The effect of the dissolved non-electrolyte is therefore quite considerable, and greater than that produced by many of the alkali salts investigated. It apparently depends upon the specific character of the dissolved substance, and its variation with the concentration is the same as that found for the alkali salts.

In the case of non-electrolytes as well as of electrolytes, therefore, Dalton's law is not obeyed, and the changes which are apparently produced in the character of the solvent remain to be explained.

In our former paper, no account was taken of the physical action of the dissolved material, but the alteration of distribution coefficient caused by this is negligibly small in the case of copper, zinc, cadmium, and nickel salts compared with that due to the formation of complexes. The physical action in these cases is that of the complex compound existing in solution, and it is impossible to accurately estimate the value of this. Even if the physical action be as great as that of any of the salts of the alkali metals examined, the conclusions arrived at in our previous communication would not be altered, whilst the actual numbers expressing the ratio of the ammonia combined per molecule of salt would be increased by not more than 2—3 per cent.

THE YORKSHIRE COLLEGE,
LEEDS.

LV.—*Influence of a Heterocyclic Group on Rotatory Power; the Ethyl and Methyl Esters of Dipyromucyltartaric Acid.*

By PERCY F. FRANKLAND and FRANCIS W. ASTON, late
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It has been shown by one of us that there is a great qualitative and quantitative difference in the rotatory effect of fatty acid groups (acetyl, chloracetyl, dichloracetyl, trichloracetyl, propionyl, phenacetyl, &c.) on the one hand, and of aromatic acid groups (benzoyl and toluyl) on the other, as exemplified by the rotatory power of the esters of the various diacyl tartaric and glyceric acids, and of the several acyl malic acids. The following table illustrates the difference in question :

Methyl glycerate ¹	$[\alpha]_D^{15^\circ}$ — 4·80°	$[M]_D^{15^\circ}$ — 5·76°
„ diacetylglycerate ²	— 12·04	— 24·56
„ di-monochloracetylglycerate ³	— 12·91	— 36·1

¹ P. Frankland and Macgregor, Trans., 1893, 63, 513.

² *Ibid.*, 1422.

³ P. Frankland and Patterson, Trans., 1898, 73, 197.

Methyl di-dichloroacetyl glycerate ¹	$[\alpha]_D^{15^\circ} - 13.96^\circ$	$[M]_D^{15^\circ} - 47.7^\circ$
„ di-trichloroacetyl glycerate ¹ ...	- 14.20	- 58.3
„ dipropionyl glycerate ²	- 10.97	- 25.45
„ diphenacetyl glycerate ²	$[\alpha]_D^{14.5^\circ} - 16.06$	$[M]_D^{14.5^\circ} - 57.17$
„ dibenzoyl glycerate ²	$[\alpha]_D^{15^\circ} + 26.89$	$[M]_D^{15^\circ} + 88.20$
„ di- <i>o</i> -toluyl glycerate ³	$[\alpha]_D^{20^\circ} + 20.19$	$[M]_D^{20^\circ} + 71.9$
„ di- <i>m</i> -toluyl glycerate ³	+ 26.40	+ 94.0
„ di- <i>p</i> -toluyl glycerate ³	+ 41.21	+ 146.7
	$[M]_D^{20^\circ}$	$[M]_D^{100^\circ}$
Diethyl tartrate	+ 15.86°	+ 27.6°
„ diacetyl tartrate ⁴	+ 9.9	+ 18.3
„ di-monochloroacetyl tartrate ⁵ ...	+ 25.5	+ 39.4
„ di-dichloroacetyl tartrate ⁵	+ 65.8	+ 68.9
„ diphenacetyl tartrate ⁴	+ 79.2	+ 39.9
„ dibenzoyl tartrate ⁶	- 247.1	- 251.6
„ di- <i>o</i> -toluyl tartrate ⁶	- 266.5	- 241.9
„ di- <i>m</i> -toluyl tartrate ⁶	- 306.3	- 281.7
„ di- <i>p</i> -toluyl tartrate ⁶	- 484.4	- 397.7

The qualitative difference in rotatory effect between the fatty and aromatic acid radicles is similarly manifested in the following series of the derivatives of diethyl malate:

Diethyl malate ⁸	$[\alpha]_D^{20^\circ} - 10.44^\circ$	$[M]_D^{20^\circ} - 19.84^\circ$
„ acetylmalate ⁷ ..	- 22.52	- 52.25
„ propionylmalate ⁷	- 22.20	- 54.61
„ butyrylmalate ⁷	- 22.22	- 57.77
„ isobutyrylacetate ⁷	- 21.99	- 57.17
„ isovalerylmalate ⁷	- 22.07	- 60.47
„ bromoacetylmalate ⁷	- 22.48	- 69.91
„ benzoylmalate ⁸	$[\alpha]_D^{21^\circ} - 3.87$	$[M]_D^{21^\circ} - 11.38$
„ <i>o</i> -toluylmalate ⁸	- 6.25	- 19.25
„ <i>m</i> -toluylmalate ⁸	- 4.67	- 14.38
„ <i>p</i> -toluylmalate ⁸	$[\alpha]_D^{20^\circ} - 0.22$	$[M]_D^{20^\circ} - 0.68$

Similarly, in the derivatives of ethyl sarcolactate, we find the same relations exhibited (P. Frankland and Henderson, Proc., 1895, 11, 54):

¹ P. Frankland and Patterson, Trans., 1898, **73**, 197.

² P. Frankland and Macgregor, Trans., 1896, **69**, 117.

³ P. Frankland and Henry Aston, Trans., 1899, **75**, 493.

⁴ McCrae and Patterson, Trans., 1900, **77**, 1098, 1103.

⁵ P. Frankland and Patterson, Trans., 1898, **73**, 189, 191.

⁶ P. Frankland and Wharton, Trans., 1896, **69**, 1591.

Walden, *Zeit. physikal. Chem.*, 1895, **17**, 245—266.

⁸ P. Frankland and Wharton, Trans., 1899, **75**, 337—347.

Ethyl sarcosylactate	$[\alpha]_D^{15^\circ} - 8.66^\circ$	$[M]_D^{15^\circ} - 10.22^\circ$
„ acetyllactate.....	- 41.47	- 66.35
„ benzoyllactate	+ 22.22	+ 49.33

The lactic acid from which these compounds were prepared was afterwards found to be partially racemised, so that the absolute values given for the rotations are, of course, too small, but the ratios are probably, and the qualitative relations certainly, correct.

The monoacyl derivatives of diethyl tartrate form another series in which a comparison of the rotatory effect of the fatty and aromatic acid radicles has been rendered possible through the recent preparation of the monoacetyl and monophenacetyltartrates by McCrae and Patterson. Thus:

	$[M]_D^{20^\circ}$	$[M]_D^{100^\circ}$
Diethyl tartrate	+ 15.86°	+ 27.6°
„ monoacetyltartrate ¹	+ 23 1	+ 33.5
„ mono-mono-chloracetyltartrate ² ..	+ 32.3	+ 48.9
„ mono-trichloracetyltartrate ³ ...	+ 54.7	+ 61.7
„ monophenacetyltartrate ¹	+ 98.5	+ 77.8
„ monobenzoyltartrate ⁴	+ 61.4	+ 54.8
„ mono- <i>o</i> -toluyltartrate ⁴	+ 38.2	+ 35.3
„ mono- <i>m</i> -toluyltartrate ⁴	+ 44.0	+ 40.8
„ mono- <i>p</i> -toluyltartrate ⁴	+ 63.5	+ 51.2

This series, in which the qualitative effect of all the acid radicles, both fatty and aromatic, appears similar, consisting as it does in raising the initial rotation of the diethyl tartrate, has been recently discussed by McCrae and Patterson (*loc. cit.*), who point out that the qualitative difference between the rotatory effect of the two classes of acid radicles only becomes apparent when the effect of introducing one and two acid radicles respectively is compared. Thus the introduction of a second fatty acid group (including phenacetyl) causes only a comparatively small diminution in the dextrorotation of the monoacyl compound, whilst the introduction of the second aromatic acid radicle (benzoyl and toluy) gives rise to such an enormous diminution in the dextrorotation that the resulting diacyl compound is powerfully lævorotatory. Judged by the standard of the influence of temperature on the rotations, it is seen that all the fatty acyl compounds of this series, as of the other, have their rotation increased by rise of tempera-

¹ McCrae and Patterson, *Trans.*, 1900, **77**, 1096—1110.

² P. Frankland and Turnbull, *Trans.*, 1898, **73**, 204. It should be noted that the preparation was not quite pure, and that the real rotation is doubtless greater.

³ P. Frankland and Patterson, *Trans.*, 1898, **73**, 186.

⁴ P. Frankland and McCrae, *Trans.*, 1898, **73**, 307—329.

ture, whilst the aromatic acyl (including phenacetyl) compounds have their rotation diminished by rise of temperature. In the series of the diacyl ethyl tartrates, there is in this respect a curious, and so far as we are aware, unique anomaly presented by diethyl benzoyltartrate, the rotation of which attains a maximum for a temperature of about 60° (P. Frankland and Wharton, Trans., 1896, 69, 1587).

The marked qualitative contrast in rotatory effect between the isomeric phenacetyl and toluyll groups is doubtless to be referred to their structural difference, the carbonyl group being attached to the benzene ring directly in the case of the toluyll, and only indirectly in the case of the phenacetyl group. It becomes, therefore, of interest to know whether other cyclic groups besides the benzene ring have the power of conferring a rotatory effect qualitatively similar to that of the benzoyl and toluyll radicles.

With the view of determining this point, we have investigated the rotatory effect of the pyromucyl group, in which the carbonyl is directly attached to the heterocyclic furfuran ring :

In connection with this investigation, we have introduced advantageous modifications in the methods of preparing pyromucic acid and pyromucyl chloride.

By means of the latter we have prepared diethyl and dimethyldipyromucyltartrates, but have so far only determined the rotatory power of the former.

The rotatory power of diethyl dipyromucyltartrate was found to be almost exactly intermediate between those of diethyl dibenzoyltartrate and diethyl di-*m*-toluylltartrate, namely, $[\text{M}]_{\text{D}}^{25} = -266.5^{\circ}$. The rotatory effect of the heterocyclic furfuran ring is thus shown to be qualitatively similar to, and quantitatively of the same order as, that of the homocyclic benzene ring.

The qualitative similarity in rotatory effect of the pyromucyl, benzoyl, and toluyll groups is further exemplified by the fact that all the compounds referred to which contain these groups have their rotation diminished by rise of temperature, whilst those containing the fatty acid radicles* increase in rotatory power as the temperature rises; in

* In respect of the effect of temperature, the dichloroacetyl and trichloroacetyl groups approximate to the phenacetyl radicle thus the rotation of ethyl di-dichloroacetyl tartrate is almost insensitive to temperature, whilst methyl di-dichloroacetyl tartrate has its rotation slightly diminished by rise of temperature; ethyl di-trichloroacetyl glycerate, again, has its rotation slightly diminished by rise of temperature.

this respect, however, it should be noticed that the phenacetyl group resembles the other aromatic and not the fatty groups. In fact the influence of temperature on rotatory power appears to differentiate between those compounds which contain and those which do not contain a cyclic group. This is at any rate true so far as the derivatives of glyceric and tartaric acids are concerned, and for these alone has this influence of temperature on rotation been fully investigated. In the case of malic acid, the aromatic acid derivatives increase in rotatory power with rise of temperature, but the influence of temperature on the fatty acid derivatives has not yet been determined.

We have in the course of this investigation devised a new method of continuous automatic esterification, by means of which we have prepared the methyl and ethyl tartrates which were required; this we think may be found of wide application in the preparation of esters.

EXPERIMENTAL.

Preparation of Pyromucic Acid.—The method first adopted was that described by Volhard (*Annalen*, 1891, 261, 380), which consists in acting on furfural with alkaline permanganate. This, although yielding good results with small quantities, was found to be extremely laborious when a large amount of the acid was to be prepared in one operation. Thus the pyromucic acid is formed in an extremely dilute solution, and its separation from the potassium chloride with which it is mixed cannot be effected by crystallisation, as both appear to have much the same solubility. After numerous modifications had been tried, we ultimately found the following method the most satisfactory.

One hundred and fifty grams of calcium hydroxide are placed in a large open vessel capable of holding about 5 litres; half a litre of water is poured over the lime, a handful of ice and then 100 grams of furfural are added, the magma being thoroughly mixed by stirring. One hundred and ten grams of potassium permanganate, dissolved in 2 litres of water, are now added very slowly at first and more rapidly towards the end, vigorous stirring being maintained throughout the whole operation, which occupies about 30 minutes. Ice is added from time to time, the temperature being thus maintained at about 10°, and on no account being allowed to rise above 20°. The coffee-coloured liquid is now heated for a short time on a bath of boiling water to complete the reaction and facilitate the subsequent filtration. The whole is now filtered hot with the aid of a pump, the manganese sludge being washed with a little boiling water and well pressed with a spatula.

The filtrate, containing calcium hydroxide, and calcium and potassium pyromucates, is placed in a large evaporating basin and hydrochloric

acid added in sufficient quantity to just set free the whole of the pyromucic acid, congo-paper being used as an indicator of free mineral acid. The liquid is now evaporated on the water-bath until the crystals of pyromucic acid appearing around the edge are only with difficulty redissolved by the hot mother liquor. After rapid filtration, the hot liquid is set aside to cool, the pyromucic acid separating out in brown needles which are mixed with a little potassium chloride. These crystals, when filtered off and washed slightly, are pure enough for transformation into pyromucyl chloride by the process described below.

The mother liquor is repeatedly extracted with ether, the ethereal extracts dried over fused sodium sulphate, and the pyromucic acid obtained by evaporation as a brown liquid which solidifies on cooling to a yellowish, crystalline mass.

In this manner, from 100 grams of furfural 60—70 grams of pyromucic acid were obtained by crystallisation from the aqueous, and 10—20 grams from the ethereal liquid, or a yield of 70—80 grams altogether.

Preparation of Pyromucyl Chloride.—This was at first prepared from the acid by heating with phosphorus pentachloride to 100°, and distilling the acid chloride at atmospheric pressure (Liès-Bodart, *Annalen*, 1856, 100, 325), but the yield by this method was extremely poor, most of the acid being apparently rapidly decomposed by the pentachloride.

Excellent results were, however, obtained by means of the following method, in which the phosphorus pentachloride is used in chloroform solution and is applied in an apparatus specially constructed for the purpose (Fig. 1).

In the flask (*B*) is placed about twice the quantity of phosphorus pentachloride theoretically required together with about 200 c.c. of pure dry chloroform; the pyromucic acid is placed in the bulb of the extraction apparatus (*A*), the lower extremity of which is plugged with glass wool, whilst the upper extremity is provided with a condenser (*D*) of the particularly compact type devised by one of us (*Chem. News*, 1899, 79, 217). The flask (*B*) is heated by means of a water-bath, the manner in which the apparatus acts being obvious, and the heating is continued until the evolution of hydrogen chloride has almost ceased. Any mineral matter (potassium chloride) with which the pyromucic acid may be mixed remains on the glass wool plug owing to its insolubility in the chloroform.

After the reaction is complete (about 6 hours), the chloroform is

FIG. 1.

distilled off on the water-bath from the flask (*B*), the residue left being then poured into a fractionating flask and submitted to vacuum distillation. Nearly all the phosphorus oxychloride passes over below 45° under 10 mm. pressure, the receiver being then changed and all the distillate which will come off when the flask is heated in a bath of boiling water is collected. This is refractionated to get rid of phosphorus oxychloride. The boiling point of pure pyromucyl chloride is 66° under 10 mm. pressure; it is a colourless, strongly refracting liquid, rapidly decomposing in strong light, and its vapour has an extremely irritating effect on the eyes. It is almost unacted on by cold water and even with boiling water the action is very slow, much slower than in the case of benzoyl chloride and water.

This method gives a practically quantitative yield of pyromucyl chloride.

New Automatic Method for Preparation of Esters of Tartaric and other Non-volatile Acids.

We have found the following method of great advantage in preparing dimethyl and diethyl tartrates, and it may doubtless be of much wider utility. The arrangement of the apparatus will be sufficiently obvious from the accompanying sketch (Fig. 2).

FIG. 2.

In the flask (*A*) are placed 100—200 grams of the acid (it need neither be specially dried nor powdered), which is then just covered with the alcohol. In the flask (*B*) is placed about one and a-half times as much of the alcohol as is required for the esterification of the whole of the acid taken; this flask (*B*) also contains a quantity of solid desiccating agent (we have always employed fused potassium carbonate). The whole apparatus forms a closed system which only com-

municates with the outer air through the open end (*G*) of the tube (*E*) which is fitted to the lower extremity of the condenser tube.

The flask (*A*) is immersed up to the neck in an oil-bath which is slowly heated to 130°, and as soon as most of the alcohol in (*A*) has distilled through the condenser (*C*) into (*B*), the latter is placed in a water-bath which is heated to boiling. The vapour from the boiling alcohol in (*B*) passes up the fractionating column (*D*) and bubbles through the mixture of acid and alcohol in (*A*), whilst the water formed in the esterification process passes along with alcohol vapour from (*A*) through the condenser and to the bottom of (*B*), where it is absorbed by the dehydrating agent. The interposition of the fractionating column (*D*) of course assists in the dehydration of the alcohol vapour passing from (*B*) to (*A*). Owing to the rigidity of the apparatus, a single clamp (not shown in the figure) on the condenser is sufficient for the support of the whole.

For the esterification of the quantity of tartaric acid by means of methyl or ethyl alcohol as indicated above, we have found that about 10 hours are requisite, and the operation can be temporarily interrupted at any time. The mixture of alcohol and ester in (*A*) is finally poured into a fractionating flask, and the two separated by vacuum distillation. Excellent yields amounting to 70–80 per cent. of the calculated quantity were thus obtained in the case of dimethyl and diethyl tartrates.

Thirty grams of diethyl tartrate and 75 grams of pyromucyl chloride (free from phosphorus oxychloride) were placed in a flask provided with a reflux air condenser, to the open upper extremity of which a calcium chloride tube was attached. The mixture was heated by means of an oil-bath to 155°, at which temperature reaction, accompanied by evolution of hydrogen chloride, took place. The temperature was finally raised to and maintained at 160–170° until this gas ceased to be evolved. Much decomposition had apparently taken place as a quantity of tarry matter was visible. On cooling overnight crystals separated out, which when filtered off were found to dissolve in a dilute solution of sodium carbonate, and were evidently pyromucic acid. The filtrate (a dark treacle) was dissolved in ether (chloroform was also sometimes used) and agitated for a day and a half with a solution of sodium carbonate on a shaking machine. The ether solution was then separated, dried with fused sodium sulphate, and

evaporated. The residue, which smelt very faintly of pyromucyl chloride, was dissolved in methylated spirit and decolorised by boiling with animal charcoal. The alcohol was distilled off and the residue poured into a dish and placed in a vacuum desiccator to crystallise. After drying the crystals on a porous plate, the yield of crude product did not amount to more than 10 grams. This was recrystallised from carbon disulphide until the melting point, 76° , was constant; the crystals were colourless, odourless, very soluble in alcohol or ether, a little less so in chloroform, benzene, or carbon disulphide, and quite insoluble in light petroleum. From a chloroform solution, on slow evaporation, the ester separated in long, flat plates over half an inch in length.

0.2203 gave 0.4435 CO_2 and 0.0975 H_2O . $\text{C} = 54.90$; $\text{H} = 4.92$.

$\text{C}_{18}\text{H}_{18}\text{O}_{10}$ requires $\text{C} = 54.82$; $\text{H} = 4.57$ per cent.

The substance could not be maintained in the liquid state below its melting point, hence all the density and polarimetric determinations were made above 76° .

$d_{99.5^{\circ}/4^{\circ}} = 1.1914$; $109.5^{\circ}/4^{\circ} = 1.1831$; $140^{\circ}/4^{\circ} = 1.1524$.

Rotation of diethyl dipyromucyltartrate.

Temp.	α_D , $l = 0.4991$.	α_D , $l = 1$.	$[\alpha]_D$.	$[M]_D$.
99.5°	-40.23°	-80.60°	-67.65°	-266.54°
109.5	-39.22	-78.58	-66.42	-261.69
140	-34.83	-69.78	-60.55	-238.57
$[20$	(calculated)		-81.56	$-321.44]$

The values for the specific rotation at the three observed temperatures, when plotted on a rotation-temperature diagram, lie practically on a straight line, and the value for 20° has therefore been calculated on the assumption that the influence of temperature on the rotation is uniform.

Rotation of diethyl dipyromucyltartrate in ethyl alcohol solution.

($l = 2.998$ *dec.*)

Weight of solution, grams.	Weight of substance, gram.	Grams substances in 100 grams solution.	$d_{20^{\circ}/4^{\circ}}$.	$\alpha_D^{20^{\circ}}$.	$[\alpha]_D^{20^{\circ}}$.	$[M]_D^{20^{\circ}}$.
10.2325	0.0515	0.503	0.7939	-1.18°	-98.54°	-388.2
10.2561	0.1191	1.161	0.7966	-2.43	-87.62	-345.2
8.7215	0.1700	1.949	0.7993	-3.97	-85.00	-334.9
17.5542	0.5140	2.928	0.8004	-6.09	-86.66	-341.4
10.5345	0.5200	4.936	0.8078	-10.38	-86.82	-342.1

Thus the specific rotation in alcoholic solution at first very rapidly diminishes with increase in concentration from 0.50 to 1.16 per cent., after which, to 4.94 per cent., it remains practically constant. The rotation at higher concentrations could not be investigated owing to the limited solubility of the compound. The rotation in alcoholic solution, from 1.95 to 4.94 per cent., approximates closely to the rotatory power of the liquid compound calculated for 20° ($[\alpha]_D^{20} - 81.56^{\circ}$).

Dimethyl Dipyromucyltartrate.

Dimethyl dipyromucyltartrate was prepared in the same way as the ethyl ester. It was crystallised from carbon disulphide until of constant melting point 131° .

0.3322 gave 0.6385 CO_2 and 0.1178 H_2O . C = 52.41 ; H = 3.94.

$\text{C}_{16}\text{H}_{14}\text{O}_{10}$ requires C = 52.46 ; H = 3.83 per cent.

Molecular volume of diethyl dipyromucyltartrate.

Taking $d\ 15^{\circ}/4^{\circ} = 1.2728$.

$$\text{Mol. vol.} = \frac{394}{1.2728} = 309.5.$$

Calculated from Traube's formula (*Ber.*, 1895, **28**, 2724, 2924):

$\text{C}_{18} = 9.9 \times 18 = 178.2$; $\text{H}_{18} = 3.1 \times 18 = 55.8$; $\text{O}_{10} = 5.5 \times 10 = 55$;

Co-volume = 25.9 ; mol. vol. = 314.9.

For compounds containing an ethylene linking, Traube deducts 1.7 ; for a hexamethylene ring, 8.1 ; for a benzene ring, 13.2 (that is, 8.1 for the 6-carbon ring, and $3 \times 1.7 = 5.1$ for the three ethylene unions). The influence of the furfuran ring on molecular volume has not yet been determined.

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