XXI.—*The Amyl (secondary Butyl-methyl) Derivatives of Glyceric, Diacetylgyceric, and Dibenzoylgyceric Acids, Active and Inactive.*

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THE preparation of the above derivatives is attended with particular interest for several reasons. Firstly, because, in the series of glycerates and diacetylgycerates, it has been shown by one of us that a maximum rotation is attained,* and that this maximum falls, either on the butylic, amylic, or hexylic terms of each series, and of these three terms hitherto only the butylic has been prepared. One of the objects of this investigation was, therefore, to ascertain whether the possession of the maximum really rests with the butylic term, or whether the rotation of the latter is surpassed by that of the amylic compound. Again, in the case of the series of the dibenzoylgycerates, only the methylic, ethylic, and propylic compounds† have so far been studied, so that the preparation of the amylic term should materially increase our knowledge of the rotation phenomena exhibited by this series. Lastly, the amyl radicle can be introduced in both an active and an inactive (racemised) form, so that the effect of one asymmetric carbon atom on another can be submitted to examination. It might at first sight appear unfortunate for the success of this investigation that active amylic alcohol is not known in a pure state, but it will be readily understood that, for the first two purposes mentioned above, the principal interest lay in the introduction of the inactive (racemised) amyl radicle, so as to enable a comparison to be instituted between the rotation of the amylic compound of the active acids in question, and that of the compounds of these acids already prepared, all of which compounds have contained inactive radicles only. Again, as regards the last purpose referred to above, it has been repeatedly shown‡ that comparative rotation results are obtained in working with a mixture of an active compound and its racemoid, provided the proportion between the two constituents of the mixture remains invariable throughout.

The amylic compounds which we have prepared have all been obtained from one and the same amylic alcohol, exhibiting a lævo-rotation,

$$[\alpha]_D^{11} = -4.62^\circ,$$

* Percy Frankland and MacGregor, *Trans.*, 1893, 1410; 1894, 750.

† Percy Frankland and MacGregor, *Trans.*, 1896, 104.

‡ Guye and Chavanne, *Compt. rend.*, 1894.

and, for the purposes of this investigation, this may be regarded as the rotation of pure lævo-amylic alcohol.

It is obvious that, of any of the above three acids, no less than nine amylic compounds can be prepared; for instance, in the case of glyceric acid,

(1) Amylic (dextro) glycerate (dextro).	(2) Amylic (lævo) glycerate (lævo).
(3) Amylic (lævo) glycerate (dextro).	(4) Amylic (dextro) glycerate (lævo).
(5) Amylic (inactive) glycerate (dextro).	(6) Amylic (inactive) glycerate (lævo).
(7) Amylic (dextro) glycerate (inactive).	(8) Amylic (lævo) glycerate (inactive).
(9) Amyl (inactive) glycerate (inactive).	

Of these (5) is really a mixture or compound of (1) and (3)

„ (6) „ „ „ „ (2) „ (4)

„ (7) „ „ „ „ (1) „ (4)

„ (8) „ „ „ „ (2) „ (3)

„ (9) „ „ „ „ (1), (2), (3), and (4),

or of (5), (6), (7), and (8).

No. (9), being devoid of rotatory power, is without interest for us, and can, therefore, be dismissed for the present.

The materials at present at our disposal for the preparation of these compounds are (*a*) inactive amylic alcohol (secondary butylcarbinol) (obtained by racemising the original alcohol), (*b*) lævo-amylic alcohol, (*c*) inactive glyceric acid, and (*d*) dextro-glyceric acid (obtained by fermentation of the inactive calcium glycerate by the *bacillus ethaceticus**). To these might be added dextro-amylic alcohol obtained by Le Bel (*Bull. Soc. Chim.*, 1879 [2], 31, 104, and *Compt. rend.*, 1878, 87, 213) by the growth of moulds in the racemised alcohol, but for practical purposes this material may be excluded from the list. The rotation properties of all these eight ethereal salts can, however, be evaluated from a knowledge of those properties for (5) and (8) alone, by the use of two principles.

a. That the optical antipodes have the same rotation, but with opposite sign.

β. That the optical effect of each asymmetric carbon atom is exerted independently of that of the other asymmetric carbon atoms which may be present in the molecule, the optical effect of the whole molecule being the algebraic sum of the optical effects of the several asymmetric carbon atoms which it contains.†

Thus let the rotations of

(1) = A, (2) = B, (3) = C, (4) = D, (5) = E, (6) = F, (7) = G, (8) = H,

then $E + H = C$, but $C = -D$,

again $E = -F$ and $H = -G$,

but $E + G = A$ and $A = -B$.

Thus A, B, C, D, E, F, G, and H are all known.

* Percy Frankland and Frew, *Trans.*, 59, 1891, 96.

† Guye and Gautier, *Compt. rend.*, 1894.

In the present investigation, we have prepared (5) and (8), as well as (1), not only for glyceric, but also for diacetyl glyceric and dibenzoyl glyceric acids respectively. We have thus tested the second of the above principles, and it will be shown that we have found it to hold good; the first principle is so well established that it would be almost waste of time to test it further, so that by means of the above formulæ, the rotation of all the eight compounds can be calculated. Thus, of the three acids, we have obtained the rotation of 24 compounds and molecular mixtures by the actual preparation of 9, and have thus shown that the preparation of 6 would have been really sufficient for the purpose.

The amylic alcohol used in this investigation was lævo-rotatory, giving $\alpha_D = -7.53^\circ$ in a 200 mm. tube at 15.3° .

An attempt was made to further purify it by fractional distillation, and in this way two fractions were obtained, distilling at $128-130^\circ$ and $130-131^\circ$ respectively. The activity of these two fractions was, however, so similar, namely $\alpha_D = -7.64^\circ$ and -7.42° in a 200 mm. tube, that it would have served no useful purpose to employ them separately, and, therefore, the original alcohol was used throughout. Its density was $d_{11^\circ/4^\circ} = 0.8237$, and its specific rotation at 11° $[\alpha]_D^{11^\circ} = -4.62^\circ$.

As, for some of our proposed compounds, this alcohol was required in an inactive state, we endeavoured, in the first instance, to racemise it by means of sodium hydroxide. For this purpose, 30 c.c. of the alcohol were boiled with 0.5 gram sodium hydroxide for 4 hours, using a reflux condenser. On subsequent distillation, it passed over at $129-131^\circ$, and on polarimetric examination gave,

$$\alpha_D = -7.52^\circ \text{ in a 200 mm. tube at } 15^\circ.$$

This treatment had, therefore, practically left its activity unchanged. The treatment was repeated, using a much larger quantity of sodium hydroxide; 45 grams of the alcohol were heated on the water bath with 40 grams of sodium hydroxide for 7 hours. The sodium hydroxide was appreciably dissolved, but a large excess remained unaffected. The alcohol was poured off from the sodium hydroxide, and the latter washed several times with cold water, the washings being added to the alcohol. The alcoholic liquid was then acidified with sulphuric acid, and the alcohol separated from the aqueous layer. The former was dried with sodium hydroxide and then distilled; it passed over at $127-129^\circ$, and gave,

$$\alpha_D = -7.1^\circ \text{ in a 200 mm. tube at } 16^\circ.$$

The activity had thus been but little affected by the treatment.

In the next instance, 25 c.c. of the alcohol, which had been treated as above, were heated in a sealed tube with 0.5 gram of sodium hydroxide at 170° for 7 hours. On subsequent distillation, the alcohol came over at 129° and exhibited

$$\alpha_D = -4.85^{\circ} \text{ in a 200 mm. tube at } 15.5^{\circ}.$$

The activity had thus been materially reduced, but by no means destroyed.

Finally, the racemisation was effected by heating 40 grams of the alcohol on a water bath and adding 4 grams of metallic sodium in small portions at a time; the whole of the sodium, however, did not dissolve. The amylate, which was liquid at 100° , was poured off from the sodium into a pressure tube, which was then sealed and heated for 3 hours at 206° . The amylate was then treated with a slight excess of hydrochloric acid, and the alcohol separated and dried over lime; the greater part of it distilled at 129° , and was found to be quite inactive. All the inactive alcohol referred to in the following pages was prepared in this way.

Amylic (active) Glycerate (inactive.)

This was prepared in the manner already frequently described by one of us in connection with other ethereal salts of glyceric acid. The glyceric acid, obtained from 35 grams of inactive calcium glycerate, was divided into two portions, concentrated to a syrup, and each portion heated along with 40 c.c. of active amylic alcohol in a sealed tube for 8 hours at 150° . On opening the tube, the excess of alcohol* was distilled off under reduced pressure below 80° , the amylic glycerate subsequently passing over at 150 — 157° (about 9 mm. pressure). The yield was 25 grams. This crude product was dried over calcium chloride, and then purified by fractional distillation until of constant rotation; the final boiling point was 144 — 147° (about 5 mm. press.). The amylic glycerate thus obtained was a fairly mobile liquid of unpleasant odour and bitter taste. On combustion, the following results were obtained.

0.2542 gave 0.5073 CO_2 and 0.2192 H_2O . C = 54.42; H = 9.58

0.2580 „ 0.5150 „ „ 0.2170 „ C = 54.43; H = 9.34

0.2181 „ 0.4350 „ „ 0.1796 „ C = 54.39; H = 9.15

$\text{C}_8\text{H}_{16}\text{O}_4$ requires C = 54.54 and H = 9.09 per cent.

* This excess of alcohol was dried over lime, and after distillation (b. p. 126 — 129°) it gave a specific rotation $[\alpha]_D^{11.4^{\circ}} = -4.76^{\circ}$ and density $11.4^{\circ}/4^{\circ} = 0.8233$. The rotation is thus slightly higher than that of the original alcohol, showing that one of the constituents had etherified more perfectly than the other. This does not, however, necessarily mean that the dextro-amyl alcohol had etherified more rapidly than the laevo-compound, for all active amylic alcohols hitherto prepared probably contain some iso-amyl alcohol, $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, and this is known to etherify more easily than the active alcohol—in fact, on this property depends Le Bel's method (*Compt. rend.*, **77**, 1021) of purifying the active alcohol.

Rotation of Amylic (active) Glycerate (inactive).

Temp.	Observed rotation α_D in 92.35 mm. tube	Density compared with water at 4°.	$[\alpha]_D$
11°	+2.85°	1.0807 (experiment)	+2.86°
47	+2.71	1.0505 („)	+2.79
25.5	+2.75	1.0685 (interpolated)	+2.79
11.6	+2.90	1.0802 („)	+2.91

The activity of this substance is, therefore, hardly at all influenced by temperature; if anything, with increase of temperature, the positive rotation diminishes very slightly, but the change is hardly, if at all, beyond the range of experimental error as can be seen from Fig. 1.

FIG. 1.—Specific Rotation of Amylic Glycerates.

Amylic (active) Diacetyl glycerate (inactive).

Twelve grams of the above amylic glycerate were gradually added to twice the calculated quantity of acetyl chloride heated to 50°. When the reaction had ceased, the excess of acetyl chloride was distilled off under reduced pressure, the diacetyl glycerate subsequently passing over at 163—165° (about 12 mm. press.). Sixteen grams of this crude product were obtained, which was distilled until of constant rotation. The amylic diacetyl glycerate is a more mobile liquid than the amylic glycerate; it has a peculiar odour and bitter taste.

On combustion, it gave the following results,

·2286 gave 0·4620 CO_2 and 0·1600 H_2O . $\text{C} = 55\cdot12$; $\text{H} = 7\cdot77$.

·2138 „ 0·4327 „ „ 0·1524 „ „ $\text{C} = 55\cdot19$; $\text{H} = 7\cdot92$.

$\text{C}_{12}\text{H}_{20}\text{O}_6$ requires $\text{C} = 55\cdot38$ and $\text{H} = 7\cdot69$ per cent.

Rotation of Amylic (active) Diacetylgllycerate (inactive).

Temp.	Observed rotation α_D in 92·35 mm. tube.	Density compared with water at 4°.	$[\alpha]_D$.
11°	+1·67°	1·0863	+1·66
49·7	+1·62	1·0488	+1·67

The density determinations made were $d_{11^\circ/4^\circ} = 1\cdot0863$ and $d_{50^\circ/4^\circ} = 1\cdot0485$. The substance is, therefore, practically insensitive to temperature as regards specific rotation. (See Fig. 2.)

FIG. 2 — Specific Rotation of Amylic Diacetylgllycerates.

Amylic (active) Dibenzoylglycerate (inactive).

14·5 grams of amylic (active) glycerate (inactive) were added slowly to twice the theoretical quantity of benzoyl chloride, which was heated to 135°, and finally to 160°, until reaction was complete. The excess of benzoyl chloride was distilled off under reduced pressure, the crude product, which weighed 17 grams, subsequently passing over at 262—268° (about 7 mm. press.). After redistillation, the ethereal salt

crystallised for the most part; it was repeatedly recrystallised from methylated spirit until of constant melting point ($36-36.5^\circ$). It was also obtained in a crystalline form from light petroleum, methylic alcohol, ethylic alcohol, ether, acetone, and benzene. Recrystallisation from isobutylic alcohol did not affect the melting point. The crystals were prismatic, and terminated by pyramidal faces.

0.15775 gave 0.3958 CO_2 and 0.0900 H_2O . $\text{C} = 68.43$; $\text{H} = 6.34$.

0.2029 „ 0.5101 „ „ 0.1151 „ „ $\text{C} = 68.56$; $\text{H} = 6.30$.

$\text{C}_{22}\text{H}_{24}\text{O}_6$ requires $\text{C} = 68.75$; $\text{H} = 6.25$ per cent.

Rotation of Amylic (active) Dibenzoylglycerate (inactive).

Temp.	Observed rotation α_D in 92.35 mm. tube.	Density compared with water at 4° .	$[\alpha]_D$.
36.6°	$+1.77^\circ$	1.1265	$+1.70^\circ$
37	$+1.79$	1.1262	$+1.72$
99	$+1.59$	1.0755	$+1.60$

The density determinations actually made were $d_{40}^{40} = 1.1237$ and $d_{99}^{99} = 1.0749$.

FIG. 3.—Specific Rotation of Amylic Dibenzoylglycerates.

The specific rotation is thus hardly affected by temperature (see Fig. 3); its rotation in benzene solution was also determined for several concentrations.

Rotation of Amylic (active) Dibenzoylelycerate (inactive) in Benzene Solution.—It has been shown by one of us (Percy Frankland and Pickard, *Trans.*, 1896, 69, 128) that methylic dibenzoylelycerate (active) gives a higher specific rotation in benzene solution than when examined in the superfused state, and, further, that the specific rotation is the greater the more dilute the solution. It appeared, therefore, of interest to ascertain what would be the behaviour in this respect of amylic (active) dibenzoylelycerate (inactive); the rotation of the latter in benzene solution was determined with the following results.

Rotation of Amylic (active) Dibenzoylelycerate (inactive) in Benzene Solution. $[\alpha]_D$ in liquid state = $+1.70^\circ$

Temp.	Grams of ester.	Grams of solvent.	Grams of ester in 100 grams solution.	Density compared with water at 4° .	Observed rotation α_D in 198.4 mm. tube.	$[\alpha]_D$.
16°	1.0026	17.8874	5.31	0.8941	$+0.20^\circ$	$+2.12^\circ$
16	3.6531	15.3407	19.23	0.9247	$+0.74$	$+2.10$
18	5.1362	13.6831	27.29	0.9409	$+0.97$	$+1.90$

The specific rotation in benzene solution was thus found to be slightly but distinctly in excess of that of the pure substance in the fused state, and to diminish slightly with increasing concentration.

We have also determined the rotation of the active amylic alcohol in benzene solution with the following results.

Rotation of Active Amylic Alcohol in Benzene Solution. Rotation of the pure alcohol $[\alpha]_D = -4.62$.

Temp.	Grams of alcohol.	Grams of solution.	Grams of alcohol in 100 grams solution.	Density compared with water at 4° .	Observed rotation in 198.4 mm. tube.	$[\alpha]_D$.
16°	1.0743	18.7769	5.72	0.8779	-0.41°	-4.11°
16	3.3642	18.8512	17.85	0.8688	-1.26	-4.10
16	5.3199	19.9857	26.62	0.8626	-1.83	-4.02
16	6.1978	19.6058	31.61	0.8595	-2.24	-4.15

Thus the negative specific rotation of the amylic alcohol is less in benzene solution than in the pure state.

Saponification of Amylic (active) Dibenzoylelycerate (inactive).—This was effected in order to ascertain whether the amylic alcohol recovered had the same activity as the amylic alcohol originally employed, or whether any change had been effected through its transformation, firstly, into amylic glycerate, and subsequently into amylic dibenzoylelycerate.

Twenty-five grams of the ethereal salt were mixed with twice the theoretical quantity of baryta dissolved in water, and heated for 55 hours on a water bath, using a reflux condenser, it had disappeared. The liberated alcohol was removed by steam distillation, and separated from the aqueous distillate by adding common salt, and ultimately by

shaking out with ether. After drying with potassium carbonate and distilling off the ether, the amylic alcohol passed over at 128—129°. A blank experiment was also made, in which some of the original amylic alcohol was digested with baryta and otherwise similarly treated in every particular. On polarimetric examination, these two specimens of amylic alcohol gave the following results.

Amylic alcohol (from blank experiment).

$\alpha_D = -1.86^\circ$ in 50 mm. tube at 17.8° . $d\ 17.8^\circ/4^\circ = 0.8192$

$\therefore [\alpha]_D^{17.8^\circ} = -4.54^\circ$.

Amylic alcohol (from saponification of the ethereal salt.)

$[\alpha]_D = -1.94^\circ$ in 50 mm. tube at 17° , assuming this to have the same density as the other specimen, then

$[\alpha]_D^{17^\circ} = -4.73^\circ$

the original alcohol had the specific rotation $[\alpha]_D^{11^\circ} = -4.62^\circ$, thus the difference between the two is very slight.

Amylic (active) Glycerate (active).

This was prepared in the same way as the amylic glycerate described above, excepting that active glyceric acid (dextro) was used. It distilled at 144—148° (about 6mm. press.).

0.2034 gave 0.4063 CO₂ and 0.1662 H₂O. C = 54.48 ; H = 9.08.

0.1799 „ 0.35805 „ 0.1500 „ C = 54.28 ; H = 9.26.

C₈H₁₆O₄ requires C = 54.54 ; H = 9.09 per cent.

Rotation of Amylic (active) Glycerate (active).

Temp.	Observed rotation α in 92.35 mm. tube.	Density compared with water at 4°.	$[\alpha]_D$.
12.5°	-11.48° and -11.51°	1.0785	-11.54°
45	-11.44°	1.0512	-11.78

The density determinations actually made were $d\ 12^\circ/4^\circ = 1.0789$ and $d\ 45^\circ/4^\circ = 1.0512$.

The specific rotation of this substance is, therefore, but slightly affected by temperature, but in so far as it is, the negative rotation increases with rise of temperature, as has already been found by one of us (P. Frankland and MacGregor, Trans., 1894, 65, 760) to be the case with other simple ethereal glycerates.

The excess of amylic alcohol recovered in the preparation of this amylic glycerate was dried, distilled, and found to possess the rotation $[\alpha]_D^{11.6^\circ} = -4.71^\circ$ and density $d\ 11.6^\circ/4^\circ = 0.8228$.

Thus, like the excess alcohol recovered in the preparation of amylic (active) glycerate (inactive), it had a slightly higher rotation than the original alcohol employed (see p. 255).

Amylic (active) Diacetylglycerate (active).

This was prepared in the same way as the corresponding compound described on p. 257. As usual, it was fractionally distilled until of constant rotation. The boiling point was 152–157° (under a pressure of about 6 mm.).

0.1876 gave 0.3786 CO₂ and 0.1290 H₂O. C = 55.04; H = 7.64.

0.1867 „ 0.3768 „ 0.1322 „ C = 55.04; H = 7.87.

C₁₂H₂₀O₆ requires C = 55.38; H = 7.69 per cent.

Rotation of Amylic (active) Diacetylglycerate (active).

Temp.	Observed rotation α_D in 44 mm. tube.	Density compared with water at 4°.	$[\alpha]_D$.
11.4°	– 8.25°	1.0855	– 17.27°
37.7	– 8.67	1.0587	– 18.61
99.5	– 9.35	0.9990	– 21.27

After taking the rotation at this high temperature, it was again observed at 11.4°, and found to be exactly the same as at first. The density determinations actually made were $d_{11.4/4} = 1.0855$, $d_{38/4} = 1.0584$, $d_{100/4} = 0.9985$.

Thus the specific rotation of this compound, like all the other diacetylglycerates previously examined by one of us, is very markedly affected by temperature, the negative rotation increasing with rise of temperature. As seen from the diagram, the increase in specific rotation is almost exactly proportional to the increase in temperature (see Fig. 2, p. 258).

Amylic (active) Dibenzoylglycerate (active).

I. This was prepared in exactly the same way as the corresponding compound described on p. 258, excepting that amylic (active) glycerate (active) was employed. It distilled at 255–270° (at about 4 mm. pressure); it was slightly yellow, and was viscid, but less so than the amylic (active) dibenzoylglycerate (inactive). As all attempts to obtain it in a solid form were unsuccessful, it was dissolved in ether, washed with a strong solution of sodium carbonate, and then with water; the ether was removed by distillation, and the residue dried in a vacuum-desiccator. The rotation was then found to be

$$\alpha_D = +11.49^\circ \text{ in a 50 mm. tube at } 14^\circ.$$

It was again distilled under reduced pressure, but at the end of the process the flask burst, and the distillate was darkened. The latter was, therefore, again distilled, the distillate being further washed and dried as above. The rotation was then found to be

$$\alpha_D = +11.26^\circ \text{ in a 50 mm. tube at } 16^\circ.$$

The rotation was thus slightly lower than before, but the temperature was higher, and it will be seen below that the rotation is very sensitive to temperature. Analysis also showed it to be as pure as we were able to obtain any of the other liquid dibenzoyl compounds, thus,

0.19875	gave	0.4968	CO ₂	and	0.1131	H ₂ O.	C = 68.17 ; H = 6.32.
0.1944	„	0.4877	„		0.1131	„	C = 68.42 ; H = 6.46.
0.19195	„	0.4797	„		0.1097	„	C = 68.16 ; H = 6.35.
0.2000	„	0.4997	„		0.1161	„	C = 68.14 ; H = 6.45.
C ₂₂ H ₂₄ O ₆ requires C = 68.75 ; H = 6.25 per cent.							

*Rotation of Amylic (active) Dibenzoylglycerate (active).
(First specimen).*

Temp.	Observed rotation α_D in 44 mm. tube.	Density compared with water at 4°.	$[\alpha]_D$.
16° *	+ 9.96°	1.1456	+ 19.76°
17	+ 9.84	1.1446	+ 19.54
42.5	+ 9.10	1.1213	+ 18.44
51.8	+ 8.75	1.11336	+ 17.86
99.3	+ 6.59	1.0750	+ 13.93

The density determinations actually made were $d_{16.5^\circ/4^\circ} = 1.1451$, $d_{43^\circ/4^\circ} = 1.1208$, $d_{52^\circ/4^\circ} = 1.1132$, $d_{99.8^\circ/4^\circ} = 1.0746$.

From the above figures, it will be seen that the rotation is extremely sensitive to temperature, and, as in the case of those dibenzoylglycerates previously investigated by one of us, the positive rotation diminishes with rise of temperature. On plotting the rotations as a curve, it will be seen (see Fig. 3, p. 259) that the latter approaches more and more to a straight line the higher the temperature, the rotation becoming also more sensitive as the temperature rises. The figures for the density, on the other hand, show that this diminishes more and more slowly with rise of temperature.

II. In consequence of the accident which happened to the above specimen of amylic (active) dibenzoylglycerate (active), and the possibility of this having influenced the rotation observed, we deemed it desirable to prepare a further quantity. Unfortunately, we had exhausted our original supply of active amylic alcohol, and the new preparation had to be made from a fresh sample. The rotation of the new amylic alcohol employed was found to be very slightly higher than that of the former one, namely, $\alpha_D = -7.61^\circ$ in a 200 mm. tube at 12.5° .

The amylic (active) glycerate (active) prepared from it had also a slightly, but distinctly higher, rotation than the former specimen, thus

* This observation was made at the end of the series, and thus shows that the rotation has not been affected by raising the substance to the temperatures employed in the other observations.

$$\alpha_D = -6.60^\circ \text{ in a 50 mm. tube at } 20.5^\circ \text{ (new specimen).}$$

$$\alpha_D = -6.14^\circ \quad , \quad , \quad 19^\circ \text{ (former specimen).}$$

From this new specimen of amylic (active) glycerate (active), the dibenzoyl-compound was prepared as before. On combustion,

0.1841 gave 0.4608 CO₂ and 0.1078 H₂O. C = 68.26; H = 6.50.

The substance was thus of about the same degree of purity as before. It was again distilled, but the distillation was not found to have altered the rotation. On combustion again,

0.1808 gave 0.4520 CO₂ and 0.1034 H₂O. C = 68.18; H = 6.35.

C₂₂H₂₄O₆ requires C = 68.75; H = 6.25 per cent.,

thus showing that no further purification could be effected by distillation.

The rotation was then determined over the following range of temperature.

*Rotation of Amylic (active) Dibenzoylglycerate (active).
(Second specimen.)*

Temp.	Observed rotation α_D in 44 mm. tube.	Density compared with water at 4°.	$[\alpha]_D$.
17°	+ 10.31°	1.1425	+ 20.51°
45.5	+ 9.35	1.1180	+ 19.01
74	+ 8.11	1.0943	+ 16.84
99.5	+ 6.87	1.0739	+ 14.54

The density determinations actually made were $d_{17.5}^{4^\circ} = 1.1421$; $d_{46}^{4^\circ} = 1.1176$; $d_{74}^{4^\circ} = 1.0943$; $d_{99.5}^{4^\circ} = 1.0739$. The alterations, both in density and rotation, are of exactly the same character as in the case of the previous specimen.

It is worthy of remark that, of the two specimens of amylic (active) glycerate (active), the one with the higher rotation also gave the more active dibenzoyl-compound, showing how the rotation of a derivative is proportional to the rotation of the original mixture of the active compound and the racemoid from which it is prepared, as pointed out in the introduction.

Amylic (inactive) Glycerate (active).

This was prepared in the same manner as the corresponding compounds already described, excepting that inactive amylic alcohol was employed instead of the active; twenty-six grams of crude ethereal salt were obtained from 35 grams of calcium glycerate (active) and 80 c.c. of amylic alcohol (inactive).

It had a rotation, which was constant on redistillation, of $\alpha_D = -7.66^\circ$ in a 50 mm. tube at 20°.

On combustion,

0.1736 gave 0.3450 CO₂ and 0.1425 H₂O. C = 54.20 ; H = 9.12.

0.1593 „ 0.3183 „ 0.1316 „ C = 54.49 ; H = 9.18.

C₈H₁₆O₄ requires C = 54.54 ; H = 9.09 per cent.

Rotation of Amylic (inactive) Glycerate (active).

Temp.	Observed rotation α_D in 44 mm. tube.	Density compared with water at 4°.	$[\alpha]_D$.
14.3°	- 6.72°	1.0783	- 14.16°
15	- 6.70	1.0777	- 14.13
48	- 6.68	1.0496	- 14.46

The density determinations actually made were $d_{14.8^\circ/4^\circ} = 1.0779$; $d_{48^\circ/4^\circ} = 1.0496$.

The negative specific rotation of this ethereal salt thus increases very slightly indeed with rise of temperature (see Fig. 1, p. 257).

The excess of alcohol recovered in the preparation of this amylic (inactive) glycerate (active) proved to be slightly active, thus,

$$[\alpha]_D^{17^\circ} = -0.085^\circ ; d_{17^\circ/4^\circ} = 0.8189.$$

It has been pointed out (see pp. 256 footnote, and 261) that the alcohol recovered in the preparation of amylic (active) glycerate (inactive) and of amylic (active) glycerate (active) exhibited a slightly increased negative rotation as compared with the alcohol used, the increase in each case being about the same in amount. In these cases, as already pointed out, this may be due to the iso-amylic alcohol (isobutylcarbinol), which is doubtless also present, etherifying more readily than the active amylic alcohol (secondary butylcarbinol), but in the present case the slight activity of the recovered alcohol cannot be thus explained, and can only be accounted for on the supposition that the dextro-amylic isomer of the racemised alcohol is more readily etherified by the dextro-glyceric acid than the lævo-amyl isomeride. This result, although suggestive, involves such a very small absolute rotation, that it would be premature to draw conclusions from it yet, and we propose submitting the matter to further investigation. The possibility of some of the ethereal salt having passed over with the alcohol must also be kept in view.

Amylic (inactive) Diacetylgllycerate (active).

This was prepared from the above amylic (inactive) glycerate (active) in precisely the same manner as already described in the case of the corresponding compounds. Seven grams of amylic glycerate yielded 11 grams of crude amylic diacetylgllycerate. The pure product distilled at 156—159° (about 4 mm. press.), the oil-bath being at 200°.

On combustion,

0.1623 gave 0.32905 CO₂, 0.1162 H₂O. C = 55.29 ; H = 7.95.

0.1585 „ 0.32105 „ 0.1115 „ C = 55.24 ; H = 7.82.

C₁₂H₂₀O₆ requires C = 55.38 ; H = 7.69 per cent.

Rotation of Amylic (inactive) Diacetyl-glycerate (active).

Temp.	Observed rotation α_D in 44 mm. tube.	Density compared with water at 4°.	$[\alpha]_D$.
15·2°	- 9·26°	1·0813	- 19·46°
52	- 9·81	1·0447	- 21·34
99·7	- 10·22	0·9980	- 23·27

The density determinations actually made were $d_{15\cdot2/4^\circ} = 1\cdot0813$; $d_{52/4^\circ} = 1\cdot0447$; $d_{100/4^\circ} = 0\cdot9977$.

The specific rotation is thus highly sensitive to temperature, its negative value rising with increase of temperature. The influence of temperature on the rotation is exhibited in the diagram (see Fig. 2, p. 258).

Amylic (inactive) Dibenzoyl-glycerate (active).

The method of preparation was the same as that pursued in the case of the two similar compounds described above, the amylic (inactive) glycerate (active) referred to on p. 264 being used as the source. It could not be obtained in a solid state.

On combustion,

0·19825 gave 0·4949 CO_2 and 0·1155 H_2O . C = 68·08; H = 6·47.

0·1936 „ 0·4836 „ 0·1142 „ C = 68·12; H = 6·55.

$\text{C}_{22}\text{H}_{24}\text{O}_6$ requires C = 68·75; H = 6·25 per cent.

It was, therefore, of about the same degree of purity as the other liquid dibenzoyl-compounds described above.

Rotation of Amylic (inactive) Dibenzoyl-glycerate (active).

Temp.	Observed rotation α_D in 44 mm. tube.	Density compared with water at 4°.	$[\alpha]_D$.
16°	+ 9·205°	1·1452	+ 18·27°
38·8	+ 8·60	1·1238	+ 17·39
63	+ 7·66	1·1032	+ 15·78
100	+ 5·93	1·0730	+ 12·56

The density determinations actually made were $d_{16/4^\circ} = 1\cdot1452$; $d_{39/4^\circ} = 1\cdot1236$; $d_{63/4^\circ} = 1\cdot1032$; $d_{100/4^\circ} = 1\cdot0730$. Thus the density diminishes less and less rapidly with rise of temperature, as in the dibenzoyl-compound described on p. 263, as, in the latter case also, the specific rotation diminishes more and more rapidly with rise of temperature. These relations are best seen in the diagram (Fig. 3, p. 259).

Superposition of the Optical Effects of Two Asymmetric Carbon Atoms.

One of the points of interest in connection with the compounds described in this paper lies in the circumstance that in all of them there are present two asymmetric carbons, each of which can be present (a) in the dextro-rotatory, (b) the lævo-rotatory, and (c) in the

racemoid form. In the liquid state, however, there is no evidence that the racemoid form is anything else than a mixture in equal proportions of the dextro- and lævo-rotatory forms. As the optical activity of asymmetric carbon compounds, moreover, has reference to the liquid state only, it is obvious that the true racemoid form disappears from consideration.

The several amylic glycerates described above may therefore be thus regarded.

1. Amylic (<i>lævo-act.</i>) glycerate (<i>dextro-act.</i>)	{	1 molecule lævo-amylic
$[\alpha]_D = C^*$		dextro-glycerate.
2. Amylic (<i>lævo-act.</i>) glycerate (<i>inact.</i>)	{	1 molecule lævo-amylic
$[\alpha]_D = H$		dextro-glycerate.
3. Amylic (<i>inact.</i>) glycerate (<i>dextro-act.</i>)	{	1 molecule lævo-amylic
$[\alpha]_D = E$		1 molecule lævo-amylic
lævo-glycerate.
	{	1 molecule lævo-amylic
		dextro-glycerate.
	{	1 molecule dextro-amylic
		dextro-glycerate.

If, then, the optical effect of (2) be algebraically added to the optical effect of (3), the optical effect of (1) should be obtained, because the optical effect of 1 mol. *l*-amylic *l*-glycerate will be equal, but opposite in sign, to that of 1 mol. *d*-amylic *d*-glycerate, and therefore these will destroy each other, and there will remain the optical effect of 1 mol. *l*-amylic *d*-glycerate from (2) + the optical effect of 1 mol. *l*-amylic *d*-glycerate from (3), which sum will thus equal the optical effect of (1). In other words, $H + E = C$.

This is actually found to be the case, thus, comparing the specific rotations at the same temperatures,

Amylic (lævo-active) glycerate (inactive).

$$H \quad [\alpha]_D^{11^\circ} = +2.86^\circ. \quad [\alpha]_D^{47^\circ} = +2.79^\circ.$$

Amylic (inactive) glycerate (dextro-active).

$$E \quad [\alpha]_D^{11^\circ} = -14.13^\circ. \quad [\alpha]_D^{47^\circ} = -14.45^\circ.$$

$$H + E = C$$

Then, for 11° . $2.86 - 14.13 = -11.27^\circ = [\alpha]_D$ amylic (*lævo-active*) glycerate (*dextro-active*) (by calculation).

Amylic (*lævo-active*) glycerate (*dextro-active*) $[\alpha]_D^{11^\circ} = -11.53^\circ$ (by experiment).

Difference between calculation and experiment = 0.26° .

Again, for 47° .

* We have adopted the same lettering here as in the introduction, p. 254.

$2.79 - 14.45 = -11.66^\circ = [\alpha]_D$ amylic (lævo-active) glycerate (dextro-active) (by calculation).

Amylic (lævo-active) glycerate (dextro-active) $[\alpha]_D^{47^\circ} = -11.79^\circ$ (by experiment).

Difference between calculation and experiment $= 0.13^\circ$.

Applying the same reasoning to the amyl diacetylgllycerates, we have,

Amylic (lævo-active) diacetylgllycerate (inactive).

H $[\alpha]_D^{11^\circ} = +1.66^\circ$. $[\alpha]_D^{52^\circ} = +1.67^\circ$. $[\alpha]_D^{99.7^\circ} = +1.68^\circ$.

Amyl (inactive) diacetylgllycerate (dextro-active).

E $[\alpha]_D^{11^\circ} = -19.25^\circ$. $[\alpha]_D^{52^\circ} = -21.34^\circ$. $[\alpha]_D^{99.7^\circ} = -23.27^\circ$.

Then $H + E = C$ $[\alpha]_D$ for amylic (lævo-active) diacetylgllycerate (dextro-active),

	Calculated.	Found.	Difference.
At 11°	$1.66^\circ - 19.25^\circ = -17.59^\circ$	-17.25°	0.34°
„ 52	$1.67 - 21.34 = -19.67$	-19.22	0.45
„ 99.7	$1.68 - 23.27 = -21.59$	-21.28	0.31

Similarly, in the case of the amylic dibenzoylgllycerates,

Amylic (lævo-active) dibenzoylgllycerate (inactive).

H $\left\{ \begin{array}{l} [\alpha]_D^{16^\circ} = +1.76^\circ. \\ [\alpha]_D^{38.8^\circ} = +1.72. \end{array} \right.$ $\left\{ \begin{array}{l} [\alpha]_D^{63^\circ} = +1.67^\circ. \\ [\alpha]_D^{100^\circ} = +1.60. \end{array} \right.$

Amylic (inactive) dibenzoylgllycerate (dextro-active).

E $\left\{ \begin{array}{l} [\alpha]_D^{16^\circ} = +18.27^\circ. \\ [\alpha]_D^{38.8^\circ} = +17.39^\circ \end{array} \right.$ $\left\{ \begin{array}{l} [\alpha]_D^{63^\circ} = +15.78^\circ. \\ [\alpha]_D^{100^\circ} = +12.56. \end{array} \right.$

Then $H + E = C = [\alpha]_D$ for amylic (lævo-active) dibenzoylgllycerate (dextro-active).

	Calculated.	Found.	Difference.
At 16°	$1.76^\circ + 18.27^\circ = +20.03^\circ$	$+19.76^\circ$	0.27°
„ 38.8	$1.72 + 17.39 = +19.11$	$+18.62$	0.49
„ 63	$1.67 + 15.78 = +17.45$	$+16.93$	0.52
„ 100	$1.60 + 12.56 = +14.16$	$+13.87$	0.29

The experimental are thus in all cases in close agreement with the calculated results, and thus show the feasibility of calculating the rotation values of all the optically isomeric amylic glycerates, diacetylgllycerates, and dibenzoylgllycerates, provided the values H and E are determined in each series, as indicated in the introduction on p. 254.

Density of the Amylic Salts of Glyceric Acid.

In the following table, we have collected the densities, calculated for equal temperatures, of the several amylic salts of glyceric acid described above; the densities are referred to water at 4° .

	Temp.	From act. alcohol, inactive acid.	From act. alcohol, active acid.	From inact. alcohol, active acid.
Amylic	{ 11°	1·0807	1·0797	1·0811
Glycerates	{ 47	1·0505	1·0495	1·0505
Amylic	{ 11	1·0863	1·0859	1·0855
Diacetyl-glycerates	{ 50	1·0485	1·0468	1·0466
	{ 100	1·0000	0·9985	0·9977
Amylic	{ 16	1·1433	1·1456	1·1452
Dibenzoyl-	{ 40	1·1237	1·1236	1·1227
glycerates	{ 63	1·1049	1·1044	1·1032
	{ 99·8	1·0749	1·0746	1·0732

The above figures show that the densities of the optical isomers are in each case in very close agreement.

Comparison of the Amylic Salts of Glyceric Acid with those previously prepared.

In order to compare the constants given above for the amylic salts with those of the derivatives previously prepared by one of us (Percy Frankland and MacGregor, *Trans.* 1893, **63**, 1415; 1894, **65**, 754), it is necessary to calculate the densities to 15°/15°, and the specific and molecular rotations, as well as the molecular deviations to 15°. Thus,

Ethereal Salt	Density 15°/15°	Molecular volume.	Specific rotation at 15° [α] _D	Molecular rotation. M [α] _D 100	Molecular deviation $\frac{\alpha}{l} \sqrt{\frac{M}{d}}$	Product of asym- metry. P $\times 10^6$
<i>Amylic Glycerates, from</i>						
Active alcohol.....	1·0783	163·2	+ 2·83°	+ 4·98°	+ 16·69°	324·3
Inactive acid						
Active alcohol.....	1·0773	163·4	- 11·55	- 20·33	- 68·05	324·3
Active acid						
Inactive alcohol	1·0786	163·2	- 14·12	- 24·85	- 83·20	324·3
Active acid						
<i>Amylic Diacetyl- glycerates, from</i>						
Active alcohol.....	1·0834	240·0	+ 1·67	+ 4·34	+ 11·24	67·3
Inactive acid						
Active alcohol	1·0828	240·1	- 17·44	- 45·34	- 117·4	67·3
Active acid						
Inactive alcohol	1·0824	240·2	- 19·44	- 50·54	- 130·8	67·3
Active acid						

Note.—In the above table, “active alcohol” = lævo-amyl alcohol, “inactive alcohol” = racemised amylic alcohol (secondary butylcarbinol); “active acid” = dextro-glyceric acid; “inactive acid” = (racemised) glyceric acid.

Of the above compounds, the ones which can be directly compared with the previously prepared glycerates and diacetylgycerates are those obtained from the inactive (racemised) amylic alcohol. From the following table it will be seen how these derivatives of the inactive (racemised) amylic alcohol fall into line with the corresponding derivatives of the other alcohols hitherto examined by one of us.

Ethereal Salts of Active Glyceric Acid.

Ethereal Salt.	Density 15°/15°	Molecular volume.	Differ- ence.	Specific rotation, $M[\alpha]_D^{15}$	Molecular rotation, $\frac{M[\alpha]_D}{100}$	Molecular deviation, $[\delta]_D = \frac{\alpha}{\tau} \sqrt{\frac{M}{d}}$	Product of asym- metry, $P \times 10^6$.
Methylic.....	1·2798	93·8	18·6	- 4·80°	- 5·76°	- 27·9°	288·8
Ethylic	1·1921	112·4		- 9·18	- 12·30	- 52·8	344·8
Propylic	1·1448	129·3	16·9	- 12·94	- 19·15	- 74·9	358·2
Isopropylic.....	1·1303	130·9		- 11·82	- 17·49	- 67·8	358·2
Butylic (norm.)	1·1084	146·2	15·7	- 13·19	- 21·37	- 77·0	346·8
Isobutylic	1·1051	146·6		- 14·23	- 23·05	- 82·9	346·8
Amylic (second- ary butylme- thyl)	1·0786	163·2	16·6 $\frac{3}{50·1}$	- 14·12	- 24·85	- 83·2	324·3
Heptylic(norm.)	1·0390	196·3		- 11·30	- 23·05	- 68·3	268·7
Octylic (norm.)	1·0263	212·4	16·1	- 10·22	- 22·28	- 62·6	241·8

Ethereal Salts of Active Diacetylgyceric Acid.

Methylic.....	1·1998	170·0	18·4	- 12·04°	- 24·56°	- 80·0°	0
Ethylic	1·1574	188·4		- 16·31	- 35·56	- 108·2	0
Propylic	1·1263	206·0	17·6	- 19·47	- 45·17	- 129·5	17·4
Isopropylic.....	1·1193	207·3		- 17·97	- 41·69	- 119·1	17·4
Isobutylic	1·0990	223·8	16·4	- 20·48	- 50·38	- 136·7	41·9
Amylic (second- ary butylme- thyl)	1·0824	240·2		- 19·44	- 50·54	- 130·8	67·3
Heptylic	1·0537	273·3	16·9	- 16·63	- 47·89	- 113·6	110·4
Octylic	1·0408	290·2		- 15·87	- 47·92	- 109·3	126·2

Note.—Product of asymmetry for hexylic glycerate = 296·8.

„ „ „ diacetylgycerate = 90·7.

The results contained in the above table, and which are more easily followed from the curves in the appended diagrams (Figs. 4, 5, 6,) show that (1) the density, in the case of the glycerates, diminishes more rapidly with increasing molecular weight than is the case with the diacetylgycerates, and as was already pointed out by one of us (*Trans.*, 1893, 63, 1428) the curves should intersect between the butylic and amylic compounds. This is now actually found to be the case, for whilst isobutylic glycerate has a greater density than isobutylic

diacetylgyerate, the density of amylic gyerate is less than that of amylic diacetylgyerate.

FIG. 4.—Densities of Ethereal Salts of Glyceric and Diacetylgyeric Acids $\left(15^{\circ}\right)$.

(2) As has been already shown, both in the series of the glycerates and in that of the diacetylgyerates, there is a maximum rotation

FIG. 5.—Molecular Volumes of Ethereal Salts of Glyceric and Diacetylgyeric Acids $\left(15^{\circ}\right)$.

which occurs in each case between the butylic and the heptylic compounds, the highest rotation in each series having hitherto been found for the butylic compound. The addition now of the amylic term to

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each of these series becomes, therefore, of particular interest. The above figures show that in respect of specific rotation $[\alpha]_D$, the maximum falls on the isobutyl term, both in the glycerate and in the diacetyl-glycerate series; on the other hand, in respect of molecular rotation $\frac{M[\alpha]_D}{100}$ the maximum falls on the amyl term in both series, whilst in respect of molecular deviation $[\delta]_D$, it falls on the amyl term in the glycerate series, and on the isobutyl term in the diacetyl-glycerate series. The differences between these two terms are, however, com-

FIG. 6.—Molecular Rotations $[M]_D$ and Molecular Deviations $[\delta]_D$ of Ethereal Salts of Glyceric and Diacetyl-glyceric Acids, 15° .

paratively small, as the curves in this part are almost straight lines parallel to the horizontal axis.

It should, however, be pointed out in this connection that, inasmuch as in the preparation of the amylic (inactive) glycerate (active) the excess alcohol recovered had a slight negative rotation (see p. 265), it follows that the alcohol actually etherified must have had a slight positive rotation, and it must therefore be concluded that, had the C₅H₁₁ which entered the glyceric acid been quite inactive, the rotation of the amylic glycerate produced would have been slightly more negative than it was found to be. Thus the rotations given above for the amylic (inactive) glycerate (active) and the amylic (inactive) diacetyl-glycerate (active) are probably a little below the truth, in consequence

of the slightly unequal etherification of the optical isomerides of which the inactive amylic alcohol is composed. Of course, this remark is subject to the reservation made on p. 265 with regard to the apparent inequality of the etherification. From their structure, it is obvious that the amyl compounds we have prepared are more directly comparable with the isopropyl and isobutyl compounds than with those of normal structure, and thus in the diagrams they have been treated as iso-amyl compounds.

The Dibenzoyl Derivatives of Active Glyceric Acid.—In the following table we have compared the densities and rotations of the dibenzoyl derivatives of active glyceric acid, as far as we have yet prepared and studied them.

Ethereal Salts of Active Dibenzoylglyceric Acid.

Ethereal salt.	Density 15°/4°.	Molecular volume 15°	Density 100°/4°.	Molecular volume 100°.	Specific rotation 15° [α] _D .	Specific rotation 100° [α] _D .	Molecular rotation 15° $\frac{M[\alpha]_D}{100}$	Molecular rotation 100° $\frac{M[\alpha]_D}{100}$	Molecular deviation 15° $\frac{a \sqrt{M}}{l \cdot d}$	Molecular deviation 100° $\frac{a \sqrt{M}}{l \cdot d}$	Product of asymmetry $P \times 10^6$
Methylic ...	1.2211	268.6	1.1574	283.4	+26.89°	+17.80°	+88.20°	+58.38°	211.8	135.3	-61.8
Ethylic ...	1.2010	284.8	1.1270	303.5	+26.58	+18.05	+90.90	+61.73	210.0	136.7	-37.4
Propylic ...	1.1807	301.5	1.1067	321.7	+21.00	+14.20	+74.76	+50.55	166.3	107.6	-19.1
Butylic ...	—	—	—	—	—	—	—	—	—	—	-7.3
Amylic (inactive) ...	1.1461	335.0	1.0730	357.9	+18.31	+12.56	+70.31	+48.2	145.7	95.7	-1.2
Hexylic ...	—	—	—	—	—	—	—	—	—	—	+0.4
Heptylic ...	—	—	—	—	—	—	—	—	—	—	+1.4
Octylic ...	—	—	—	—	—	—	—	—	—	—	+5.5

The above table shows, as already pointed out by one of us (Trans., 1894, 65, 758; 1896, 69, 104), that the introduction of the two benzoyl groups reverses the sign of the rotation, all the dibenzoylglycerates having a positive, whilst the glycerates, diacetylglycerates, dipropionylglycerates, and diphenacetylglycerates have a negative rotation. The tendency of the positive rotation in this series of dibenzoylglycerates is obviously to diminish as the magnitude of the alkyl radicle increases. There is, however, a slight departure from this general tendency apparent in the case of the methyl and ethyl compounds, as it would be anticipated that the positive rotation of the methyl should be considerably in excess of that of the ethyl compound, whilst, as a matter of fact, the specific rotations of these two compounds was found to be almost exactly equal over a wide range of temperature.

At first sight, it might be suggested that the rotation of the methyl compound is abnormally low, owing to its forming molecular aggregates (the methyl compound melts at 58—59°, the ethyl at 25°), but at higher temperatures, which should lead to the breaking up of such aggregates, the rotation of the ethyl compound is more distinctly in

excess of that of the methyl compound. The general relationship of the rotations in this series, excluding this anomaly in the case of the first term, indicates that the lævo-rotation conditioned by the alkyl-group tends to counteract the dextro-rotation which is conditioned by the benzoyl-groups; thus, in the simple glycerates, as has been shown above, the lævo-rotation increases from the methyl to the amyl compound, the same is the case in the diacetylglycerate series, whilst in this dibenzoylglycerate series the positive rotation diminishes from the methyl to the amyl compound. Just as, therefore, in the glycerate and diacetylglycerate series, the negative rotation passes through a *maximum* at the butyl or amyl compound, so in this dibenzoylglycerate series, it is to be anticipated that the positive rotation will pass through a *minimum* at the same terms of the series. Thus we should expect that the heptylic and octylic dibenzoylglycerates would have a greater positive rotation than the amyl-compound. It remains to be seen whether a further study of the higher members of this interesting series will confirm this prediction. The 'product of asymmetry,' as seen from the above table, also predicts such a minimum at the hexyl term, with the noticeable feature that the sign of the product of asymmetry actually changes for the hexyl-compound, changing back again for the heptyl and higher terms of the series. The further study of these compounds will, therefore, be attended with special interest.

Influence of Temperature on the Rotation of the Amylic Salts of Glyceric Acid.

Attention has repeatedly been drawn by one of us to the influence of temperature on the rotation of optically active organic compounds, and the active compounds described in this paper exhibit some interesting points in this connection.

1. The rotation of the amylic salts of active diacetylglyceric acid and of active dibenzoylglyceric acid is very sensitive to temperature, whilst that of the amylic salts of the corresponding inactive acids is insensitive to temperature, showing, therefore, that the sensitiveness is dependent on the active acid radicle.

2. The rotation of all the simple amylic glycerates, amylic (active) glycerate (active), amylic (active) glycerate (inactive), and amylic (inactive) glycerate (active) is insensitive to temperature. It has been shown in a previous paper (Trans., 1894, 65, 769), that the rotation of methylic glycerate is more sensitive to temperature than that of ethylic glycerate, and it thus appears that in the series of the glycerates, as far as it has been yet investigated, as the alkyl radicle increases in magnitude the sensitiveness of the rotation to temperature diminishes.

3. The sensitiveness of the diacetylglycerates has been more fully investigated (*loc. cit.*), with the result that it was found to diminish with the increase in the magnitude of the alkyl radicle as far as the isobutyl compound, the rotation of the heptyl and octyl being slightly more sensitive than that of the isobutyl compound. The sensitiveness of the rotation of amylic (inactive) diacetylglycerate (active) is now found to be exactly the same as that of the isobutyl compound. These two compounds have also nearly the same specific rotation. It would thus appear that the sensitiveness attains a minimum in those terms of the series in which the actual rotation reaches a maximum, or in which the addition of CH_2 produces the least effect on the rotation. Throughout the glycerates and diacetylglycerates, the negative rotation increases with rise of temperature.

4. In the dibenzoylglycerate series, the positive rotation diminishes with rise of temperature. In this series, again, the sensitiveness of the rotation diminishes in passing from the methyl to the amyl compound.

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