH \cdot O | C_2H_3O$$
$$COOC_2H_5$$

Ethylic diacetylglycerate
(lævorotatory).
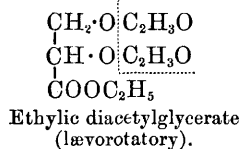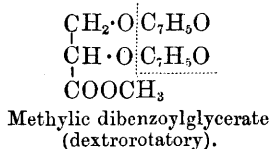
But we know that the dextrorotation of the dibenzoylglycerates is conditioned by the benzoyl groups, and the methylglyceryl and ethylglyceryl ions could not possibly differ in rotation to the extent which the ions in question actually do, hence we regard the dissociation as almost certainly taking place as indicated below

$$CH_2 \cdot OC_7H_5O$$
$$CH \cdot OC_7H_5O \quad ,$$
$$COO | CH_3$$

$$CH_2 \cdot OC_2H_3O$$
$$CH \cdot OC_2H_3O$$
$$COO | C_2H_5$$
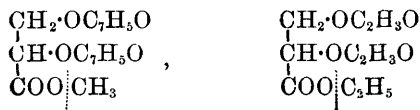
* This supposition is quite out of harmony with Perkin's experiments on diethylic benzoyltartrate, in which it was found that by hydrolising with an insufficient quantity of alcoholic potash benzoyltartaric acid was formed, the ethyl groups being eliminated, whilst the benzoyl groups remained attached (Trans., 1867, **20**, 141).

(FRANKLAND & PICKARD)

SPECIFIC ROTATION OF METHYL DIBENZOYLGLYCERATE IN VARIOUS SOLVENTS.
(BENZENE, ACETIC ACID, NITROBENZENE AND ETHYLENE DIBROMIDE.)

Parts of Methyl dibenzoylglycerate in 100 parts of Solution.

$[\alpha]_D = +$

Benzene

Acetic acid

Nitrobenzene

Ethylene dibromide

⊙ Nitrobenzene.
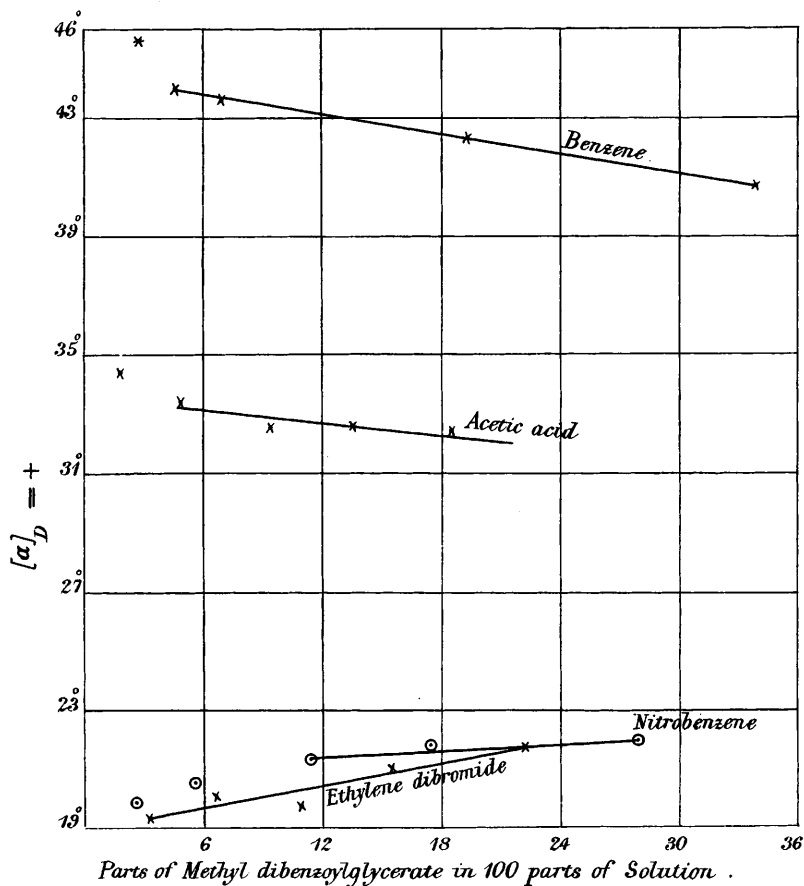
This process would leave the active ions differing profoundly in constitution as they do in rotation.

We have recently obtained further evidence bearing on this point, in connection with the rotation of ethylic monobenzoylglycerate. This substance which has been prepared by one of us in conjunction with Mr. MacGregor is in all probability the β-compound, of the formula

$$CH_2 \cdot OC_7H_5O$$
$$CH \cdot OH$$
$$COOC_2H_5$$
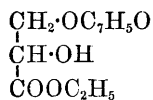
In a state of fusion, the specific rotation of this substance is $[\alpha]_D = -9 \cdot 80°$, whilst, with a benzene solution, the following result was obtained.

Weight of benzene solution, grams.	Weight of substance in grams.	Grams of substance in 100 grams solution.	Observed rotation α_D in 198·4 mm. tube.	Density of solution compared with water at same temperature.	Temp. of observation of rotation.	$[\alpha]_D$.
9 ·5558	1 ·3701	14 ·3	$-0 \cdot 925°$	0 ·9194	15 ·5°	$-3 \cdot 5°$

Thus the activity of the substance in benzene solution was far less lævorotatory than in the pure state, a circumstance which is quite in harmony with the supposition that in benzene solution the molecule is more or less dissociated into a C_2H_5-ion and the complex active ion $C_{10}H_9O_5$. For, as already pointed out, in these ethereal salts of glyceric acid, dextrorotation is conditioned by the presence of benzoyl groups in place of the hydroxylic hydrogen atoms; whilst lævorotation is conditioned by the positive radicles replacing the carboxylic hydrogen; now if, in the above substance the benzoyl group were split off in the dissociation supposed to take place in the benzene solution, then the molecule should become more lævorotatory; on the other hand, if it is the ethyl group that is split off we should anticipate that the molecule would become more dextrorotatory by virtue of the more preponderating influence obtained by the benzoyl group; and this is precisely what takes place, for in benzene solution the substance actually becomes more dextrorotatory, or rather its lævorotation is greatly diminished.

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