

CCCXCV.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XXVI. The Optical Activity of Malic Acid in the Presence of Sodium Molybdate.*

By THOMAS STEWART PATTERSON and CHARLES BUCHANAN.

IN connexion with earlier work by one of us on the general problem of the rotation of optically active compounds, in which the influence of inactive solvents upon the rotation of active compounds was

studied, we thought it worth while to investigate some of those remarkable cases discovered by Biot and by Gernez in which substances such as borax and salts of molybdc and tungstic acids greatly influence the rotation of certain compounds like malic acid and tartaric acid. Perhaps the most remarkable effects of this character are those recorded by Gernez (*Compt. rend.*, 1889, **109**, 769), who studied solutions in which, to a fixed quantity of malic acid, gradually increasing amounts of sodium molybdate were added. He found the rotation to vary in such a manner that two minima of negative rotation and one positive maximum were developed, whilst between these three different concentrations were observed at which the rotation was zero. Gernez accounted for this behaviour by assuming that each maximum or minimum corresponds to the formation of a definite additive compound having a composition represented by the relative amounts of malic acid and sodium molybdate in solution at that particular concentration.

A summary of further work on this subject is given by Darmois (*J. Phys. Radium*, 1923, **4**, 49), who claims to have isolated three compounds: $(\text{MoO}_4)_2\text{C}_4\text{H}_6\text{O}_4\text{Na}_2, 3\text{H}_2\text{O}$, with $[\alpha]_{5780} +184^\circ$ ($c = 0.95$); $\text{MoO}_3, 2\text{C}_4\text{H}_6\text{O}_5, 2\text{NaOH}$, $[\alpha]_{5780} -55.1^\circ$ ($c = 20$); and $\text{MoO}_3, 2\text{C}_4\text{H}_6\text{O}_5, 4\text{NaOH}$, for which no rotation value seems to be given.

The interesting phenomena described by Gernez have hitherto only been examined by means of light of one refrangibility and, with one exception, at the ordinary temperature,* and we deemed it of interest to investigate a number of these solutions at different temperatures and for different colours of light, especially for those concentrations at which the rotation changes from a positive to a negative value through zero, and *vice versa*, with increasing concentration of molybdc acid.

Preparation of Solutions.—The malic acid used was recrystallised from water and made thoroughly anhydrous. It had m. p. 100—103°, $[\alpha]_{5790}^{20} -1.99^\circ$ (1.861 g. in 20 c.c. of water); Gernez found -2.0° at the same temperature for *sodium yellow* (λ 5890).

Our first series of solutions was made up to correspond to those of Gernez, who used 1.1166 g. of malic acid in 12 c.c. of water. A

* Grossman and Pötter (*Z. physikal. Chem.*, 1906, **56**, 577) examined solutions containing malic acid and sodium molybdate up to temperatures of 95° and concluded that various complexes are formed, some dextro and some lævo, which on dilution decompose, yielding a complex of one molecule of Na_2MoO_4 and one molecule of malic acid. The work to be described, however, shows that above 60° such solutions undergo permanent change. They turn blue, and on cooling the rotation does not revert to its original value. Darmois (*loc. cit.*, pp. 63, 69) states that he used three different colours of light, but he records only dispersion ratios.

solution of malic acid in water was prepared of as nearly as possible 18.61 g. in 100 c.c. of solution, and its strength determined accurately by titration. Various quantities of sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$; recrystallised from water) were weighed into a 20 c.c. graduated flask to which 10 c.c. of the malic acid solution were added, and the solution was made up to 20 c.c. with water. The rotation of each solution was then examined for several colours of light and usually at different temperatures. The specific rotation was calculated relative to the amount of malic acid in the solution: $[\alpha] = 100\alpha/ldp$, where $p = \text{g. of malic acid per 100 g. of solution}$, or $[\alpha] = 100\alpha/lc$, where $c = \text{g. of malic acid per 100 c.c.}$

Fig. 1* shows the specific rotation for three colours of light at 17° plotted relative to *concentration of sodium molybdate*, the quantity of malic acid present remaining, of course, constant throughout.

The specific rotation of the malic acid solution without addition is so small that it can hardly be indicated on the diagram, but the addition of sodium molybdate increases the negative rotation very rapidly, and almost linearly, for all three colours of light, until the first minimum is reached with the addition of a quantity of sodium molybdate corresponding to approximately 0.5 mol. per mol. of malic acid present in the solution (*A* in Fig. 1). On further addition of molybdate the rotation then rapidly becomes less negative and reaches zero at a concentration of sodium molybdate corresponding to about 0.7 mol. per mol. of malic acid. Zero rotation is not reached, however, at exactly the same concentration of molybdate for each colour of light; the three curves do not all intersect on the line of zero rotation (*B* in Fig. 1).

With further addition of molybdate the rotation rapidly rises again, almost linearly, and reaches a positive maximum at or near a concentration of 1 mol. of molybdate per mol. of malic acid (*C* in Fig. 1). The rotation then rapidly diminishes, passing through zero rotation at *D*, where the concentration of molybdate is 1.4 mols. per mol. of malic acid, but it is difficult to decide whether the zero for all three colours is at the same concentration. The three curves appear to intersect in a region where the rotation has a slight negative value of about -4° ; the diagram does not show this very well. With further addition of molybdate, a second minimum, *E*, is reached at a concentration of about 1.75 mols. of molybdate to 1 mol. of acid and, later, a third passage through zero rotation takes place at a concentration of about 2.07 mols. of molybdate to 1 of acid. The rotation then increases steadily until no more molybdate can be got into solution.

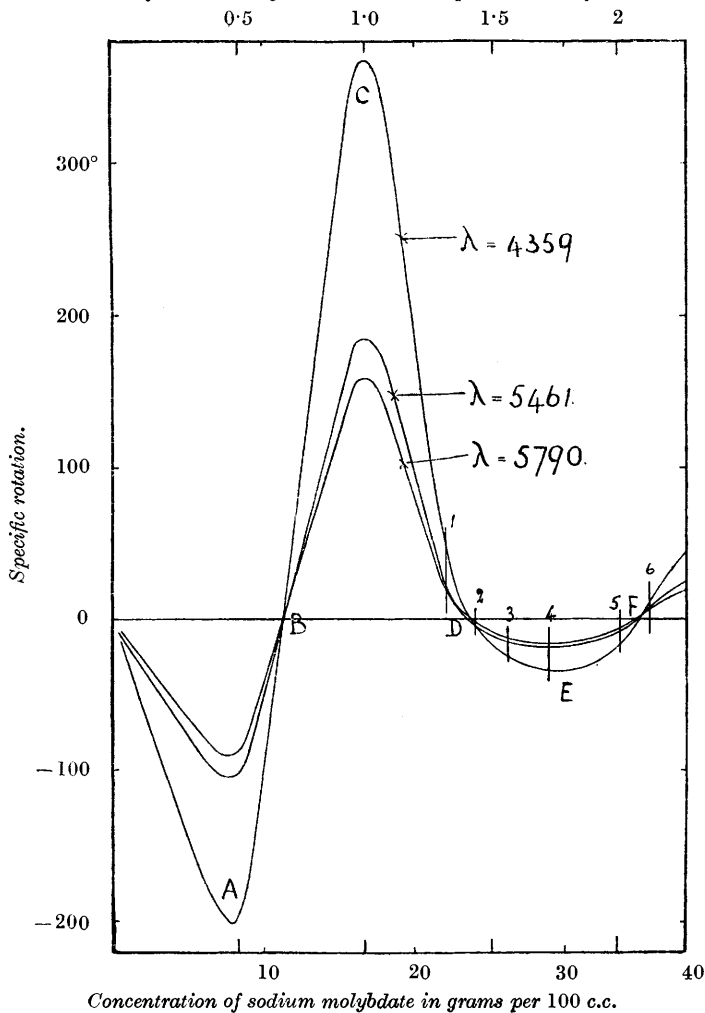
* To avoid confusion we have not indicated the individual experimental data on the diagrams.

These phenomena are very difficult to account for. It is easy to say that various compounds are formed in solution between the malic acid and the molybdate; but even on this hypothesis it is

FIG. 1.

Malic acid: $c = 9.3$; $t = 17^\circ$.

Concentration of sodium molybdate in molecules per molecule of malic acid.



difficult to give any consistent explanation of the phenomena. It might seem that at least four different kinds of combination must be postulated, with a reversal of sign of rotation between each

form. Any discussion of the matter can only be undertaken by making so many quite arbitrary assumptions that for the present we do not propose to enter on it. The strongest argument in favour of this idea is that compounds of malic acid and sodium molybdate can be isolated in the solid form, Darmois claiming to have isolated three, as already mentioned. An alternative suggestion is that the sodium molybdate produces this effect by ordinary solvent action, and to show that this is not utterly improbable we may point to the facts that (1) salts such as barium chloride, potassium bromide, ammonium sulphate, etc., have very powerful depressing effects upon the rotation of aqueous solutions of ethyl tartrate (J., 1912, 101, 1834), and (2) ethyl tartrate dissolved in benzene, in toluene and in *o*- and *m*-xylene apparently exhibits in dilute solution both a maximum and a minimum value in a manner not altogether unlike this, although, of course, in very different degree (J., 1902, 81, 1099).

We wished particularly to examine the rotations of solutions in the neighbourhood of the points *B*, *D*, and *F* (Fig. 1) as regards the effect of temperature change, since from our previous work we should have expected, at these points, rapid change of rotation in correspondence with the very rapid change of rotation due to alteration in concentration of the sodium molybdate.

Fig. 2* shows some of these temperature-rotation curves which are numbered to correspond to the numbers shown in Fig. 1. It will be noticed that in all cases change of temperature does produce rapid alteration of rotation, and also that this alteration of rotation with change in temperature is consistent.

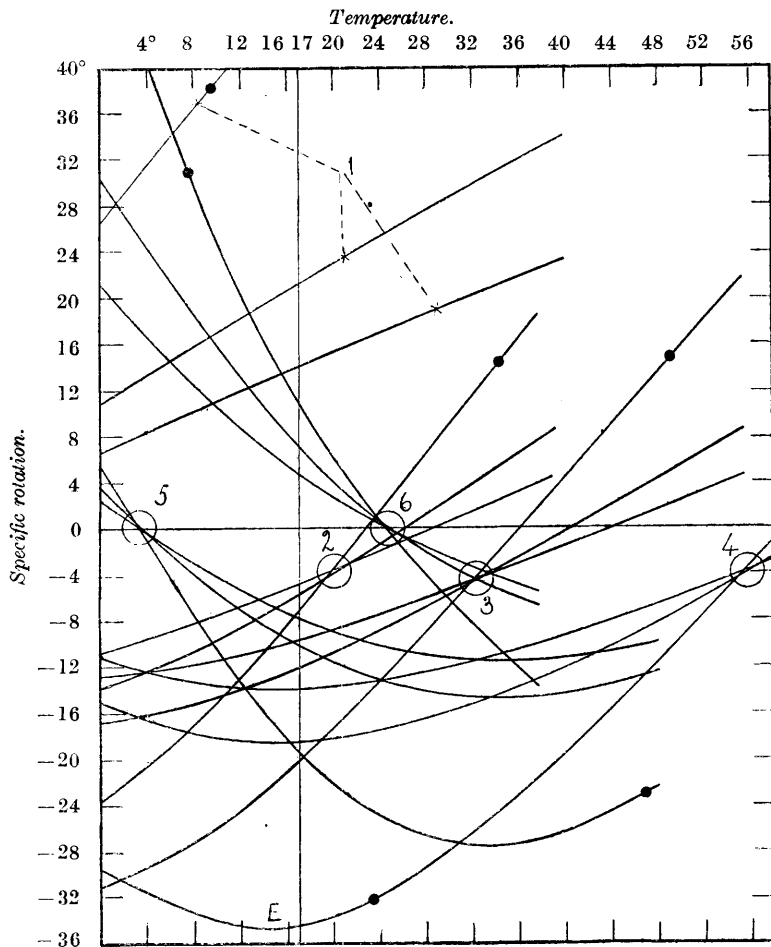
The general behaviour will be understood by considering the solutions marked 1, 2, 3, 4, 5, and 6 in Fig. 1. Of these, solution 2 may be first considered. The data shown on Fig. 1 are those for a temperature of 17° as marked by a vertical line in Fig. 2. When this solution is cooled, the rotation diminishes and the curves spread out from one another, but when it is heated above 17° the curves rapidly approach each other and intersect at, or very near, a point where the temperature is 20° and the specific rotation for the various colours is in the neighbourhood of -4.0°. It is difficult to decide whether the curves meet accurately at a point or over a slight range of temperature. On further heating of the solution, the rotation for all colours of light increases and the curves spread apart.

When solution 1 is heated the rotation for all the various colours of light rapidly increases, but clearly if it were possible to cool the solution much beyond zero, these curves would intersect one another

* It should be noted that only two of the curves in Figs. 1 and 2 are for the same wave-lengths. In Fig. 1, the third curve is for $\lambda = 5790$ (yellow) and in Fig. 2, for $\lambda = 6234$ (red). This is not likely, however, to cause any confusion.

at a lower temperature, which, since extrapolation would have to be carried out over a considerable range, cannot be estimated with accuracy.

FIG. 2.



Temperature-rotation curves for certain aqueous solutions of l-malic acid and sodium molybdate, for $\lambda = 6234, 5461, 4359$. The curve for $\lambda = 4359$ is, in each case, marked with a black circle; the other two can then easily be identified. See also note on p. 3010.

In solution 3 we find that, on heating from 0° , the rotation rapidly increases in such a way that the curves intersect one another at a temperature of approximately 33° and at a rotation value in the neighbourhood of -4° , after which the rotation continues to increase, the curves spreading out as in other cases.

The data shown for solution 4 (the point *E* in Fig. 1) lie at the minimum of the concentration curve, and are represented at *E* in Fig. 2, and are of a particularly interesting character. On cooling, the rotation of this solution diminishes (becomes more negative) to show a distinct minimum and then rises again on further cooling to zero temperature. On heating, the curves show a behaviour very similar to that exhibited by those already dealt with : the rotation rapidly increases, and again the various curves intersect one another at the same rotation as before, namely -4° , but at a temperature of 55° . Thus when the three solutions 4, 3, and 2 are heated, the curves for the different colours of light are found to intersect at practically the same rotation value, but at gradually diminishing temperatures.

In solution 5 we find, as in the last case, distinct minima in the curves, but here the data shown in Fig. 1 at 5 lie on the left of the minimum in Fig. 2, whereas for solution 4 they lie to the right (point *E*, Fig. 2). On cooling, the curves for solution 5 gradually approach one another and intersect at a temperature of about -4° and a rotation value in the neighbourhood of zero; on heating, the rotation diminishes and reaches a distinct minimum value, after which the curves rise again, but could not be followed to higher temperatures on account of the liability of the solution to decompose.

The temperature-rotation curves for solution 6 are also shown. In this case the rotation rapidly diminishes with rising temperature, and the curves intersect one another apparently over a slight range of temperature in the neighbourhood of zero rotation.

Thus, the behaviour throughout is entirely consistent; on heating the solutions 2, 3, and 4, the curves are made to intersect one another at practically the same rotation, -4° , but at different temperatures, *viz.*, 20° , 33° , and 55° respectively. It seems indisputable that, on heating, these solutions are brought into the condition represented on Fig. 1 at the point *D*, and, from analogy, it will probably be admitted that when solution 1 is cooled, its temperature-rotation curves would be caused to intersect at this same point. On the other hand, by cooling solution 5 and by heating solution 6, the curves are caused to intersect at a rotation value at or very close to zero, but at temperatures of 4° and 24° respectively, and this region of intersection is that represented at *F* in Fig. 1.

We had hoped that with one of these solutions, such as number 4, we should be able to demonstrate both of these regions of intersection of the temperature-rotation curves : that by heating the solution we should be able to reach the point *D* on Fig. 1 and, by cooling it, reach the point *F*, but in this we were disappointed, as it

is not possible to heat any of these solutions over a sufficient range of temperature.

It appears from this, however, that the behaviour of these solutions is closely similar to that of other simple active compounds dissolved in "indifferent" solvents, for it has been shown by one of us that, although the temperature-rotation curves of an active compound may be very greatly modified either by different solvents or by change of concentration in one solvent, yet the rotation value at which any two such curves intersect one another has, in general, one definite value, although it may occur at very different temperatures.

The data we have collected furnish interesting and unique material in connexion with the characteristic diagram. In a previous paper by one of us (J., 1916, **109**, 1202), it was suggested that in consequence of the apparently periodic character of the temperature-rotation curves for active compounds, "any given substance may very probably have several characteristic diagrams and several rational zeros. If these rational zeros are very different in value it might be possible readily to detect the trend of the two separate diagrams." And in a later paper (*Proc. Roy. Soc. Edinburgh*, 1918—19, **39**, 27) indications of the existence of two characteristic diagrams in the case of *isobutyl dibenzoyltartrate* were described. In the present instance, since there are four points (including the point of origin of the diagram) at which the rotation becomes zero, it might be possible to draw four separate characteristic diagrams. There should be one from the point of origin up to the region *A*; another from the region *A* through *B* to the region *C*; a third from the region *C* through *D* to the region *E*; and another from *E* through *F* onwards. Since the points of intersection lie so close to zero, it is not easy to distinguish clearly between these separate characteristic diagrams, but on account of the fact that the intersections at *D* and at *F* lie, quite definitely, (Fig. 2) at different rotation values, it is also certain that the two characteristic diagrams which could be drawn for these two regions of the curves are different. We do not wish to dwell upon the point now; we may have occasion to refer to it in connexion with later work. We may add, however, that in consequence of intersection taking place very near zero rotation in each case, dispersion ratios remain fairly constant throughout, the constancy being somewhat improved by calculating from the rational zero in each case.

If these curves are considered from the point of view of a combination of malic acid and sodium molybdate in solution, they might possibly be interpreted by supposing that heating the solutions has the effect of dissociating any compound which may be formed, and that cooling has the opposite effect.

The portion of the curve in the neighbourhood of the second minimum is possibly the most interesting on account of the comparatively easy recognisability of the two regions of intersection. We have not examined the other portions of the curve in so complete a fashion, but, except for solutions represented on the part of the curve from the origin up to *A*, it appears that heating the solutions causes a change of rotation similar to that obtained by travelling along the concentration curve to the left as in the cases referred to above. For solutions from the origin up to *A*, a different behaviour is noticeable: on heating such solutions it might be expected from the previous observations that the rotation should diminish, whereas the opposite takes place—the rotation increases slightly.

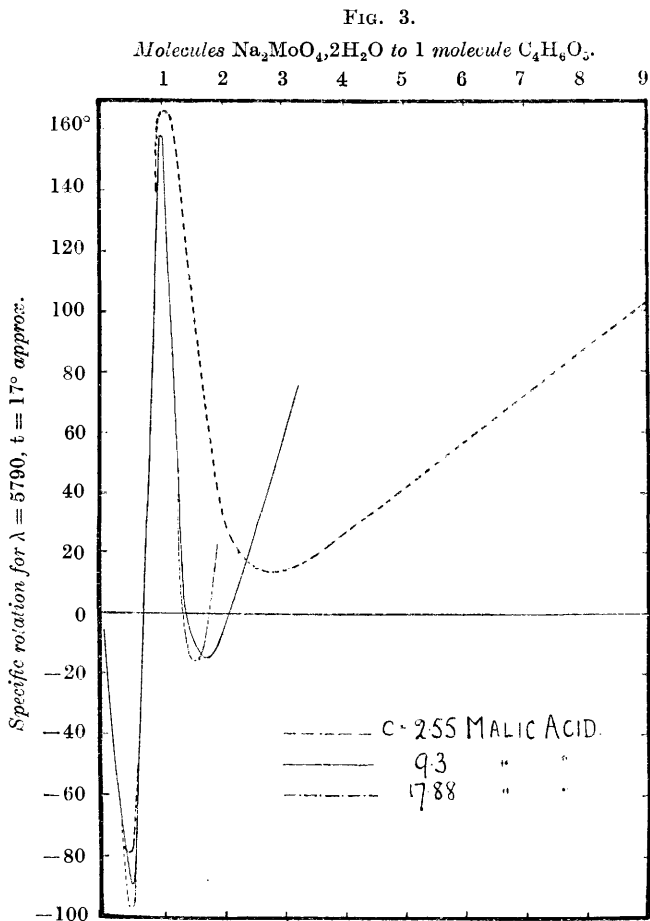
Since the number of colours of light used by us is only small, we have not examined very specially the dispersion curves for these solutions—they seem to us much like these for most other active compounds. By plotting λ^2 against $1/\alpha$ we find for the solution indicated by 1 in Figs. 1 and 2, at 16° and 36° , an approximately linear relationship, but for 2 and 3 at zero, 4 at 17° and 5 at 30° , this is not the case.

The foregoing experiments were carried out with practically the same concentration of malic acid as was used by Gernez, the concentration of sodium molybdate being increased as far as possible. In order to increase the proportion of molybdate to malic acid to a still greater extent, we used a more dilute solution of malic acid ($c = 2.55$ g./100 c.c. of solution), the rotation being examined for three different colours of light at approximately 20° . The results for mercury yellow (λ 5790) are shown in Fig. 3. The curve obtained shows that the variation of the rotation for this proportion of malic acid with gradual increase in the quantity of molybdate present is, on the whole, similar to that previously described. The first minimum occurs very near the same position as before, but seems to have a slightly less negative value, whilst the first maximum has a slightly higher value. A greater difference is to be observed in the second minimum which, for this solution, has a positive instead of a negative value. There is no definite indication, however, of a second maximum although the quantity of molybdate to malic acid was more than twice as much as in the previous case.

We also examined a solution of greater concentration as regards malic acid, and its behaviour is also shown in Fig. 3. The curve obtained is, on the whole, very similar to the first one described, and, in general, it may perhaps be said that increase in concentration of the malic acid compresses the whole concentration curve towards the left of the diagram, increased dilution having the opposite effect.

Since these changes have been attributed to formation of com-

pounds of sodium molybdate and malic acid, we examined for comparison a solid compound obtained by dissolving 9 g. of malic acid and 8.1 g. of sodium molybdate in a small quantity of water, and then adding warm alcohol until a slight turbidity was produced. On standing, light crystals filled the liquid and were



filtered off, $[\alpha]_D^{17} -48.55$ ($c = 2.5$). On recrystallisation from aqueous alcohol, the rotation rose to -50.45° and remained constant on further recrystallisation, but analytical results agreed only approximately with the formula $2\text{C}_4\text{H}_6\text{O}_5 \cdot \text{Na}_2\text{MoO}_4$. A rough estimate of the change of rotation with concentration indicated that the specific rotation decreases on dilution.

Attempts were made to find an organic solvent for this compound,

but without success. The rotation was therefore observed in aqueous solution for six colours of light at different temperatures. The temperature-rotation curves showed no very characteristic peculiarity; the rotation increased in much the same way as for solutions in the neighbourhood of *A*, Fig. 1.

We thought it worth while also to ascertain whether, on mixing solutions of malic acid and of sodium molybdate, any gradual change of rotation with lapse of time—any lag—could be observed. In our first experiment, the two separate solutions were kept at room temperature for a considerable time, then mixed and immediately placed in the polarimeter. The rotation showed quite a considerable and steady change during about $\frac{1}{2}$ hour. We found, however, that this was, in fact, a temperature effect. On mixing the two solutions there is a rise of temperature—which, of course, may indicate the formation of some compound—and, as the solution cooled, its rotation changed, in the manner of one of the curves in Fig. 2. If, after mixing, the solutions were quickly cooled to the original temperature by immersing the containing flask in water, no lag could be observed.

Experimental Data.

The colours of light used were the following and, to save space, will be denoted in the sequel by letters :

r_1	r_2	y	g	b	v
λ 6716.	6234.	5790.	5461.	4916.	4359.

Data used for Fig. 1.

(*M* = g. of malic acid per 100 c.c.; *S* = g. of sodium molybdate per 100 c.c.)

<i>M.</i>	<i>S.</i>	$[\alpha]_y^{17^\circ}$.	$[\alpha]_g^{17^\circ}$.	$[\alpha]_v^{17^\circ}$.
9-325	0-4785	— 8-05°	— 9-40°	— 14-40°
9-307	4-00	— 53-0	— 61-4	— 115-2
9-305	6-03	— 80-7	— 93-5	— 176-8
9-323	7-99	— 90-72	— 105-4	— 202-1
9-322	8-41	— 86-44	— 100-4	— 191-9
9-325	9-07	— 71-45	— 82-44	— 154-8
9-322	10-04	— 39-83	— 45-86	— 84-96
9-325	10-59	— 22-52	— 26-61	— 46-45
9-322	12-00	+ 23-41	+ 27-29	+ 58-39
9-322	14-07	+ 90-57	+ 105-4	+ 213-1
9-322	16-28	+ 154-5	+ 180-6	+ 360-8
9-322	16-51	+ 156-6	+ 183-1	+ 366-7
9-322	18-05	+ 141-8	+ 166-5	+ 332-9
9-322	20-00	+ 78-59	+ 92-82	+ 188-4
9-307	22-00	+ 17-45	+ 21-10	+ 47-00
9-307	24-00	— 5-40	— 5-60	— 6-70
9-325	26-22	— 10-70	— 12-10	— 19-85
9-285	28-91	— 16-01	— 18-40	— 34-38
9-325	33-61	— 9-10	— 9-70	— 19-80
9-307	35-77	+ 6-20	+ 7-00	+ 10-40
9-322	53-55	+ 69-92	+ 81-27	+ 147-9

Solution 1.

 Malic acid, $c = 9.307$, $p = 7.849$; sodium molybdate, $c = 22.00$.

t .	d .	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_p$.	$[\alpha]_p$.	$[\alpha]_b$.	$[\alpha]_b$.
0°	1.1932	+ 5.21°	+ 6.56°	+ 8.54°	+ 10.81°	+ 15.55°	+ 26.43°
16	1.1871	11.47	13.75	17.37	20.79	29.71	45.81
27	1.1821	14.62	17.92	22.43	26.74	37.38	57.79
35.8	1.1775	17.11	21.57	26.58	31.65	44.36	67.76

Solution 2.

 Malic acid, $c = 9.307$, $p = 7.775$; sodium molybdate, $c = 24.00$.

t .	d .	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_p$.	$[\alpha]_p$.	$[\alpha]_b$.	$[\alpha]_b$.
0°	1.2127	-9.08°	-10.61°	-12.10°	-13.59°	-16.44°	-23.47°
11	1.2075	-5.92	-7.02	-8.32	-9.19	-10.38	-13.98
16	1.2050	-4.60	-5.14	-6.00	-6.27	-6.80	-7.60
19.5	1.2032	-4.01	-4.28	-4.31	-4.28	-3.94	-4.01
22.5	1.2018	-2.94	-2.74	-2.54	-2.34	-1.81	-0.69
27.5	1.199	-1.21	-0.47	+ 0.13	+ 0.94	+ 2.48	+ 6.17
37.5	1.1935	+3.06	+ 3.74	+ 5.79	+ 7.21	+ 11.15	+ 19.03

Solution 3.

 Malic acid, $c = 9.325$, $p = 7.711$; sodium molybdate, $c = 26.22$.

t .	d .	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_p$.	$[\alpha]_p$.	$[\alpha]_b$.	$[\alpha]_b$.
0°	1.221	-10.83°	-12.74°	-14.60°	-16.79°	-21.94°	-31.10°
13	1.2148	-9.61	-10.48	-11.94	-13.51	-16.88	-23.69
35	1.2034	-3.17	-3.23	-3.03	-2.96	-2.29	-1.35
44.8	1.1976	± 0	+ 0.41	+ 1.49	+ 2.40	+ 4.74	+ 9.95
55.5	1.1910	+ 3.69	+ 4.70	+ 6.74	+ 8.54	+ 13.20	+ 21.64

Solution 4.

 Malic acid, $c = 9.285$, $p = 7.566$; sodium molybdate, $c = 28.91$.

t .	d .	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_p$.	$[\alpha]_p$.	$[\alpha]_b$.	$[\alpha]_b$.
0°	1.2384	-9.81°	-11.15°	-12.94°	-14.94°	-19.88°	-29.28°
11	1.2335	—	—	-15.77	-18.22	—	-34.19
17	1.2306	-12.09	-13.97	-16.01	-18.40	-24.24	-34.38
37.5	1.2195	-8.81	-10.03	-11.72	-13.18	-15.92	-22.10
49.5	1.2123	-5.66	-6.13	-6.95	-7.53	-8.59	-10.22
58.5	1.2065	-2.64	-2.60	-2.53	-2.40	-1.64	+ 0.75

Solution 5.

 Malic acid, $c = 9.325$, $p = 7.455$; sodium molybdate, $c = 33.61$.

t .	d .	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_p$.	$[\alpha]_p$.	$[\alpha]_b$.	$[\alpha]_b$.
0°	1.2660	+2.10°	+ 2.32°	+ 4.07°	+ 3.84°	+ 4.37°	+ 5.63°
19	1.2562	-7.27	-8.48	-9.94	-10.41	-14.42	-21.22
30	1.2502	-9.39	-11.23	-12.54	-14.35	-18.64	-27.13
40.4	1.2440	-9.84	-11.26	-12.27	-14.22	-18.53	-26.15
48.2	1.2390	-9.00	-9.81	-11.44	-12.42	-16.17	-22.19

Solution 6.

 Malic acid, $c = 9.307$, $p = 7.285$; sodium molybdate, $c = 35.77$.

t .	d .	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_p$.	$[\alpha]_p$.	$[\alpha]_b$.	$[\alpha]_b$.
0°	1.2938	+18.37°	+21.48°	+26.19°	+30.04°	+38.46°	+52.18°
16	1.2854	+ 4.77	+ 5.81	+ 7.14	+ 8.28	+ 10.35	+ 12.75
20.5	1.2828	+ 1.94	+ 2.41	+ 3.38	+ 3.68	+ 4.95	+ 5.15
24.2	1.2806	+ 0.33	+ 0.54	+ 0.87	+ 0.94	+ 0.87	+ 0.60
25.5	1.2800	- 0.44	- 0.47	± 0.00	- 0.27	- 0.60	- 2.01
29.2	1.2778	- 1.95	- 2.15	- 2.35	- 2.89	- 3.83	- 7.42
37.8	1.2725	- 4.92	- 5.60	- 6.14	- 6.67	- 8.97	- 13.69

Data used for Fig. 3.

(S = g. of sodium molybdate per 100 c.c.; n = mols. of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ per mol. of $\text{C}_4\text{H}_6\text{O}_5$.)

Malic acid, $c = 17.88$.

Rotations ($t = 17^\circ$, approx.).

S .	n .	$[\alpha]_D$.	$[\alpha]_D$.	$[\alpha]_D$.
5.127	0.1588	- 36.13°	- 42.34°	- 78.64°
10.201	0.3159	- 70.81	- 82.55	- 156.9
15.24	0.4719	- 98.49	- 114.5	- 218.5
20.13	0.6233	- 38.48	- 50.28	- 82.77
21.899	0.6780	- 3.84	- 4.05	-
22.51	0.6971	+ 6.33	+ 7.38	+ 18.79
24.966	0.7732	+ 41.61	+ 47.48	+ 97.99
30.37	0.9404	+ 132.2	+ 154.8	+ 310.9
32.01	0.991	+ 153.6	+ 179.3	+ 359.6
32.23	0.998	+ 155.4	+ 182.3	-
32.35	1.00	+ 157.4	+ 184.5	+ 370.2
35.00	1.084	+ 121.5	+ 142.3	+ 359.6
40.15	1.243	+ 38.31	+ 45.58	+ 96.25
42.71	1.323	+ 13.02	+ 15.45	-
45.06	1.395	- 11.07	- 12.64	- 20.75
50.04	1.550	- 17.00	- 19.96	-
55.10	1.706	- 6.77	- 7.83	- 17.28
60.78	1.882	+ 18.46	+ 21.08	-

Malic acid, $c = 2.55$.

Rotations ($t = 17^\circ$, approx.).

S .	n .	$[\alpha]_D$.	$[\alpha]_D$.	$[\alpha]_D$.
0.96	0.2084	- 47.45	- 54.13	- 105.9
2.017	0.438	- 90.59	- 106.3	- 199.6
2.395	0.5201	- 72.16	- 87.46	- 166.7
2.60	0.5646	- 54.91	- 64.71	- 121.6
4.033	0.8758	+ 114.5	+ 132.5	+ 264.3
4.348	0.9443	+ 143.5	+ 166.3	+ 334.1
4.612	1.0002	+ 156.9	+ 183.1	+ 364.8
5.03	1.092	+ 164.7	+ 193.7	+ 382.3
5.437	1.181	+ 160.1	+ 187.5	+ 370.2
5.922	1.286	+ 145.5	+ 171.4	+ 339.2
7.01	1.523	+ 97.27	+ 115.3	+ 230.2
8.093	1.758	+ 57.27	+ 67.45	+ 137.4
9.433	2.048	+ 28.63	+ 33.73	+ 69.42
9.905	2.151	+ 23.14	+ 27.06	+ 54.90
10.76	2.336	+ 16.87	+ 19.61	+ 41.97
11.40	2.476	+ 14.51	+ 15.69	+ 34.90
12.15	2.638	+ 12.94	+ 14.51	+ 28.23
12.975	2.818	+ 12.55	+ 14.51	+ 29.81
13.404	2.911	+ 12.55	+ 15.30	+ 29.81
15.018	3.262	+ 14.90	+ 17.65	+ 32.95
16.404	3.562	+ 19.22	+ 22.75	+ 40.00
19.146	4.158	+ 27.06	+ 32.16	+ 60.39
25.11	5.464	+ 48.23	+ 56.48	+ 103.1
29.732	6.457	+ 64.71	+ 72.56	+ 135.7
34.97	7.595	+ 81.96	+ 95.3	+ 177.6
39.81	8.646	+ 94.52	+ 108.6	+ 203.9
45.00	9.772	+ 112.9	+ 129.0	+ 238.9
50.08	10.87	+ 127.8	+ 146.3	+ 272.2

Rotations of sodium molybdomalate, $2C_4H_6O_5, Na_2MoO_4$, in water
($p = 23.37$).

$t.$	$d.$	$[\alpha]_{r_1}.$	$[\alpha]_{r_2}.$	$[\alpha]_y.$	$[\alpha]_g.$	$[\alpha]_v.$
0°	1.1540	-35.34°	-41.65°	-49.97°	-58.38°	-112.9°
16	1.1484	37.22	44.18	52.43	61.53	116.7
25.5	1.1444	38.35	45.53	54.29	63.36	121.3
37	1.1390	39.03	46.29	55.35	64.58	122.4
45.5	1.1345	39.42	46.85	56.04	64.88	122.9

For this solution the rotation for blue could not be read.

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UNIVERSITY OF GLASGOW.

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