LXII.—*The Rotatory Dispersive Power of Organic Compounds. Part X. The Preparation and Properties of Pure Ethyl Tartrate.*

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IN a series of experiments to determine the form of the curves of rotatory dispersion of the tartaric esters (Lowry and Dickson, T., 1915, 107, 1176; Lowry and Abram, *ibid.*, p. 1187), difficulty was experienced in obtaining accurate data for ethyl tartrate, since it was found that the samples used not only varied in rotatory power, but could also be separated by distillation into fractions of

unequal optical activity, the middle fractions giving higher readings than the two end fractions. In the case of methyl tartrate, this difficulty was not experienced, and the methyl ester was therefore selected as affording the most trustworthy material for determining the mathematical equation for the dispersion curves. No further attempt was made at that time to isolate pure ethyl tartrate, but it was suggested (*loc. cit.*, p. 1177) that, in view of the large amount of work that had been done with this ester, it was very desirable that a complete fractionation should be carried out sooner or later, in order that the properties of the compound might be determined with the help of fully purified material.

In response to this suggestion, Professor Franchimont of Leiden wrote to say that more than twenty years previously the ester had been prepared in his laboratory as a crystalline solid, which, after purification with the help of a centrifugal machine, melted at 16–17°, and remained for many years in the solid state when stored in a cellar below this temperature. The crystalline ester had been prepared again in his laboratory in 1907, and on this occasion the melting point had been raised to 19°. Since it was evident that material which had been purified by crystallisation was likely to be better than any that could be obtained by fractional distillation only, Professor Franchimont very kindly prepared and sent to London two fresh specimens of the crystalline ester. The first specimen melted at 6° and about half of it remained liquid at 0°. The low melting point showed that it was not completely purified, but its rotatory power, $\alpha_{5461} = +55.86^\circ$, $\alpha_{4358} = +13.06^\circ$, measured in a 6-decimetres tube at 20°, was already almost equal to the highest value that had been obtained with material purified by fractional distillation. The second specimen had been fully purified in Holland, although its melting point had not been determined. As it had become liquid in transit, and the package had been opened by the Customs officers, the specimen was refrozen in London, when it was found that it began to melt at 19°, whilst its rotatory power was $\alpha_{5461} = +56.48^\circ$, $\alpha_{4358} = +14.34^\circ$.

After the samples of ethyl tartrate which had been purified in Holland had been persuaded to crystallise in London (by freezing to a glass with solid carbon dioxide and then thawing in an ice-chest), no difficulty was experienced in inoculating other specimens of the tartrate with the crystals, and obtaining in this way several kilograms of the solid ester. This was purified by draining in a centrifugal machine and freed from the last traces of water by distillation under very low pressure. The purification was continued until both the rotatory power and the melting point were constant. Thus, fractions prepared by different methods and puri-

fied independently melted concordantly at 18.7° and gave an observed rotation $\alpha_{5461} = +56.9^{\circ}$ for a 6-decimetre column at 20° .

With the help of this pure material the most important of the physical constants of the ester were determined, including the density at three temperatures, the viscosity, the refractive index for eight wave-lengths in the visible spectrum, and finally the optical rotatory power for a long series of lines in the visible and early ultra-violet regions of the spectrum. The last series of readings was of special significance, as showing that pure ethyl tartrate gives, like the methyl ester, a curve of rotatory dispersion which can be expressed right up to the limits of experimental accuracy by two terms of the Drude equation. In the case of the acid, the dispersion is apparently rendered more complex as a result of electrolytic dissociation, since small but systematic differences are found between the observed rotations of the acid, in aqueous solutions of different concentrations, and the values calculated from the two-term equation (Lowry and Austin, Bakerian Lecture, *Phil. Trans.*, 1922). In the case of the ethyl ester, however, the largest deviation between the observed and calculated values for the specific rotatory power is only 0.03° (for a very difficult zinc blue line) in a series of eighteen visual readings and 0.3° for the worst of the photographic readings in the ultra-violet region of the spectrum; for two-thirds of the readings the differences are $\pm$, and the remaining errors are distributed casually. It is therefore clear that the two-term formula expresses perfectly the rotatory dispersion of the ester, as at present determined, and will probably remain as an exact representation of that dispersion until entirely new methods of measurement shall be developed.

EXPERIMENTAL.

Preparation of Ethyl Tartrate.

(a) The material used for these experiments was at first prepared as described by Patterson (T., 1910, **79**, 168), using hydrogen chloride as a condensing agent; but the yields obtained were low (56 per cent.), and even after two distillations under a pressure of 10 to 12 mm. the product still contained chlorine.

(b) Much better results were obtained by using a modified form of the method described by Rodger and Brame (T., 1898, **73**, 302), in which the acid is first converted into ethyl hydrogen tartrate by boiling with alcohol and distilling off the aqueous liquor, and then into the normal tartrate by boiling with more alcohol and fractionating out the ester under reduced pressure. In practice, 1,200 grams of tartaric acid were boiled for seven hours with 2,000

grams of freshly distilled 98 per cent. alcohol in a 5-litre flask heated in an oil-bath at 115° ; the aqueous liquor was then distilled off rapidly by raising the temperature of the oil-bath to 250° . The syrupy residue was heated with 400 grams of fresh alcohol during a further period of seven hours, the temperature of the oil-bath being 150 – 160° , after which the aqueous liquor was again distilled off as before. The crude ester was distilled, in quantities of 150 to 200 grams at a time, in a $1\frac{1}{2}$ -litre distilling flask under a pressure of 10 to 12 mm.; when the pressure rose to 15 mm., distillation was stopped. In this way an immediate yield of 700 to 800 grams of a water-white ester was obtained from 1,200 grams of acid. The residues from the vacuum distillation were boiled with a further quantity of alcohol for another period of seven hours, and distilled as described above to obtain a further quantity of the ester; but this process could not be repeated more than three times owing to excessive frothing in the final distillation. Altogether, 7,800 grams of the ester were prepared by this method, with a yield of about 80 per cent.

(c) A small quantity of the ester was also prepared by heating the crude ethyl hydrogen tartrate [prepared as described under (b) above] with four times its weight of 98 per cent. alcohol during a period of five hours at 160° in a rotating autoclave (Morgan and Vining, T., 1920, **117**, 780) at a pressure of 200 lb. per square inch. The subsequent distillation was carried out as before, but there was no frothing, and an immediate yield of more than 90 per cent. of very pure material was obtained. This method has also been applied with great advantage in the preparation of propyl tartrate.

Purification.

The ester, prepared as described above, was cooled in ice, inoculated with a crystal of ethyl tartrate, and frozen to a solid block. The mass was broken up and the lumps were crushed, in which process they were partly melted, giving rise to a sludge of crystals in a very syrupy liquid. This was transferred to a small centrifuge, the cage of which had been lined with silk. After draining, the crystals were again partly melted and centrifuged, whilst the mother-liquors were frozen to produce a further crop of crystals.

Ethyl tartrate appears to be almost as hygroscopic as sulphuric acid; the crystals therefore always absorb moisture during the process of freezing and draining. This is not altogether a disadvantage, since it provides a liquor of lower melting point which may very well serve as a rinsing agent to remove the impurities;

but in order to obtain the pure ester, the crystals must be melted and distilled to get rid of the last traces of water. This distillation was at first carried out under a pressure of 11 to 12 mm. with the help of two water-pumps arranged in parallel. In the later stages of the work a Langmuir mercury-vapour pump was used, in conjunction with an oil-pump of the Siemens type, the oil-pump being backed by two water-pumps in parallel. The capacity of this combination is enormous, since that of the mercury-pump is said to be fifteen times as great as that of the oil-pump, which is itself very large. In practice, the distillation of the ester could be carried out under pressures of 0.03–0.001 mm. as recorded by a McLeod gauge. In contrast to the high capacity of this combination, it may be stated that a Gaede mercury-pump of the ordinary type gave results which were no better than those obtained by means of a water-pump alone, since the pressure always rose to several millimetres of mercury as soon as distillation began.

In order to secure useful results in this system of low-pressure distillation, the whole of the distillation apparatus was made of glass, with ground joints lubricated and sealed with ethyl tartrate; and all the connexions were at least 1 centimetre, and usually 2 centimetres, in diameter. A drying tube of large diameter containing phosphoric oxide was inserted between the distillation apparatus and the Langmuir pump in order to keep out all traces of moisture. The liquid was heated in an oil-bath, and evaporated quietly without any bumping or even formation of bubbles; indeed, the only indication that distillation was proceeding was the gradual accumulation of liquid in the iced receiver. In this apparatus the temperature of distillation was brought down from 160–170° to 98–110°, although by rapid heating the temperature could be raised to 115°.

Fractionation.

The two samples used were :

- (i) 4,000 grams; $\alpha_{5461} = 53.62^\circ$ (6 dm.). Freezing point 7°.
- (ii) 3,800 grams; $\alpha_{5461} = 54.68^\circ$. Freezing point 7°.

After freezing, partial melting, and centrifuging, the values of the constants were :

- (i) $\alpha_{5461} = 55.06^\circ$. Freezing point 14.5°.
- (ii) $\alpha_{5461} = 55.02^\circ$. Freezing point 13.4°.

Three further freezings, after mixing these two fractions, and one distillation under 10 mm. pressure, gave the values :

$$\alpha_{5461} = 56.62^\circ. \text{ Freezing point } 18.7^\circ;$$

and similar treatment of all the mother-liquors obtained up to this point gave :

$$\alpha_{5461} = 56.60^{\circ}. \text{ Freezing point } 17.8^{\circ}.$$

These two fractions, when mixed and fractionally crystallised, gave :

$$\begin{array}{ll} \text{Solid} & \alpha_{5461} = 56.62^{\circ}. \text{ Freezing point } 17.8^{\circ}. \\ \text{Liquid} & \alpha_{5461} = 56.60^{\circ}. \text{ Freezing point } 17.8^{\circ}, \end{array}$$

but when redistilled a fortnight later the rotatory power was found to have fallen from 56.6° to 56.2° . We believe that this drop of rotatory power is the direct result of distilling the ester in a relatively poor vacuum, and all the rotatory powers given above may be too low from this cause, since every fraction was distilled before its rotatory power was determined. By using the Langmuir pump for the final distillation, higher rotatory powers were obtained, although the quantity of material only allowed 2-decimetre tubes to be used, for example, the sample described above gave the following fractions :

Fraction	1*	$\alpha_{5461} = 18.8^{\circ}$ (2 dm.).	Freezing point	18.4° .
"	2a	" = 19.01° .	" "	18.7° .
"	2b	" = 19.02° .	" "	18.7° .
"	3	" = 18.99° .	" "	18.7° .

* Probably moist.

The 500 grams prepared in an autoclave gave on distillation a large middle fraction of 450 grams, and on redistillation another middle fraction of 400 grams; the values for the latter were :

$$\alpha_{5461} = 19.01^{\circ}. \text{ Freezing point } 18.7^{\circ}.$$

It appears, therefore, that preparation in an autoclave followed by two distillations under a pressure of less than 0.1 mm. provides an alternative method of preparing the ester in a pure condition.

Coloration.

Almost all commercial samples of ethyl tartrate are yellow in colour, perhaps as a result of careless distillation. A similar colour was also seen in one of our own samples. This colour is undoubtedly due to an impurity, since it can be removed by freezing out and centrifuging the crystalline ester. When this permanent coloration had been removed, it did not reappear in six successive distillations under 10 mm. pressure; but after the rotatory power had risen to 56.28° , the purified ester developed a yellow colour when heated in the distilling flask, and gave a yellow distillate, the colour of which disappeared, however, after a few hours. This

transient yellow colour reappeared in every subsequent distillation and became very pronounced when the rotatory power had risen to 56.62° .

The yellow colour, which thus appears when highly purified samples are distilled, does not produce any substantial alteration of rotatory power. Thus when two separate samples were distilled and their rotations taken, first whilst still coloured, and secondly after becoming colourless, the readings in 2-decimetre tubes were :

Sample 1. Coloured, 18.90° . Colourless, 18.85° .

Sample 2. Coloured, 18.88° . Colourless, 18.85° .

In the same way, of two samples which (as set out in a previous paragraph) gave rotations of 56.62° and 56.60° in 6-decimetre tubes, one was quite light in tint, whilst the other developed an intense yellow in the last distillation.

Slow or rapid distillation, and the presence of rubber stoppers in the apparatus, were suspected as causes producing the transient yellow coloration, but without justification. Thus, the sample of ethyl tartrate which was prepared in an autoclave never came into contact with rubber; it was distilled once in the vacuum of the Langmuir pump, in an apparatus composed entirely of glass, and gave a perfectly colourless distillate; but when the pure middle fraction was again distilled under the same conditions, it developed the familiar transient yellow colour. This colour must, indeed, be regarded as a test which serves to establish the *purity* rather than the *impurity* of the sample.

The failure of the yellow colour to appear in the early stages of purification might have been attributed to the presence in the distillation flask of a little ethyl hydrogen tartrate; but the addition of this compound to a purified sample did not prevent the yellow colour from appearing. It seems more probable that the inhibiting impurity is water and that the yellow coloration may be due to the reversible formation of a yellow anhydride, possibly a member of the keten class. The formation of this yellow anhydride would then be, like the formation of a white fume of sulphur trioxide on heating concentrated sulphuric acid, a sign of the absence of all but small traces of water.

Determinations of Freezing Point.

As a result of the very great viscosity of the ester, the determination of the freezing point was more difficult than in the case of the majority of organic compounds. Relatively large quantities of material were used in order to secure a satisfactory equilibrium of

temperature between solid and liquid, and the actual mass taken for each determination was seldom less than 500 grams. In making a measurement, the freshly distilled sample was cooled in ice, inoculated with a few crystals, and stirred vigorously; the maximum temperature was noted and the experiment was then repeated, but after the initial cooling the sample was now surrounded by water at a temperature about 1° below the maximum previously noted, in order that the temperature at which the liquid and solid were in equilibrium might be influenced to the smallest possible extent by external heating or cooling. Since most of the samples tested were substantially pure, the extent to which crystallisation proceeded was not important.

We have obtained some indications that ethyl tartrate may perhaps be dimorphous, like methyl tartrate, since from time to time we have observed freezing points substantially below those which we expected to find in view of the purity of the sample under examination. Thus, the low melting point, 6° , of the first sample received from Holland, in marked contrast with its high rotatory power, $55\text{--}68^{\circ}$ (which should correspond with a melting point of 16° or more), may perhaps be explained in this way. Again, we have seen a very large crystal, perhaps $3 \times 1\frac{1}{2}$ cm., which had grown on the surface of a sample of pure tartrate (m. p. about 18.5°) go to pieces and redissolve at a room temperature of about 13° . These observations have, however, not been frequent, and, in view of the extreme difficulty of persuading the liquid to crystallise without inoculation, are beyond the range of systematic experiment. Although, therefore, we have very good grounds for suspecting that ethyl tartrate is dimorphous, we have not been able to obtain a direct experimental verification of our suspicions.

A remarkable change of freezing point which cannot be attributed to dimorphism was observed on exposing the purified ester to the high vacuum of a Langmuir pump in a vessel containing phosphoric oxide. Under these conditions the compound gave off bubbles (perhaps of alcohol or water-vapour) and liquefied, although the temperature of the room was below the original melting point of the crystals. In this experiment the melting point actually fell from 18.6° to 12.7° , and more than half of the solid melted, as a result of exposure under very low pressure in presence of phosphoric oxide. Subsequent exposure in presence of 50 per cent. sulphuric acid, giving a vapour pressure of about 3 mm. of water-vapour, or of alcohol, did not cause the liquid to become solid again, and we are therefore unable to state which of these compounds was eliminated by the phosphoric oxide.

Determinations of Density.

The density of the viscous ester was determined in a pyknometer with a capillary neck. It was filled by means of the apparatus devised by Wade and Merriman (T., 1912, **101**, 2429) for measuring the density of pure liquids, free from air and without any risk of absorption of moisture. The level of the liquid was adjusted roughly when the pyknometer had stood at constant temperature in a thermostat for three hours; after a further period of half an hour the level of the liquid was again adjusted, and the neck of the flask was cleaned with cotton wool moistened with ether; the correctness of the adjustment was checked by observing the meniscus again after the pyknometer had remained in the thermostat another half hour. The pyknometer was calibrated by filling it with air-free water at the same temperature. The results of the observations were as follow :

$$D_4^{20^\circ} = 1.2028; \quad D_4^{25^\circ} = 1.1980; \quad D_4^{34.8^\circ} = 1.1895.$$

Previous observations have given the values

$$\left. \begin{array}{l} D_4^{20^\circ} 1.2059 \text{ (Pictet, } \textit{Jahresberichte}, 1882, 856); \\ D_4^{20^\circ} 1.1989 \text{ (Landolt, } \textit{Annalen}, 1877, \textbf{188}, 324); \\ D_4^{20^\circ} 1.2036 \\ D_4^{30^\circ} 1.1840 \end{array} \right\} \text{ (Winther, } \textit{Z. physikal. Chem.}, 1902, \textbf{41}, 174).$$

Determinations of Viscosity.

The absolute measurement of very high viscosities is a problem which has been studied but little. Sheppard (*J. Ind. Eng. Chem.*, 1917, **9**, 523) and Jacobs (T., 1920, **117**, 473) have used the falling-sphere viscosimeter, but in our experiments we have followed Bingham (*J. Ind. Eng. Chem.*, 1914, **6**, 233; *Bull. Bureau of Standards*, U.S.A., 1918, **14**, [I], 60), who has made a careful study of the Ostwald viscosimeter for media of high viscosity and has given absolute values for a series of strong solutions of sucrose. In our experiments, the viscosimeter had a capillary tube 12.2 cm. in length and approximately 0.1 cm. radius, the volume of liquid passing through the capillary being 12.1 c.c. Special precautions were taken to prevent the absorption of moisture by the liquid both during the filling and during the measurements. The time of flow was measured for five independent fillings of the viscosimeter and was observed, as a rule, three times for each sample at intervals of half an hour. The times were compared with those of a 60 per cent. solution of dried sucrose, the strength of which was found to be 60.01 per cent. by the polarimeter as compared with 60.05 per cent. by direct weighing. The times of flow at 19.96° were as follow :

Ethyl Tartrate.

(i) 1467·6	(ii) 1459·0	(iii) 1467·0	(iv) 1460·0	(v) 1464·0
1467·4	1459·8	1467·2		1460·4
1468·6	1459·8	1460·0		1460·6

Average time 1463·5 secs.

Sucrose (60 per cent. by weight).

(i) 347·8	(ii) 349·8	(iii) 347·4	(iv) 348·4
347·8	348·0	347·0	348·4
346·8	345·4	346·8	

Average time, 347·9 secs.

The times of flow, repeated at intervals over a period of twenty-four hours in one series of experiments, were as follow :

	0	0·5	1	4	8·5	12	24 hrs.
Ethyl tartrate	1467·6	1467·0	1468·0	1467·0	1465·0	1460·2	1450·4
Sucrose (60 per cent.)	350·4	349·6	350·2	348·4	—	—	343·3

Although the times recorded at the end of twenty-four hours are a few seconds lower, the ratio $1450·4/343·3 = 4·225$ agrees very closely with the ratio $1463·5/347·9 = 4·207$ of the average times set out above.

It will be seen that the viscosity of the ester is more than four times as great as that of the strongest sugar-solution used by Bingham. The correction for kinetic energy (Hoskins, *Phil. Mag.*, 1909, [vi], 17, 503) was calculated to be only 0·00016 *C.G.S.* unit for the sugar solution and 0·000036 unit for the ester, and was negligible in both cases. The density of the sugar solution was 1·28644, whilst that of the tartrate was 1·2028 at 20°. Taking Bingham's value $\eta = 56·5$ for 60 per cent. sucrose at 20°, the absolute viscosity of the ester at 20° is found to be $\eta = 221·7$ centipoises or 2·217 *C.G.S.* units.

Refractive Indices.

The refractive index was determined with a Pulfrich refractometer made by Hilger, which was provided with a water-jacket round the liquid in addition to the usual tube dipping into the liquid (compare Lowry, *Proc. Opt. Convention*, 1912, II, 292). The instrument had been calibrated to give readings for the principal lines in the arc spectra of mercury and cadmium in addition to the usual sodium and hydrogen lines. The instrument was arranged so that the two constituents of the yellow sodium and mercury doublets could be seen separately, but readings were taken only of the less refrangible constituents. The results obtained were as follow :

TABLE I.
Refractive Indices of Ethyl Tartrate at 20°.

Line.	Wave-length.	Re-fractive index.	Line.	Wave-length.	Re-fractive index.
Cadmium red	6438	1.44481	Cadmium green	5086	1.45082
Sodium yellow	5896	1.44677	Cadmium blue	4800	1.45269
Mercury yellow	5790	1.44722	Cadmium dark blue	4678	1.45331
Mercury green	5461	1.44873	Mercury violet	4359	1.45659

These values can be plotted out as a smooth curve, but this is not reproduced in the paper.

TABLE II.
Rotatory Dispersion in Ethyl Tartrate at 20°.

		$\alpha = \frac{180.462}{\lambda^2 - 0.03} - \frac{149.216}{\lambda^2 - 0.056}$	$[\alpha] = \frac{25.005}{\lambda^2 - 0.03} - \frac{20.678}{\lambda^2 - 0.056}$			
Wave-length. $\lambda \times 10000.$		Rotations in 6-dcm. tube.		Specific rotations.		
		Obs.	Calc.	Obs.	Calc. Diff.	
Li	6707.8	49.60°	49.60°	6.87°	6.87°	±
Cd	6438.5	53.30	53.27	7.38	7.38	±
Zn	6362.3	53.65	53.65	7.43	7.43	±
Na	5893.0	56.45	56.46	7.82	7.82	±
Hg	5790.7	56.84	56.81	7.87	7.87	±
Cu	5782.2	56.82	56.85	7.87	7.87	±
Hg	5769.6	56.90	56.89	7.88	7.88	±
Cu	5700.2	56.88	57.03	7.88	7.90	-0.02
Hg	5460.7	56.86	56.75	7.87	7.86	+0.01
Cu	5218.2	54.93	54.91	7.61	7.61	±
Cu	5153.3	53.98	54.03	7.48	7.48	±
Cu	5105.5	53.15	53.30	7.36	7.38	-0.02
Cd	5085.8	53.00	52.91	7.34	7.33	+0.01
Zn	4810.5	45.11	45.31	6.25	6.28	-0.03
Cd	4799.9	44.88	44.87	6.22	6.22	±
Zn	4722.2	41.52	41.50	5.75	5.75	±
Cd	4678.2	39.34	39.42	5.45	5.46	-0.01
Hg	4358.3	14.35	14.30	1.98	1.98	±

(b) Photographic Readings.						
Fe	4603	35.0	35.0	4.9	4.9	±
Fe	4475	25.0	25.5	3.5	3.5	±
Fe	4415	20.0	20.1	2.8	2.8	±
Fe	4359	15.0	14.3	2.1	2.0	+0.1
Fe	4315	10.0	9.3	1.4	1.3	+0.1
Fe	4271	5.0	3.6	0.7	0.5	+0.2
Fe	4240	0.0	0.6	0	0.1	+0.1
Fe	4210	- 5.0	- 5.0	- 0.7	- 0.7	±
Fe	4148	- 15.0	- 15.3	- 2.1	- 2.1	±
Fe	4119	- 20.0	- 20.3	- 2.8	- 2.8	±
Fe	4071	- 30.5	- 30.1	- 4.2	- 4.2	±
Fe	4005	- 45.0	- 45.1	- 6.2	- 6.2	±
Fe	3967	- 55.5	- 55.0	- 7.7	- 7.7	±
Fe	3900	- 74.0	- 74.7	- 10.3	- 10.4	- 0.1
Fe	3889	- 80.0	- 78.2	- 11.1	- 10.8	+0.3
Fe	3872	- 83.0	- 83.9	- 11.5	- 11.6	- 0.1
Fe	3868	- 85.0	- 85.2	- 11.8	- 11.8	±
Fe	3860	- 88.0	- 88.1	- 12.2	- 12.2	±

Measurements of Rotatory Dispersion.

The optical rotatory power of the pure ester was measured at 20° for a series of eighteen lines, with an eyepiece, and for eighteen

FIG. 1.

Rotatory dispersion in ethyl tartrate.

lines in the dark-blue, violet, and ultra-violet regions by a photographic method. The visual readings have been recorded to two decimal places, but except in the yellow and green the second

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decimal is of very little value; the specific rotations, which are about seven times smaller, and are also given to two decimals, show much more clearly the degree of accuracy that is claimed for these observations. In the same way, in the photographic readings, the analyser was set to exact degrees, but the accuracy of the readings is certainly not closer than 0.5° ; the single decimal shown in the specific rotations therefore again corresponds closely with the limits of experimental error.

Fig. 1 shows the curve of observed rotations, ranging from a positive maximum of 57° in the green to a negative value of -88° in the last photographic reading. The figure also shows, plotted against λ^2 , the curve of molecular rotations, in which the anomalies of maximum, reversal of sign, etc., are clearly seen, together with the two rectangular hyperbolas of which this complex curve is the algebraic sum. In our opinion, these two curves represent the simple rotatory dispersions of two isodynamic constituents of the ester, the constitution of which we have not yet ascertained.

Summary.

1. Ethyl tartrate, purified by distillation, freezing, and redistillation in the vacuum of a Langmuir pump, freezes at 18.7° , and gives $\alpha_{5461} + 56.9^\circ$ in a 6-dcm. tube at 20° , $[\alpha]_{5461} + 7.87^\circ$. The density of the ester at 20° is 1.2028, and its viscosity 2.217 *C.G.S.* units.

2. The rotatory dispersion of the ester at 20° is given accurately by the formulæ

$$\alpha = \frac{180.462}{\lambda^2 - 0.03} - \frac{149.216}{\lambda^2 - 0.056}; \quad [\alpha] = \frac{25.005}{\lambda^2 - 0.03} - \frac{20.678}{\lambda^2 - 0.056}$$

where α is for a 6-dcm. column.

3. When sufficiently purified, the ester becomes yellow on heating, perhaps as a result of a reversible dehydration; the pure ester also appears to decompose at atmospheric temperatures when in a high vacuum in presence of phosphoric oxide.

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