

LXXIII.—*The Magnetic Rotation of Compounds supposed to Contain Acetyl, or to be of Ketonic Origin.*

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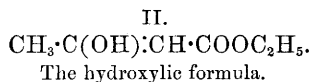
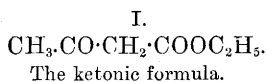
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INTRODUCTION.

EVER since the discovery of ethyl acetoacetate by Geuther in 1863, the constitution of this ethereal salt has been the subject of much discussion, and notwithstanding the fact that it has been more fully investigated than almost any other chemical compound, this question of its constitution is still disputed. This is the more remarkable when it is considered that only two formulæ can be brought forward to account for the properties of this substance, namely :—



The ketonic formula was first suggested by Frankland and Duppa; the hydroxylic formula is the one which was proposed by Geuther.

The difficulty of deciding between these formulæ lies in the fact that either may be taken as almost equally well explaining the reactions of the substance, and, again, it is conceivable that it may at times act as a ketonic compound, and at others as a hydroxy-derivative; in other words, the two formulæ may be called tautomeric.

Among the latest contributions to the discussion of this question of the constitution of ethyl acetoacetate is a long and important paper by Nef (*Annalen*, 266, 52), who, from the results of a number of interesting experiments, concludes that the hydroxylic formula is the correct one, and that the ketonic constitution, and also the idea of tautomerism, of the two formulæ must be regarded as disproved.

In support of the ketonic formula v. Pechmann brings forward a number of new arguments. He compares side by side the properties of ethyl acetoacetate and ethyl formylacetate, and argues that as

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these substances differ so materially in properties, they cannot be analogously constituted.

For the ethyl formylacetate, as for the ethyl acetoacetate, two formulæ are possible:—



The first, suggested by W. Wislicenus (*Ber.*, **20**, 2930), represents the substance as an aldehyde, and analogously constituted to the ketonic form of ethyl acetoacetate. The second, suggested by Claisen (*Sitzungsbericht d. k. Bayer Akademie der Wissenschaften*, **20**, 264), represents the substance as a derivative of vinyl alcohol corresponding to the hydroxy-form of ethyl acetoacetate, and v. Pechmann argues that from its behaviour with different reagents, it is impossible that ethyl formylacetate and ethyl acetoacetate can be analogously constituted. Having shown that ethyl formylacetate has the hydroxylic formula, he concludes that ethyl acetoacetate can only have the ketonic formula.

Claisen has likewise written a valuable paper on this subject, strongly advocating the ketonic constitution of ethyl acetoacetate (*Ber.*, **25**, 1776), and just recently Nef again refers to this subject, objecting to the arguments which have been used by v. Pechmann (*Proc. Amer. Acad.*, 1892, 160). Michael has also lately written another paper (*J. pr. Chem.*, **46**, 189), in which he calls in question the correctness of some of Nef's experiments, especially those from which he has drawn the most important conclusions.

On considering this subject, it appeared to me that it must be always a matter of great difficulty to decide definitely the constitution of substances of the nature of ethyl acetoacetate or other ketonic derivatives from the study of their chemical properties alone, more especially when it is considered that, even if they usually possess the ketonic constitution, they may in many of their reactions act in a tautomeric form, and that it would therefore be valuable if some physical method could be used which would discriminate clearly between the ketonic and hydroxylic forms of such substances.

The most important point of difference between these two classes of substances is that the ketones are saturated compounds, whereas their hydroxylic isomers are unsaturated.

To distinguish between these, the study of their refractive powers is one method which can be adopted, and Brühl (*Ber.*, **25**, 369) has lately shown that in the case of ethyl acetoacetate numbers are obtained which are in favour of the ketonic formula.

In my previous researches I have repeatedly called attention to the fact that very considerable differences are observed between the magnetic rotation of saturated and unsaturated compounds, the latter

giving much larger numbers than the former, and it appeared to me that this method might in the present instance be very valuable in distinguishing between saturated ketonic substances and their unsaturated hydroxylic isomers, especially if in some cases the refractive and dispersive powers were likewise examined in confirmation of the results.

A preliminary account of some of the results in connection with this subject are published in the Proceedings of this Society (May 19, 1892, p. 100).

In the paper by Professor Claisen (*Ber.*, 25, 1779), on the constitution of ethyl acetoacetate, already referred to, he also draws attention to my determination of the magnetic rotation of this substance, showing that this strongly favours the ketonic formula for that body.

Methods of Estimating the Magnetic Rotations.

Before considering the results I have obtained, it will be best to consider what are likely to be the differences in the rotations between these ketonic and isomeric hydroxylic compounds, and how they can best be deduced.

The difference in rotation between a saturated and an unsaturated compound of a similar kind differing by H_2 is in most cases approximately the same; in allyl compounds, however, as allyl alcohol and carboxylic compounds, with which it is associated, it is lower than in most other compounds (0.914); leaving this special case out, the following is a list of the most important comparisons between the rotations of saturated and unsaturated bodies:—

Ethyl α -crotonate and butyrate	1.112
Ethyl oleate and stearate	1.112
Methyl isobutenyl ketone (mesityl oxide), and methyl isobutyl ketone	1.145
Ethyl itaconate and glutarate	1.120
Ethyl citraconate and glutarate	1.170
Average	1.132

In this list an exceptionally high result found between ethyl maleate and succinate, namely, 1.245, has been left out; but if this and that of an allyl compound be introduced, it will give an average which is not very different, about 1.117. In the past I have usually employed 1.112, and, as this is not far from the above, it will, I think, be best to still continue its use.

This number, 1.112, refers to the rotations of bodies differing in composition by H_2 , but in the case of the ketonic and hydroxylic

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class of compounds under consideration this difference does not exist as they are isomeric; consequently the unsaturated or hydroxy-derivative will have a larger rotation than the ketonic by 1.112 + the value of the difference for H_2 , and for dihydroxylic as compared with diketonic compounds twice this.

The value of H_2 as deduced from the rotations of the paraffins is 0.504 (Trans., 1882, **41**, 572); if this be added to the rotation of a ketonic compound, as well as 1.112, a number is obtained which approximates pretty well to that of its hydroxylic isomer. Thus:—

Mol. rot. ethyl acetoacetate.....	6.501
Difference for unsaturation by H_2	1.112
Difference for H_2	0.508
	<hr/>
	8.121

This hydroxylic compound is ethyl hydroxycrotonate, and as the rotation of ethyl crotonate is known, that of its hydroxy-derivative can be estimated probably more accurately than by the above method, by adding to it the value of OH replacing hydrogen, thus:—

Mol. rot. ethyl crotonate	7.589
„ OH replacing hydrogen as in alcohols	0.194
	<hr/>
	7.783

This indicates that the previous method gives numbers which are a little too high. On examination, this is found to arise from the fact that between the rotations of compounds varying in composition from each other by H_2 , the difference does not amount to 0.508, but may be more or less. This is not because the value of hydrogen changes materially, but because the products are of different types, each having its own special rotation, for example, ketones differ from primary alcohols by 0.324, from secondary by 0.409, and from tertiary by 0.646. Aldehydes also differ from primary alcohols by 0.438. As this amount for the difference in composition for H_2 is a variable quantity, to find the rotations of the unsaturated hydroxylic isomers of ketonic bodies as accurately as our present information will permit, it has been found best first to ascertain the rotations of the saturated compounds corresponding to them, and then to add to these the usual amount for unsaturation by H_2 , namely, 1.112. Taking ethyl acetoacetate again as an example, its isomeric unsaturated isomer, ethyl hydroxycrotonate, corresponds to the saturated compound ethyl hydroxybutyrate; then we get—

Mol. rot. ethyl hydroxybutyrate*	6·737
Difference for saturation by H ₂	1·112
Ethyl hydroxycrotonate	7·849

This amount of variation between ethyl hydroxybutyrate and ethyl acetoacetate for the difference of composition by H₂ will be found to be 0·236.

It is interesting to find all the above methods give numbers which are not very wide apart, but I believe the last to be the most trustworthy.

Unfortunately, not many of the saturated compounds required have been as yet examined, and therefore it is also desirable to have some means of controlling any estimate which may be made for them, besides the ordinary method of adding or subtracting the known values of different products, and an interesting method has been found which, it will be seen, does this at any rate approximately. It is based on the system of series constants already described in this Journal (Trans., 1884, **45**, 574). From the numbers and diagrams which are given in the paper just referred to, it is seen that each series of saturated compounds has a special value of its own, and on the diagrams they will be seen to run in parallel lines, and not in one line, even where the composition is the same as in the monobasic acids and their ethyl and methyl salts. Now if from the rotation of any substance 1·023 (the value of CH₂) be taken as many times as it contains carbon atoms, the remainder is what has been called the series constant, and if the rotation of another member of the homologous series to which this compound belongs be required, it is only necessary to add to the series constant 1·023, the number of times the substance contains atoms of carbon.

With complex bodies, the use of these series constants promises to be valuable, because it is difficult to estimate by the ordinary way what will be the rotation of a substance which represents two or more classes of compounds such as ethyl lactate, which is an ethereal salt and secondary alcohol, ethyl acetoacetate, which is an ethereal salt, and a ketone, &c.

From determinations of the magnetic rotation of such compounds, it appears that their series constant is the *mean*, or very nearly so, of

* The rotation of ethyl hydroxybutyrate has not yet been directly determined, but is calculated from that of ethyl lactate by the addition of the value for CH₂ (1·023). Although this is an α - and the above a β -hydroxy-compound, this is not likely to influence the estimate practically. It has been shown that the ethereal salts of tartaric and racemic acid gave the same rotations (Trans., 1887, **51**, 364). Therefore we may expect the *lævo*- and *dextro*-ethyl lactates will also have the same rotations.

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the series constants of the compounds they represent; thus, taking ethyl lactate, which is a secondary alcohol and ethereal salt:—

Ser. const. of sec. alcohol	0·844
„ ethyl salt	0·337
	<u>2)1·181</u>
Estimated ser. const. of ethyl lactate.....	0·590
1·023 × 5.....	<u>5·115</u>
Estimated mol. rot. ethyl lactate.....	5·705
Found.....	<u>5·720</u>

For methyl lactate we get—

Ser. const. of sec. alcohol	0·844
„ methyl salt.....	0·273
	<u>2)1·117</u>
Estimated ser. const. methyl lactate	0·558
1·023 × 4	<u>4·092</u>
Estimated mol. rot. methyl lactate.....	4·650
Found	<u>4·658</u>

Ethyl acetoacetate—

Ser. const. of acetic ethereal salt	0·370
„ ketone.....	0·375
	<u>2)0·745</u>
Estimated ser. const. ethyl acetoacetate...	0·372
1·023 × 6.....	<u>6·138</u>
Mol. rot. of ethyl acetoacetate.....	6·510
Found	<u>6·501</u>

Ethyl tartrate may be taken as another example. This substance represents an ethereal salt of succinic acid and a glycol,

Ser. const. of glycol.....	0·897
„ ethyl succinate	0·196
	<u>2)1·093</u>
Estimated ser. const. ethyl tartrate	0·546
1·023 × 8	<u>8·184</u>
Mol. rot. ethyl tartrate.....	8·730
Found.....	<u>8·766</u>

It is desirable in these calculations to take the series constant of

the products most nearly related to the substances the rotation of which it is desired to estimate.

In this paper I have mostly used the ordinary method of finding the rotation, supplemented by this method in which series constants are employed, and have described the process somewhat in detail, so that an idea may be formed as to how far some of the curious results obtained in this investigation are to be relied upon.

Through the kindness of my chemical friends, I have had placed at my disposal for this inquiry a number of specimens of rare products; this has made it possible to examine a somewhat systematic series of substances bearing on this subject. The following is a list:—

Fatty Series.

- Pyruvic acid.
- Ethyl acetoacetate.
- Ethyl ethylacetoacetate.
- Ethyl allylacetoacetate.
- × Ethyl ethylideneacetoacetate.
- Levulinic acid.
- †† Ethyl acetonedicarboxylate.
- × * Acetylacetone.
- × * Methylacetylacetone.
- × Ethylacetylacetone.
- × Ethyl acetonoxyalate.
- × Methyl acetonoxyalate.
- × Ethyl diacetoacetate.
- † Diacetylacetone.
- † Ethyl β -amidocrotonate.

Aromatic Series.

- × Benzoylacetone.
- Ethyl benzoylacetate.
- × Methyl acetophenonoxyalate.
- × Ethyl acetophenonoxyalate.

For the substances marked × I am indebted to the kindness of Professor Claisen, those marked † to Dr. Collie, those marked * to Professor Dunstan, and the one marked †† to Professor v. Pechmann.

It will be convenient to follow this list in the above order, to discuss the bearing of the results obtained first, and afterwards give the experimental data from which they are obtained.

THEORETICAL CONSIDERATIONS.

Pyruvic Acid.

The interest attaching to this substance is that there is but little likelihood of its possessing any other than a ketonic constitution, $\text{CH}_3\cdot\text{CO}\cdot\text{COOH}$.

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Its magnetic rotation was found to be 3·567.

If this compound be considered as acetoformic acid, its rotation, according to the series constant, would be

Ser. const. formic acid.	0·648
„ of ketone	0·375
	<u>2)1·023</u>
	0·511
1 023 × 3	3·069
Estimated rot. of pyruvic acid	<u>3·580</u>

So that although pyruvic acid is not usually a very pure product, the rotation obtained is probably not far from correct; at any rate it is the rotation of a *saturated* compound.

Ethyl Acetoacetate.

The rotation found for this substance some years since was 6·501. I have shown when discussing the methods of calculation used in this paper (p. 806) that from the series constants it should be 6·510. That is viewing it as an acetic compound; if taken as the ether of a C_3 acid it is slightly lower, namely 6·494; the series constant for acetic ethereal salt being 0·370, whereas that of ethereal salts of monocarboxylic acids containing C_3 and upwards is 0·337.

From this agreement with the series constants and the size of the rotation, there can be no doubt that it is a *ketonic saturated* compound. Had it been an unsaturated compound, its rotation would have been about 7·849, or 1·348 higher than that found.

As a very slight internal rearrangement in the molecule of acetoacetic acid would be required for it to become an hydroxylic unsaturated body, it was thought that it would be interesting to determine its magnetic rotation at a considerably higher temperature than those previously employed, so as to see if heat were conducive to such a change.

The following is a comparison of the rotation obtained with that at ordinary temperatures:—

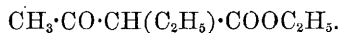
Mol. rot. ethyl acetoacetate at 16°....	6·501
„ „ 90°....	6·470
Difference	<u>74·3°....0·031</u>

The results, therefore, show that practically no change takes place when ethyl acetoacetate is heated. From observations on other substances described further on in this paper, it will be seen that this

was not likely to happen, but that cooling would be more likely to have an influence in causing the formation of an unsaturated isomer. I have mentioned on previous occasions that magnetic rotations are slightly lower when determined at high than when determined at low temperatures; therefore, the above results being a little lower at 90.5° is consistent with this.

Ethyl Ethylacetoacetate.

The examination of this substance is interesting as it enables a comparison to be made with ethyl ethylmalonate, where no question as to the existence of hydroxyl can arise; the ethyl in this body being in union with carbon. Therefore if the rotation of ethyl ethylacetoacetate differs from that of ethyl acetoacetate in the same way, or approximately so, as that of ethyl ethylmalonate differs from malonate, it will be good evidence that the ethyl is in union with the carbon, thus—



The rotation of ethyl ethylacetoacetate was found to be 8.329 .

The following are the comparisons:—

Mol. rot. of ethyl ethylmalonate	9.272
„ malonate	7.410
Increase due to rep. of H in CH_2 by ethyl.	1.862
Mol. rot. of ethyl ethylacetoacetate	8.329
„ ethyl acetoacetate.....	6.501
	<hr/> 1.828

The increase in both cases is practically the same. These numbers then establish the analogy of the replacement in this compound to that in ethyl ethylmalonate, and also show that it is a *saturated* or *ketonic* compound.

Ethyl Allylacetoacetate.

This substance was examined several years ago, and was found to have a rotation of 10.382 . It is an example of the introduction of an unsaturated radicle into ethyl acetoacetate by single combination,

its formula being $\text{CH}_3 \cdot \text{CO} \cdot \text{CH} \cdot \text{COOC}_2\text{H}_5$
 $\quad \quad \quad |$
 $\quad \quad \quad \text{CH}_2 \cdot \text{CH} : \text{CH}_2$

From the following comparisons with ethyl allylacetate, it will be seen that this also has the ketonic formula:—

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Mol. rot. of ethyl allylacetate.....	6.426
„ ethyl acetate.....	2.525
Difference due to allyl replacing H.....	3.901
Mol. rot. of ethyl allylacetoacetate	10.382
„ ethyl acetoacetate.....	6.501
Difference due to allyl replacing H.....	3.881

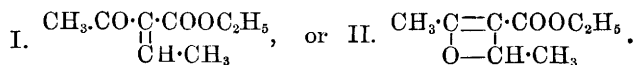
These differences are practically the same, and as ethyl allylacetate cannot contain allyl replacing the hydrogen of hydroxyl, it must be in union with the carbon; the same is evidently the case in ethyl allylacetoacetate.

Ethyl Ethylideneacetoacetate.

This substance, which is prepared from ethyl acetoacetate and aldehyde, differs in composition from ethyl allylacetoacetate by CH_2 . Its rotation was found to be 9.370. This is less than that of ethyl allylacetoacetate by practically the amount required for the difference of CH_2 (1.023).

Mol. rot. ethyl allylacetoacetate.....	10.382
„ ethyl ethylideneacetoacetate	9.370
	1.012

It might, therefore, be thought to be a vinyl compound, but from all we know of such bodies they do not have such a high rotation relatively as allyl compounds, that is, judging from the rotation of vinyl bromide; and on the other hand the formation of this substance from ethyl acetoacetate and aldehyde renders it improbable that it has this composition. Claisen considers it may have either of the two following formulæ:—

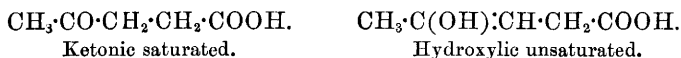


It is not easy to decide between these, as both are unsaturated compounds; the first on account of its containing ethylidene replacing two hydrogens in the CH_2 group of ethyl acetoacetate, and the second on account of ethylidene replacing one hydrogen in the CH group and another in the hydroxyl group of ethyl ethylhydroxycrotonate. As this, however, represents an oxide as well as an ethereal salt, its rotation would probably be rather higher than it is. This point could probably be best decided by treating the body with

nascent hydrogen. If the first formula be correct, it might yield ethyl hydroxyethylbutyrate, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{C}_2\text{H}_5)\cdot\text{COOC}_2\text{H}_5$.

Levulinic Acid.

β -Acetopropionic Acid.—This acid, like acetoacetic acid and its compounds, might exist as a ketonic compound, or change into the hydroxy-unsaturated isomer, thus—



As no free acid likely to be capable of changing from a ketonic to a hydroxylic compound had been examined, and it was thought that the ethereal salt might be less mobile in this particular, the examination of the acid was undertaken. It was examined twice in the melted state, and also in aqueous solution to see whether this condition affected it in reference to its constitution. The results obtained were as follows :—

Mol. rot.	I. Fused	5.543
,,	II. „	5.509
,,	III. Aqueous solution	5.503
		5.518
	Average	5.518

On comparing this result with the rotation of propionic acid, we get

Mol. rot. levulinic acid.....	5.518
,, propionic acid	3.462
	2.056
Diff. = acetyl rep. hydrogen ..	2.056

This is very nearly the same as the value of acetyl replacing hydrogen in ethyl acetoacetate, namely, 2.039.

Calculated by series constants, it is—

Ser. const. of acid, $\text{C}_n\text{H}_{2n}\text{O}_2$	0.393
,, ketone	0.375
	2)0.768
Estimated ser. const. of levulinic acid	0.384
1.023 \times 5.....	5.115
	5.499
,, rotation of levulinic acid	5.499

This differs from the result found by only 0.019. Again, if the acid have the increment added which is necessary to give the rotation of the ethereal salt, it can be compared with ethyl acetoacetate.

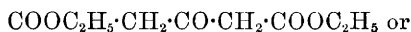
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Levulinic acid	5.518
Increment for ethereal salt.....	1.990
<hr/>	
Ethyl levulinate	7.508
Ethyl acetoacetate	6.501
<hr/>	
	1.007

This difference is very close to that required for CH_2 , namely, 1.023. From these results, levulinic acid is seen to be a *ketonic saturated* compound.

Ethyl Acetonedicarboxylate.

The interest attaching to the examination of this substance consists in its representing ethyl acetoacetate with hydrogen of the methyl group replaced by a second ethyl carboxyl group, and as this is of a negative character, it was possible that it might influence the ketonic nature of the compound. It might exist as



Ketonic, saturated.



Hydroxylic, unsaturated.

v. Pechmann, who discovered this interesting substance, has lately discussed the question of its constitution from a chemical point of view (*Ber.*, **24**, 4095), and concludes that it must possess a ketonic formula.

Brühl has also determined its refractive power, and found it to behave as a saturated compound.

Nef, on the other hand, disputes the validity of v. Pechmann's conclusions (*Proc. Amer. Acad.*, 1892, 158).

The magnetic rotation of the compound confirms to a great extent the views of v. Pechmann showing that the substance is chiefly ketonic, but it also indicates that at ordinary temperatures it also probably contains a small amount of a hydroxylic or unsaturated compound.

The rotation for the formula $\text{COOC}_2\text{H}_5 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$ may be estimated as follows—

Mol. rot. of ethyl acetoacetate	6.501
„ COOC_2H_5 rep. hydrogen	2.951
<hr/>	
	9.452

or taking acetone as the basis of the calculation,

Mol. rot. of acetone	3.514
„ $2\text{COOC}_2\text{H}_5$ rep. hydrogen	5.902
<hr/>	
	9.416

From the series constants, it is

Ser. const. ethereal salt of bibasic acid	
(glutaric)	0.140
Ser. const. of ketone	0.375
	<hr/>
	2) 0.515
	<hr/>
	0.257
1.023 × 9	9.207
	<hr/>
	9.464

The first and the last calculations come very close; the average of all, 9.444, will be used in this paper.

The rotation determined at 16.5° gives 9.604 or 0.160 in excess of the calculated; this is greater than would arise from experimental error. The rotation was, therefore, again determined, but at a much higher temperature, and at 94° it gave 9.374 or 0.070 less than the calculated rotation; a result which, if its rotation at 16.5° had been about the same as the calculated, would be consistent with experience. As already mentioned in the case of ethyl acetoacetate, rotations are always slightly lower at high than at low temperatures (of course allowing for change of density).

Mol. rot. ethyl acetonedicarboxylate at	16.5°	9.604
" " " "	94.0°	9.374
	<hr/>	<hr/>
Difference	77.5°	0.230

This difference calculated for 100° is 0.297.

This would point to some change taking place in the substance, and as will be seen farther on, indicates that any hydroxylic isomer present changes when heated into the ketonic compound, so that at 94°, and perhaps somewhat lower, it is apparently a pure ketonic product, but at ordinary temperatures contains a small quantity of a hydroxylic or unsaturated isomer.

Diketonic Compounds.

Acetylacetone, Methylacetylacetone, and Ethylacetylacetone.

Ordinary monoketones, so far as they have been examined, do not seem to have any tendency to pass into unsaturated or hydroxylic compounds. It was important, therefore, to see in what condition the so-called diketones exist at ordinary and elevated temperatures.

As monoketones might possibly change into monhydroxylic or unsaturated compounds, so diketones might change either into monhydroxyketones or into dihydroxy-derivatives or glycols, thus —

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Acetylacetone	$\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$,
Hydroxyketone.....	$\text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_3$,
Dihydroxy - derivative or	
glycol	$\text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{C}\cdot\text{C}(\text{OH})\cdot\text{CH}_3$.

I. The rotation of *acetylacetone* may be calculated thus—

Mol. rot. of acetone	3.514
„ acetyl replacing hydrogen...	2.039
„ acetylacetone.....	5.553

In calculating diketones from series constants, the series constant of a monoketone has to be employed, because that of a diketone is not known, but possibly this is correct or nearly so, because when a second carboxyl is introduced into a compound its series constant is *lowered*, but when a second hydroxyl is introduced its series constant is *increased*; therefore, in the case of an aldehyde, or a ketone, which stands between these, it is probable that the introduction of a second ketonic group would practically not alter the series constant.

On calculating acetylacetone in this way, the following result is obtained, which goes to confirm this; the series constant of acetone being taken, as it is a derivative of that compound—

Ser. const. of acetone	0.445
1.023 \times 5	5.115
Mol. rot. acetylacetone.....	5.560

This is very close to that given above.

II. The rotation of *methylacetylacetone* may be calculated on the basis of methyl ethyl ketone, this substance being in fact an acetyl derivative of the latter, thus, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{CO}\cdot\text{CH}_3)\cdot\text{CH}_3$.

Mol. rot. of methyl ethyl ketone	4.480
„ acetyl replacing hydrogen.	2.039
„ methylacetylacetone.....	6.519

From the series constant,

Ser. const. of ketone	0.375
1.023 \times 6	6.138
Mol. rot. of methylacetylacetone	6.513

These two calculations likewise agree closely.

III. The molecular rotation of *ethylacetylacetone*.

This substance may, in the same way as the above, be regarded as an acetyl methyl propyl ketone, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{CO}\cdot\text{CH}_3)\cdot\text{CH}_2\cdot\text{CH}_3$.

Mol. rot. of methyl propyl ketone	5.499
„ acetyl replacing hydrogen.	2.039
„ ethylacetylacetone	7.538
From series constants,	
Ketone	0.373
1.023 × 7	7.161
Mol. rot. of ethyl acetylacetone	7.534

Before comparing the rotations found, it will be best to find the probable rotations of the isomeric monhydroxyketones.

The saturated compounds corresponding to these are—

- I. Sec. acetopropyl alcohol.
- II. „ acetobutyl „
- III. „ acetoamyl „

The rotation found for normal acetopropyl alcohol is 5.544; if to this the difference between normal and secondary propyl alcohol be added, 0.251, the rotation of the secondary acetopropyl alcohol will be found to be 5.795, and if to this 1.112 be also added, the rotation of the hydroxyketone isomeric with acetylacetone will be obtained, viz., 6.907.

Calculating from series constants, the following results are obtained :—

I. Sec. const. isopropyl alcohol	0.950
„ ketone	0.375
	2) 1.325
	0.662
1.023 × 5	5.115
Sec. acetopropyl alcohol	5.777
For unsaturation	1.112
	6.889
II. Ser. const. sec. butyl alcohol	0.844
„ ketone	0.375
	2) 1.219
	0.609
1.023 × 6	6.138
Sec. acetobutyl alcohol	6.747
For unsaturation	1.112
	7.859

III. This will be the same as II, with the addition of 1.023 or 8.882.

The dihydroxy-derivatives would be unsaturated glycols. Combes (*Bull. Soc. Chim.*, **48**, 474—483) has shown that when acetylacetone is treated with nascent hydrogen it yields amylic glycol boiling at 177°. The rotation of this and the corresponding unsaturated compound can be estimated thus—

Glycol.....	2.943
CH ₂ × 3.....	3.069
	<hr/>
	6.012
For unsaturation × 2 ..	2.224
	<hr/>
	8.236

The difference between the hydroxyketonic compound and the ketonic is 1.336. If this be added to the former, it will give 8.225 for the dihydroxylic compound, so that both methods of calculation practically agree. By adding this difference to the other two compounds, we get for the dihydroxylic isomers of methyl- and ethylacetyl acetone 9.295 and 10.218 respectively.

The following is a table giving a comparison of the calculated rotations as compared with those found:—

	Ketonic calc.	Hydroxy- ketonic calc.	Dihydrox- ylic calc.	<i>t.</i>	Found.
Acetylacetone.....	5.553	6.889	8.236	16.6°	7.166
Methylacetylacetone	6.519	7.859	9.295	16.3	7.237
Ethylacetylacetone..	7.534	8.882	10.218	18.8	7.890

From this it is seen that all these substances give rotations considerably higher than those required by the ketonic constitution; that ethylacetylacetone is nearest to the calculated number for the latter; that methylacetylacetone comes nearly midway between the ketonic and hydroxyketonic constitution, and *acetylacetone* has a rotation which is even a little in excess of that required by the hydroxyketonic constitution, indicating the presence of a small quantity of dihydroxylic compound, apparently about 20 per cent.

As methylacetone has a rotation lying nearly midway between the ketonic and hydroxyketonic, it was thought possible that this substance might be a mixture of these two bodies in a state of unstable equilibrium, and that its constitution might vary with temperature. It was, therefore, measured at a much higher temperature than that at first employed, and the result confirmed this supposi-

tion, the rotation becoming considerably less. Acetylacetone and also ethylacetylacetone were likewise examined under similar conditions, and the rotations of these substances also were modified. The following are the results:—

	<i>t.</i>	Mol. rot.	<i>t.</i>	Mol. rot.	<i>t.</i> diff.	Mol. rot. difference.	Mol. rot. diff. for 100°.
Acetylacetone..	16·7°	7·175	93·0°	6·599	76·3°	−0·576	0·755
Methylacetyl- acetone	17·4	7·290	96·4	6·670	79·0	−0·620	0·785
Ethylacetyl- acetone	18·8	7·890	92·9	7·562	74·1	−0·328	0·443

On comparing these results with the calculated numbers in the previous table, it will be seen that ethylacetylacetone at 92·9° has a rotation which is nearly identical with that required by the *ketonic* constitution, and also that methylacetylacetone gives a number very close to that required by this kind of structure,* thus—

	Calculated ketonic.	<i>t.</i>	Found.
Acetylacetone.....	5·553	93·0°	6·599
Methylacetylacetone ..	6·519	96·4	6·670
Ethylacetylacetone ..	7·536	92·9	7·562

Acetylacetone at 93° has also assumed a position between the ketonic and hydroxyketonic rotations, and thus, at this temperature, to a great extent corresponds in character to methylacetylacetone at ordinary temperatures.

Acetylacetone, after being heated, appears quickly to regain its ordinary rotation when cooled, but this is not the case with methylacetylacetone. The rotation taken at 92° was 6·675; the same specimen examined two or three hours afterwards at 15·2° gave 6·765, and had thus only increased 0·090, but when examined a few weeks afterwards, was found to have regained its normal rotation.

The density of methylacetylacetone which has been heated and then cooled is lower than it is under ordinary circumstances, or after it has rested some considerable time. The following experiment was made in reference to this. A dilatometer was quickly filled with a freshly boiled specimen of methylacetylacetone. On placing this in water at 15°, some minutes elapsed before it became stationary in the

* In making these comparisons, a small allowance of, say, about 0·100 should be added for the influence of temperature on the rotation made at the higher temperature; this will slightly reduce the difference of rotation.

stem, some change apparently taking place; its position was then noted; in two hours it had contracted so that it was 5 mm. below its previous position, and in 24 hours it had fallen 12 mm., and it then required to be heated to 19.7° before it reached the position it originally occupied at 15° . This would correspond to a difference in density of about 0.0036. From the above results there can be no doubt that the character of these compounds changes with alterations of temperature, high temperatures favouring the ketonic or more stable condition, low temperatures the hydroxyketonic condition. It would be interesting to examine the vapours of these substances under varying conditions.

To confirm the interpretation given of the remarkable rotation of these bodies, the refractive and dispersive powers of two of them were examined at different temperatures. The refractive power should, like the rotation, show whether they are saturated or unsaturated compounds, becoming less with rise of temperature as they become saturated; and as the dispersion should also become less as they pass from saturated towards unsaturated compounds, this would give additional evidence if there were a change. The full details are given in the Experimental Part of this paper. The following numbers for three lines will show the results:—

Refraction and Dispersion of Acetylacetone at Temperatures wide apart.

<i>t.</i>	$\frac{\mu_A - 1}{d} p.$	$\frac{\mu_F - 1}{d} p.$	$\frac{\mu_G - 1}{d} p.$
11.0°	45.17	47.46	48.72
99.3°	44.14	46.12	47.17
<hr/>			
Reduction from rise of temperature... } 88.3°	1.03	1.34	1.55

The refractive power of this substance at ordinary temperatures is remarkably high. For the unsaturated compound it should be 42.2; with Brühl's estimate for one ethylene combination = 2.30, it would be 44.5, and for two, 46.8; so, like the rotation, this shows that it is the hydroxyketone containing some dihydroxy-derivative. To be sure these results were correct, I asked Dr. Gladstone if he would also examine this substance, and he was kind enough to do so; he used Dr. Claisen's specimen, whereas I employed Professor Dunstan's, and obtained:—

<i>t.</i>	$\frac{\mu_A - 1}{d} p.$	$\frac{\mu_F - 1}{d} p.$	$\frac{\mu_H - 1}{d} p.$
18.4°	45.62	47.99	50.70

These confirm the foregoing. Dr. Gladstone remarks—"That the

molecular refraction observed is higher than the theoretical, but only to an extent that might be explained on the supposition of the substances being unsaturated; thus acetylacetone, if it contained two double bonds, would give, theoretically, 45.4.* 2nd. That the dispersion is enormous and far beyond anything that can be accounted for by the double linking." In my results the dispersion between A and G amounts to no less than 3.55, and Dr. Gladstone found, between A and H, 5.08, whereas the theoretical, even considering the substance as doubly unsaturated, would only amount to about 3.58 between A and H.

From the results obtained at 99.3°, it is seen that the refraction has fallen by heating to this temperature, 1.02 for the A line and 1.55 for the G line; therefore the dispersion has altered to the extent of the difference between these numbers, namely, 0.53; this is between A and G; between A and H it would be considerably more, approaching double this amount. The refraction and dispersion, therefore, support the conclusions arrived at from the magnetic rotation.

Refraction and Dispersion of Methylacetylacetone at Temperatures wide apart.

The following results were obtained:—

<i>t.</i>	$\frac{\mu_A - 1}{d} p.$	$\frac{\mu_F - 1}{d} p.$
8.3°	50.81	52.75
99.2°	49.88	51.56
<hr/>		
Reduction from rise of temperature .. } 90.9°	00.93	1.19

The refractive power is in this case too high for the ketonic or unsaturated compound, which would require 49.8, and it is too low for the unsaturated, which, by adding 2.30 on to the last number, would be 52.1; this accords with the magnetic rotation, showing that this substance is a mixture of the ketonic and hydroxyketonic compounds, and when heated to 99.2° it also gives numbers showing that at this temperature it is practically ketonic. This change is also accompanied by a reduction of the dispersion, as would be expected, but rather less than in the case of acetylacetone; it amounts to 0.26 between A and F. The dispersion of this substance at ordinary temperatures is high.

It appears, then, that when acetylacetone, which is, from its rotation, at ordinary temperatures a hydroxyketonic compound apparently containing a small quantity of a dihydroxy-isomer, is methylated or

* Taking Bruhl's numbers, this would not be high enough for two ethylene combinations.

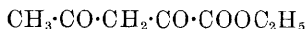
ethylated, it becomes a mixture of ketonic and hydroxyketonic compounds.

As the ethylic is more ketonic than the methylic derivative, it would appear that, the larger the hydrocarbon radicle introduced, the greater the tendency of the substance to become ketonic.

Ethyl Acetoneoxalate or Ethyl Acetylpyruvate.

This substance was discovered by Claisen and Stylos (*Ber.*, **20**, 2188—2191), by acting on ethyl oxalate with sodium alcohol and acetone. This may be regarded as acetylacetone in which methyl is replaced by COOC_2H_5 , and its examination was important, because in the case of ethyl acetoacetate the replacement of a second hydrogen by COOC_2H_5 , and consequent formation of ethyl acetonedicarboxylate, appeared to influence the ketonic group and cause the formation of a small amount of a hydroxylic compound. Therefore, if the methyl in acetylacetone—which, at ordinary temperatures, exists as the isomeric hydroxyketonic compound—is replaced by this group, COOC_2H_5 , it might be further influenced, and changed, partly or entirely, into a dihydroxy-derivative.

The magnetic rotation for the ketonic compound



may be calculated thus :—

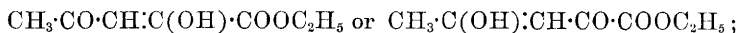
Mol. rot. of ethyl pyruvate.....	5.504
„ acetyl replacing H	2.037
	<hr/>
	7.541

Calculating from series constants—

Ser. const. ethereal salt	0.337
„ ketone $\times 2$	0.750
	<hr/>
	3)1.087
	0.362
1.023 $\times 7$	7.161
	<hr/>
	7.523

Average, 7.532.

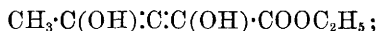
The monhydroxylic compound would be



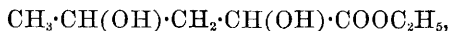
both of these would probably have the same or nearly the same rotation. Taking the first, the saturated compound corresponding to this is ethyl hydroxylevulinate, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{COOC}_2\text{H}_5$. Its rotation would be :—

Mol. rot. of ethyl levulinate	7·519
OH	0·194
„ ethyl hydroxylevulinate	7·713
For unsaturation	1·112
	<hr/> 8·825
From series constants—	
Ser. const. secondary alcohol	0·844
„ ethereal salt	0·337
„ ketone	0·375
	<hr/> 3)1·556
	0·519
1·023 × 7	7·161
	<hr/> 7·680
Ethyl hydroxylevulinate	7·680
For unsaturation	1·112
	<hr/> 8·792
Average, 8·809,	

The dihydroxylic compound would be



and the saturated compound corresponding to it,



or butyl glycol with hydrogen replaced by COOC_2H_5 . The rotation can then be calculated thus:—

Mol. rot. of butyl glycol (calculated)..	4·989
„ COOC_2H_5 replacing H....	2·950
For unsaturation × 2	2·224
	<hr/> 10·163

The difference between the estimated rotation of the ketonic and hydroxyketonic compounds is 1·277; if this be added to the rotation of the latter it gives 10·085 for the rotation of the dihydroxy-compound. These calculations are not quite so concordant as usual; their mean is 10·124, which will probably be not far from the truth.

The molecular rotation of ethyl acetoneoxalate is 10·122, which is very close to the above; therefore the substance has the *dihydroxy*-constitution $\text{CH}_3\cdot\text{C}(\text{OH})\text{:C:C}(\text{OH})\cdot\text{COOC}_2\text{H}_5$.

Its rotation was also determined at a higher temperature, and the following is a comparison of the different results obtained:—

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	<i>t.</i>	Mol. rot.	<i>t.</i>	Mol. rot.	<i>t.</i> diff.	Mol. rot. diff.
Ethyl acetoneoxalate	19.9°	10.122	89.5°	9.82	69.6°	0.302

For 100° the difference would be 0.434. This shows a reduction of rotation much greater than could result from the influence of temperature alone, and therefore indicates an alteration of a portion of the substance into the hydroxyketonic compound.

The determination of the refractive power of this substance points to the same conclusion. This was determined by myself and also by Dr. Gladstone; the detailed results will be found further on, but the following numbers will show this:—

	$\frac{\mu_A - 1}{d} p.$	$\frac{\mu_F - 1}{d} p.$	$\frac{\mu_H - 1}{d} p.$
Perkin....	$\left\{ \begin{array}{l} 17.0^\circ \quad 65.091 \\ 107.0^\circ \quad 64.676 \end{array} \right.$	$\left\{ \begin{array}{l} 68.593 \\ 68.096 \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \end{array} \right.$
Diff. ..	$\frac{83.0^\circ}{\quad} \quad \frac{0.415}{\quad}$	$\frac{0.497}{\quad}$	
Gladstone	22.1° 65.28	68.78	72.89

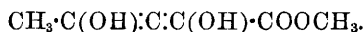
If a saturated compound, the calculated values for A would be 60.4, with a dispersion of 2.78 between A and H. With two ethylene linkings (Brühl), it would be 65.0 for A, which is close to that found. The reduction of the refraction and dispersion on heating, though not much greater than would be expected from the action of heat alone (see this vol., pp. 293, 310), tends to confirm the conclusion, namely, that this substance alters in constitution slightly, a small portion changing into the hydroxyketonic compound.

Methyl Acetoneoxalate or Methyl Acetylpyruvate.

As this substance is solid at ordinary temperatures, it had to be examined in the melted condition; it fuses at 63—64°; being a methyl salt, its rotation should differ from that of the ethyl salt by about 1.100 less; this would make it—

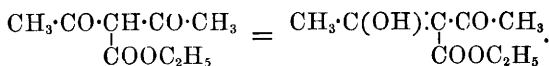
For ketonic compound.....	6.432
„ hydroxyketonic compound...	7.709
„ dihydroxy-compound.....	9.024

The rotation obtained at 66° was 8.876. Therefore at this temperature the rotation is close to that required by the dihydroxy-compound, though not quite high enough. But if the rotation of this substance changes with heat to the same extent as that of the ethylic compound, at 20° it would be 9.075, which is close to the estimated number, so that this substance has also the dihydroxylic constitution



Ethyl Diacetoacetate.

This substance, which may be regarded as acetylacetone with hydrogen replaced by the group COOC_2H_5 , as well as ethyl diacetoacetate, has special interest in reference to the subject under consideration. It has been shown from the rotations of acetylacetone at ordinary temperatures that it is a monhydroxy-compound, and as its rotation is rather higher than is required by that constitution, it may be assumed that it has a tendency to become a dihydroxy-compound. On replacing one of its methyls by COOC_2H_5 , and thus producing ethyl acetoneoxalate, this tendency is increased, and a dihydroxy-compound is formed; therefore, if, instead of replacing a methyl group, we replace one of its hydrogen atoms by COOC_2H_5 , somewhat analogous conditions are obtained which would also be expected to conduce to the formation of a dihydroxy-compound, but in this case a hydrogen of the central CH_2 is replaced; this, therefore, can now only lend one hydrogen to one of the $-\text{CO}-$ groups, and thus only a monhydroxy-compound can be formed in the ordinary manner.



If a dihydroxy-compound were formed, it would therefore be necessary for one of the methyl groups to give up hydrogen to the carbonyl and produce

$$\text{CH}_3 \cdot \text{C}(\text{OH}) \cdot \underset{\text{COOC}_2\text{H}_5}{\text{C}} \cdot \text{C}(\text{OH}) \cdot \text{CH}_2$$

The rotation of this substance may be estimated thus:—

Mol. rot. ethyl acetoacetate.....	6·501
„ acetyl rep. hydrogen.....	2·037
„ ketonic compound.....	8·538
Calculated from series constant—	
Ser. const. ketone × 2.....	0·750
Ethereal salt	0·370
	3)1·120
	0·373
1·023 × 8	8·184
Mol. rot. ketonic compound.....	8·557

Average 8·547.

To find the rotation for the monhydroxyketonic and dihydroxylic compounds the same difference of 1·277 can be used as in the case of acetoneoxalethyl ether.

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Thus—

Mol. rot. ketonic compound.....	8·547
	<hr/> 1·277
„ monhydroxyketonic compound..	9·824
	<hr/> 1·277
„ dihydroxylic compound.....	11·101

The rotation found at 18·4° was 10·699. This is considerably too high for a monhydroxyketonic compound, the difference being 0·875, whereas it is only 0·402 lower than that required by the dihydroxylic compound; in fact, it appears to consist of about one-third of the former and two-thirds of the latter compound.

When heated to 92·6°, its rotation was 10·449, being a reduction of 0·250 for 74·2° or 0·337 for 100°. This is larger than is likely to result from the influence of heat alone, showing that a change takes place, the quantity of the monhydroxyketonic compound present becoming slightly larger.

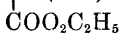
The determinations of the refractive power of this substance made by Dr. Gladstone and also by myself confirm the above results, as the following numbers will show :—

	<i>t.</i>	$\frac{\mu_A - 1}{d} p.$	$\frac{\mu_F - 1}{d} p.$	$\frac{\mu_H - 1}{d} p.$
Perkin....	17·6°	71·952	75·030	—
	99·8°	71·641	74·666	—
Diff. ..	82·2°	0·311	0·364	
Gladstone	22·8°	71·91	75·27	78·65

$$\text{Dispersion H—A} = 6·774.$$

If a saturated compound, the calculated value for A would be 68·0, with a dispersion of 3·12 between A and H. With one ethylene linking (Brühl), it would be 70·3, and for two 72·6. The refractive power, therefore, like the rotation, shows that it consists of a mixture of a mono- and di-hydroxylic compound; the dispersion is even in excess of that required by this constitution, and this is further indicated by the reduction of the refraction and also of the dispersion on heating, which, however, is not much greater than might arise from the action of heat.

These results, therefore, indicate the unexpected existence of the compound $\text{CH}_3\text{C}(\text{OH})\text{:C}(\text{OH})\text{CH}_2$, as forming the chief constituent of ethyl dioacetacetate at ordinary temperatures.



Diacetylacetone.

This substance might exist in four conditions, or, in other words, have three isomers:—

- I. Triketonic $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$.
 II. Hydroxydiketonic $\text{CH}_3 \cdot \text{C}(\text{OH}) : \text{CH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$.
 III. Dihydroxyketonic $\text{CH}_3 \cdot \text{C}(\text{OH}) : \text{CH} \cdot \text{CO} \cdot \text{CH} : \text{C}(\text{OH}) \cdot \text{CH}_3$.
 IV. Trihydroxy- $\text{CH}_3 \cdot \text{C}(\text{OH}) : \text{C} : \text{C}(\text{OH}) \cdot \text{CH} : \text{C}(\text{OH}) \cdot \text{CH}_3$.

The rotation may be estimated as follows:—

I. *Triketonic formula*—

Mol. rot. of acetone	3.514
„ acetyl rep. hydrogen $\times 2$	4.074
	<hr/> 7.588

According to series constant—

Ser. const. acetone $\times 3 \div 3$	0.445
1.023 $\times 7$	7.161
	<hr/> 7.606

Average 7.597.

II. *Hydroxydiketonic Formula*.—The saturated form of this would be $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$, or acetylmethyl hydroxy-propyl ketone.

Methyl propyl ketone may, therefore, be taken as the basis.

Mol. rot. of methyl propyl ketone	5.499
„ acetyl replacing hydrogen	2.037
	<hr/> 7.536
OH	0.194
	<hr/> 7.730
For unsaturation	1.112
	<hr/> 8.842

By series constant, the saturated compound being viewed as an isopropyl alcohol derivative,

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Ser. const. isopropyl alcohol	0.950
„ ketone $\times 2$	0.750
	<hr/> 3)1.700
	0.566
1.023×7	<hr/> 7.161
	<hr/> 7.727
For unsaturation	<hr/> 1.112
	<hr/> 8.839

Average, 8.840.

III. *Dihydroxyketonic Formula*.—The saturated form of this would be $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_3$. This is a dihydroxydipropyl ketone.

Taking dipropyl ketone as the basis of the calculation, the following result is obtained:—

Mol. rot. of dipropyl ketone	7.536
$(\text{OH})_2$ 194×2	0.398
	<hr/> 7.934
For unsaturation $\times 2$..	<hr/> 2.224
	<hr/> 10.158

By series constant, regarding the saturated compound as a ketonic dimethyl glycol,

Ser. const. dimethyl glycol (calc.)	1.078
„ ketone	0.375
	<hr/> 2)1.453
	0.726
1.023×7	<hr/> 7.161
	<hr/> 7.887
For unsaturation $\times 2$.	<hr/> 2.224
	<hr/> 10.111

Average, 10.134.

IV. *Trihydroxylic Formula*.—The saturated form of this would be $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_3$. This is a heptane glycerol.

Mol. rot. of heptane glycerol (calc.) ..	8.204
For unsaturation $\times 3$..	3.336
	<hr/> 11.540

If the difference of 1.277 found between similar formulæ in some of

the calculations be used, the numbers obtained are not very different to the above.

I. Triketone	7.597
	1.277
II. Hydroxydiketone	8.874
	1.277
III. Dihydroxyketone	10.151
	1.277
IV. Trihydroxy-.....	11.428

The last is the least concordant, differing by 0.112.

As diacetylacetone is a solid, it was examined in the fused state at 60.4°; it then gave 10.223 for its molecular rotation. This evidently agrees nearly with III or the dihydroxyketonic constitution



though it is even a little high for this.

The rotation was also determined at 96.3°, and then gave 9.587 for its molecular rotation, which shows a very large reduction considering the temperature is only 36.4° above the previous number, thus:—

<i>t.</i>	Mol. rot.	<i>t.</i>	Mol. rot.	<i>t. diff.</i>	Mol. rot. diff.
59.3°	10.223	96.3°	9.587	37.3°	0.635

For 100°, supposing the change to take place equally (which is improbable, as it is likely to become more rapid as the temperature rises), it would amount to 1.704.

From this it will be found that if heated up to about 137° it would have passed into II, the hydroxydiketonic compound, with a rotation of 8.874, and if it could be kept liquid whilst cooled to about -6.7° it would have passed into IV, the trihydroxy-compound, with a rotation of 11.428.

The refraction and dispersion powers of this substance were determined at two different temperatures; the following numbers show the result:—

<i>t.</i>	$\frac{\mu_A - 1}{d} p.$	$\frac{\mu_F - 1}{d} p.$
60.0°	63.599	67.509
99.8°	62.643	66.180
Diff. ..	0.956	1.329

The calculated refraction for A, if a saturated compound, would be 58.2, but with two ethylene linkings (Brühl) 62.80. This is somewhat lower than that obtained, but for three ethylene linkings it

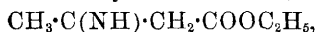
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would be 65.1 , which is too high; therefore these results show, like the rotation, that it is a dihydroxylic compound at this temperature. As with the rotation, the effect of heat on this substance alters it to a very large extent, both in refraction and dispersion. The above differences are only for about 40° ; for 100° they would be 2.402 and 3.417 respectively, giving a difference of dispersion of no less than about 1.015 .

Ethyl β -Imidobutyrate, or Ethyl β -Amidocrotonate.

This substance, which is known by both the above names, is produced by the action of ammonia on ethyl acetoacetate; its constitution is, however, disputed, some regarding it as having that represented by the first name, and others as corresponding to the second name.

The constitution indicated by the first name, namely,



is explained very easily if the reaction be taken as occurring between ammonia and ethyl acetoacetate, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COOC}_2\text{H}_5$. In this case it would be a saturated compound; but if it be indicated by the second name, that is, $\text{CH}_3\cdot\text{C}(\text{NH}_2)\cdot\text{CH}\cdot\text{COOC}_2\text{H}_5$, its formation is most easily explained by taking ethyl acetoacetate as $\text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{COOC}_2\text{H}_5$. In this form it would be an unsaturated compound. It was, therefore, interesting to examine the rotation of this substance.

Its rotation may be estimated thus:

I. As ethyl imidobutyrate—

Mol. rot. of ethyl butyrate	6.477
Less H	0.254
	<hr/>
	6.223
Plus nitrogen in amines ..	0.717
	<hr/>
„ ethyl imidobutyrate	6.940

II. As ethyl amidocrotonate—

Mol. rot. of ethyl α -crotonate	7.589
NH ₂ rep. H	0.971
	<hr/>
„ ethyl amidocrotonate	8.560

The rotation of the substance in a state of surfusion at 15° was 10.770 ; it was also examined at 86.5° , and gave 10.494 , giving a difference of 0.276 for 71.5° ; but it would not be wise to lay much stress upon this, as, when kept heated, this substance undergoes decomposition very quickly with evolution of ammonia.

The rotation found is no less than 2.210 higher than that estimated, even for the unsaturated compound; so that there cannot be

a doubt that it is a compound of that nature; but why it is so abnormally high it is difficult to understand. Very little, however, is known as to the rotation of unsaturated amido-derivatives (allylamine being the only one examined; this, however, does not give an abnormal rotation), but that the NH_2 has a remarkable influence, in some instances, is certain; this is seen in the aromatic series, where aniline and other bases are found to give remarkably high rotations. For example, benzene has a rotation of 11.295 ; the introduction of NH_2 and formation of aniline raises this to 16.097 . Therefore the method of estimating the rotation of this substance may be at fault to some extent. It also might possibly be that this compound is a fumaroid modification; this would raise the rotation, but not sufficiently to account for all the difference found.

On account of obtaining these high numbers, it was thought desirable to examine the refractive power of this substance; this gave for

$t.$	$\frac{\mu_A - 1}{d} p.$	$\frac{\mu_G - 1}{d} p.$
16°	61.67	67.08

The substance was then allowed to crystallise, and well pressed between bibulous paper to remove any changed product it might contain from having been heated a little; it then gave—

$t.$	$\frac{\mu_A - 1}{d} p.$	$\frac{\mu_G - 1}{d} p.$
15.8°	61.80	67.17

These two determinations thus give practically the same results.

These numbers, like the rotation, are remarkably high. The calculated values, $\text{C}_6\text{H}_{11}\text{NO}_2$, are—

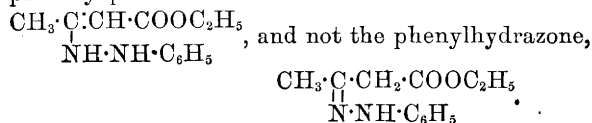
As saturated	55.5
As unsaturated	57.8

The dispersion $G-A$ is 5.37 , which is enormous.

The refractive and dispersive powers, therefore, confirm the magnetic rotations.

Had it not been known that ethyl acetoacetate was a ketonic compound, the formation of this substance might have been considered as favouring its hydroxylic constitution.

The action of ammonia on ethyl acetoacetate is analogous to that of phenylhydrazine, as Nef has shown (*Annalen*, **266**, 64) that the primary product formed in the latter case is the phenylhydrazide,



Aromatic Compounds.

The examination of the following compounds, which correspond to some of the foregoing, in which methyl is replaced by phenyl, namely:—

Ethyl benzoylacetate,
Benzoylacetone,
Methyl acetophenoneoxalate,
Ethyl acetophenoneoxalate,

is interesting, because the introduction of phenyl into a compound affects its properties in a different way from that of the alcohol radicles, being less basic in its character.

The magnetic rotations of a very large number of aromatic compounds have been determined but not yet published, and thus some help can be obtained in calculating the rotations the above substances should have. No set of series constants has as yet been formed, so that this means of corroborating the numbers obtained by other methods cannot be used, but, as the differences to be dealt with are large, any small errors will not invalidate the conclusions arrived at.

In the aromatic series, the average value of C_6H_5 replacing hydrogen is 10·400. This, however, fluctuates; thus in ethyl benzoate it is 10·301, in acetophenone 10·122, and in benzyl alcohol 10·760.

The difference between the rotation of saturated and unsaturated compounds containing C_6H_5 is much greater than in the fatty series. The following comparisons will show this:—

	Mol. rot.	Diff.
Cinnamene	16·081	} 2·690.
Ethylbenzene	13·391	
Allylbenzene	17·577	} 3·027.
Propylbenzene.....	14·550	
β -Butenylbenzene	18·325	} 2·735.
Butylbenzene (calc.) ..	15·590	

The average of these is 2·817.

This value is for substances differing in composition by H_2 . But the above ketonic compounds and their unsaturated hydroxylic isomers do not differ in composition by H_2 , so that this will have to be taken into account.

The difference of rotation due to the variation of composition by H_2 in the aromatic series, which would apply to the calculation of the rotation of the unsaturated hydroxylic compounds under consideration, cannot be obtained directly, but may be arrived at by analogy from the fatty series, thus—

The rotation of benzylic alcohol is 12.400, and that of benzaldehyde 11.846; the difference between these rotations for variation of composition by H_2 is 0.554.

If we compare aldehydes and alcohols in the fatty series, the difference found is about 0.436.

In the fatty series the amount for unsaturation by H_2 (1.112) will be found to have required the addition of 0.224 to make it suitable to represent the difference for unsaturation in the case of the hydroxylic isomers of ethyl acetoacetate and acetylacetone, and 0.165 in the case of the monohydroxylic isomers of ethyl and methyl acetoneoxalate.

Now, as the difference between alcohols and aldehydes of the fatty series is to the above quantities, so will most probably be the difference between the aromatic alcohols and aldehydes to the numbers required.

For ethyl benzoylacetate and benzoylacetone this would be 0.284; this, added to the amount for unsaturation, namely, 2.817, will give 3.101 as the difference in rotation which exists between the rotation of these two substances and their hydroxylic unsaturated isomers. For ethyl and methyl acetophenoneoxalate it will be 0.209; this, with 2.817, will give 3.026 as the difference for this class of compound.

The influence of $COOC_2H_5$ and $COOCH_3$ replacing hydrogen in the aromatic series is about 2.800 and 1.340 respectively.

The value of CH_2 is slightly higher than in the fatty series, namely, 1.040.

With these particulars it will be possible to get pretty close approximations to the molecular rotation of the substances under consideration and their possible hydroxylic isomers.

Ethyl Benzoylacetate.

The rotation of this compound and its unsaturated hydroxylic isomer may be calculated thus:—

Mol. rot. of ethyl acetoacetate.....	6.501
Less CH_2	1.023
	<hr/> 5.478
„ phenyl replacing hydrogen as in acetophenone.....	10.122
	<hr/>
„ ethyl benzoylacetate... ..	15.600
For unsaturation	3.101
	<hr/>
Hydroxylic compound	18.701

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The molecular rotation found for ethyl benzoylacetate was 16.393 at 18.8°; this is higher than that required by the ketonic constitution by 0.793, but less than is required by the hydroxylic constitution by 2.321; it would, therefore, appear to be a mixture consisting of about 3 parts of the ketonic to 1 of the hydroxylic compound. This substance was, therefore, measured at a higher temperature, namely, 100.6°, and it then gave 16.192 (corrected for influence of temperature; see p. 862). The following shows clearly this influence of temperature:—

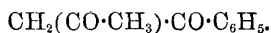
<i>t.</i>	Mol. rot.	<i>t.</i>	Mol. rot.	<i>t.</i> diff.	Mol. rot. diff.	Diff. 100°.
18.8°	16.393	100.6°	16.191	81.8°	0.202	0.247

These results indicate that this substance becomes somewhat more ketonic in composition by rise of temperature in the same way as do many of the fatty compounds previously examined.

From the rotation of ethyl benzoylacetate it is seen that phenyl favours the hydroxylic condition more than methyl, because ethyl acetoacetate appears to be ketonic only.

Benzoylacetone.

This substance, which is the phenylic representative of acetylacetone, may also be regarded as acetylacetophenone,



Its rotation and that of its hydroxylic isomers may be estimated thus:—

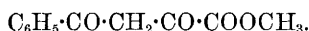
Mol. rot. of acetophenone	12.591
„ acetyl rep. H	2.039
„ benzoylacetone	14.630
For unsaturation	3.101
„ hydroxyketonic com- pound	17.731
For unsaturation	3.101
„ dihydroxylic compound	20.832

Benzoylacetone melts at 58°. Its rotation was determined at 63.3°, and gave 18.782. It is evidently nearest to that of the hydroxyketonic compound, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}:\text{C}(\text{OH})\cdot\text{C}_6\text{H}_5$, but at the same time it is 1.039 above that number, indicating that it contains about 30 per cent. of the dihydroxylic compound, $\text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{CH}:\text{C}(\text{OH})\cdot\text{C}_6\text{H}_5$. Acetylacetone was found to consist of a hydroxyketonic compound with

about 20 per cent. of the dihydroxylic compound. This comparison again shows that phenyl favours the hydroxylic condition more than methyl does.

Methyl Acetophenoneoxalate.

This substance corresponds to methyl acetoneoxalate, in which a methyl group is replaced by phenyl; its composition is



It may be viewed as benzoylacetone in which methyl is replaced by COOCH_3 , and its rotation estimated for its ketonic and hydroxylic forms; thus:—

Mol. rot. of benzoylacetone	14·630
Less CH_2	1·040
	<hr/>
„ COOCH_3 rep. H	1·340
	<hr/>
„ methyl acetophenoneoxalate	14·930
For unsaturation.....	3·026
	<hr/>
„ hydroxyketonic compound..	17·956
For unsaturation.....	3·026
	<hr/>
Dihydroxylic compound....	20·982

This substance melts at 61° . Its rotation was determined in the fused state at $66\cdot5^\circ$, and gave $21\cdot511$. This agrees nearest with that of the dihydroxy-compound, $\text{C}_6\text{H}_5\cdot\text{C}(\text{OH})\text{:C:C}(\text{OH})\cdot\text{COOCH}_3$; it is, however, a little higher ($0\cdot529$); but as there is no probability of a trihydroxy-compound existing, and much difficulty was experienced in determining its rotation, this may be due to experimental error.

The result agrees with that obtained with methyl acetoneoxalate.

Ethyl Acetophenoneoxalate.

The rotations of this substance for the three forms in which it might exist should be about $1\cdot100$ higher than for the methyl salt. This would give the following numbers:—

Mol. rot. for ketonic compound	16·030
„ hydroxyketonic com-	
pound	19·056
„ dihydroxylic compound.	22·082

This substance, which melts at 42° , was examined at $47\cdot1^\circ$, and

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gave for its molecular rotation 22.175. This again is for the dihydroxylic constitution $C_6H_5 \cdot C(OH) : C : C(OH) \cdot COOC_2H_5$, ethyl acetone-oxalate also giving numbers for an analogous compound.

Conclusions.

Monoketonic Compounds.—With the exception of ethyl acetonedicarboxylate, all those which have been examined for their magnetic rotation, as well as for their refractive power (where this has been observed), are shown to be saturated, and therefore ketonic. In the case of ethyl acetonedicarboxylate, a small quantity of a hydroxylic compound is apparently present owing to the influence of the two negative $COOC_2H_5$ groups, which are seen to have such a large influence in other cases.

Besides the compounds examined in this paper, this has also been found to be the case in the following instances:—

Ethyl acetosuccinate,
Acetobutyl alcohol,
Acetopropyl alcohol,
Acetylcarbinol,
Dichloroacetone,
Acetylmethylpentamethylene.

Diketonic Compounds.—Acetylacetone at about 17° is found to be, both by its magnetic rotation and refractive power, an unsaturated hydroxyketonic compound containing about 20 per cent. of a dihydroxylic compound.

Methyl and ethyl acetoneoxalate, which differ from the foregoing in containing the positive groups $COOCH_3$ and $COOC_2H_5$ in place of methyl, are dihydroxylic at about 20° .

Ethyl diacetoacetate at 18° consists of a mixture of about 32 per cent. of monhydroxylic and 68 per cent. of dihydroxylic compounds.

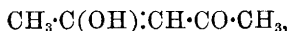
Triketonic Compounds.—The only one of these examined, namely, diacetylacetone, when fused, is at about 60° a dihydroxylic compound.

From the rotation of methyl- and ethyl-acetylacetone, it appears that the alcohol radicles replacing hydrogen in acetylacetone, render the compound more ketonic, the larger radicle having the greater influence in this respect; thus the composition of these bodies at ordinary temperatures may be represented:—

	Per cent. of ketonic.	Per cent. of hydroxylic.	Per cent. of dihydroxylic.
Acetylacetone.....	—	80.0	20
Methylacetylacetone ..	46.4	53.6	—
Ethylacetylacetone ..	74.0	26.0	—

From this it may be inferred that, if still larger radicles were introduced, it is probable that the hydroxyketonic compound would cease to exist, and the body be simply ketonic.

This has an important bearing upon the subject of judging as to what the constitution of compounds of this class will be from those they are derived from, or *vice versâ*. For example, both these substances are produced from unsaturated acetylacetone,



or from its sodium compound, $\text{CH}_3\cdot\text{C}(\text{ONa})\text{:CH}\cdot\text{CO}\cdot\text{CH}_3$; yet ethylacetylacetone consists chiefly of the saturated ketonic product $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{C}_2\text{H}_5)\cdot\text{CO}\cdot\text{CH}_3$.

From this it is seen that the presence of hydrocarbon radicles of the fatty series favours the ketonic form, just as the positive radicle COOC_2H_5 favours the hydroxylic form.

The magnetic rotations of the aromatic compounds confirm those obtained with the corresponding compounds in the fatty series, but, at the same time, phenyl being a more positive compound than methyl, the hydroxylic condition is favoured to a greater extent, even ethyl benzoylacetate containing apparently about 20 per cent. of its hydroxylic isomer.

Ethyl acetoacetate, being a ketonic compound, is not changed when heated, but the small amount of hydroxylic isomer present in ethyl acetonedicarboxylate disappears below 100° .

Ethyl β -imidobutyrate or β -amidocrotonate is evidently an unsaturated compound, and, therefore, is correctly described by the second name.

All the diketonic compounds of the fatty series examined are more or less hydroxylic, and change when heated, becoming less hydroxylic, acetylacetone and methylacetylacetone being the most largely affected. This is also true of ethyl benzoylacetate, and probably the other aromatic compounds examined.

The triketone diacetylacetone changes to a much greater extent than any of the other substances examined with rise of temperature, becoming less hydroxylic.

It is seen from the above observations that the influence of heat on the hydroxylic isomers of the ketonic compounds tends to cause them to change into the more stable ketonic form.

The existence of products consisting of two or more isomeric compounds in a state of unstable equilibrium, their relative proportions varying with temperature, is remarkable, especially as they differ considerably in constitution, some being saturated, and others unsaturated: so that it is difficult to tell why the presence of one should be necessary to the existence of the other or others. This may have

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something to do with the way these products behave with reagents, because it is just possible that the addition of other substances may disturb the equilibrium that exists, and the product may become either entirely, or to a much larger extent, ketonic, or (which is less probable) hydroxylic, and this may account for results obtained which are different from those expected.

It would, therefore, be interesting to examine the magnetic rotations of mixtures of some of these compounds, such as acetylacetone, with different reagents, as this would show whether they do have any influence of this kind. I hope to do this when I have the opportunity. When high temperatures are employed to induce chemical change, it is well to remember that these substances will probably, in many cases, be ketonic compounds.

EXPERIMENTAL RESULTS.

Pyruvic Acid.

The acid was obtained from Kahlbaum; as the purity of the acid is always doubtful, however carefully prepared, it was examined by titration with sodium hydrate solution. The result obtained showed 99.89 per cent. of acid.

The density determinations gave—

$d\ 4^{\circ}/4^{\circ}$	1.2881.	$d\ 15^{\circ}/15^{\circ}$	1.2752.
$d\ 10^{\circ}/10^{\circ}$	1.2808.	$d\ 20^{\circ}/20^{\circ}$	1.2700.
	$d\ 25^{\circ}/25^{\circ}$		1.2649.

The magnetic rotations gave—

$t.$	Sp. rotation.	Mol. rotation.
14.5°	0.9282	3.557
14.5	0.9279	3.556
14.5	0.9294	3.561
14.5	0.9272	3.553
Average 14.5	0.9282	3.557

Ethyl Acetoacetate.

The boiling point of the specimen used was 181—182° (corr.).

The density determinations gave—

$d\ 70^{\circ}/70^{\circ}$	0.9941.	$d\ 85^{\circ}/85^{\circ}$	0.9865.
$d\ 75^{\circ}/75^{\circ}$	0.9913.	$d\ 90^{\circ}/90^{\circ}$	0.9843.
$d\ 80^{\circ}/80^{\circ}$	0.9888.	$d\ 95^{\circ}/95^{\circ}$	0.9824.
	$d\ 100^{\circ}/100^{\circ}$		0.9809.

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
90·5°	0·8894	6·527
90·5	0·8817	6·470
90·5	0·8774	6·439
90·5	0·8801	6·459
90·5	0·8789	6·450
90·5	0·8824	6·476
Average 90·5	0·8816	6·470

Ethyl Ethylacetoacetate.

This was prepared from ethyl sodacetoacetate and ethyl iodide in the usual manner. It boiled at 197·7—198·8° (corr.).

The density determinations gave—

$d_{4^{\circ}/4^{\circ}}$	0·9937.	$d_{15^{\circ}/15^{\circ}}$	0·9838.
$d_{10^{\circ}/10^{\circ}}$	0·9879.	$d_{20^{\circ}/20^{\circ}}$	0·9800.
	$d_{25^{\circ}/25^{\circ}}$	0·9767.	

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17·8°	0·9286	8·304
17·8	0·9233	8·346
17·8	0·9308	8·324
17·8	0·9304	8·320
17·8	0·9348	8·360
17·8	0·9304	8·320
Average 17·8	0·9314	8·329

Ethyl Ethylideneacetoacetate.

The specimen of this substance examined boiled at 112° at 15 mm. (Claisen).

The density determinations gave—

$d_{4^{\circ}/4^{\circ}}$	1·1082.	$d_{15^{\circ}/15^{\circ}}$	1·0986.
$d_{10^{\circ}/10^{\circ}}$	1·1027.	$d_{20^{\circ}/20^{\circ}}$	1·0950.
	$d_{25^{\circ}/25^{\circ}}$	1·0914.	

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
19·6°	1·1096	9·361
19·6	1·1136	9·394
19·6	1·1077	9·345
19·8	1·1122	9·382
19·6	1·1103	9·367
Average 19·6	1·1107	9·370

Levulinic Acid.

The crystallised acid was rapidly distilled and collected in two fractions.

Fraction I.—This boiled at 249·5—251·5° (corr.) and was examined in a state of surfusion.

The density determinations gave—

$d\ 4^{\circ}/4^{\circ}$	1·1524.	$d\ 15^{\circ}/15^{\circ}$	1·1421.
$d\ 10^{\circ}/10^{\circ}$	1·1462.	$d\ 20^{\circ}/20^{\circ}$	1·1386.
	$d\ 25^{\circ}/25^{\circ}$	1·1358.	

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13·7°	0·9802	5·526
13·6	0·9817	5·534
13·6	0·9842	5·549
13·7	0·9802	5·526
15·3	0·9815	5·540
15·2	0·9856	5·563
15·2	0·9874	5·574
15·2	0·9867	5·569
15·3	0·9830	5·548
Average 14·5	0·9834	5·548

Fraction II.—This boiled at 251—253° corr.

The density determinations gave—

$d\ 4^{\circ}/4^{\circ}$	1·1537.	$d\ 15^{\circ}/15^{\circ}$	1·1438.
$d\ 10^{\circ}/10^{\circ}$	1·1478.	$d\ 20^{\circ}/20^{\circ}$	1·1404.
	$d\ 25^{\circ}/25^{\circ}$	1·1376.	

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16°	0·9718	5·479
16	0·9740	5·491
16	0·9788	5·518
16	0·9822	5·537
16	0·9792	5·521
Average 16	0·9772	5·509

Levulinic Acid + 2H₂O.

This solution was made with the acid of Fraction I.

The density determinations gave—

$$d_{15^{\circ}/15^{\circ}} \quad 1\cdot1228.$$

$$d_{20^{\circ}/20^{\circ}} \quad 1\cdot1197.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
14·2°	0·9973	7·497
14·2	0·9984	7·503
14·2	1·0037	7·545
14·2	0·9939	7·471
Average 14·2	0·9983	7·504
Less 2 mols. OH ₂		2
		5·504

The numbers obtained from the determination of the fused acid and the solution in water being very similar, the average of the three results may be taken, namely, 5·520, as the molecular rotation of this acid.

Ethyl Acetonedicarboxylate.

Professor v. Pechmann was kind enough to furnish me with a very pure specimen of this substance. Its boiling point was 165° at 38 mm. (Pechmann).

The density determinations gave—

$d_{4^{\circ}/4^{\circ}}$	1·1269.	$d_{30^{\circ}/30^{\circ}}$	1·1046.
$d_{10^{\circ}/10^{\circ}}$	1·1269.	$d_{35^{\circ}/35^{\circ}}$	1·1023.
$d_{15^{\circ}/15^{\circ}}$	1·1165.	$d_{40^{\circ}/40^{\circ}}$	1·0993.
$d_{20^{\circ}/20^{\circ}}$	1·1126.	$d_{45^{\circ}/45^{\circ}}$	1·0963.
$d_{25^{\circ}/25^{\circ}}$	1·1090.	$d_{50^{\circ}/50^{\circ}}$	1·0934.

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$d\ 55^\circ/55^\circ$	1.0908.	$d\ 80^\circ/80^\circ$	1.0801.
$d\ 60^\circ/60^\circ$	1.0885	$d\ 85^\circ/85^\circ$	1.0783.
$d\ 65^\circ/65^\circ$	1.0863.	$d\ 90^\circ/90^\circ$	1.0767.
$d\ 70^\circ/70^\circ$	1.0841.	$d\ 95^\circ/95^\circ$	1.0753.
$d\ 75^\circ/75^\circ$	1.0821.	$d\ 100^\circ/100^\circ$	1.0740.

The magnetic rotations gave—

$t.$	Sp. rotation.	Mol. rotation.
13.2°	0.9598	9.633
13.2	0.9598	9.633
13.2	0.9613	9.648
13.5	0.9604	9.641
14.2	0.9571	9.622
19.7	0.9493	9.574
19.7	0.9505	9.586
19.7	0.9479	9.559
19.7	0.9493	9.574
Average 16.2	0.9550	9.608

$t.$	Sp. rotation.	Mol. rotation.
94°	0.8949	9.337
94	0.9003	9.393
94	0.8967	9.356
94	0.8987	9.377
94	0.9018	9.409
Average 94	0.8985	9.374

Acetylacetone, Methylacetylacetone, and Ethylacetylacetone.

Acetylacetone, Specimen I.

The first specimen of this substance examined was prepared by Professor Dunstan and Mr. T. S. Dymond for their interesting experiments on the synthesis of trimethylisoxazole* (Trans., 1891, 59,

* Dunstan and Dymond, in their paper "On the Action of Alkalis on the Nitro-compounds of the Paraffin Series" (Trans., 1891, 59, 415), have misunderstood my remarks on the magnetic rotation of trimethylisoxazole. They state that the results might "indicate that the compound is unsaturated to the extent of four equivalents of hydrogen (H_4)."

The rotation of this substance is peculiar; it is too high for a saturated compound, and at the same time is scarcely high enough for a body unsaturated to the extent of H_2 , and consequently agrees best with the formula they propose, which requires it to be unsaturated to this extent only.

428). It was made by Claisen's method (*Ber.*, **22**, 1010), and purified by conversion into its copper derivative, from which it was afterwards liberated by means of dilute sulphuric acid. This was examined both last year and also this year, and it will be seen that the results on both occasions were practically the same, showing that it does not change to any appreciable extent on keeping, though there is a slight difference in the densities taken on the two occasions.

Examined 1891. The boiling point of the product was 137—140° (D. and D.).

The density determinations gave—

$d\ 4^{\circ}/4^{\circ}$	0.9897.	$d\ 15^{\circ}/15^{\circ}$	0.9792.
$d\ 10^{\circ}/10^{\circ}$	0.9838.	$d\ 20^{\circ}/20^{\circ}$	0.9750.
	$d\ 25^{\circ}/25^{\circ}$		0.9712.

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15.0°	1.2502	7.092
15.5	1.2590	7.146
15.5	1.2658	7.184
15.5	1.2583	7.142
15.5	1.2524	7.108
15.5	1.2539	7.116
16.0	1.2553	7.127
Average 15.5	1.2564	7.131

Examined 1892.

The density determinations gave—

$d\ 4^{\circ}/4^{\circ}$	0.9925.	$d\ 55^{\circ}/55^{\circ}$	0.9560.
$d\ 10^{\circ}/10^{\circ}$	0.9863.	$d\ 60^{\circ}/60^{\circ}$	0.9533.
$d\ 15^{\circ}/15^{\circ}$	0.9819.	$d\ 65^{\circ}/65^{\circ}$	0.9506.
$d\ 20^{\circ}/20^{\circ}$	0.9781.	$d\ 70^{\circ}/70^{\circ}$	0.9481.
$d\ 25^{\circ}/25^{\circ}$	0.9745.	$d\ 75^{\circ}/75^{\circ}$	0.9457.
$d\ 30^{\circ}/30^{\circ}$	0.9709.	$d\ 80^{\circ}/80^{\circ}$	0.9434.
$d\ 35^{\circ}/35^{\circ}$	0.9676.	$d\ 85^{\circ}/85^{\circ}$	0.9413.
$d\ 40^{\circ}/40^{\circ}$	0.9645.	$d\ 90^{\circ}/90^{\circ}$	0.9394.
$d\ 45^{\circ}/45^{\circ}$	0.9615.	$d\ 95^{\circ}/95^{\circ}$	0.9376.
$d\ 50^{\circ}/50^{\circ}$	0.9587.	$d\ 100^{\circ}/100^{\circ}$	0.9359.

The magnetic rotations gave—

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<i>t.</i>	Sp. rotation.	Mol. rotation.
15·4°	1·2589	7·125
15·4	1·2585	7·122
15·4	1·2580	7·120
15·4	1·2580	7·120
15·7	1·2595	7·129
15·6	1·2602	7·133
15·7	1·2642	7·156
15·6	1·2605	7·135
Average 15·2	1·2597	7·130

The rotation was also determined at a higher temperature, and gave the following result:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
85·7°	1·1131	6·571
85·7	1·1158	6·587
85·7	1·1182	6·601
85·7	1·1135	6·574
Average 85·7	1·1151	6·583

These numbers show a remarkable reduction in the rotation when determined at higher temperatures.

Methylacetylacetone, Specimen I.

This was prepared by Professor Dunstan and Mr. Dymond by heating the sodium compound of acetylacetone with methyl iodide at 140°. It was purified by fractional distillation. The boiling point of this specimen was 168·5—169° (D. and D.).

The density determinations gave—

$$\begin{array}{ll}
 d\ 4^{\circ}/4^{\circ} & 0\cdot9920. \\
 d\ 10^{\circ}/10^{\circ} & 0\cdot9865. \\
 d\ 25^{\circ}/25^{\circ} & 0\cdot9753.
 \end{array}
 \qquad
 \begin{array}{ll}
 d\ 15^{\circ}/15^{\circ} & 0\cdot9824. \\
 d\ 20^{\circ}/20^{\circ} & 0\cdot9787.
 \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15·5°	1·1306	7·291
15·5	1·1262	7·263
15·5	1·1262	7·263
15·5	1·1292	7·282
15·5	1·1226	7·240
15·5	1·1268	7·266
15·5	1·1216	7·233
Average 15·5	1·1261	7·263

As this substance was kept a long time before the following determinations were made, and had become yellow, evidently owing to some slight decomposition, it was redistilled, and the fraction boiling at 170—172·5° (corr.) taken for examination.

The density determinations gave—

$d\ 4^{\circ}/4^{\circ}$	0·9925.	$d\ 55^{\circ}/55^{\circ}$	0·9596.
$d\ 10^{\circ}/10^{\circ}$	0·9878.	$d\ 60^{\circ}/60^{\circ}$	0·9570.
$d\ 15^{\circ}/15^{\circ}$	0·9837.	$d\ 65^{\circ}/65^{\circ}$	0·9544.
$d\ 20^{\circ}/20^{\circ}$	0·9801.	$d\ 70^{\circ}/70^{\circ}$	0·9518.
$d\ 25^{\circ}/25^{\circ}$	0·9768.	$d\ 75^{\circ}/75^{\circ}$	0·9494.
$d\ 30^{\circ}/30^{\circ}$	0·9736.	$d\ 80^{\circ}/80^{\circ}$	0·9472.
$d\ 35^{\circ}/35^{\circ}$	0·9707.	$d\ 85^{\circ}/85^{\circ}$	0·9451.
$d\ 40^{\circ}/40^{\circ}$	0·9678.	$d\ 90^{\circ}/90^{\circ}$	0·9434.
$d\ 45^{\circ}/45^{\circ}$	0·9651.	$d\ 95^{\circ}/95^{\circ}$	0·9419.
$d\ 50^{\circ}/50^{\circ}$	0·9623.	$d\ 100^{\circ}/100^{\circ}$	0·9405.

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
92°	0·9976	6·701
92	0·9961	6·691
92	0·9930	6·670
92	0·9930	6·670
92	0·9891	6·644
Average 92	0·9937	6·675

Two or three hours after these determinations were made, and the substance having cooled down, it was remeasured and gave the following results :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15·2°	1·0488	6·752
15·2	1·0488	6·752
15·2	1·0525	6·776
15·2	1·0503	6·762
15·2	1·0532	6·781
Average 15·2	1·0507	6·765

From these it is seen that the rotation is much smaller than when previously examined at about this temperature, but, on re-examination a few weeks afterwards, it was found to have regained its normal rotation. From this it is evident that the substance undergoes a considerable amount of change on heating, and does not at once regain its original character on cooling, but requires time to do so. The density of the product also becomes lower after it is heated, and this does not rise to the normal for some time. To get an idea of the rate of change of density, an experiment was made in a dilatometer, the particulars of which are given in the earlier part of this paper (p. 817).

After obtaining these remarkable results, it was thought that it would be interesting to examine a different specimen of this substance, and also of acetylacetone, and Professor Claisen very kindly prepared them for me with great care; he also furnished me with a specimen of ethylacetylacetone.

The following results were obtained with these new specimens:—

Acetylacetone, Specimen II.

This boiled at 138—138·5°, and was nearly colourless. The density determinations gave—

<i>d</i> 4°/4°	0·9897.	<i>d</i> 55°/55°	0·9517.
<i>d</i> 10°/10°	0·9837.	<i>d</i> 60°/60°	0·9492.
<i>d</i> 15°/15°	0·9791.	<i>d</i> 65°/65°	0·9468.
<i>d</i> 20°/20°	0·9748.	<i>d</i> 70°/70°	0·9445.
<i>d</i> 25°/25°	0·9710.	<i>d</i> 75°/75°	0·9425.
<i>d</i> 30°/30°	0·9674.	<i>d</i> 80°/80°	0·9404.
<i>d</i> 35°/35°	0·9639.	<i>d</i> 85°/85°	0·9385.
<i>d</i> 40°/40°	0·9606.	<i>d</i> 90°/90°	0·9366.
<i>d</i> 45°/45°	0·9574.	<i>d</i> 95°/95°	0·9348.
<i>d</i> 50°/50°	0·9545.	<i>d</i> 100°/100°	0·9334.

These are nearly identical with those obtained from specimen I, examined in 1891.

The magnetic rotations gave—

TABLE I.

<i>t.</i>	Sp. rotation.	Mol. rotation.
19·5°	1·2623	7·191
19·5	1·2643	7·202
19·5	1·2643	7·202
19·5	1·2638	7·200
Average 19·5	1·2637	7·199

As it had been found that methylacetylacetone when heated does not at once regain its ordinary condition, it was thought that it would be interesting to see whether long cooling would influence this substance; it was therefore kept in ice for seven days. As it was not possible to measure its rotation at 0° in warm weather on account of dew forming on the glass ends of the measuring tubes, the substance was rapidly brought to the atmospheric temperature and quickly measured. It then gave the following results:—

TABLE II.

<i>t.</i>	Sp rotation.	Mol. rotation.
17°	1·2746	7·246
17	1·2725	7·234
17	1·2731	7·238
Average 17	1·2734	7·239

Determinations were then made at higher temperatures, and gave—

TABLE III.

<i>t.</i>	Sp. rotation.	Mol. rotation.
93°	1·1182	6·640
93	1·1213	6·658
93	1·1186	6·642
93	1·1182	6·639
93	1·1209	6·656
Average 93	1·1194	6·647

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The following were obtained with some of this substance which had been boiled and cooled to 100° directly before measurement:—

TABLE IV.

<i>t.</i>	Sp. rotation.	Mol. rotation.
100·2°	1·1040	6·571
100·2	1·1022	6·560
100·2	1·1037	6·569
100·2	1·1045	6·573
Average 100·2	1·1036	6·568

It will be seen that the cooled specimen, Table II, gave only slightly higher results than the specimen which was examined under ordinary conditions. The boiled specimen cooled to 100°, Table IV, also gave only slightly lower results than the unboiled, if difference of temperature be considered. This might be expected from the densities of the product cooled and heated in these different ways, which gave normal results.

The examination of both specimens of acetylacetone gave practically the same rotations, as the following comparisons will show:—

<i>t.</i>	Spec. I.	<i>t.</i>	Spec. II.
15·5°	7·131 (1891)	19·5°	7·199
15·2	7·130 (1892)	17·0	7·239 (cooled in ice)
85·7	6·583	93·0	6·647
—	—	100·2	6·568 (boiled and cooled to 100°)

The average of the low temperature results is t 16·7°, mol. rot. 7·175; and for the high temperature t 93°, mol. rot. 6·599, making a difference between them of 0·576 for 76·3°, or 0·755 for 100°.

The refractive and dispersive power of this substance was determined at temperatures wide apart with specimen I with the following results (see p. 847).

Dr. Gladstone was good enough to examine specimen II, obtained from Professor Claisen; the following are his results:—

Line.	<i>t.</i>	μ .	$\frac{\mu - 1}{d}p$.
A.....	18·4°	1·4447	45·62
F.....	18·4	1·4678	47·49
H.....	18·4	1·4943	50·70

Dispersion H—A = 5·08.

$d\ 11^{\circ}/4^{\circ}\ 0.98506. \quad d\ 99.3^{\circ}/4^{\circ}\ 0.89787.$

Line.	$\mu.$		Diff. for 88°3'.	$\frac{\mu-1}{d}.$		Diff. for 88°3'.	$\frac{\mu-1}{d}p.$		Diff. for 88°3'.
	$t.$			$t.$			$t.$		
	11°.	99°3'.		11°.	99°3'.		11°.	99°3'.	
A	1.444932	1.396344	0.048588	0.451680	0.441427	0.010253	45.168	44.143	1.025
C	1.450067	1.400321	0.049746	0.456893	0.445856	0.011037	45.689	44.586	1.103
D	1.454957	1.404135	0.050462	0.461492	0.450104	0.011388	46.149	45.010	1.139
F	1.467571	1.414139	0.053432	0.471662	0.461246	0.013416	47.466	46.125	1.341
G	1.479223	1.423518	0.056405	0.487201	0.471692	0.015509	48.720	47.169	1.551

Dispersion $G-A = 3.552$ at $11^{\circ}.$
 " " = 3.026 " $99.3^{\circ}.$

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Specimen II gives slightly higher results than specimen I, but the difference is but small.

The large difference obtained at temperatures 88.3° apart is consistent with the rotations, and it will be observed that a considerable decrease in the dispersion also takes place at the higher temperature.

Methylacetylacetone, Specimen II.

Professor Claisen gives the following particulars of the preparation of this specimen:—Acetylacetone was first converted into the potassium salt by dissolving it in ether and precipitating it with a solution of potash in methyl alcohol. This salt was dried, dissolved in methyl alcohol, and boiled some hours with methyl iodide until the mixture was neutral to test paper. Ether was then added, and the liquid filtered from potassium iodide, and, after evaporating the ether, the product was distilled under reduced pressure (about 20 mm.). It was further purified by dissolving it in ether, and precipitating with potash in methyl alcohol, and the potassium derivative, $\text{CH}_3\cdot\text{CO}\cdot\text{CK}(\text{CH}_3)\cdot\text{CO}\cdot\text{CH}_3$, thus obtained, was well washed with ether, and dried. It was then dissolved in water, decomposed with dilute sulphuric acid, and the product distilled three times under reduced pressure; all came over between 74° and 75° under a pressure of 20 mm. This was the highest temperature this specimen of methylacetylacetone was subjected to in its preparation.

The density determinations gave—

$d\ 4^{\circ}/4^{\circ}$	0.9941.	$d\ 10^{\circ}/10^{\circ}$	0.9887.
$d\ 15^{\circ}/15^{\circ}$	0.9845.	$d\ 20^{\circ}/20^{\circ}$	0.9808.
$d\ 25^{\circ}/25^{\circ}$	0.9773.	$d\ 100^{\circ}/100^{\circ}$	0.9408.

The magnetic rotations gave—

$t.$	Sp. rotation.	Mol. rotation.
19.2°	1.1286	7.284
19.2	1.1330	7.312
19.2	1.1330	7.312
19.2	1.1345	7.322
19.2	1.1308	7.298
Average 19.2	1.1320	7.306

After being kept in ice for seven days,

The density determinations gave—

$d\ 4^{\circ}/4^{\circ}$	0.9964.	$d\ 15^{\circ}/15^{\circ}$	0.9866.
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The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17·5°	1·1360	7·306
17·5	1·1319	7·279
17·5	1·1368	7·310
17·5	1·1363	7·308
Average 17·5	1·1352	7·301

Determination at a Higher Temperature.

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
100·7°	0·9934	6·689
100·7	0·9872	6·647
100·7	0·9919	6·678
100·7	0·9872	6·647
Average 100·7	0·9899	6·665

It was thought that probably the specimen cooled in ice would have given rather higher numbers than that which had been kept at the atmospheric temperature, but although the density is a trifle higher, the molecular rotation has come out practically the same.

The following is a comparison of the molecular rotations obtained from the two different specimens of methylacetylacetone.

<i>t.</i>	Spec. I.	<i>t.</i>	Spec. II.
15·5°	7·263	19·2°	7·306
—	—	17·5	7·301
92·0	6·675	100·7	6·665

These results agree very closely, showing that both preparations behaved in the same manner.

The average rotations are—

<i>t.</i>	Mol. rotation.
17·4°	7·290
96·4	6·670
Difference ..	79·0
	0·620

The difference for 100° would be 0·785, or a trifle more than that found for acetylacetone.

Dispersion F—A	= 1·940 at 8·34°.
" "	" = 1·673 " 99·2°.

The determination of the refractive and dispersive powers of this substance, made with specimen I at temperatures wide apart, gave results in table, p. 850. The substance being rather yellow, the line G could not be measured.

A corresponding set of determinations was made with specimen II. This, however, had become yellow by keeping; it was therefore distilled, and the fraction boiling at 170—172° (corr.) taken. This was kept in ice five days after distillation before it was examined (see p. 852).

These numbers are remarkably near to those obtained with specimen I, those for the higher temperature being practically identical, and those for the lower only differing on an average by +0.155, probably due to the product having been kept at a low temperature before examination, and the presence consequently of a slightly larger proportion to the hydroxylic compound.

As in the case of acetylacetone, large differences are seen to exist at temperatures wide apart, and also a considerable decrease in the dispersion is observable at the higher temperatures. These results are consistent with the magnetic rotation.

Ethylacetylacetone.

This substance boiled at 180—184° (Claisen).

The density determinations gave—

$d\ 4^{\circ}/4^{\circ}$	0.9711.	$d\ 55^{\circ}/55^{\circ}$	0.9382.
$d\ 10^{\circ}/10^{\circ}$	0.9660.	$d\ 60^{\circ}/60^{\circ}$	0.9359.
$d\ 15^{\circ}/15^{\circ}$	0.9620.	$d\ 65^{\circ}/65^{\circ}$	0.9338.
$d\ 20^{\circ}/20^{\circ}$	0.9584.	$d\ 70^{\circ}/70^{\circ}$	0.9317.
$d\ 25^{\circ}/25^{\circ}$	0.9541.	$d\ 75^{\circ}/75^{\circ}$	0.9295.
$d\ 30^{\circ}/30^{\circ}$	0.9519.	$d\ 80^{\circ}/80^{\circ}$	0.9275.
$d\ 35^{\circ}/35^{\circ}$	0.9488.	$d\ 85^{\circ}/85^{\circ}$	0.9255.
$d\ 40^{\circ}/40^{\circ}$	0.9460.	$d\ 90^{\circ}/90^{\circ}$	0.9238.
$d\ 45^{\circ}/45^{\circ}$	0.9433.	$d\ 95^{\circ}/95^{\circ}$	0.9223.
$d\ 50^{\circ}/50^{\circ}$	0.9407.	$d\ 100^{\circ}/100^{\circ}$	0.9208.

The magnetic rotations gave—

$t.$	Sp. rotation.	Mol. rotation.
18.8°	1.0589	7.850
18.8	1.0645	7.891
18.8	1.0616	7.869
18.8	1.0726	7.952
18.8	1.0645	7.891
Average 18.8	1.0644	7.890

Dispersion F—A = 1.916 at 15.4°.
 " " = 1.691 at 100.3°.

Dispersion F-A = 1.916 at 15.4°.

<i>t.</i>	Sp. rotation.	Mol. rotation.
92·9°	0·9840	7·582
92·9	0·9806	7·556
92·9	0·9794	7·547
92·9	0·9791	7·544
92·9	0·9840	7·582
Average 92·9	0·9814	7·562

The difference between the rotations of this substance at the temperatures employed is 0·328 for 74·1° or 0·443 for 100°, which is only a little more than half that obtained in the case of acetylacetone and methylacetylacetone, the larger radicle evidently having a retarding influence in this respect.

Methyl Acetoneoxalate.

This substance melts at 63—64° (Claisen), and had, therefore, to be examined in a fused condition.

The density determinations gave—

$d_{60^{\circ}/60^{\circ}}$	1·1589.	$d_{80^{\circ}/80^{\circ}}$	1·1489.
$d_{65^{\circ}/65^{\circ}}$	1·1562.	$d_{85^{\circ}/85^{\circ}}$	1·1467.
$d_{70^{\circ}/70^{\circ}}$	1·1536.	$d_{90^{\circ}/90^{\circ}}$	1·1450.
$d_{75^{\circ}/75^{\circ}}$	1·1512.	$d_{95^{\circ}/95^{\circ}}$	1·1439.
	$d_{100^{\circ}/100^{\circ}}$		1·1432.

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
66°	1·2829	8·880
66	1·2826	8·878
66	1·2882	8·917
66	1·2897	8·927
66	1·2791	8·846
66	1·2728	8·810
Average 66	1·2825	8·876

Ethyl Acetoneoxalate.

The boiling point of this specimen was 113—116° under 19 mm. (Claisen).

The density determinations gave—

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$d\ 15^\circ/15^\circ$	1.1318.	$d\ 60^\circ/60^\circ$	1.1026.
$d\ 20^\circ/20^\circ$	1.1277.	$d\ 65^\circ/65^\circ$	1.1000.
$d\ 25^\circ/25^\circ$	1.1239.	$d\ 70^\circ/70^\circ$	1.0976.
$d\ 30^\circ/30^\circ$	1.1203.	$d\ 75^\circ/75^\circ$	1.0952.
$d\ 35^\circ/35^\circ$	1.1169.	$d\ 80^\circ/80^\circ$	1.0928.
$d\ 40^\circ/40^\circ$	1.1137.	$d\ 85^\circ/85^\circ$	1.0906.
$d\ 45^\circ/45^\circ$	1.1107.	$d\ 90^\circ/90^\circ$	1.0888.
$d\ 50^\circ/50^\circ$	1.1079.	$d\ 95^\circ/95^\circ$	1.0872.
$d\ 55^\circ/55^\circ$	1.1052.	$d\ 100^\circ/100^\circ$	1.0860.

The magnetic rotations gave—

$t.$	Sp. rotation.	Mol. rotation.
19.8°	1.2995	10.111
19.7	1.2995	10.111
19.7	1.2980	10.100
19.7	1.3035	10.143
19.7	1.3013	10.125
20.2	1.2991	10.112
20.2	1.3067	10.172
20.2	1.3027	10.140
Average 20.0	1.3013	10.127

$t.$	Sp. rotation.	Mol. rotation.
89.5°	1.2197	9.829
89.5	1.2182	9.818
89.5	1.2167	9.805
89.5	1.2197	9.829
89.5	1.2182	9.818
Average 89.5	1.2185	9.820

The refraction determinations gave the results in table, p. 855.

Dr. Gladstone also determined the refractive power of this substance, and obtained—

Line.	$t.$	$\mu.$	$\frac{\mu-1}{d}p.$
A	22.1°	1.4643	65.28
F	22.1°	1.4892	68.78
H	22.1°	1.5185	72.89

Dispersion H—A = 7.61 at 22.1°.

Ethyl Diacetoacetate.

Prepared by the action of acetyl chloride on ethyl sodacetoacetate. Its boiling point was 103—105° at 19 mm. (Claisen).

$\alpha\ 17^{\circ}/4^{\circ}\ 1.12879.$

Line.	$\mu.$		Diff. for 83°.	$\frac{\mu - 1}{d}.$		Diff. for 83°.	$\frac{\mu - 1}{d} p.$		Diff. for 83°.
	$t.$			$t.$			$t.$		
	17°.	100°.		17°.	100°.		17°.	100°.	
A	1·465028	1·426166	0·038862	0·411970	0·409344	0·002626	65·091	64·676	0·415
C	1·470244	1·430845	0·039399	0·416591	0·413838	0·002753	65·821	65·386	0·435
D	1·475699	1·435508	0·040191	0·421424	0·418317	0·003107	66·585	66·094	0·491
F	1·490047	1·448699	0·041348	0·434135	0·430988	0·003147	68·593	68·096	0·497

Dispersion F—A = 3.502 at 17°.
 " " = 3.420 " 100°.

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The density determinations gave—

$d\ 4^{\circ}/4^{\circ}$	1.1073.	$d\ 55^{\circ}/55^{\circ}$	1.0696.
$d\ 10^{\circ}/10^{\circ}$	1.1012.	$d\ 60^{\circ}/60^{\circ}$	1.0670.
$d\ 15^{\circ}/15^{\circ}$	1.0967.	$d\ 65^{\circ}/65^{\circ}$	1.0646.
$d\ 20^{\circ}/20^{\circ}$	1.0950.	$d\ 70^{\circ}/70^{\circ}$	1.0622.
$d\ 25^{\circ}/25^{\circ}$	1.0889.	$d\ 75^{\circ}/75^{\circ}$	1.0598.
$d\ 30^{\circ}/30^{\circ}$	1.0854.	$d\ 80^{\circ}/80^{\circ}$	1.0575.
$d\ 35^{\circ}/35^{\circ}$	1.0819.	$d\ 85^{\circ}/85^{\circ}$	1.0553.
$d\ 40^{\circ}/40^{\circ}$	1.0786.	$d\ 90^{\circ}/90^{\circ}$	1.0534.
$d\ 45^{\circ}/45^{\circ}$	1.0754.	$d\ 95^{\circ}/95^{\circ}$	1.0516.
$d\ 50^{\circ}/50^{\circ}$	1.0724.	$d\ 100^{\circ}/100^{\circ}$	1.0499.

The magnetic rotations gave—

$t.$	Sp. rotation.	Mol. rotation.
19.8°	1.2202	10.670
19.8	1.2217	10.683
19.8	1.2179	10.651
19.8	1.2214	10.681
19.8	1.2243	10.707
Average 19.8	1.2211	10.678

After being in ice for seven days,

$t.$	Sp. rotation.	Mol. rotation.
17°	1.2275	10.717
17	1.2290	10.730
17	1.2275	10.717
Average 17	1.2280	10.721

Average of above, 10.699 at 18.4°.

The magnetic rotations gave—

$t.$	Sp. rotation.	Mol. rotation.
92.6°	1.1499	10.441
92.6	1.1510	10.451
92.6	1.1507	10.448
92.6	1.1518	10.458
Average 92.6	1.1508	10.449

$d\,17.6^{\circ}/4^{\circ}\quad 1.09313.$

Dispersion G—A	= 4.705 at 17.6°.
"	= 4.591 " 99.8°.

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Dr. Gladstone has likewise examined this substance, and obtained the following result:—

Line.	t .	μ .	$\frac{\mu - 1}{d} p$.
A	22·8°	1·4549	71·91
F	22·8°	1·4761	75·27
H	22·8°	1·4975	78·65

Dispersion H—A = 6·74 at 22·8°.

Diacetylacetone.

Dr. Collie very kindly prepared the specimen of this substance for me from dehydracetic acid; when fused, it becomes coloured slightly red, and this rendered the readings for the magnetic rotations a little difficult.

The density determinations gave—

$d\ 40^\circ/40^\circ$	1·0681.	$d\ 70^\circ/70^\circ$	1·0564.
$d\ 45^\circ/45^\circ$	1·0660.	$d\ 75^\circ/75^\circ$	1·0547.
$d\ 50^\circ/50^\circ$	1·0639.	$d\ 80^\circ/80^\circ$	1·0531.
$d\ 55^\circ/55^\circ$	1·0620.	$d\ 85^\circ/85^\circ$	1·0515.
$d\ 60^\circ/60^\circ$	1·0601.	$d\ 90^\circ/90^\circ$	1·0504.
$d\ 65^\circ/65^\circ$	1·0583.	$d\ 95^\circ/95^\circ$	1·0497.
	$d\ 100^\circ/100^\circ$		1·0494.

The magnetic rotations gave—

t .	Sp. rotation.	Mol. rotation.
56·0°	1·3870	10·307
56·0	1·3837	10·282
56·0	1·3780	10·240
56·0	1·3779	10·240
56·0	1·3930	10·352
57·5	1·3913	10·345
57·5	1·3937	10·363
57·5	1·3811	10·269
57·5	1·3762	10·233
64·2	1·3530	10·084
64·2	1·3533	10·086
64·2	1·3472	10·041
64·2	1·3499	10·061
Average 59·0	1·3742	10·223

<i>t.</i>	Sp. rotation.	Mol. rotation.
92·75°	1·2730	9·565
96·0	1·2826	9·637
97·5	1·2716	9·555
99·0	1·2764	9·591
Average 96·3	1·2759	7·587

The difference in the rotation of this and the previous amounts to 0·635 for 37·3°, or 1·704 for 100°.

The refraction determinations gave results in table, p. 860.

Ethyl β-Amidocrotonate.

This was examined at two temperatures; for the first it was used in a state of surfusion.

The density determinations gave—

<i>d</i> 15°/15°	1·0273.	<i>d</i> 60°/60°	1·0034.
<i>d</i> 20°/20°	1·0239.	<i>d</i> 65°/65°	1·0015.
<i>d</i> 25°/25°	1·0207.	<i>d</i> 70°/70°	0·9997.
<i>d</i> 30°/30°	1·0178.	<i>d</i> 75°/75°	0·9981.
<i>d</i> 35°/35°	1·0150.	<i>d</i> 80°/80°	0·9965.
<i>d</i> 40°/40°	1·0124.	<i>d</i> 85°/85°	0·9950.
<i>d</i> 45°/45°	1·0099.	<i>d</i> 90°/90°	0·9937.
<i>d</i> 50°/50°	1·0076.	<i>d</i> 95°/95°	0·9925.
<i>d</i> 55°/55°	1·0054.	<i>d</i> 100°/100°	0·9913.

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15·0°	1·5467	10·790
15·0	1·5482	10·800
15·2	1·5455	10·782
15·2	1·5381	10·732
15·2	1·5452	10·780
15·2	1·5425	10·761
15·2	1·5474	10·795
16·2	1·5437	10·778
17·4	1·5430	10·781
19·0	1·5370	10·750
Average 15·8	1·5437	10·775

Dispersion F—A	= 3.919 at 60°.
" "	= 3.537 " 99.8°.

<i>t.</i>	Sp. rotation.	Mol. rotation.
86.5°	1.4508	10.454
86.5	1.4631	10.543
86.5	1.4573	10.500
86.5	1.4536	10.498
86.5	1.4542	10.478
Average 86.5	1.4558	10.494

The determination of its refractive and dispersive powers gave—

$$d\ 16^{\circ}/4^{\circ}\ 1.02578.$$

$$d\ 15.8^{\circ}/4^{\circ}\ 1.02551.$$

Line.	<i>t.</i>	μ .	$\frac{\mu - 1}{d}$.	$\frac{\mu - 1}{d} p$.
A	16°	1.49032	0.47805	61.668
C	16	1.49633	0.48390	62.423
D	16	1.50209	0.48952	63.148
F	16	1.51806	0.50509	65.157
G	16	1.53334	0.51998	67.078

Dispersion G—A = 5.410 at 16°.

A second set of determinations were made with this product after it had been allowed to crystallise, and was thoroughly pressed between bibulous paper, to remove any traces of oily products which had been produced by the action of heat.

Line.	<i>t.</i>	μ .	$\frac{\mu - 1}{d}$.	$\frac{\mu - 1}{d} p$.
A	15.8°	1.49131	0.47908	61.802
C	15.8	1.49672	0.48436	62.482
D	15.8	1.50273	0.49022	63.239
F	15.8	1.51863	0.50573	65.239
G	15.8	1.53403	0.52075	67.176

Dispersion G—A = 5.374 at 15.8°.

Ethyl Benzoylacetate.

The specimen examined was obtained from Kahlbaum.

The density determinations gave—

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$d\ 4^\circ/4^\circ$	1.1311.	$d\ 55^\circ/55^\circ$	1.1008.
$d\ 10^\circ/10^\circ$	1.1259.	$d\ 60^\circ/60^\circ$	1.0990.
$d\ 15^\circ/15^\circ$	1.1219.	$d\ 65^\circ/65^\circ$	1.0973.
$d\ 20^\circ/20^\circ$	1.1186.	$d\ 70^\circ/70^\circ$	1.0957.
$d\ 25^\circ/25^\circ$	1.1154.	$d\ 75^\circ/75^\circ$	1.0943.
$d\ 30^\circ/30^\circ$	1.1126.	$d\ 80^\circ/80^\circ$	1.0930.
$d\ 35^\circ/35^\circ$	1.1099.	$d\ 85^\circ/85^\circ$	1.0919.
$d\ 40^\circ/40^\circ$	1.1073.	$d\ 90^\circ/90^\circ$	1.0910.
$d\ 45^\circ/45^\circ$	1.1050.	$d\ 95^\circ/95^\circ$	1.0903.
$d\ 50^\circ/50^\circ$	1.1029.	$d\ 100^\circ/100^\circ$	1.0896.

The magnetic rotations gave—

$t.$	Sp. rotation.	Mol. rotation.
17.5°	1.7224	16.402
17.5	1.7182	16.362
17.5	1.7220	16.398
17.5	1.7242	16.419
20.5	1.7136	16.347
20.5	1.7188	16.397
20.5	1.7217	16.425
Average 18.8	1.7201	16.393

$t.$	Sp. rotation.	Mol. rotation.
99.0°	1.6285	15.941
99.7	1.6251	15.909
100.7	1.6273	15.930
100.7	1.6229	15.887
100.7	1.6207	15.867
100.7	1.6253	15.913
Average 100.6	1.6249	15.908

As the influence of heat on the rotation of stable aromatic compounds is much greater than on those of the fatty series, it is necessary to allow for this before considering what the influence of temperature is on the chemical constitution of the substance. In this instance it will probably be most accurate to take the average of the difference found for a ketone and carboxylic acid, thus:—

Influence of heat on the rotation of acetophenone per 100° = 0.298

Influence of heat on the rotation of ethereal salt

of an aromatic carboxylic acid „ = 0.399

Average „ 0.348

Therefore, on the above rotation, 81.8° above the preceding one, this will be 0.284 . The rotation will then be

$$15.908 + 0.284 = 16.192.$$

Benzoylacetone.

Dr. Claisen purified this substance by precipitating it from its alkaline solution with carbonic acid. It melted at 58° , and was examined in the fused state.

The density determinations gave—

$d\ 60^\circ/60^\circ$	1.0899.	$d\ 85^\circ/85^\circ$	1.0812.
$d\ 65^\circ/65^\circ$	1.0862.	$d\ 90^\circ/90^\circ$	1.0805.
$d\ 70^\circ/70^\circ$	1.0898.	$d\ 95^\circ/95^\circ$	1.0801.
$d\ 75^\circ/75^\circ$	1.0834.	$d\ 100^\circ/100^\circ$	1.0800.
$d\ 80^\circ/80^\circ$	1.0823.		

As this substance was slightly brownish when fused, and became more so when kept in this condition, it was found impossible to measure it in a tube of the length usually employed (102 mm.); one of about half that length was therefore used, but even in this the colour obstructed the passage of the light to a very large extent, and made the readings difficult.

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
61.0°	2.2673	18.762
63.0	2.2688	18.787
64.0	2.2749	18.824
64.0	2.2662	18.773
64.0	2.2651	18.763
Average 63.2	2.2684	18.782

Methyl Acetophenoneoxalate.

This substance was examined in the fused state; it melts at 61° .

The density determinations gave—

$d\ 65^\circ/65^\circ$	1.1574.	$d\ 75^\circ/75^\circ$	1.1528.
$d\ 70^\circ/70^\circ$	1.1551.	$d\ 80^\circ/80^\circ$	1.1504.
	$d\ 85^\circ/85^\circ$	1.1481.	

The remarks made in reference to benzoylacetone also apply to this substance, but, besides, the colour obstructing the light, there was a slight opalescence which could not be got rid of by filtering

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the fused substance, and it was only with great difficulty readings could be obtained in a tube half the ordinary length. The results were, therefore, rather rough, but the averages given, being obtained from 64 readings, are probably not far from the truth; they are:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
66·5°	2·1739	21·511

Ethyl Acetophenoneoxalate.

The melting point of this substance was 42° (Claisen).

The density determinations gave—

<i>d</i> 20°/20°	1·1867.	<i>d</i> 60°/60°	1·1674.
<i>d</i> 25°/25°	1·1839.	<i>d</i> 65°/65°	1·1657.
<i>d</i> 30°/30°	1·1811.	<i>d</i> 70°/70°	1·1641.
<i>d</i> 35°/35°	1·1784.	<i>d</i> 75°/75°	1·1625.
<i>d</i> 40°/40°	1·1758.	<i>d</i> 80°/80°	1·1611.
<i>d</i> 45°/45°	1·1734.	<i>d</i> 85°/85°	1·1600.
<i>d</i> 50°/50°	1·1702.	<i>d</i> 90°/90°	1·1592.
<i>d</i> 55°/55°	1·1682.	<i>d</i> 95°/95°	1·1589.
	<i>d</i> 100°/100°	1·1588.	

The magnetic rotation gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
47·3°	2·1254	22·152
49·5	2·1207	22·124
48·3	2·1300	22·212
47·1	2·1255	22·158
45·5	2·1266	22·154
Average 47·5	2·1256	22·160

This substance, when melted, was of a yellowish colour, and was measured in an ordinary tube of 102 mm. in length; it was, however, very slightly cloudy, and could not be rendered quite clear by filtration, this cloudiness was evidently due to the presence of a trace of some crystalline substance, as it interfered with the polarised light, and thus impaired the sensitiveness of the observations; to overcome as much as possible the errors which might arise from this source, a very large number of observations were made, and each of the five series given above are averages of about 20 (making in all 100), whereas, in most cases, they are averages of 8 or 10 only.