XLIII.—*On the Magnetic Rotatory Power of some of the Saturated and Unsaturated Bibasic Acids and their Derivatives; also of Mesityl Oxide.*

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NEARLY a year since I brought before the Society an account of some experiments upon the magnetic rotatory power of the ethereal salts of maleic and citraconic acid and their isomers (Proc., 1887-8, p. 98), but owing to a desire to re-examine these substances when prepared by a process different from that previously used, and to extend my experiments on unsaturated compounds, and also to determine the magnetic rotation of some of the saturated bibasic compounds running parallel with them, I delayed sending in any detailed account of my experiments until this additional work was completed. So far as the re-examination of the ethereal salts of the unsaturated acids is concerned, it will be found that the numbers now given do not vary appreciably from those given last year, except in the case of ethylic itaconate, which was a little too high, owing to impurity in the product examined. Before considering, however, the bearing of the results which have been obtained, it will be most convenient first to give the

details of the preparation, properties, and magnetic rotation of the substances examined.

Malonic Acid.

This was examined in aqueous solutions, the proportions corresponding to 1 mol. of acid to 4 mols. of water ($\text{C}_3\text{H}_4\text{O}_4 + 4\text{H}_2\text{O}$). This is a supersaturated solution at ordinary temperatures. The density determinations gave—

$$d_{15}^{15^\circ} 1.2543, \quad d_{20}^{20^\circ} 1.2514,$$

$$d_{25}^{25^\circ} 1.2488.$$

The following are the numbers obtained for the magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
23.5°	0.9537	7.460
23.5	0.9543	7.465
23.5	0.9546	7.467
23.5	0.9555	7.474
23.0	0.9605	7.514
23.0	0.9536	7.466
23.0	0.9557	7.477
23.0	0.9545	7.468
Average 23.2	0.9553	7.474
Less mol. rot. of 4 mols. of water		4.000
Malonic acid		3.474

Propyl Succinate.

This ether, which does not appear to have been previously described, was prepared by passing gaseous hydrochloric acid through a hot mixture of succinic acid, and about twice as much propyl alcohol as was necessary for the formation of the ether; when partially saturated with hydrochloric acid, it was gently boiled, so that more succinic acid might go into solution, and again partially saturated with acid, this operation being repeated until all the acid had disappeared; it was then well saturated with hydrochloric acid and allowed to stand about 24 hours. At the end of this time, the product was heated, and the unchanged propyl alcohol distilled off. The crude ether was diluted with ordinary ether, and the solution washed with water and sodium carbonate, after which it was dried over anhydrous potassium

carbonate and distilled. The propyl succinate thus prepared came over within about half a degree, but on taking the densities of different fractions they were not found to agree quite so closely as was desired; the product was therefore carefully fractioned, and was obtained boiling practically constant at $250\cdot8^{\circ}$ (corr.), when distilled and collected in two fractions. These gave densities fairly close to each other, viz. :—

$$\text{Fraction I. } d_{15^{\circ}}^{15^{\circ}} 1\cdot0063,$$

$$,, \quad \text{II. } d_{15^{\circ}}^{15^{\circ}} 1\cdot0061,$$

The densities found for the other temperatures were—

$$d_{4^{\circ}}^{4^{\circ}} 1\cdot0157, \quad d_{25^{\circ}}^{25^{\circ}} 0\cdot9986.$$

Propyl succinate is a colourless oil, boiling without decomposition; when cooled in ice and hydrochloric acid, it solidifies to a crystalline mass which fuses below 0° .

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
$10\cdot3^{\circ}$	0·9324	10·353
10·3	0·9343	10·373
10·3	0·9345	10·377
13·0	0·9285	10·340
13·0	0·9316	10·374
Average 11·4	0·9323	10·363

Succinyl Chloride.

This was prepared in the ordinary way by means of succinic acid and phosphorus pentachloride. After the oxychloride of phosphorus formed has been mostly distilled off, it is best to fraction the product under reduced pressure, otherwise carbonisation takes place to a considerable extent, especially if a Wurtz flask is used with a neck sufficiently long to contain the thermometer scale in the vapour, and the distillation is conducted slowly. The chloride of succinyl used boiled at $150\text{—}152^{\circ}$ (corr.) at 214 mm., and was a bright yellow liquid. At 760° it boiled at $190\text{—}192^{\circ}$ (corr.).

The density determinations gave the following results :—

$$\begin{array}{ll}
 d_{\frac{4}{40}}^{40} 1.4252, & d_{\frac{20}{20}}^{20} 1.4073, \\
 d_{\frac{10}{10}}^{10} 1.4178, & d_{\frac{25}{25}}^{25} 1.4028, \\
 d_{\frac{15}{15}}^{15} 1.4123, & d_{\frac{30}{30}}^{30} 1.3809.
 \end{array}$$

<i>t.</i>	Sp. rotation.	Mol. rotation.
10.4°	1.1893	7.224
10.0	1.1888	7.219
10.0	1.1870	7.209
10.0	1.1879	7.214
9.0	1.1966	7.261
9.2	1.1996	7.280
9.5	1.1957	7.255
9.7	1.1951	7.256
11.0	1.1901	7.234
12.0	1.1946	7.267
13.0	1.1871	7.227
14.0	1.1916	7.265
Average 10.6	1.1919	7.242

Pyrotartaric Anhydride and Chloride.

The method given for the preparation of pyrotartaric anhydride consists in heating pyrotartaric acid with phosphorus pentasulphide (Böttiger, *Ber.*, **11**, 1352). At first it was intended to prepare it by heating pyrotartaric chloride with the acid, but the yield of chloride obtained was very unsatisfactory, as carbonisation took place to a considerable extent. The chloride boiled at about 210—220° under 760 mm., and at about 158° at 214 mm. If the operation had been conducted from the first under reduced pressure, probably a more satisfactory yield might have been obtained. The process, which was found to work well for the production of the anhydride, consists in digesting the powdered acid with an excess of acetyl chloride until all action is over, and slowly fractioning the product, when the anhydride is eventually obtained as a rather thick colourless oil, boiling constantly at 247.4 (corr.). This boiling point is lower than that of succinic anhydride, which is given as 250°, whilst that of glutaric anhydride is given as 282—287°. Pyrotartaric anhydride has little or no odour; it sinks as an oil in cold water, but when agitated with hot water it soon dissolves, yielding a perfectly clear solution. It remains fluid even if cooled down to near 0°, and has been described as an oil, but if rubbed with a glass rod crystallisation sets

in and it soon becomes a white confused crystallised mass. This fuses at $31\cdot5$ — 32° , but not sharply.

The relative density determinations gave—

$$\begin{array}{ll} d_{6\cdot5^\circ}^{6\cdot5^\circ} 1\cdot2458, & d_{40^\circ}^{40^\circ} 1\cdot2203, \\ d_{15^\circ}^{15^\circ} 1\cdot2378, & d_{55\cdot8^\circ}^{55\cdot8^\circ} 1\cdot2122. \\ d_{25^\circ}^{25^\circ} 1\cdot2303, & \end{array}$$

From these the following true densities were deduced :—

<i>t.</i>	<i>d.</i>	Difference.
0°	1·2526	
10	1·2422	0·0104
20	1·2318	0·0104
30	1·2214	0·0104
40	1·2110	0·0104
50	1·2006	0·0104
60	1·1902	0·0104

The determinations of the magnetic rotation gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
$9\cdot4^\circ$	0·9323	4·750
9·0	0·9335	4·755
9·0	0·9359	4·767
8·5	0·9383	4·777
17·2	0·9259	4·744
16·3	0·9371	4·789
Average 11·6	0·9338	4·764

The following were made at higher temperatures :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
$47\cdot8^\circ$	0·9096	4·738
49·4	0·9104	4·743
50·9	0·9075	4·730
52·1	0·9079	4·737
Average 50·0	0·9088	4·737

Glutaric Acid.

This acid was prepared from the cyanide of trimethylene which is obtained on digesting bromide of trimethylene with cyanide of potassium and alcohol. The cyanide was purified by distillation and then saponified with aqueous potash. The reaction takes place easily, ammonia being evolved very freely on heating the mixture. The resulting solution was acidified with hydrochloric acid and the glutaric acid taken up with ether; it is necessary to agitate the solution many times successively with fresh quantities of ether before all the acid is taken up. In one operation the acidified mixture was evaporated to dryness before extraction with ether, but the acid obtained was coloured and difficult to get quite pure.

The acid obtained from the ethereal solution was dried over the water-bath and crystallised from benzene. This was found to be a convenient solvent, glutaric acid being moderately soluble in it when boiling, and but slightly so when cold. After two crystallisations it was obtained in white, non-deliquescent plates melting at 96—97°. Rebout gives 96·5° (*Ann. Chem. Phys.* [5], **14**, 501).

The strongest solution of this acid which could be conveniently used for the examination of its magnetic rotation was in the proportion of 1 mol. of acid to 10 mols. of water ($C_5H_8O_4 + 10OH_2$). Two such solutions were made, for the second the acid was recrystallised from water. They had the following densities:—

Sol. I.	Sol. II.
$d_{4^{\circ}}^{4^{\circ}}$ 1·1224,	
$d_{15^{\circ}}^{15^{\circ}}$ 1·1166,	$d_{15^{\circ}}^{15^{\circ}}$ 1·1162.
$d_{25^{\circ}}^{25^{\circ}}$ 1·1126,	

The following numbers were obtained for the magnetic rotation:—

Solution I.

<i>t.</i>	Sp. rotation.	Mol. rotation.
12·6°	1·0001	15·509
13·0	1·0008	15·521
13·0	1·0005	15·516
13·3	0·9992	15·500
13·6	0·9933	15·410
13·6	0·9992	15·502
14·2	0·9980	15·500
Average 13·3	0·9987	15·494

Solution II.

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·4°	0·9911	15·428
16·4	0·9949	15·488
16·4	0·9934	15·465
16·4	0·9946	15·483
16·4	0·9970	15·492
Average 16·4	0·9942	15·471

These numbers are as close as could be expected; the average of the molecular rotation, less the molecular rotation of 10 mols. of water, should give that of glutaric acid, thus:—

$$\text{Average mol. rot. of } \text{C}_5\text{H}_8\text{O}_4 + 10\text{OH}_2 = 15\cdot482$$

$$\text{Less molecular rotation of } 10\text{OH}_2 \dots = 10\cdot000$$

$$\text{Molecular rotation of glutaric acid } \dots = 5\cdot482$$

Ethyl Glutarate.

The ethyl compound of glutaric acid was prepared by saturating its alcoholic solution with hydrochloric acid. The ether, after being separated by means of water, was washed with sodium carbonate, dried with potassium carbonate, and distilled. It nearly all came over at 236° (corr.), a little of the first and last being rejected. Rebout gives 236·5—237° (corr.) as the boiling point he observed. The density determinations gave:—

$$d_{\frac{4}{4}}^{\frac{4}{4}} 1\cdot0382, \quad d_{\frac{20}{20}}^{\frac{20}{20}} 1\cdot0243,$$

$$d_{\frac{10}{10}}^{\frac{10}{10}} 1\cdot0327, \quad d_{\frac{25}{25}}^{\frac{25}{25}} 1\cdot0204,$$

$$d_{\frac{15}{15}}^{\frac{15}{15}} 1\cdot0284, \quad d_{\frac{30}{30}}^{\frac{30}{30}} 1\cdot0167.$$

The following are the numbers obtained for the magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
12·6°	0·9219	9·345
12·6	0·9232	9·357
12·6	0·9235	9·361
12·9	0·9250	9·379
12·9	0·9259	9·388
12·9	0·9251	9·380
11·3	0·9206	9·322
11·3	0·9221	9·337
11·3	0·9243	9·359
11·3	0·9243	9·359
12·0	0·9221	9·342
13·3	0·9240	9·372
13·6	0·9195	9·329
13·9	0·9214	9·350
Average 12·5	0·9231	9·356

Ethyl Sebate.

The specimen examined was the same as that described in my previous paper (Trans., 1884, 518). The following fresh measurements were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
11·2°	0·9773	14·423
11·2	0·9782	14·436
11·3	0·9802	14·467
11·5	0·9829	14·508
12·0	0·9791	14·459
Average 11·4	0·9795	14·459

Maleic Anhydride.

This was prepared by the process described by me in a paper brought before the Society some years since (Trans., 1881, 561), and consists in digesting maleic acid with acetyl chloride, and decomposing the resulting aceto-maleic anhydride by distillation. Considerable quantities were made and the process was found to work very satisfactorily. It was found safest to use a good excess of acetyl chloride, otherwise, if too little be used, fumaric acid will be formed and come over with the last portion of maleic anhydride. The latter should be distilled three or four times to ensure the complete decomposition of the aceto-maleic anhydride, and fraction off the acetic acid formed.

The boiling points of these preparations were taken with different thermometers, and gave:—I, 199·5° corr.; II, 200° corr.; III, 200° corr.; so that practically the boiling point of maleic anhydride may be taken as 200°.

Maleic anhydride may be crystallised from absolute alcohol if the operation be conducted quickly, but if left to stand afterwards the crystals gradually disappear.

This substance being solid its magnetic rotation was determined from its solutions in acetic acid, acetic anhydride, and citraconic anhydride.

Solution of Maleic Anhydride in Acetic Acid.

The acetic acid solution was made in the proportion of 2 mols. of acetic acid to 1 mol. of maleic anhydride, $2\text{C}_2\text{H}_4\text{O}_2 + \text{C}_4\text{H}_2\text{O}_3$. This solution was a supersaturated one and the anhydride crystallised out on standing, but, after warming, the solution remained free from crystals sufficiently long for the required determination. The acetic acid used was perfectly free from water. The density determinations gave the following numbers:—

$$\begin{array}{ll} d_{10}^{10^\circ} 1.1880, & d_{17}^{17^\circ} 1.1804, \\ & d_{25}^{25^\circ} 1.1733. \end{array}$$

The magnetic rotation found was as follows:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
23·0°	0·9219	9·502
24·0	0·9204	9·494
24·5	0·9204	9·498
25·0	0·9201	9·498
Average 24·1	0·9207	9·498
Less mol. rot. of 2 mols. $\text{C}_2\text{H}_4\text{O}_2$		5·050
Mol. rot. of 1 mol. $\text{C}_4\text{H}_2\text{O}_3$. . .		4·448

Solution of Maleic Anhydride in Acetic Anhydride.

The solution of maleic anhydride in acetic anhydride was in the proportion of 5 mols. of maleic anhydride to 2 mols. of acetic anhydride, $5\text{C}_4\text{H}_2\text{O}_3 + 2\text{C}_4\text{H}_6\text{O}_3$. This forms a supersaturated solution which sometimes will remain liquid for a long time, but is very

uncertain in this particular. Its relative density determinations gave the following numbers:—

$$\begin{array}{ll} d_{\frac{6.6}{6.6}}^{6.6} 1.2781, & d_{\frac{60}{60}}^{60} 1.2345, \\ d_{\frac{25}{25}}^{25} 1.2595, & d_{\frac{98}{98}}^{98} 1.2158. \\ d_{\frac{39.9}{39.9}}^{39.9} 1.2480, \end{array}$$

From these the following true densities were deduced:—

<i>t.</i>	<i>d.</i>	Difference.	<i>t.</i>	<i>d.</i>	Difference.
10°	1.2740	0.0118	60°	1.2142	0.0121
20	1.2622	0.0119	70	1.2019	0.0123
30	1.2503	0.0120	80	1.1896	0.0123
40	1.2383	0.0120	90	1.1772	0.0124
50	1.2263		100	1.1648	0.0124

The magnetic rotation gave the following numbers. Owing to the tendency of the solution to crystallise, the determinations had to be made at a rather high temperature. This will make the results probably a little low:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
32°	0.9972	30.661
31	0.9999	30.733
30	0.9973	30.645
29.2	0.9958	30.564
Average 30.7	0.9975	30.651
Less mol. rot. of 2 mols. C ₄ H ₆ O ₃		8.564
Mol. rot. of 5 mols. C ₄ H ₂ O ₃	..	22.087
„ 1 mol. „	..	4.417

Solution of Maleic Anhydride in Citraconic Anhydride.

Maleic anhydride dissolves easily in citraconic anhydride; the proportions used were equimolecular, C₄H₂O₃ + C₅H₄O₃. This solution deposits maleic anhydride in cold weather. The density determinations of this solution gave—

$$d_{15^{\circ}}^{15^{\circ}} 1.2983,$$

$$d_{20^{\circ}}^{20^{\circ}} 1.2938,$$

$$d_{25^{\circ}}^{25^{\circ}} 1.2896.$$

The magnetic rotations gave the following numbers :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
19.5°	1.1206	10.101
19.0	1.1198	10.091
18.5	1.1216	10.103
18.0	1.1193	10.080
Average 18.8	1.1203	10.069
Less mol. rot. of specimen of } C ₅ H ₄ O ₃ used		5.527
Mol. rot. C ₄ H ₂ O ₃		4.542

A second solution of maleic anhydride in citraconic anhydride was also examined, the citraconic anhydride used as the solvent being that purified with phosphoric anhydride, and described further on in this paper; the proportions used were equimolecular. The density determinations of this product gave—

$$d_{10^{\circ}}^{10^{\circ}} 1.3039,$$

$$d_{15^{\circ}}^{15^{\circ}} 1.2992,$$

$$d_{25^{\circ}}^{25^{\circ}} 1.2946.$$

These numbers are slightly higher than those obtained with the previous preparations, owing to the density of the citraconic anhydride used being higher. The magnetic rotation gave the following numbers :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
12.1°	1.1250	10.075
10.6	1.1262	10.090
9.75	1.1296	10.105
9.40	1.1296	10.103
9.0	1.1275	10.081
9.0	1.1269	10.076
Average 9.94	1.1275	10.088
Less mol. rot. of specimen of } C ₅ H ₄ O ₃ used		5.540
Mol rot. C ₄ H ₂ O ₃		4.548

Maleic Acid.

The acid being solid and not easily fusible had to be examined in solution. The strongest solution it was found practical to use was in the proportion of 1 mol. of maleic acid to 8 mols. of water ($C_4H_4O_4 + 8OH_2$). This was a supersaturated solution, and the acid was deposited to some extent on standing. Its density determinations gave—

$$d_{15^\circ}^{15^\circ} 1.1694, \quad d_{20^\circ}^{20^\circ} 1.1676,$$

$$d_{25^\circ}^{25^\circ} 1.1656.$$

The magnetic rotation found was as follows :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
26.0°	1.0972	13.609
26.0	1.1002	13.646
26.0	1.0981	13.621
26.0	1.0975	13.644
24.0	1.0994	13.628
24.0	1.1028	13.670
23.0	1.1002	13.627
23.0	1.0999	13.624
Average 24.8	1.0994	13.633
Less mol. rot. of 8 mols. OH_2 ..		8.000
Maleic acid		5.633

Ethyl Maleate.

Several experiments were made on the preparation of this compound which it may be useful to describe. Attempts were first made to produce it directly from alcohol and maleic anhydride, but to get a neutral ether it is necessary to employ a high temperature; the mixture was therefore heated in sealed tubes at 180—190° for four or five hours, but in this way the product obtained consisted chiefly of ethyl fumarate. Maleic anhydride was then digested with alcohol, the mixture cooled in ice and salt, and saturated with hydrochloric acid gas previously cooled by passing through a worm placed in a freezing mixture; at this low temperature the action did not take place, and it was necessary to allow the product to attain a temperature of 18° or 19° to induce etherification. The product obtained consisted chiefly of ethyl maleate, but it contained a little ethyl

fumarate and a small quantity of some chlorine addition product. As these methods did not yield satisfactory products, recourse was had to the process of preparing this ether from silver maleate by acting on it with ethyl iodide. In carrying this out, the silver salt was added to an excess of ethyl iodide little by little, the heat of a water-bath being applied to set up the reaction after each addition; the product was then digested on the water-bath for a short time. The ethyl maleate was then extracted from the silver iodide by means of dry ether, and the ethereal solution distilled until the residual liquid had attained a temperature of about 160° , this was then fractioned under reduced pressure. The ethyl maleate thus prepared came over at 180.5 (corr.) at 212 mm.; it also boiled at 223.5° at 760 mm. (Anschutz found 225°). It was found to be free from ethyl fumarate.

The following has been found the most satisfactory method of testing ethyl maleate for small quantities of ethyl fumarate. About 2 or 3 c.c. of the ether are saponified with alcoholic potash to which some *water* has been added, the mixture is then diluted with water and the alcohol boiled off. After cooling, dilute hydrochloric acid is added in excess, and if no fumaric acid crystallises out, the solution is treated with ether, which will remove every trace of fumaric acid, but scarcely any maleic acid, so that on evaporation the former, if present, will be found to constitute most of the residue.

Neutral salts of maleic acid give with ferric salts a red solution similar to that formed by an acetate, but fumarates give a bulky, pale-brown precipitate; probably these reactions might be used for testing the purity of ethyl maleate, but in this case it is especially necessary to saponify the ether with alcoholic potash diluted with water, otherwise, apparently an addition product is formed with the ethyl maleate which yields a potash salt, precipitating ferric salts in a similar way to fumarates.

The relative density determinations of ethyl maleate gave—

$$\begin{array}{ll} d_{10}^{10^{\circ}} 1.0780, & d_{20}^{20^{\circ}} 1.0695, \\ d_{15}^{15^{\circ}} 1.0735, & d_{25}^{25^{\circ}} 1.0658. \end{array}$$

The following numbers were obtained for the magnetic rotation of this compound:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
12·0°	1·0871	9·649
11·6	1·0861	9·637
11·6	1·0856	9·632
11·6	1·0842	9·620
12·5	1·0857	9·640
12·5	1·0857	9·640
12·5	1·0879	9·660
11·0	1·0877	9·646
10·5	1·0878	9·643
23·0	1·0730	9·608
23·0	1·0702	9·582
22·0	1·0702	9·576
22·0	1·0725	9·596
Average 15·1	1·0818	9·625

Ethyl Fumarate.

The first specimen examined was prepared by saturating a mixture of alcohol and fumaric acid with gaseous hydrochloric acid, the mixture being heated now and then until the acid disappeared. The ether was washed first with water, and then with sodium carbonate, dried and fractioned. It boiled at 219–220° (corr.), but contained a small quantity of chlorine from the formation of ethyl chlorosuccinate. Dr. Purdie also observed the formation of ethyl chlorosuccinate when preparing ethyl fumarate by this method, though he evidently obtained more of it than I did, probably on account of continuing the application of heat to the mixture whilst passing the hydrochloric acid (Trans., 1881, **39**, 346).

The density determination gave—

$$d_{15}^{15^{\circ}} 1\cdot0623, \quad d_{25}^{25^{\circ}} 1\cdot0539.$$

The magnetic rotation determinations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
9·5°	1·1247	10·073
9·5	1·1231	10·064
12·8	1·1273	10·165
12·8	1·1251	10·145
Average 11·1	1·1250	10·112

As this ether was not quite pure, other experiments were made on its preparation, and it was found that etherification might be

effected by heating the acid and alcohol in a sealed tube to a high temperature. The proportions used were one of fumaric acid to three of absolute alcohol, the mixture being heated at 180—190° for seven or eight hours. The excess of alcohol was then distilled off, and the ethyl fumarate washed with water and sodium carbonate, dried, and distilled; it boiled at 219·3° (corr.). Its density determinations gave—

$$\begin{array}{ll} d_{10}^{10^{\circ}} 1\cdot0626, & d_{20}^{20^{\circ}} 1\cdot0535, \\ d_{15}^{15^{\circ}} 1\cdot0578, & d_{25}^{25^{\circ}} 1\cdot0496. \end{array}$$

As might be expected these densities are somewhat lower than those of the ether containing chlorine.

The magnetic rotations found were as follows:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10·0°	1·1256	10·119
10·0	1·1280	10·150
10·5	1·1253	10·130
10·5	1·1232	10·111
22·5	1·1135	10·119
21·7	1·1133	10·111
21·5	1·1126	10·103
Average 15·2	1·1202	10·120

The numbers are therefore almost identical with those obtained with the previous less pure specimen of ethyl fumarate; the influence of a small quantity of ethyl chlorosuccinate would only very slightly reduce the rotation. The rotation of ethyl chlorosuccinate deduced from other compounds which have lately been examined, is 9·72, or very close to that number.

Fumaryl Chloride.

This was prepared from fumaric acid by means of phosphorus pentachloride. It was obtained as a pale-yellow fuming liquid boiling at 161—164°. Its density determinations gave—

$$\begin{array}{ll} d_{15}^{15^{\circ}} 1\cdot4202, & d_{20}^{20^{\circ}} 1\cdot4149, \\ & d_{25}^{25^{\circ}} 1\cdot4095. \end{array}$$

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17·0°	1·4579	8·739
17·0	1·4567	8·732
16·8	1·4564	8·729
16·8	1·4579	8·738
14·3	1·4641	8·758
13·9	1·4652	8·763
13·2	1·4637	8·769
Average 15·6	1·4607	8·747

Citraconic Anhydride.

This was prepared in the ordinary way by the distillation of citric acid. It was fractioned many times. The product selected for examination boiled at 213·5—214° (corr.). Its density determinations gave—

$$\begin{array}{ll}
 d_{4^{\circ}}^{4^{\circ}} 1\cdot2605, & d_{15^{\circ}}^{15^{\circ}} 1\cdot2493, \\
 d_{10^{\circ}}^{10^{\circ}} 1\cdot2540, & d_{20^{\circ}}^{20^{\circ}} 1\cdot2450, \\
 & d_{25^{\circ}}^{25^{\circ}} 1\cdot2409.
 \end{array}$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15·5°	1·1014	5·488
17·0	1·1125	5·547
18·5	1·1113	5·548
14·0	1·1113	5·530
13·5	1·1141	5·544
14·0	1·1100	5·525
22·0	1·1014	5·512
21·5	1·1011	5·509
21·0	1·1011	5·494
20·5	1·1039	5·519
Average 17·7	1·1068	5·522

As these numbers were not so high as was expected, it was thought that the citraconic anhydride might contain some citraconic acid; it was, therefore, heated with phosphoric anhydride up to its boiling point. As the latter was apparently a good deal hydrated, and also blackened, the citraconic anhydride was decanted, and heated with fresh phosphoric anhydride, this operation being repeated a third

time; altogether a considerable quantity of phosphoric anhydride was used. The citraconic anhydride was then decanted from the phosphoric anhydride and fractioned; it commenced to distil at 213.5° (corr.), and about nine-tenths came over within a degree of this. This distillate was again treated with phosphoric anhydride, and heated up to its boiling point for a short time with it, when the phosphoric anhydride was now only a little discoloured; after decanting off the citraconic anhydride it was again distilled, when it came over nearly constantly at 213.5° , a few drops at the last which were rejected coming over at 215° .

Citraconic anhydride thus purified was perfectly colourless, and a more mobile fluid than the ordinary product. Its relative density determinations gave—

$d_{4}^{4^{\circ}}$ 1.2617,	$d_{51.45^{\circ}}^{51.45^{\circ}}$ 1.2246,
$d_{15^{\circ}}^{15^{\circ}}$ 1.2504,	$d_{59.75^{\circ}}^{59.75^{\circ}}$ 1.2205,
$d_{20^{\circ}}^{20^{\circ}}$ 1.2461,	$d_{65^{\circ}}^{65^{\circ}}$ 1.2178,
$d_{25^{\circ}}^{25^{\circ}}$ 1.2420,	$d_{77.5^{\circ}}^{77.5^{\circ}}$ 1.2119,
$d_{25.92^{\circ}}^{25.92^{\circ}}$ 1.2418,	$d_{87.75^{\circ}}^{87.75^{\circ}}$ 1.2081,
$d_{37.4^{\circ}}^{37.4^{\circ}}$ 1.2335,	$d_{98.6^{\circ}}^{98.6^{\circ}}$ 1.2055.

These numbers are averages of two and in some cases of three determinations. The following true densities were deduced from them:—

<i>t.</i>	<i>d.</i>	Diff.
0°	1.2659	
10	1.2549	0.0110
20	1.2439	0.0110
30	1.2328	0.0111
40	1.2218	0.0110
50	1.2107	0.0111
60	1.1997	0.0110
70	1.1886	0.0111
80	1.1775	0.0111
90	1.1664	0.0111
100	1.1553	0.0111

The following numbers were obtained for its magnetic rotation.

Two series of determinations were made—one at the ordinary temperature, and one at a high temperature for reasons explained further on.

Series I. Ordinary Temperature.

<i>t.</i>	Sp. rotation.	Mol. rotation.
17·8°	1·1101	5·535
17·8	1·1131	5·550
17·8	1·1098	5·533
17·8	1·1137	5·553
16·5	1·1131	5·544
17·0	1·1107	5·534
17·5	1·1101	5·534
Average 17·4	1·1115	5·540

It will be observed that the specific rotation of this purified citraconic anhydride is higher than that of the ordinary product, but that the molecular rotation is practically the same. This is accounted for by the increase of the density resulting from the purification.

Series II. High Temperatures.

<i>t.</i>	Sp. rotation.	Mol. rotation.
60·5°	1·0693	5·451
64·7	1·0790	5·511
66·2	1·0687	5·461
67·1	1·0708	5·461
67·4	1·0708	5·475
67·7	1·0714	5·477
Average 65·7	1·0717	5·473

Citraconic Anhydride and Acetic Acid.

This mixture was made to correspond to the analogous one containing maleic anhydride, being in the proportions of 1 mol. of anhydride to 2 mols. of acetic acid. The density determinations gave—

$$\begin{array}{ll}
 d_{10}^{10} 1\cdot1508, & d_{20}^{20} 1\cdot1413, \\
 d_{15}^{15} 1\cdot1459, & d_{25}^{25} 1\cdot1371.
 \end{array}$$

The numbers obtained for the magnetic rotation were as follows:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
23·2°	0·9294	10·519
23·2	0·9261	10·483
23·2	0·9281	10·506
23·2	0·9261	10·482
Average 23·2	0·9274	10·498
Less 2 mols. acetic acid		5·050
Citraconic anhydride		5·448

Citraconic Anhydride and Acetic Anhydride.

This mixture was also examined so as to compare the results with those obtained with maleic anhydride and acetic anhydride. The quantities used were in the proportion of 5 mols. of citraconic anhydride to 2 mols. of acetic anhydride.

The relative density determinations gave the following results:—

$$\begin{array}{ll}
 d_{\frac{6\cdot7^\circ}{6\cdot7^\circ}} 1\cdot2116, & d_{\frac{59\cdot8^\circ}{59\cdot8^\circ}} 1\cdot1704, \\
 d_{\frac{15^\circ}{15^\circ}} 1\cdot2028, & d_{\frac{64\cdot75^\circ}{64\cdot75^\circ}} 1\cdot1676, \\
 d_{\frac{25^\circ}{25^\circ}} 1\cdot1941, & d_{\frac{98\cdot05^\circ}{98\cdot05^\circ}} 1\cdot1544.
 \end{array}$$

The true densities deduced from these are as follows:—

<i>t.</i>		Difference.
10°	1·2078	0·0118
20	1·1960	0·0116
30	1·1844	0·0114
40	1·1730	0·0112
50	1·1618	0·0112
60	1·1506	0·0112
70	1·1394	0·0111
80	1·1283	0·0111
90	1·1172	0·0111
100	1·1061	0·0111

The following results were obtained for the magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·0	1·0192	35·982
15·5	1·0198	36·003
15·5	1·0198	36·005
15·5	1·0186	35·961
Average 15·6	1·0193	35·988
Less 2 mols. acetic anhydride ..		8·564
		5) 27·485
Citraconic anhydride		5·497

Citraconic Acid.

As this acid is solid, it was found necessary to examine its solutions. The solution employed was made in the proportions of 1 mol. of citraconic acid to 2 mols. of water ($C_6H_8O_4 + 2OH_2$), and was prepared by mixing citraconic anhydride with water in the proportion of 1 mol. of anhydride to 3 mols. of water. The resulting product was a supersaturated solution, depositing part of the acid on standing. A solution of citraconic acid when evaporated on the water-bath decomposes, and on adding water to it citraconic anhydride separates as an oil. Crystallised citraconic acid kept over sulphuric acid under a bell-jar smells strongly of the anhydride.

The density determinations of the above aqueous solution of citraconic acid gave the following results:—

$$d_{15^{\circ}}^{15^{\circ}} 1.2410, \quad d_{20^{\circ}}^{20^{\circ}} 1.2392.$$

$$d_{25^{\circ}}^{25^{\circ}} 1.2366,$$

The numbers obtained for the magnetic rotation were as follows:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
25·0°	1·1469	8·553
25·0	1·1471	8·555
25·0	1·1480	8·562
25·0	1·1496	8·573
23·0	1·1504	8·572
23·0	1·1525	8·689
23·0	1·1492	8·564
Average 24·1	1·1491	8·567
Less 2 mols. water.....		2·000
Citraconic acid		6·567

Ethyl Citraconate.

This was in the first instance prepared by saturating an alcoholic solution of citraconic anhydride with hydrochloric acid gas, keeping the mixture cool. After standing a few hours, the ether was separated by the addition of water, washed with dilute sodium carbonate, dried over potassium carbonate, and distilled. Thus obtained it boiled at 230.5 (corr.). The density determinations gave—

$$d_{15}^{15^{\circ}} 1.0486, \quad d_{20}^{20^{\circ}} 1.0445,$$

$$d_{25}^{25^{\circ}} 1.0414.$$

The magnetic rotation determinations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
19.0	1.0650	10.524
16.0	1.0705	10.557
17.5	1.0651	10.514
18.8	1.0638	10.510
21.5	1.0573	10.490
20.0	1.0598	10.481
Average 18.4	1.0636	10.513

On treating this ether with alcoholic soda, and testing the resulting product, it was found to contain a little chlorine, showing the presence of some chlorine addition product resulting from the union of the ethyl citraconate with the hydrochloric acid used in its preparation.

Experiments were therefore made to obtain this ether in a purer condition by heating citraconic anhydride with absolute alcohol in sealed tubes. By employing a temperature of 120—130° for a day, a considerable quantity of an oily product was obtained, but as it mostly dissolved in a solution of sodium carbonate, it was evidently the acid ether; a temperature of about 180—200° was therefore used and maintained for six or seven hours; after distilling off the alcohol, the product was washed with sodium carbonate solution, dried over potassium carbonate and distilled, it boiled almost constantly at 230.3°. The density determinations gave—

$$d_{15}^{15^{\circ}} 1.0485, \quad d_{20}^{20^{\circ}} 1.0446,$$

$$d_{25}^{25^{\circ}} 1.0409.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10·0°	1·0707	10·515
10·4	1·0673	10·484
10·8	1·0689	10·503
11·2	1·0666	10·483
11·5	1·0695	10·514
13·5	1·0497	10·484
13·5	1·0526	10·513
Average 11·6	1·0636	10·499

Some time after these experiments were made, a quantity of the ethyl citraconate used for them was saponified, the solution acidified, and the liberated acid taken up with ether. On gently evaporating this, citraconic acid was left as a syrupy liquid owing to the presence of a little water; but after standing for several days it deposited small crystals of a less soluble acid, evidently either itaconic or citraconic acid, which had been formed by the high temperature used when preparing the ether, it was therefore finally resolved to prepare some pure ethyl citraconate from silver citraconate and ethyl iodide.

Silver citraconate comes down as a very bulky precipitate, quite different in character from silver itaconate, and does not become dense when heated to 100°. It is difficult to wash, unless a vacuum pump is used with a considerable reduction of pressure. It was dried at 100°, and gradually added to a large excess of colourless ethyl iodide. The action did not set in quickly in the cold, but when gently heated, local boiling took place on each addition of the salt. After all the silver salt had been added, the mixture was heated on the water-bath for a short time, and the silver iodide collected on a filter and washed with ethyl iodide. The filtrate was then freed from ethyl iodide by distillation, and the ethyl citraconate washed with sodium carbonate solution, dried by means of potassium carbonate, and distilled. The ethyl citraconate thus obtained boiled constantly at 230·3°, and was perfectly colourless. Its density determinations gave—

$$\begin{array}{ll}
 d_{4^{\circ}}^{4^{\circ}} 1\cdot0567, & d_{15^{\circ}}^{15^{\circ}} 1\cdot0468, \\
 d_{10^{\circ}}^{10^{\circ}} 1\cdot0514, & d_{20^{\circ}}^{20^{\circ}} 1\cdot0429, \\
 & d_{25^{\circ}}^{25^{\circ}} 1\cdot0395.
 \end{array}$$

It will be observed that the density of the ethyl citraconate

prepared in this manner is slightly lower than that of the products previously described.

The numbers obtained for its magnetic rotation are as follows :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18·3°	1·0651	10·540
18·4	1·0655	10·543
18·3	1·0643	10·532
18·4	1·0604	10·494
17·0	1·0613	10·492
17·0	1·0632	10·514
17·0	1·0627	10·507
Average 17·8	1·0632	10·517

The three specimens have therefore given numbers very close to each other, the influence of the small amount of impurities in the two first being compensated to a great extent by the variation in density, &c. The average of all the numbers gives 10·500 practically.

Methyl Citraconate.

This was prepared from silver citraconate and methyl iodide in the same way as the ethylic salt just described; it boiled very nearly constantly at 210·5° (corr.), and was perfectly colourless. The density determinations gave—

$$\begin{array}{ll}
 d_{4^{\circ}}^{4^{\circ}} 1\cdot1312, & d_{20^{\circ}}^{20^{\circ}} 1\cdot1168, \\
 d_{10^{\circ}}^{10^{\circ}} 1\cdot1251, & d_{25^{\circ}}^{25^{\circ}} 1\cdot1131, \\
 d_{15^{\circ}}^{15^{\circ}} 1\cdot1208, & d_{30^{\circ}}^{30^{\circ}} 1\cdot1098.
 \end{array}$$

The following are the numbers obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13·3°	1·0675	8·349
13·0	1·0689	8·359
13·0	1·0703	8·370
12·6	1·0634	8·371
12·6	1·0709	8·372
Average 12·9	1·0682	8·364

Ethyl Itaconate.

The acid used in the following experiment was obtained from Kahlbaum. An attempt was made to etherify the acid by means of alcohol and hydrochloric acid, but as it seemed to rapidly form an additive product with the hydrochloric acid it was abandoned. The method employed for the preparation of ethyl fumarate already described was then adopted, the mixture of itaconic acid and absolute alcohol being heated for seven or eight hours at 180—190°. The ether thus prepared boiled at 227.5—228°, and its density determinations gave—

$$d_{\overline{7}^{\circ}}^{7^{\circ}} 1.0563, \quad d_{\overline{15}^{\circ}}^{15^{\circ}} 1.0490,$$

$$d_{\overline{25}^{\circ}}^{25^{\circ}} 1.0412.$$

The magnetic rotation determined from 15 series of observations gave a *molecular rotation* of 10.630, the details of which it is useless to give, as the ether made by the above process is evidently not pure. Suspicion was aroused on account of the rotation of the compound being higher than it was expected to be; the impurity is probably due to ethyl mesaconate formed by the high temperature employed. This ether was prepared more than 12 months since and kept in the dark, but on redetermining its density it was found that a certain amount of change, probably polymerisation, had taken place. The density at $d_{\overline{15}^{\circ}}^{15^{\circ}}$ had increased to 1.0537 or 0.0047, and, on distilling, about four-fifths came over at 227.7—228°, some higher boiling product being left behind.

To obtain the ether pure, the method of treating the silver salt with ethyl iodide was again resorted to. Silver itaconate is apparently crystalline, and much more dense than silver citraconate, moreover, it is not so easily acted on by ethyl iodide as that salt, and requires digesting with it for some time on the water-bath to complete the reaction. On distilling the ethyl itaconate prepared by this method, about five-sixths came over below 230°, leaving a residue which partly came over only after being strongly heated, in fact, the residue appears to consist of ethyl itaconate more or less polymerised.

The first portion of the distillate on being fractioned gave ethyl itaconate with a boiling point of 227.7—227.9°. The density determinations gave—

$$d_{\overline{4}^{\circ}}^{4^{\circ}} 1.0607, \quad d_{\overline{10}^{\circ}}^{10^{\circ}} 1.0546,$$

$$d_{15}^{15^{\circ}} 1.0504,$$

$$d_{20}^{20^{\circ}} 1.0464,$$

$$d_{25}^{25^{\circ}} 1.0427.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18.0°	1.0598	10.449
18.0	1.0601	10.453
18.0	1.0601	10.453
18.0	1.0607	10.457
17.0	1.0647	10.491
17.0	1.0640	10.484
17.0	1.0647	10.484
Average 17.6	1.0620	10.467

It will be seen that this ether prepared from the silver salt does not differ in boiling point from that obtained by heating itaconic acid with alcohol; its density, however, is slightly higher, whilst the specific and molecular rotations are appreciably lower.

Ethyl Meseaconate.

This ether was prepared by saturating a mixture of alcohol and meseaconic acid with gaseous hydrochloric acid. The ether was washed with dilute sodium carbonate, dried, and distilled. It was free from chlorine. The boiling point was 228° (corr.).

The density determinations gave the following numbers :—

$$d_{4}^{4^{\circ}} 1.0598,$$

$$d_{15}^{15^{\circ}} 1.0492,$$

$$d_{10}^{10^{\circ}} 1.0539,$$

$$d_{20}^{20^{\circ}} 1.0453,$$

$$d_{25}^{25^{\circ}} 1.0415.$$

The magnetic rotation determinations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
14·0°	1·1400	11·219
14·4	1·1406	11·229
14·8	1·1397	11·229
13·0	1·1469	11·278
13·5	1·1431	11·244
13·5	1·1429	11·243
14·0	1·1421	11·240
22·5	1·1322	11·215
22·0	1·1320	11·207
21·5	1·1340	11·224
Average 16·3	1·1393	11·233

Methyl Meseaconate.

This was prepared by saturating a mixture of mesaconic acid and methyl alcohol with hydrochloric acid. The ether was washed with sodium carbonate. It boiled at 205·5—206·5° (corr.). The density determinations gave—

$$\begin{array}{ll}
 d_{\frac{4}{4}}^{\frac{4}{4}} 1\cdot1360, & d_{\frac{15}{15}}^{\frac{15}{15}} 1\cdot1253, \\
 d_{\frac{10}{10}}^{\frac{10}{10}} 1\cdot1302, & d_{\frac{20}{20}}^{\frac{20}{20}} 1\cdot1207, \\
 d_{\frac{25}{25}}^{\frac{25}{25}} 1\cdot1170.
 \end{array}$$

The determinations of the magnetic rotation gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15·2°	1·1631	9·073
14·3	1·1645	9·077
14·0	1·1610	9·047
14·0	1·1610	9·047
Average 14·4	1·1619	9·061

Mesityl Oxide. Methyl Isobutenyl Ketone.

The product examined was obtained from Kahlbaum. It was dried by means of anhydrous potassium carbonate, and repeatedly fractionated. The specimen selected boiled at 129·5—130° (corr.). The density determinations gave—

$$d_{\frac{4}{4}}^{4^{\circ}} 0.8706,$$

$$d_{\frac{15}{15}}^{15^{\circ}} 0.8612,$$

$$d_{\frac{25}{25}}^{25^{\circ}} 0.8548.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
11.6°	1.2336	7.775
11.6	1.2366	7.794
11.6	1.2333	7.773
11.6	1.2333	7.773
Average 11.6	1.2342	7.778

Observations on the Results obtained with Saturated Compounds.

Malonic, Succinic, and Glutaric Compounds.

From previous experiments (Trans., 1884, 570) it appeared that succinic acid was the first member of the homologous series of the bibasic acids, though from analogy it was more probable that it should commence with glutaric acid. The results obtained from the examination of glutaric acid given in this paper show that the latter supposition is apparently correct, as its series constant is lower than that of ethyl succinate, thus :—

Molecular rotation of ethyl succinate	8.380
Less $\text{CH}_2 \times 8 = 1.023 \times 8$	8.184
Series constant	0.196
Molecular rotation of ethyl glutarate.....	9.356
Less $\text{CH}_2 \times 9 = 1.023 \times 9$	9.207
Series constant	0.149

Numbers obtained by a fresh examination of ethyl sebate give results a little lower than these previously obtained, these give a series constant very nearly the same as that of ethyl glutarate, thus—

Molecular rotation of ethyl sebate	14.459
Less $\text{CH}_2 \times 14 = 1.023 \times 14$	14.322
	0.137

The number previously obtained for the mol. rot. of ethyl sebate

was 14.496, if this be averaged with the new results it gives 14.477, and this has a series constant of 0.155, so that there can be no doubt that glutaric and sebacic acids are true members of the homologous series. It is quite probable that a re-examination of ethyl suberate would also give somewhat lower numbers than those previously obtained, and thus also would be found to have the correct series constant. The molecular rotation required for this substance would be 12.425, the number found was 12.461, and a very small error in reading would cause this, as the molecular weight of the ether is high.

The molecular rotation found for propyl succinate also gives a lower series constant than ethyl succinate, this is quite in accordance with other observations, the propyl-groups usually having this influence. The series constant is much the same as that of ethyl glutarate and sebate.

Molecular rotation of propyl succinate....	10.363
Less $\text{CH}_2 \times 10 = 1.023 \times 10$	10.230
	<hr/> 0.133

The molecular rotation of ethyl glutarate is nearly identical with methyl succinate (pyrotartarate) of ethyl, which is 9.347.

The accompanying diagram shows the relative position of the molecular rotations of the ethers of the bibasic acids, those of some of the isomeric compounds being also given. In the diagram in my previous paper, the homologous series was supposed to follow the direction which is indicated by the dotted line, this is now substituted by the line starting from ethyl glutarate, and following on to ethyl sebate.

It is interesting to notice that in the case of the monobasic acids and ethereal salts that the molecular rotation drops from formic to acetic acid and again, but in a less degree, to propionic acid, the true homologous series then commencing (see Diagram VI, Trans., 1884, 548). In the case of the ethers of bibasic acids, we get this peculiarity to a greater extent, the drop occurring three times before the true homologous series commences. (See accompanying diagram.)

The relationships of the magnetic rotations of the ethers of the bibasic acids to the acids themselves have hitherto been only inferred from the results obtained from the examination of the monobasic acids and of their ethereal salts; some experiments were therefore made in this direction, but as the bibasic acids are solid and not easily fusible, solutions had to be employed, this makes accurate results more difficult to obtain. Two of the most soluble acids were taken,

namely, malonic and glutaric acids. Succinic acid was not considered to be sufficiently soluble.

The numbers obtained show the following relationships to the ethers :—

Ethyl malonate	7.410
Malonic acid	3.474
Diff. for replacement of H ₂ by (C ₂ H ₅) ₂ ..	3.936
Ethyl glutarate	9.356
Glutaric acid	5.482
Diff. for replacement of H ₂ by (C ₂ H ₅) ₂ ..	3.874

In the case of the fatty acids best comparable with these, we get—

Ethyl acetate.....	4.462
Acetic acid.....	2.525
Difference for replacement of H by C ₂ H ₅	1.937 = { for replacement of H ₂ by (C ₂ H ₅) ₂ = 3.874.
Ethyl propionate.....	5.452
Propionic acid.....	3.462
Difference for replacement of H by C ₂ H ₅	1.990 = { for replacement of H ₂ by (C ₂ H ₅) ₂ = 3.980.

These comparisons show that the influence of etherification in the case of the bibasic acids is very similar to that of the monobasic acids. These results, however, are not quite so consistent as might be expected, because the difference between the propionic and glutaric compounds and between the acetic and malonic compounds should compare, instead of which they are reversed; this, however, may be caused by some small error due to examining the malonic and glutaric acids in solution.

Pyrotartaric Anhydride.

The primary object in examining this compound was to compare it with the anhydrides of the unsaturated acids, as well as to study its rotation in reference to that of pyrotartaric acid itself. The latter relationship will be considered here, the former further on.

The rotation of pyrotartaric (methylosuccinic) acid has not been determined, but as its ether gives numbers nearly identical with those of ethyl glutarate, there can be no doubt its rotation is practically the same as that of glutaric acid.

Pyrotartaric acid (estimated).....	5.482
„ anhydride	4.750
	<hr/>
	0.732

This number is about that which would be expected, and shows that this anhydride when uniting with water to form the acid gives a rotation which is *less* than the sum of the rotation of the anhydride plus the rotation of water; this agrees with all previous observations of saturated compounds when uniting with water to form new compounds.

Acetyl and Succinyl Chlorides.

Acetyl chloride was examined chiefly to get an idea of the value of chlorine in such compounds, as it was evident that by comparing it with aldehyde, the value of this element when replacing hydrogen could be obtained, thus :—

Acetyl chloride	3.800
Aldehyde	2.385
	<hr/>
Influence of Cl replacing H.....	1.415
Value of H.....	0.254
	<hr/>
Value of Cl.....	1.669

This is a little lower than the value of chlorine in propyl chloride, which is 1.733.

With respect to succinyl chloride, the only compound it can at present be compared with is ethyl succinate.

Ethyl succinate.....	8.380
Succinyl chloride	7.242
	<hr/>
Difference	1.138

If a similar comparison be made with acetyl chloride and ethyl acetate, thus—

Ethyl acetate.....	4.463
Acetyl chloride	3.800
	<hr/>
Difference	$0.662 \times 2 = 1.324$

we get a result which is not very much more than half of that obtained with the succinic compound. At any rate it shows there must be a pretty close analogy between the rotation of the chlorides of acetyl and acetic compounds and the chlorides of succinyl and succinic

compounds. The above difference would at the same time indicate that the value of chlorine in succinyl chloride is slightly higher than in acetyl chloride.

Mesityl Oxide. Methyl Isobutenyl Ketone.

As no unsaturated ketone had been examined in reference to its magnetic rotation, I was anxious to know whether this substance would bear to analogous saturated compounds the usual relationship. As this is an iso-compound it is necessary to compare it with a saturated isoketone or allow for the influence of this group, the latter will be the simplest method; methyl butyl ketone has not been examined but methyl propyl ketone has, so that by adding the value of CH_2 to this the desired rotation will be found.

Molecular rotation of mesityl oxide	7.778
Methyl propyl ketone, $5.499 + 1.023$	6.522
	<hr/>
	1.256
Less influence of iso-group	0.111
	<hr/>
	1.145

This is a difference only slightly in excess of that found to exist between ethyl α -crotonate and ethyl butyrate. This ketone therefore behaves in a manner similar to other unsaturated compounds as regards its magnetic rotation.

Maleic, Citraconic, and Itaconic Acids.

When considering the rotation of mesityl oxide, reference was made to the difference of rotation between saturated and unsaturated compounds, the latter having a larger rotation to the extent of a little more or less than 1.0, with the exception of allyl compounds, it has been found to be a little greater than 1.0 as in ethyl α -crotonate and ethyl oleate, where it is 1.112. The following is a comparison of the ethereal salts of maleic, citraconic, and itaconic acids with saturated acids:—

Ethyl maleate	9.625
Ethyl succinate	8.380
	<hr/>
	1.245
Ethyl citraconate	10.517
Ethyl pyrotartarate	9.347
	<hr/>
	1.170

Ethyl itaconate	10·467
Ethyl pyrotartarate	9·347
	<hr/>
	1·120

In all these cases, the difference is only a little higher than 1·0, and these acids may therefore be regarded as ordinary unsaturated compounds related to succinic and pyrotartaric (methylsuccinic) acids in the same way as α -crotonic and oleic acids are to butyric and stearic acids.

The relationship of maleic and citraconic acids to their ethers is also analogous to that existing between the saturated monobasic and bibasic acid and their ethers, thus :—

Ethyl maleate	9·625
Maleic acid.....	5·633
	<hr/>
Difference	3·992
Ethyl citraconate.....	10·517
Citraconic acid	6·567
	<hr/>
Difference	3·950

It has been shown that in the case of malonic and glutaric acids and their ethers the differences are respectively 3·936 and 3·874, and with acetic and propionic acids 1·937 and 1·990 respectively, which multiplied by 2 give 3·874 and 3·980. These results go to show that in the formation of the ethers of these unsaturated acids the same kind of chemical change takes place as with the saturated acids, and therefore that they are of similar structure, that is, each acid contains two COOH groups.

The relationship of ethyl and methyl citraconate to each other is also analogous to that of ethyl and methyl succinate :—

Ethyl citraconate ...	10·517	Ethyl succinate	8·380
Methyl citraconate..	8·364	Methyl succinate....	6·232
	<hr/>		<hr/>
Difference.....	2·153	Difference.....	2·158

Fumaric and Mesaconic Acids.

From the magnetic rotation of the ethereal salts of these acids, they are evidently abnormal compounds, the numbers they give being remarkably high, nearly as high as would be given by an unsaturated compound differing from a saturated one by H_4 , thus :—

Ethyl fumarate	10·116
Ethyl succinate	8·380
	<hr/>
Difference	1·736
Ethyl mesaconate	11·233
Ethyl pyrotartarate.....	9·347
	<hr/>
	1·886

It may be as well to notice here that the relationship of ethyl and methyl mesaconate is analogous to that of ethyl and methyl succinate :—

Ethyl mesaconate	11·233
Methyl mesaconate.....	9·061
	<hr/>
	2·172

As shown previously, the difference in the case of the succinate is 2·158.

As bearing upon the general structure of fumaric acid, we may consider its chloride. The only comparison we have in this case is its relationship to its ether :—

Ethyl fumarate	10·116
Fumaryl chloride.....	8·747
	<hr/>
	1·369

This is a little higher than the difference found between ethyl succinate and succinyl chloride, which is 1·138; but it is nearly the same as twice the difference found between ethyl acetate and acetyl chloride, which comes to 1·324. So that there is no reason to think that their structure, so far as the existence of carboxyl-groups is concerned, differs from that of ordinary acids. If, then, maleic and fumaric acids contain these groups, the cause of their isomerism must be related to the part of the acid they are attached to.

From the high magnetic rotation of fumaric acid, as well as its greater stability and smaller solubility than maleic acid, it is natural to infer that in the case of the former there is some kind of condensation or closer union between the molecules than in the latter, and I have previously brought this view forward (Trans., 1881, 560). This idea coincides to some extent with the views advanced by Kekulé, in which an explanation of the isomerism is sought in the idea of saturated and free affinities. If this, however, holds good, probably all unsaturated compounds, except fumaric and mesaconic acids and perhaps one or two others, would have to be regarded as

having free affinities, judging from the magnetic rotation of those already examined. But this idea of condensation or closer union of the molecules in fumaric and mesaconic acids is negatived by some of the physical properties of these substances. If it existed, we should expect that the ethereal salts of these compounds would have higher boiling points and greater densities than those of maleic and citraconic acids. The following comparison shows how they stand to each other:—

Ethyl maleate, b. p.	225·0°	$d_{15}^{15^\circ}$	1·0740
Ethyl fumarate, „	218·5°	„	1·0623
	<hr/> 6·5°		<hr/> 0·0017
Ethyl citraconate, b. p....	230·3°	$d_{15}^{15^\circ}$	1·0468
Ethyl mesaconate, „	228·0°	„	1·0492
	<hr/> 2·3°		<hr/> + 0·0024

Ethyl itaconate boils at 227·8°, and has a density of $d_{15}^{15^\circ}$ 1·0504, so that we find the boiling points of ethyl maleate, citraconate, and itaconate are actually *higher* than those of ethyl fumarate and mesaconate. The densities of ethyl maleate and itaconate are also *higher* than those of these ethers, that of the citraconate being, however, a trifle lower than that of the mesaconate.

No doubt the most striking peculiarity of fumaric and mesaconic acids is their apparent inability to form anhydrides, and in this respect they resemble terephthalic acid; maleic, citraconic, and itaconic acids behave like phthalic acid, which easily gives an anhydride. The isomerism between phthalic acid and terephthalic acid being due to difference of position, can such an explanation be used in reference to the compounds under consideration? Van't Hoff, I believe, was the first to suggest this view. The difference of position in these compounds can be represented either by his figure, or on a plane by assuming the existence of a two-carbon chain. Taking maleic and fumaric acids as instances, we get—

In this way, maleic, citraconic, and itaconic acids would most resemble ortho-compounds, and fumaric and mesaconic acids para-

compounds; but if this be so, are these differences of position likely to cause the ethers of the latter acids to give larger magnetic rotation than those of the former? This is difficult to answer at present. Difference of position in the aromatic series does affect the magnetic rotation of bodies very considerably, and I may mention that I have examined the ethers of phthalic and isophthalic acids, and find that the latter gives a slightly *higher* rotation than the former, but the difference is very small. The more correct comparison, however, would most probably be between phthalic and terephthalic acids. The latter I hope to measure before long. At the present moment, the position theory appears to afford the best means of explaining the isomerism of these unsaturated acids.

As to the difference of constitution of citraconic and itaconic acids, the magnetic rotation does not give much light. If they be represented thus—

the difference will be in reference to displacements by CH_3 — and CH_2 —, and we have no perfectly parallel cases examined as regards the influence such displacements would have on the magnetic rotation of substances. The only comparisons we have which are near to this are between the ethereal salts of succinic and methylmalonic acid and those of pyrotartaric and glutaric acids. In the former, the rotation varies by 0.05, and in the latter by only 0.01, the lower rotations being for the methyl replacements. The rotation of ethyl itaconate is 0.05 lower than that of the citraconate, so that, if anything, these comparisons would be in favour of itaconic acid containing methyl.

The boiling points of the ethereal salts of methylmalonic and pyrotartaric acids are a good deal lower than those of the ordinary succinic and glutaric acids. The boiling point of ethyl itaconate is also lower than that of ethyl citraconate, but only about 2.5° .

A number of experiments were made on the oxidation of citraconic, mesaconic, and itaconic acids with chromic mixture and by fusion with alkali, but they all gave acetic acid; in the case of citraconic acid, when fused with alkali, the silver salt prepared from the distilled acid gave numbers indicating the presence of propionic acid in small quantities.

The oxidation of these acids with permanganate takes place with different degrees of rapidity. Thus when a small quantity is added to

a dilute solution of citraconic acid slightly acidified with sulphuric acid, the colour disappears after about 15 seconds, whilst with exactly similar solutions of mesaconic and itaconic acids the colour vanishes almost immediately. With alkaline permanganate, moreover, these acids do not behave in the same way; thus, with dilute alkaline solutions of the three acids made exactly alike, the alkaline permanganate does not become green with the citraconic solution until about 20 seconds have elapsed, it then slowly becomes turbid; the mesaconic solution becomes green at once, and then gradually opaque and greenish-yellow; whilst the itaconic solution becomes green at once, and remains bright. These three acids when thoroughly oxidised with alkaline permanganate yield oxalic acid; no acetic acid was found.

Maleic and Citraconic Anhydrides.

These anhydrides were measured in different ways. Maleic anhydride being solid was examined in solution only, and citraconic both in the pure state and dissolved. From the examination of the latter in the pure state, there can be no doubt about its rotation, but when dealing with solutions of these anhydrides in different solvents, it is necessary to bear in mind that they are unsaturated compounds, and may combine more or less with the solvents, and produce saturated compounds, therefore when doing those of maleic anhydride in acetic acid or acetic anhydride, corresponding experiments were always made with citraconic anhydride and these solvents, because the true value of this compound had been obtained with the pure substance. It was found that these solvents did slightly alter the rotation of citraconic anhydride, and at last citraconic anhydride itself was used as the solvent for maleic anhydride, as these two compounds being of the same kind and so nearly related, were not likely to influence each other. The following are the results obtained:—

I.

Rotation obtained for maleic anhydride in acetic acid	4·448
Maleic anhydride in acetic anhydride	4·417
Maleic anhydride in citraconic anhydride	4·545

II.

Citraconic anhydride in acetic acid	5·448
Citraconic anhydride in acetic anhydride	5·488
Citraconic anhydride alone	5·540

so that the solutions in Series I give numbers about 0·10—0·13 lower than do the mixture of maleic anhydride and citraconic

anhydride. In Series II they are from 0.052—0.092 lower than those given by pure citraconic anhydride.

Density determinations were made with the solutions of maleic and citraconic anhydride in acetic anhydride from 10° to 100°, thinking that they might throw some light on the cause of the small difference of rotation, but they do not give any definite evidence on the subject. It was, however, thought best to give the determinations, as they may be useful for future reference.

There can be no reason to doubt, however, that the magnetic rotation obtained for maleic anhydride when determined in its solution in citraconic anhydride is practically correct, and this is borne out by the following comparisons of this substance, and citraconic anhydride with their respective ethers, with which they show practically the same difference:—

Ethyl maleate	9.625	Ethyl citraconate . . .	10.517
Maleic anhydride	4.545	Citraconic anhydride	5.540
Difference	5.080	Difference	5.077

In previous papers I have drawn attention to the fact, that when water unites with a substance so as to produce a new product, the rotation of the latter is less than the sum of the rotations of water and the substance with which it has chemically united, but in the case of maleic and citraconic anhydrides, when they unite with water to form their respective acids, we get the extraordinary result that the acids possess rotations actually *greater* than the sum of the rotation of the anhydrides and the water they have united with.

Maleic acid	5.633	Citraconic acid	6.567
Maleic anhydride	4.545	Citraconic anhydride .	5.540
OH ₂	1.088	OH ₂	1.027

Now if the water had been present even in an uncombined way its value would have been only 1.000, and yet there is no doubt that in this case its union with the anhydrides has resulted in the formation of new compounds. As no anhydrides of the bibasic acids had been examined, the experiments on pyrotartaric anhydride already given were made (p. 565) to see whether it behaved in a normal or abnormal manner when hydrated. From the comparisons already given, it is seen that the difference between the rotation of this anhydride and its acid is only 0.732, or considerably less than 1.000, a result consistent with all previous observations.

Citraconic anhydride behaves as an unsaturated compound, giving

a rotation which is considerably higher than the corresponding saturated anhydride thus:—

Citraconic anhydride	5·540
Pyrotartaric anhydride.	4·764
	<hr/>
	0·776

but this difference is much smaller than that existing between most unsaturated compounds, especially those related to it, which give from 1·120 to 1·245, as already shown. This peculiarity of the rotations of maleic and citraconic anhydrides leads to the inference that there is something anomalous in their constitution, or that when in the fluid condition they do not consist of simple molecules of the formulæ $C_4H_2O_3$ and $C_6H_4O_3$, but of those with more complex ones formed by one molecule saturating another, and thus reducing the rotation (when in the state of vapour, maleic anhydride has the ordinary formula: Hübner and Schrieber, *Z.*, 1871, 713). Some experiments were therefore made with citraconic anhydride, to see, if such molecules existed, whether they would break up on heating. The magnetic rotation determinations of this substance were made along with comparable ones of pyrotartaric anhydride, because it is found that the molecular rotation of a substance is not quite constant for all temperatures, falling off a little with rise of temperature; this matter is at present occupying my attention. The numbers obtained were—

Citraconic anhydride at 17·4°	5·540
Citraconic anhydride at 65·7°	5·473
	<hr/>
	0·077
Pyrotartaric anhydride at 11·6°	4·764
Pyrotartaric anhydride at 50°	4·737
	<hr/>
	0·027

The citraconic anhydride determinations at high temperature show us a difference slightly in excess of those of the pyrotartaric anhydride; this would favour the idea of dissociation taking place to a very slight extent, but the variation is almost within the errors of experiment, and cannot be taken as any evidence of this. A large number of density determinations of citraconic anhydride were also made from 0—100° (p. 577), but it was found that these change in a very regular manner with the temperature, and within this range do not indicate dissociation. Endeavours were made to take the density of this substance at its boiling point, and also at the boiling point of aniline,

but in both cases decomposition with evolution of gas gradually took place, and rendered it impossible to do this.

The method of determining molecular weights proposed by Raoult was brought under my notice, and I have applied it to the determination of the molecular weight of these anhydrides and most of the substances referred to in this paper. The solvent used was glacial acetic acid, and the proportions of the substance used varied from about 1·4 to 1·6 to 100 of acid.

The following results were obtained :—

Substance.	Mol. wt. found.	Mol. wt. calculated.	Difference.
Citraconic acid.....	134·4	130	+ 4·4
Itaconic acid	134·8	130	4·8
Mesaconic acid.....	134·2	130	4·2
Ethyl citraconate.....	189·9	186	3·9
Ethyl itaconate	188·7	186	2·1
Ethyl mesaconate	187·7	186	1·1
Ethyl succinate	180·6	174	6·6
Ethyl maleate	179·1	172	7·1
Ethyl fumarate	177·3	172	5·3
Succinic anhydride	115·4	100	15·4
Pyrotartaric anhydride	131·2	114	17·2
Maleic anhydride	108·9	98	10·9
Citraconic anhydride.....	129·8	112	18·6

From the results of this method of determining the molecular weight, it appears that all the above acids and ethers have the molecular weight usually assigned to them, the variation in the number being but small and probably due to experimental errors. In the case of the anhydrides, however, the variations are somewhat larger and moderately consistent, and therefore probably not due to errors of experiment, but as both saturated and unsaturated anhydrides behave in the same way, their molecular conditions would appear to be the same, so that these results afford no help in explaining the peculiarities of the magnetic rotation of maleic and citraconic anhydrides. So far the evidence of the magnetic rotation of citraconic anhydride at high temperatures, the density determination through the range of temperature 0° to 100°, and Raoult's method of determining molecular weights, all give evidence against the existence of complex molecules. It may be there is some peculiarity in the constitution of these bodies we are not acquainted with; if so, it is difficult to conceive what it can be. I have been struck, however, with the peculiar behaviour of these anhydrides towards tertiary amines

with which we should not expect them to react easily. For example, if citraconic anhydride be added to triethylamine action sets in with great energy, the product becomes brown and strongly heated, and a brown pitch results which is partially soluble in water and partially insoluble. Maleic anhydride acts similarly. Citraconic anhydride also reacts with picoline, but not so freely as with triethylamine. Succinic anhydride does not behave in the same way with these bases; but whether the greater chemical activity of these unsaturated anhydrides is due to their being unsaturated compounds or to difference in structure from ordinary anhydrides, we have no means of proving at present; any explanation of their peculiar magnetic rotations, therefore, must be allowed to stand until more compounds of this class have been obtained and examined. Our knowledge of unsaturated compounds and their physical characteristics is at present very incomplete, that they are very different from those of saturated compounds the following instances in relation to boiling points will show:—

Saturated Compounds.

Ethyl succinate,	b. p.	216·5°	} +34·5.
Succinic anhydride,	„	250·0	
Ethyl pyrotartarate,	„	218·0	} +29·4.
Pyrotartaric anhydride,	„	247·0	

Unsaturated Compounds.

Ethyl maleate,	b. p.	225°	} -25.
Maleic anhydride,	„	200	
Ethyl citraconate,	„	230	} -17.
Citraconic anhydride,	„	213	

The anhydrides in the case of the saturated compounds boil much higher than the ethers, but in unsaturated anhydrides boil considerably lower than the ethers.

The chief conclusions resulting from this inquiry may be briefly summarised:—

1. That glutaric acid appears to be the first true member of the homologous series of bibasic acids.

2. That the propyl ether of succinic acid has a lower series constant than the ethylic ether, a result which is consistent with analogous observations on some of the compounds of the fatty acids.

3. That pyrotartaric anhydride has a rotation which shows that when it unites with water condensation takes place as with other anhydrides, the rotation of the resulting acid being less than the sum of the rotation of the anhydride plus the rotation of water.

4. That the rotation of mesityl oxide shows that unsaturated ketones have rotations consistent with those of other unsaturated bodies.

5. That the ethereal salts of maleic, citraconic, and itaconic acids have rotations consistent with those of other unsaturated compounds differing from the saturated ones by H_2 , and that their general structure appears to be analogous to that of ordinary bibasic acids.

6. That the ethereal salts of fumaric and mesaconic acids have much higher rotations than ordinary unsaturated compounds, being nearly sufficiently high for those represented by saturated compounds less H_4 , and that their general structure is apparently analogous to that of ordinary bibasic acids, and that this difference of character to their isomers is apparently best accounted for by difference of position, *i.e.*, by the Vant' Hoff hypothesis.

7. That the rotations of maleic and citraconic anhydrides are abnormally low, and the reason for this cannot at present be satisfactorily explained.

8. That from the determinations by Raoult's method of the molecular weights of most of the substances examined in this paper, they seem to have the molecular weights usually ascribed to them—at any rate none appear to be polymers.

The following table gives a list of the substances which have been subjected to examination, with their molecular rotations and the pages where they are referred to.

	Molecular rotation.	Page.
<i>Acids.</i>		
Citraconic	6·567	580, 591, 595, 599.
Glutaric	5·482	566, 589, 600.
Maleic.....	5·633	572, 591-593.
Malonic.....	3·474	562, 589.
<i>Ethers.</i>		
Ethyl citraconate.....	10·517	581, 591, 592, 594, 599, 601.
Ethyl fumarate	10·112	574, 593, 594, 599, 601.
Ethyl glutarate	9·356	567, 587.
Ethyl itaconate	10·467	584, 592, 594, 599, 601.
Ethyl maleate.....	9·625	572, 591, 594, 599-601.
Ethyl sebate.....	14·459	568, 587.
Ethyl mesaconate	11·233	585, 593, 594, 599-601.
Methyl citraconate	8·364	583, 592, 600.
Methyl mesaconate	9·061	586, 593, 599, 601.
Propyl succinate	10·363	562, 588, 600.
<i>Anhydrides.</i>		
Citraconic	5·540	576, 596-601.
Maleic.....	4·548	568, 596-601.
Pyrotartaric	4·764	564, 589, 598-600.

	Molecular rotation.	Page.
<i>Chlorides.</i>		
Acetyl.....	3·800	590, 593.
Fumaryl.....	8·747	575, 593.
Succinyl.....	7·242	563, 590.
<i>Ketone.</i>		
Mesityl oxide.....	7·778	587, 591, 601.