XXVII.—*The Preparation of Esters from other Esters of the same Acid.*

By T. S. PATTERSON and CYRIL DICKINSON.

SOME time ago we commenced some experiments with the object of preparing methyl ethyl tartrate, a comparison of the rotation of which with that of methyl and of ethyl tartrate could not fail to be interesting. In this work we were encouraged by the hope that methyl ethyl tartrate would prove to be a solid at the ordinary temperature, in which case its purification would present no great difficulty. Our first attempt to prepare it was made by boiling tartaric acid with ethyl alcohol for some hours, then removing the excess of alcohol first by distillation and afterwards by the evaporation of the residue in a vacuum over sulphuric acid. The very viscous substance thus obtained (83 grams) was then dissolved in excess of methyl alcohol (100 grams) and the solution saturated with hydrogen chloride. After removal of the

* This substance, as already noticed by us, was not obtained by these chemists in a pure state, but was regarded by them as a liquid additive product with hypochlorous acid.

alcohol and hydrogen chloride and distillation of the residue under low pressure, the ester obtained had a rotation of $+5.72^\circ$ ($l=2$, $t=17^\circ$), that is to say, consisted of nearly pure methyl tartrate.

The method of preparation was therefore modified. One hundred grams of tartaric acid, after being dried and powdered, were heated in a flask under a reflux condenser with 25 grams of methyl alcohol (the calculated quantity being 22 grams) on a water-bath for about 8 hours. The acid ultimately went into solution. The syrup after cooling was then saturated with hydrogen chloride, after which 33 grams (calc. 31 grams) of ethyl alcohol were added and hydrogen chloride again passed into the solution to saturation and the mixture allowed to stand overnight. The ester obtained after removal of the excess of alcohol and hydrogen chloride and distillation of the residue under reduced pressure was found to boil at $144\text{--}152^\circ$ (bath $190\text{--}210^\circ$, pressure about 12 mm.) and weighed 50 grams. It had a rotation of $+11.14^\circ$ ($l=2$, $t=18^\circ$).

This substance was then redistilled under reduced pressure. It boiled at $157\text{--}158^\circ$ (bath $194\text{--}197^\circ$, pressure 15 mm.). Three fractions were collected, the first being only a small one. The rotation of the second was $+10.9^\circ$ and of the third $+11.0^\circ$ ($l=2$, $t=15^\circ$).

This is approximately intermediate between the rotations of methyl tartrate and ethyl tartrate, so that the substance obtained was probably composed mainly of methyl ethyl tartrate, but it showed no tendency to crystallise nor did any solid separate out when a few crystals of methyl tartrate were added. No further purification could be expected by distillation, and as any other method, except crystallisation, would probably involve more labour than the result would justify and, in addition, be still uncertain, the attempt to prepare this substance in a pure condition has been for the present abandoned.

The result of the first experiment, however, seemed interesting enough to warrant further investigation, since it appeared from it that ethyl hydrogen tartrate had been almost completely converted into methyl tartrate by the action of methyl alcohol and hydrogen chloride.

Now in certain cases the preparation of an ester from the acid and the alcohol presents difficulties which could be overcome by the use of another ester in place of the acid. It is therefore of importance to ascertain whether such a method will yield a pure product.

Preparation of Ethyl Tartrate from Methyl Tartrate.

This was carried out by the method recommended by Fischer and Speier (*Ber.*, 1895, 27, 3252), except that methyl tartrate was substituted for the acid.

Hydrogen chloride was passed into 120 grams of ethyl alcohol until

5 grams had been absorbed; 30 grams of methyl tartrate were then added, and the mixture boiled for about 4 hours under a reflux condenser. The alcohol and hydrogen chloride were then removed, and the ester remaining was distilled in a vacuum. Three fractions were collected, the last of which had an observed rotation of $+8.498^\circ$ ($l=1$, $t=18.6^\circ$). Under the same circumstances, pure ethyl tartrate would have a rotation of $+9.15^\circ$. Since pure methyl tartrate has a rotation of about $+2.8^\circ$ at the same temperature, and we may assume without any great error that the rotation of a mixture of ethyl and methyl tartrates is the sum of the rotations of each constituent separately, it follows that about 90 per cent. of the original methyl tartrate had been converted into ethyl tartrate.

The three fractions of impure tartrate were then mixed and treated anew with 120 grams of ethyl alcohol containing 5 grams of hydrogen chloride. After the alcohol and hydrogen chloride had been removed and the ester fractionated several times, a product was obtained having a rotation of $+9.25^\circ$ ($l=1$, $t=18.8^\circ$), which is exactly the same as that of pure ethyl tartrate. It is thus clear that methyl tartrate may be completely converted into ethyl tartrate by the method described.

The reverse reaction was then tried.

Preparation of Methyl Tartrate from Ethyl Tartrate.

Sixty grams of methyl tartrate were boiled for about 5 hours with 240 grams of methyl alcohol containing 15 grams of hydrogen chloride. On subsequent removal of the alcohol and distillation of the residue in a vacuum, a very viscous liquid was obtained of observed rotation $+6.249^\circ$ ($l=2$, $t=16.5^\circ$), so that about 87 per cent. of the ethyl tartrate had been converted into methyl tartrate. Instead of treating this again with methyl alcohol and hydrogen chloride, a few small crystals of methyl tartrate were added. By next morning, the ester had almost completely solidified, only a small quantity of liquid refusing to crystallise. The whole mass was spread on porous earthenware. When dry, the solid weighed 37 grams. This represents a yield of 71 per cent. on the 60 grams of ethyl tartrate used, which, considering the loss of methyl tartrate incurred in the removal of a first fraction in distillation, and of the portion dissolved in the ethyl tartrate which was absorbed by the porous plate, agrees as well as could be expected with the 87 per cent. found polarimetrically.

The substance obtained was then dissolved in benzene and allowed to crystallise; 22 grams separated out. The crystals were dried on porous earthenware and then distilled. After the first small fraction had been removed, the residue boiled at 150° (bath 175° , pressure about

15 mm.). The distillate soon solidified; its melting point was not very sharp, and lay at 55—56°, which is considerably higher than that usually given, namely, 48°. Its density, relative to water at 4°, was examined at various temperatures, the following figures being obtained:

Temperature	29°	39·8°	58·2°	77·3°
Density	1·3187	1·3074	1·2878	1·2676

These figures plotted relatively to temperature are found to lie upon a straight line. By extrapolation, the density at 20° is found to be 1·3286, Pictet (*Jahresber.*, 1882, 856) giving 1·3284, and at 100°, 1·2433, Pictet giving 1·2500.

As the rotation of methyl tartrate appears to have only been examined at 18°, 20°, and 100°, we have obtained the following figures for the rotation of this specimen at intermediate temperatures, from which a curve may easily be constructed.

t° .	Rotation (100 mm.).	Density.	$[\alpha]_D^{t^{\circ}}$
18·2	+ 2·910°	1·3306	+ 2·19°
12·7	2·250	1·3363	1·68
36·1	4·766	1·3113	3·63
99	8·063	1·2444	6·48
82·1	7·580	1·2624	6·00
79·8	7·475	1·2649	5·91
71·4	7·025	1·2738	5·51
64·2	6·650	1·2815	5·19
58·6	6·305	1·2874	4·90
52·5	5·958	1·2937	4·61
28·1	4·030	1·3198	3·05

Since, from the experiments described above, it appears that methyl tartrate can be converted into pure ethyl tartrate, and *vice versa*, by Fischer's method, and as the first experiment mentioned shows that the same change can be accomplished by the saturation method at a low temperature, it seems probable that any other ester may be obtained in a pure condition by an analogous process, it being best, of course, to choose as starting point a substance whose physical condition is different from that of the ester which it is desired to prepare.

YORKSHIRE COLLEGE,
LEEDS.