

XXXV.—*On Tartaric and Racemic Acids, and the Magnetic Rotation of their Ethereal Salts.*

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IN 1867, I laid before the Society an account of some experiments on the basicity of tartaric acid (*J. Chem. Soc.*, **20**, 148, 149), in which I described some derivatives of tartaric and racemic acids which could be distilled; and from the fact that these boiled at about the same temperature, I inferred that the molecular weight of both acids must be the same, notwithstanding the fact that racemic acid is built up of dextro- and lævo-tartaric acids, and can be separated into them again. Since then, a good deal of work has been done upon these compounds, and more recently Anschütz and Pictet have not only re-examined some of the compounds I previously described, but have also prepared new ones. They have also shown that ethyl tartrate when pure can be distilled, and that tartrate and racemate of methyl have practically the same boiling points (*Ber.*, **13**, 1177—1178).

As magnetic rotary polarisation has been found capable of detecting even small difference of constitution in substances, I was induced to examine some of the compounds of tartaric and racemic acids by this method, to see if any fresh light could be obtained in reference to them. The products I used for this purpose were the ethylic derivatives.

As is well known, the preparation of the neutral ethers of these acids is troublesome. In my experiments I employed the usual method of saturating the alcoholic solution of the acids with hydrochloric acid, allowing the mixture to stand, and then resaturating. (In one operation I used sulphuric acid, but it did not appear to act any better, if so well as hydrochloric acid.) Some of the alcohol and the hydrochloric acid were then removed by distillation on the water-bath, the product mixed with ether, and the mixture washed first with a little water, and afterwards with dilute sodium carbonate solution; it was then dried over potassium carbonate, the ether distilled off, and the residue fractioned under reduced pressure. This last operation was found to be very troublesome, owing to the frothing of the product; it was stopped when decomposition set in. After the first distillation, the ethers could be redistilled under reduced pressure without much difficulty, and two or three fractionations were sufficient to obtain them with almost constant boiling points.

The tartrate and racemate of ethyl obtained in this way were

colourless liquids, viscid, like glycerol. They both boiled at the same temperature, viz., 232—233° (corr.) at 197 mm.

The permanent rotation of this tartaric ether was found to be as follows :—

$t$ .	$\alpha$ ( $l = 200$ mm.)	$[\alpha]_D$ .
12° .....	+ 17·5	+ 7·220
14 .....	18·1	7·481
16 .....	18·56	7·658
18 .....	18·97	7·807
20 .....	19·30	8·017

These results show how sensitive the rotation of this ether is to changes of temperature, as pointed out in Amé Pictet's Dissertation, *Recherches sur les Éthers Tartariques* (Geneva, 1881). My results come somewhat higher than his, which for 20° are  $\alpha$  18·47 and  $[\alpha]_D = 7·659$ .

The relative density determinations gave—

Tartaric ether ..	$d_{15^\circ}^{15^\circ}$ 1·2097	$d_{25^\circ}^{25^\circ}$ 1·2019,
Racemic ether ...	$d_{15^\circ}^{15^\circ}$ 1·2098	$d_{25^\circ}^{25^\circ}$ 1·2021.

Anschutz and Pictet found for tartaric ether at 14°, 1·2097, but it does not appear whether this is given as the relative or the true density (*Ber.*, 13, 1177).

The following are the results of the observations on the magnetic rotation of these bodies :—

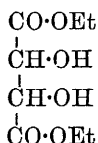
*Tartaric Ether.*

$t^\circ$ .	Sp. rot.	Mol. rot.
16·5° .....	0·9241	8·751
16·5 .....	0·9250	8·759
17·0 .....	0·9289	8·799
17·0 .....	0·9308	8·818
13·0 .....	0·9385	8·864
13·0 .....	0·9177	8·670
13·5 .....	0·9252	8·744
13·5 .....	0·9243	8·736
14·0 .....	0·9257	8·752
14·0 .....	0·9259	8·774
Average.. 14·8 .....	0·9266	8·766

*Racemic Ether.*

$t^{\circ}$ .	Sp. rot.	Mol. rot.
17.5° .....	0.9241	8.755
17.5 .....	0.9329	8.839
18.0 .....	0.9182	8.702
18.5 .....	0.9270	8.786
18.5 .....	0.9234	8.754
13.4 .....	0.9230	8.722
13.4 .....	0.9238	8.729
13.8 .....	0.9229	8.724
13.8 .....	0.9248	8.741
14.0 .....	0.9251	8.745
14.0 .....	0.9264	8.758
13.0 .....	0.9260	8.748
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15.5 .....	0.9248	8.759

From the above results we see not only that the boiling points and densities of tartaric and racemic ethers are identical, but that this is also true of the magnetic rotation. This latter is remarkably close to that which we should expect from the formula—



This is seen if we take the magnetic rotation of succinic ether, and add to it the values of two oxygens, as found for those in glycol (Trans., 1884, 515 and 559).

Ethyl succinate .....	8.380
O <sub>2</sub> .....	0.389
	<hr/>
	8.769

That tartaric and racemic ethers should have the same properties is perhaps not astonishing, because we know that racemic acid when converted into certain salts, forms not one salt, but those of right- and left-handed tartaric acids, so that when etherified it is not unlikely that it also should yield ethers of right- and left-handed tartaric acids, and this is what appears to happen. The difficulty of preparing left-handed tartaric acid has prevented me from examining it separately.

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There is one marked difference between tartaric and racemic acid, and that is that the latter always crystallises with a molecule of water, and the question arises as to whether this be water of crystallisation or part of the molecule, because it is quite easy to represent racemic acid as a single molecule derived from two of tartaric acid, with the elements of two molecules of water, and as racemic ether does not represent the ordinary crystallised racemic acid, but the compound from which water has been separated, this possibly might account for its being a mixture of the ethers of the two tartaric acids.

As most neutral silver salts are void of water of crystallisation, I had the curiosity to prepare the silver salts of tartaric and racemic acids direct from the acids themselves, by adding rather strong aqueous nitrate of silver to their moderately concentrated solutions; the salts, which were quickly formed, were filtered off, washed, and *air*-dried. They were, however, found to have the ordinary composition  $C_4H_4Ag_2O_6$ .

The densities of comparable solutions of tartaric and racemic acid were next examined, because if right- and left-handed tartaric acids are identical in properties, as we have every reason to believe they are (except as regards polarised light), racemic acid, if simply consisting of these united in virtue of their crystalline natures, would be expected to give when dissolved solutions of the same density as tartaric acid; on the other hand, if derived from the two tartaric acids plus the elements of water, it would be expected to give solutions dissimilar in density.

In the first determinations, rather dilute solutions were taken, the proportions of 1 mol. of tartaric acid to 100 mols. of water being employed, the same were used with dehydrated racemic acid, but with the crystallised acid only 99 mols. of water, as the acid itself contains one. These solutions contained 8·333 per cent.  $C_4H_6O_6$ .

The numbers obtained were as follows :—

	<i>t.</i>	I.	II.	III.
Racemic acid (dehydrated)	$\frac{15^\circ}{15^\circ}$	—	1·03714	1·03707
„ crystallised	„	1·03716	—	—
Tartaric acid .....	„	1·03703	1·03704	1·03701

Average.

$$\left. \begin{array}{l} 1·03712 \\ 1·03703 \end{array} \right\} \text{diff.} = 0·00009.$$

This difference is almost *nil*, but still it was found in all the experiments. These were made side by side, so as to get the same temperature, and the density tubes used were in the last experiment

reversed, so that any error arising from the determination of their capacity might be neutralised; this was done also in the subsequent density determinations.

To see if this was a real difference, stronger solutions were used, but as crystallised racemic acid only dissolves to the extent of 1 in 4·84 per cent. of water at 20°, it is of course difficult to get strong solutions; however, by making a hot 25 per cent. solution of the dehydrated acid, and determining its density before it had time to crystallise, the following results were obtained, as compared with tartaric acid solution of the same strength:—

	<i>t.</i>	I.	II.	Average.
25 p. c. solution of } racemic acid, de- } hydrated . . . . . }	$\frac{15\cdot3^{\circ}}{15^{\circ}}$	1·12393	1·12404	1·12398
25 p. c. tartaric acid	$\frac{15\cdot3^{\circ}}{15^{\circ}}$	1·12333	1·12360	1·12346
			Diff. . . . .	0·00052

Here we find that there is a slightly higher density in the case of racemic acid; the comparison, however, is not a rigorous one, because we are comparing a supersaturated solution of racemic acid with an unsaturated solution of tartaric acid, but although the difference is proportionally larger than in the case of the dilute solutions, still both lay in the same direction.

These results made it desirable to determine the densities of the solid acids. For this purpose they were powdered for use. Toluene was the liquid used in the experiments, and the air was removed from the powdered acid and hydrocarbon by means of the air-pump. The following results were obtained, about 21 grams of acid being used in each case.

Recrystallised racemic acid } (C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> H <sub>2</sub> O) . . . . . }	$d_{4^{\circ}}^{7^{\circ}}$	1·6873,	} Diff. = 0·0188.
Dehydrated racemic acid, } C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> . . . . . }	„	1·7782	
Recrystallised tartaric acid, } C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> . . . . . }	„	1·7594	

These numbers show that racemic acid (dehydrated) has a density considerably greater than tartaric acid, viz., 0·0188.

Now, 25 p. c. of this difference is equal to 0·00470,  
and 8·33 „ „ „ „ 0·00154.

The differences in the densities of the solutions of racemic and tartaric acids given above are very small as compared with these.

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These results, therefore, lead to the inference that racemic acid when dissolving in water separates into the two tartaric acids, a small quantity only remaining associated, even in supersaturated solutions.

To see whether racemic acid could exist as a definite body if devoid of this molecule of water, a quantity of the ordinary acid crystallised from water, was recrystallised from absolute alcohol. It was thus obtained in well-defined small transparent crystals, differing from tartaric acid in being much less soluble in alcohol. The crystals were dried between bibulous paper, and when heated at  $100^{\circ}$  neither lost weight nor did they become opaque, so that racemic acid is a definite product without the molecule of water it usually contains. This fact taken in conjunction with those above, point to the conclusion that the water which is given off on drying racemic acid at  $100^{\circ}$  exists as such in that substance, and is present as water of crystallisation only.

Mr. Pickering has very kindly determined the heat of dissolution of tartaric and racemic acids for me. The following are his results and remarks.

“The acids were dissolved in 400 gram-molecular proportions of water at an initial temperature of  $8.77^{\circ} \pm 0.04$ . The results were as follows:  $w$  being the weight of the acid taken, and  $t - t'$  the fall of temperature observed. The water equivalent of the calorimeter and its contents was 607.74 grams with the anhydrous acids, and 608.74 grams with hydrated acid, the molecular weights taken were 149.64, and 167.6 in the two cases.

Substance.	$w$ .	$(t - t')^{\circ} \text{C.}$	Molecular heat of dissolution.
Tartaric acid (dextro-) {	grams. 12.506	0.4741	-3447
	12.418	0.4729	-3461
Racemic acid, anhyd. {	12.520	0.7836	-5692
	12.583	0.7828	-5658
Racemic acid, hyd. .. {	13.956	0.9591	(-7012)
	14.042	0.9742	-7078
	14.117	0.9794	-7079

these numbers agree fairly well with those obtained by Berthelot and Jungfleisch, at  $10^{\circ}$ .

Tartaric acid .....	-3270 cal.
Anhydrous racemic acid .....	-5420 „
Hydrated „ „ .....	-6900 „

but Thomson gives a somewhat higher value for the first of these acids,  $-3596$  cal. at  $19.6^{\circ}$ .

"The heat of dissolution of hydrated racemic acid corrected for the heat of fusion of the water it contains ( $1501$  cal.) is  $-5564$  cal., and the difference between this quantity and the heat of dissolution of the anhydrous acid gives the heat of combination of the latter with its water, this is a negative quantity,  $-111$  cal.; Berthelot's figures give a value not differing very much from this, namely,  $+68$  cal. This value, it must be remembered, refers solely to the heat of combination of the substances in the solid condition, and is independent of any decomposition which they may undergo on dissolution, provided the anhydrous and hydrated acids yield identical solutions, which there is no reason to doubt. Now it is very improbable that the heat of combination of a salt with its water should be a negative quantity or even *nil*, there is indeed but one imperfectly established case in which the experimental results indicate such an occurrence (this vol., p. 77); it is more probable that the negative value is apparent not real. Two explanations may be offered: first, that the so-called hydrated acid does not contain water of crystallisation at all, but an additional  $H_2 + O$  as part of its constitution.\* The general behaviour of the acid, however, tends to discountenance such a view, especially as the molecular volume of the water deduced from Dr. Perkin's results is  $16.8$ , a quantity smaller than that ( $18.8$ ) of  $H_2 + O$ , but similar to some of the values found for water of crystallisation in feebly hydrated salts. The second and more probable explanation is that the hydrated acid is not the hydrate of the anhydrous acid, but that when the former is deprived of its water, the residual constituents enter into a state of more intimate combination, the resulting anhydrous compound being different in constitution from the hydrated compound. The quantity,  $-111$  cal., would thus represent the heat of combination of the water, less that absorbed on the alteration of structure accompanying hydration."

*Ethyl Diaceto-tartrate and Diaceto-racemate.*

Whilst making these experiments on tartaric and racemic acids, I thought it would be of interest to re-examine diacetotartaric and diaceto-racemic ethers in reference to their boiling points. As the temperature at which these boil under ordinary pressure is very high, I preferred to take their boiling points under reduced pressure. They were both found to boil at the same temperature, viz.,  $229-230^{\circ}$

\* If it is not water, the heat of formation of the so-called hydrated acid from the anhydrous acid and water will be  $(7065-5675 =) 1390$  cal., no allowance having to be made for the heat of fusion of any water in the first acid.

under 100 mm. Whilst preparing diaceto-racemic ether I succeeded in obtaining it in well-defined crystals from a solution in light petroleum. Professor Haushöfer has been so kind as to measure them for me, and obtained the following results :—

*Crystalline System Triclinic.*

Colourless, but not transparent, crystals in the form of thick tables or plates, the surfaces of which were insufficient for calculating the morphological elements. They appear to be a combination of the three pairs of surfaces  $(100) = a$ ,  $(010) = b$ , and  $(001) = c$ , parallel to the axial planes with a hemipyramid  $(110) = p$ , the different developments of which are represented by the two figures in the cut. The substance is well characterised by the fact that convergent polarised light on the surface  $b$  gives rise to a uniaxial interference image (somewhat excentric).

Angles measured.

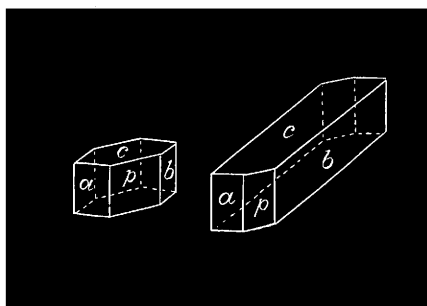
$$(0\bar{1}0)(100) = b' : a = 92^\circ 26'$$

$$(0\bar{1}0)(110) = b' : p = 53 \ 55$$

$$(0\bar{1}0)(001) = b' : c = 96 \ 45$$

$$(100)(001) = a : c = 99 \ 40$$

$$(001)(110) = c : p = 93 \ 34$$



The crystalline form of the diacetotartaric ether has already been measured by M. Ch. Soret, and described in M. Amé Pictet's Dissertation, *Recherches sur les Éthers Tartariques* (Geneva, 1881).

*Acid Tartarate of Silver.*

When preparing the tartarate of silver already referred to, by adding a somewhat strong solution of silver nitrate to a similar solution of tartaric acid, after filtering off the silver salt, and allowing the clear solution to stand for about 24 hours, it was found to contain



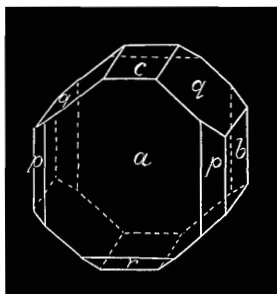
a quantity of beautiful, large, well-defined, brilliant crystals. These were washed with a little cold water, and dried first on bibulous paper and then over sulphuric acid. They gave the following numbers on analysis :—

	I.	II.	III.	IV.
Silver .....	39·27	39·39	39·35	39·28
Water .....	—	—	6·56	6·59

The water was determined by heating at  $100^{\circ}$  and also at  $110^{\circ}$ .

The formula  $C_4H_5AgO_6 \cdot H_2O$  requires silver, 39·27; water, 6·54. Several preparations were made, and Professor Haushöfer was good enough to examine some of the crystals. The following are his results :—

*Crystalline System, Monoclinic;  $a : b : c = 0·7205 : 1 : 0·8685$ ;  
 $\beta = 70^{\circ} 10'$*



Prismatic crystals usually developed in the direction of the orthopinacoid. Crystals of the combinations  $\infty P_{\infty}(100) = a$ ,  $\infty P(110) = p$ ,  $0P(001) = c$ ,  $P_{\infty}(011) = q$ ,  $\infty P_{\infty}(010) = b$ ,  $P_{\infty}(10\bar{1}) = r$ . The surface  $r$  is wanting in most of the crystals. The surfaces  $a$  and  $p$  exhibit a fine vertical striation.

	Measured.	Calculated.
$a : c = (100)(001) =$	$*109^{\circ} 50'$	— —
$p : p = (110)(1\bar{1}0) =$	$*112 \quad 5$	— — (before)
$q : q = (011)(0\bar{1}1) =$	$*101 \quad 52$	— — (above)
$q : a = (011)(100) =$	$105 \quad 1$	$105^{\circ} 16'$
$q : p = (011)(110) =$	$124 \quad 25$	$124 \quad 24$
$r : a = (10\bar{1})(100) =$	$132 \quad 30$	$132 \quad 38$
$q : c = (011)(001) =$	$140 \quad 55$	$140 \quad 56$
$b : q = (010)(011) =$	$129 \quad 5$	$129 \quad 4$
$b : p = (010)(110) =$	$123 \quad 54$	$123 \quad 58$
$a : p = (100)(110) =$	$146 \quad 0$	$146 \quad 2$

This salt when heated with water becomes opaque, and is apparently converted into the ordinary silver tartrate, with separation of tartaric acid, which dissolves some of the salt. If boiled with a strong solution of tartaric acid, it dissolves, and on cooling a white product is first deposited, which afterwards changes into small crystals, consisting apparently of the above acid silver tartrate.

An acid silver racemate appears to be formed in the same way as the tartrates, but it is much less soluble in water, and the crystals are small. I have not been able to obtain it free from the neutral racemate. One specimen of this impure salt gave 45.3 per cent. of silver; this is much lower than the ordinary salt, which requires 59.3, and is good evidence that an acid racemate exists.

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