

### 239. Acid Salts of Monobasic Organic Acids. Part I.

By JOHN D. M. ROSS and THOMAS J. MORRISON.

SOME acid salts of mandelic acid are already known. McKenzie (J., 1899, **75**, 969) mentions the existence of barium hydrogen mandelate, and McKenzie and Walker (J., 1922, **121**, 356) describe potassium and sodium hydrogen mandelates. In the present communication the existence of acid salts of *r*-mandelic acid has been investigated by a study of the solubility curves for some systems of the type mandelic acid-metal mandelate-water.

Many acid salts of monobasic organic acids have already been described. In some cases they have been investigated by a study of the freezing-point diagrams for the systems acid-metal salt. Since mandelic acid decomposes at temperatures only slightly above its melting point, such an investigation was impracticable in the present instance.

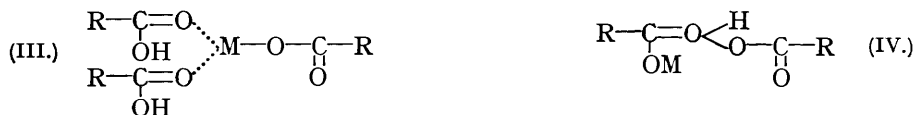
Acid salts of formic acid have been studied by Groschuff (*Ber.*, 1903, **36**, 1783) and by Kendall and Adler (*J. Amer. Chem. Soc.*, 1921, **43**, 1470), using the freezing-point method. The last authors applied the same method to the study of acid salts of acetic acid, some of which had been reported by Lescoeur (*Ann. Chim.*, 1893, **23**, 245; *Compt. rend.*, 1874, **78**, 1044; *Bull. Soc. chim.*, 1875, **24**, 517), Melsens (*Compt. rend.*, 1844, **19**, 611), Dukelski (*Z. anorg. Chem.*, 1909, **62**, 114), and Dunningham (J., 1912, **101**, 431).

Various acid salts of the following acids are on record: long-chain fatty acids (Ekwall and Mylius, *Ber.*, 1929, **62**, 1080; Ekwall, *Z. anorg. Chem.*, 1933, **210**, 337; *Ber.*, 1933, **66**, 546), benzoic acid (Farmer, J., 1903, **83**, 1440; Landrieu, *Compt. rend.*, 1920, **170**, 1452; 1920, **171**, 1066; Pfeiffer and Nakatsuka, *J. pr. Chem.*, 1933, **136**, 241), substituted benzoic acids (pyridine salts; Pfeiffer, *Ber.*, 1914, **47**, 1580), salicylic acid (Hoitsema, *Z. physikal. Chem.*, 1898, **27**, 312); and acid salts of acetic acid with rare-earth metals have been investigated by Kotovski and Lehl (*Z. anorg. Chem.*, 1931, **199**, 185).

Pfeiffer (*loc. cit.*) suggests two possible formulæ, (I) and (II), for acid salts of monobasic acids, in both of which the carbonyl group is assumed to exert a co-ordination valency.



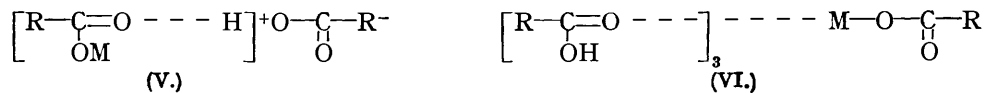
He prefers the second formula on the ground that more complex acid salts can be readily represented as in (III). Kendall (*e.g.*, *J. Amer. Chem. Soc.*, 1914, **36**, 1222, 1722; 1915, **37**, 2498; 1916, **38**, 1712) has shown that if the acidic property of the carboxyl



group is sufficiently suppressed, the basic nature of the carbonyl group becomes evident, and additive or oxonium compounds arise. The normal salt of an acid with a metal of

strongly basic nature will thus exhibit basic properties, and combine with the acid itself to form an acid salt. The formula suggested for such a salt is (IV).

This type of formula was also suggested by Farmer (*loc. cit.*). In accordance with later electronic views, it may be written as (V), which is practically identical with



(I). The most obvious disadvantage of this method of formulation is the difficulty of representing more complex acid salts containing more than one molecule of acid, which are formed in many cases. It is to be expected that the basic properties shown by the original normal salt will exist only to a slight extent, or not at all, in the acid salt, so that there should be difficulty in adding on another molecule of acid, and the most stable acid salt should be the 1 : 1 salt. We have found, however, that in the cases of potassium and sodium mandelates, the 3 : 1 salts are both stable in contact with water, while the 1 : 1 potassium acid salt is unstable.

Pfeiffer's formula (II) is consistent with these facts, and the 2 : 1 and the 3 : 1 salt are readily formulated as (III) and (VI) respectively on the same principles, by assuming that the metal takes up two or three pairs of electrons from the carboxyl oxygen atoms of the acid molecules. This is not possible in the case of hydrogen, which can form, in general, only one such co-ordination link. This also suggests an explanation of the fact that the most complex acid salt formed by the interaction of a normal salt with a monobasic organic acid is the 3 : 1 salt,  $3\text{R}\cdot\text{CO}_2\text{H}\cdot\text{R}\cdot\text{CO}_2\text{M}$ . By formation of three such co-ordination linkages, together with the linkage to the acid radical originally present (assumed to be covalent), an octet of electrons is completed round the metallic ion, thus definitely limiting the number of such acid salts.

Acid salts of the formulæ (II), (III), and (VI) may be regarded as complex acids, the hydrogen atoms being replaceable to give double salts of the type (I; with M instead of H). McKenzie (*loc. cit.*) has isolated a zinc ammonium mandelate which is probably of this type. Other examples are Purdie's zinc ammonium lactate and double salts of benzoic acid isolated by Pfeiffer and Nakatsuka (*loc. cit.*). The evidence is thus definitely in favour of structures of the types (II), (III), and (VI), in which co-ordination between oxygen and a metallic radical takes place.

The formation and the stability of such a link will depend on the nature of the metallic radical. It has been shown by Kendall and Adler (*loc. cit.*) that the electrode potential may be correlated with the extent of compound formation. Other factors, however, such as ionic size, valency, and the solubility of the normal salt may also exert some influence. In order to compare the effect of the metals in this respect, we may examine the influence of the normal salts on the solubility of mandelic acid. In every case the solubility of the acid is increased by the addition of normal salt, in agreement with the fact that acid salts can be isolated in each of the cases considered. For comparative purposes we have plotted concentrations of mandelic acid against those of metal mandelate (both as g.-equivs. per 100 g. of water) in Fig. 1. In dilute solutions of metal mandelates the slope of the curve may be taken as a measure of the extent of compound formation. The results which are tabulated below indicate that the influence of the metals is in the following order:  $\text{K} > \text{Ba} > \text{Li} > \text{Sr} > \text{Na}$ .

*Increase in solubility of mandelic acid in presence of normal mandelates.*

Solubility of $\text{C}_8\text{H}_8\text{O}_3$ in $\text{H}_2\text{O} = 0.134$ g.-equiv. per 100 g. $\text{H}_2\text{O}$ .					
Salt added .....	K	Na	Li	Ba	Sr
Concn. of salt added .....	0.0052	0.0114	0.0127	0.0062	0.0031
Solubility of acid .....	0.144	0.144	0.155	0.145	0.138
Gradient .....	2.0	0.9	1.7	1.8	1.3

The "gradient" represents the ratio of the increase in the solubility of mandelic acid to the amount of metal mandelate added. The figures for the calcium salt are not included,

as it was found that the 1 : 1 salt was formed at such low concentrations of the normal salt that no reliable data could be obtained for it. The values for the electrode potentials are as follows : Li, 2.96; K, 2.92; Sr, 2.8; Ba, 2.8; Na, 2.71, the values for barium and strontium being less accurate than those for the other metals. Allowing for the experimental errors, we see that the gradients for potassium, strontium, and barium are approximately equal, and so are the electrode potentials. Sodium, with the smallest electrode potential, gives the smallest gradient. Lithium, with the highest electrode potential, might be expected to give the greatest gradient, whereas the slope is less than that for potassium and barium. The anomalous position of lithium has been noted before (Kendall, *loc. cit.*), and a possible explanation is to be found in the fact that the lithium ion, being the smallest of those of the alkali metals, is most strongly hydrated in solution, and this hydration limits the number of co-ordination linkages which the ion can form. Lithium also shows anomalous behaviour in that it alone of the alkali metals forms only one acid salt, which is stable only in solutions containing excess of mandelic acid.

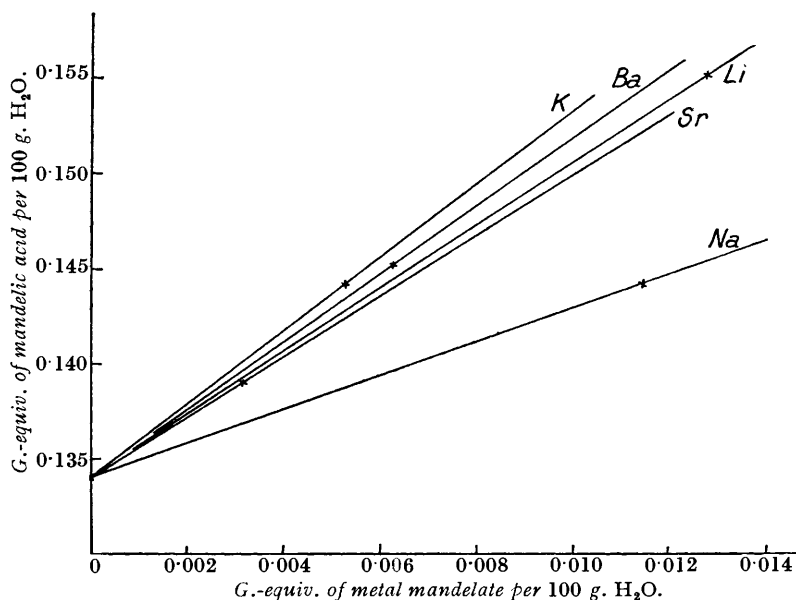


FIG. 1.

In the experiments here described we find the more soluble of the normal metal mandelates forming more than one acid salt, while the less soluble form only one such salt. We hope that further investigations will enable us to decide if this agreement is of real significance.

#### EXPERIMENTAL.

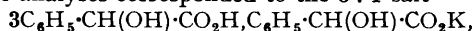
In the following experiments racemic substances were used.

*Mandelic Acid.*—This acid was purified by recrystallisation either from water or from benzene-acetone (90 : 10).

*Potassium Mandelate.*—This salt was prepared from mandelic acid repeatedly, the following being typical. 100 G. of acid and 50 g. of potassium carbonate were dissolved in 300 c.c. of water, and the solution evaporated to dryness on the water-bath. The salt was washed with ether, and dried at 90° in a vacuum. The solid (130 g.) was recrystallised from a mixture of 1000 c.c. of acetone and 100 c.c. of methyl alcohol, the solution being kept in the ice-chest over-night, and the first crop, white rosettes, removed, washed, and dried as before. The mother-liquor was evaporated to half its bulk, cooled in the ice-chest, and the further crop treated as before, giving a total yield of 80 g. The salt separating contained a considerable quantity of acetone, and prolonged drying (several hours) was necessary to remove this.

*Acid salts.* A solution of 5 g. of mandelic acid in 25 c.c. of water was neutralised with

concentrated potassium hydroxide. A further 5 g. of acid were added, and the solution warmed, filtered, and cooled. The solid was dried in a vacuum at 60°, and contained 59.8% mandelic acid. On recrystallisation from water the acid content rose to 71.0%, unchanged by further recrystallisation. As the analyses corresponded to the 3 : 1 salt



an attempt was made to prepare this salt from aqueous solution.

15.2 G. (4 equiv.) of acid and 1.7 g. (1 equiv.) of potassium carbonate were dissolved in 70 c.c. of water, and the solution warmed to remove carbon dioxide. The resulting salt was dried in a vacuum and then contained 69.9% of acid, raised on recrystallisation to 70.8% ( $3C_8H_8O_3, C_8H_7O_3K$  requires  $C_8H_8O_3$ , 70.6%).

The 1 : 1 salt was obtained by dissolving 4 g. of potassium mandelate and 4 g. of the acid in 15 c.c. of absolute alcohol by gentle warming (Found :  $C_8H_8O_3$ , 44.4. Calc. for  $C_8H_8O_3, C_8H_7O_3K$  :  $C_8H_8O_3$ , 44.4%).

**Sodium Mandelate.**—This salt was prepared by neutralising a solution of mandelic acid with an equivalent quantity of sodium carbonate, and evaporating the solution to dryness on the water-bath. It was recrystallised from alcohol, and dried in a vacuum.

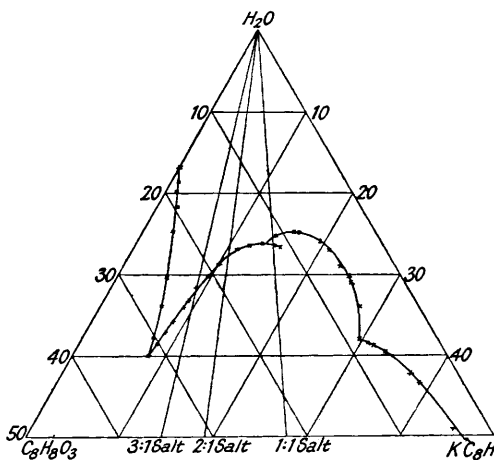


FIG. 2.

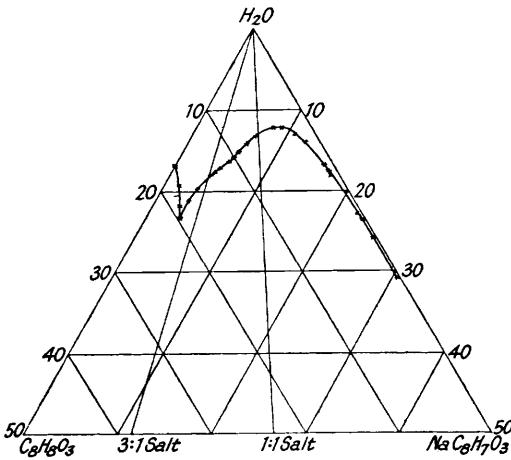


FIG. 3.

**Acid salt.** 20 G. (2 mol.) of the acid and 3.5 g. (0.5 mol.) of sodium carbonate were dissolved in water, and the solution evaporated on the water-bath until crystallisation began. The solid contained 46.7% of free acid, unchanged on recrystallisation (Calc. for  $C_8H_8O_3, C_8H_7O_3Na$  :  $C_8H_8O_3$ , 46.6%), and was identical with the compound obtained by the addition of (–) malic acid to a solution of sodium mandelate (McKenzie and Walker, *loc. cit.*).

**Lithium, Barium, and Calcium Mandelates.**—These salts, prepared in an analogous manner to the sodium salt, were recrystallised from water and dried in a vacuum.

**Strontium Mandelate.**—This salt was similarly prepared, except that the hydrated hydroxide was used.

1. **The System Mandelic Acid–Potassium Mandelate–Water.**—The solubility determinations were carried out in a gas-heated thermostat adjusted to  $25^\circ \pm 0.1^\circ$ . The apparatus was a modification of that designed by Campbell (J., 1930, 179). The solutions were stirred in flat-bottomed specimen tubes ( $3'' \times 0.5''$ ) until equilibrium was attained, and filtered in the thermostat. In many cases it was found convenient to heat the solutions till all solid had dissolved, and then allow the solid phase to separate at  $25^\circ$ . In all solubility determinations 5 c.c. of water were used.

The solutions were analysed as follows. A weighed portion was titrated with accurately standardised sodium hydroxide to determine the concentration of mandelic acid. Another weighed portion was evaporated in a platinum crucible, and ignited with sulphuric acid, the metal being estimated as sulphate.

For its analysis, the solid phase was removed from the filter, and pressed on a porous plate, its acid content being determined by titration.

The results for the system are collected below, and the corresponding curve is given in Fig. 2.

$C_8H_8O_3$ , %	$C_8H_7O_3K$ , %	$H_2O$ , %	Solid phase.	$C_8H_8O_3$ , %	$C_8H_7O_3K$ , %	$H_2O$ , %	Solid phase.
16.9	0.0	83.1	Acid.	11.6	15.0	73.4	3 : 1 Salt.
17.8	0.8	81.4		11.0	15.6	73.4	
18.6	1.1	80.3		8.4	16.5	75.1	
19.5	2.4	78.1		11.4	14.5	74.1	
21.6	3.8	74.6		8.6	16.2	75.2	
25.0	5.5	69.5		6.5	19.5	74.0	
27.1	6.7	66.2		6.1	21.0	72.9	
30.1	7.7	62.2		6.0	23.1	70.9	
31.7	8.3	60.0		5.5	24.7	69.8	
30.1	8.5	61.4		5.7	25.3	69.0	
28.7	8.7	62.6	6.3	27.7	66.0	2 : 1 Salt	
27.1	8.8	64.1	8.1	29.7	62.2		
25.2	9.1	65.7	7.7	30.8	61.5		
24.0	9.4	66.6	7.1	31.6	61.3		
22.5	9.3	68.2	6.4	33.3	60.3		
20.4	9.8	69.8	5.1	37.2	57.7		
18.5	10.4	71.1	4.6	38.7	56.7		
15.8	11.2	73.0	4.1	45.2	50.7		
14.4	12.3	73.3	3.3	47.3	49.4		
12.9	13.7	73.4					

Examination of the curve shows that, of the three acid salts formed, only the 3 : 1 salt is stable in contact with its saturated solution, while the other two are stable only in presence of solutions containing excess of potassium mandelate.

#### Analyses.

	Found, %		Calc., %			Found, %		Calc., %	
	K.	$C_8H_8O_3$ .	K.	$C_8H_8O_3$ .		K.	$C_8H_8O_3$ .	K.	$C_8H_8O_3$ .
Normal salt	20.4	—	20.6	—	2 : 1 Salt	7.6	61.6	7.9	61.5
3 : 1 Salt	6.1	70.8	6.0	70.6	1 : 1 Salt	11.4	44.3	11.4	44.4

2. *The System Mandelic Acid-Sodium Mandelate-Water.*—The results for this system are collected below, the corresponding curve being in Fig. 3. Examination of the curve shows that both acid salts formed are stable in presence of water.

$C_8H_8O_3$ , %	$C_8H_7O_3Na$ , %	$H_2O$ , %	Solid phase.	$C_8H_8O_3$ , %	$C_8H_7O_3Na$ , %	$H_2O$ , %	Solid phase.
16.9	0.0	83.1	Acid	7.8	6.4	85.8	1 : 1 Salt
17.7	1.6	80.7		6.3	6.9	86.8	
18.9	2.9	78.2		4.0	8.3	87.7	
19.7	3.7	76.6		3.1	9.2	87.7	
17.6	3.7	78.7		2.0	10.9	87.1	
15.9	3.9	80.2		1.5	12.5	86.0	
13.7	4.5	81.8		0.9	15.8	83.3	
13.0	4.8	82.2		0.8	16.6	82.6	
12.4	4.9	82.7		0.7	17.1	82.2	
10.9	5.5	83.6		0.5	22.3	77.2	
10.4	5.7	83.9	0.4	23.7	75.9		
9.2	6.0	84.8	0.4	25.5	74.1		
			0.3	30.6	69.1		

#### Analyses.

	Found, %		Calc., %			Found, %		Calc., %	
	Na.	$C_8H_8O_3$ .	Na.	$C_8H_8O_3$ .		Na.	$C_8H_8O_3$ .	Na.	$C_8H_8O_3$ .
Normal salt	13.0	—	13.2	—	1 : 1 Salt	6.9	46.4	7.1	46.6
3 : 1 Salt	3.8	72.3	3.7	72.3					

3. *The System Mandelic Acid-Lithium Mandelate-Water.*—The results for this system are collected below, and shown in Fig. 4. The curve shows that the acid salt is just stable in presence of water.

$C_8H_8O_3$ , %	$C_8H_7O_3Li$ , %	$H_2O$ , %	Solid phase.	$C_8H_8O_3$ , %	$C_8H_7O_3Li$ , %	$H_2O$ , %	Solid phase.
16.9	0.0	83.1	Acid	13.0	3.3	83.7	1 : 1 Salt
18.8	1.6	79.6		11.1	3.6	89.3	
20.1	3.0	76.9	Acid +	9.9	3.6	86.5	
19.0	3.0	78.0	1 : 1 salt	8.3	3.9	87.8	
18.2	3.1	78.7		6.6	4.2	89.2	
16.2	3.1	80.7		4.7	5.0	90.3	
15.3	3.2	81.5	1 : 1 Salt	4.0	4.7	91.3	
14.6	3.2	82.2		0.9	4.7	94.4	
13.7	3.3	83.0		0.0	4.9	95.1	

Analyses.

	Found, %.		Calc., %.		1 : 1 Salt	Found, %.		Calc., %.	
	Li.	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub> .	Li.	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub> .		Li.	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub> .	Li.	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub> .
Normal salt	4.4	—	4.4	—		2.3	49.1	2.2	49.1

4. The System Mandelic Acid–Barium Mandelate–Water.—The results for this system are exhibited below and in Fig. 5. The acid salt is stable in presence of water.

C <sub>8</sub> H <sub>8</sub> O <sub>3</sub> , %.	(C <sub>8</sub> H <sub>7</sub> O <sub>3</sub> ) <sub>2</sub> Ba, %.	H <sub>2</sub> O, %.	Solid phase.	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub> , %.	(C <sub>8</sub> H <sub>7</sub> O <sub>3</sub> ) <sub>2</sub> Ba, %.	H <sub>2</sub> O, %.	Solid phase.
16.9	0.0	83.1	Acid	7.8	1.4	90.8	} 1 : 1 Salt
17.9	1.1	81.0	Acid +	6.6	1.7	91.7	
17.0	1.1	81.9	1 : 1 Salt *	3.8	2.3	93.9	
15.2	1.1	83.7	} 1 : 1 Salt	3.2	2.6	94.2	
14.1	1.0	84.9		2.0	4.2	93.8	
13.4	1.0	85.6		1.7	4.7	93.6	
11.5	1.1	87.4		1.2	6.4	92.4	
9.1	1.3	89.6	0.3	7.8	91.9	} Ba salt	
			0.0	7.9	92.1		

\* 1 : 1 Salt = (C<sub>8</sub>H<sub>7</sub>O<sub>3</sub>)<sub>2</sub>Ba.(C<sub>8</sub>H<sub>8</sub>O<sub>3</sub>)<sub>2</sub>.H<sub>2</sub>O (cf. McKenzie, *loc. cit.*).

Analyses.

	Ba.	Found, %.	H <sub>2</sub> O.	Ba.	Calc., %.	H <sub>2</sub> O.
		C <sub>8</sub> H <sub>8</sub> O <sub>3</sub> .			C <sub>8</sub> H <sub>8</sub> O <sub>3</sub> .	
Ba(C <sub>8</sub> H <sub>7</sub> O <sub>3</sub> ) <sub>2</sub> .½H <sub>2</sub> O	30.4	—	2.1	30.4	—	2.0
1 : 1 Salt	18.0	40.1	2.7	18.0	40.0	2.4

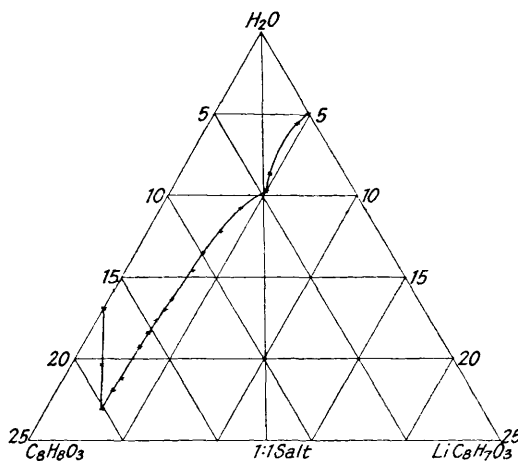


FIG. 4.

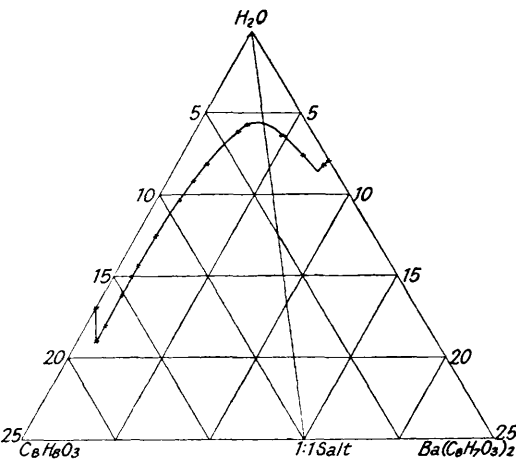


FIG. 5.

5. The System Mandelic Acid–Strontium Mandelate–Water.—The results of this system are given below and in Fig. 6. The acid salt is stable in presence of water.

C <sub>8</sub> H <sub>8</sub> O <sub>3</sub> , %.	(C <sub>8</sub> H <sub>7</sub> O <sub>3</sub> ) <sub>2</sub> Sr, %.	H <sub>2</sub> O, %.	Solid phase.	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub> , %.	(C <sub>8</sub> H <sub>7</sub> O <sub>3</sub> ) <sub>2</sub> Sr, %.	H <sub>2</sub> O, %.	Solid phase.
16.9	0.0	83.1	Acid	3.9	1.0	95.9	} 1 : 1 Salt
17.3	0.5	82.2	Acid +	1.4	2.2	96.4	
14.7	0.6	84.7	1 : 1 salt *	1.0	2.9	96.1	
11.6	0.5	87.9	} 1 : 1 Salt	0.3	3.6	96.1	
10.7	0.6	88.7		0.1	3.7	96.2	
6.8	0.6	92.6		0.0	3.8	96.2	

\* Sr(C<sub>8</sub>H<sub>7</sub>O<sub>3</sub>)<sub>2</sub>.(C<sub>8</sub>H<sub>8</sub>O<sub>3</sub>)<sub>2</sub>.

Analyses.

	Found, %.	Calc., %.		Found, %.	Calc., %.
Normal salt	Sr, 22.6	Sr, 22.5	1 : 1 Salt	Sr, 12.5; C <sub>8</sub> H <sub>8</sub> O <sub>3</sub> , 43.9	Sr, 12.6; C <sub>8</sub> H <sub>8</sub> O <sub>3</sub> , 43.8

6. *The System Mandelic Acid-Calcium Mandelate-Water.*—The following results for this system are plotted in Fig. 7. At concentrations of mandelic acid greater than the value 14.1,

$C_8H_8O_3$ , %	$(C_8H_7O_3)_2Ca$ , %	$H_2O$ , %	Solid phase.	$C_8H_8O_3$ , %	$(C_8H_7O_3)_2Ca$ , %	$H_2O$ , %	Solid phase.
16.9	0.0	83.1	Acid	4.2	0.2	95.6	} 1 : 1 Salt
14.1	0.1	85.8	} 1 : 1 Salt	1.2	0.7	98.1	
12.2	0.1	87.7		0.4	1.7	97.9	} 1 : 1 Salt and Ca salt
10.5	0.1	89.4		0.0	1.8	98.2	
6.5	0.1	93.4					

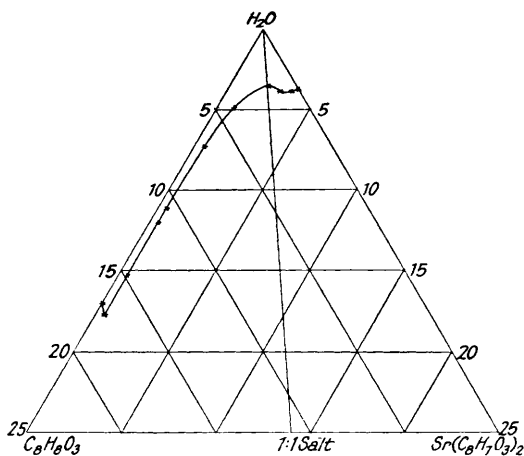


FIG. 6.

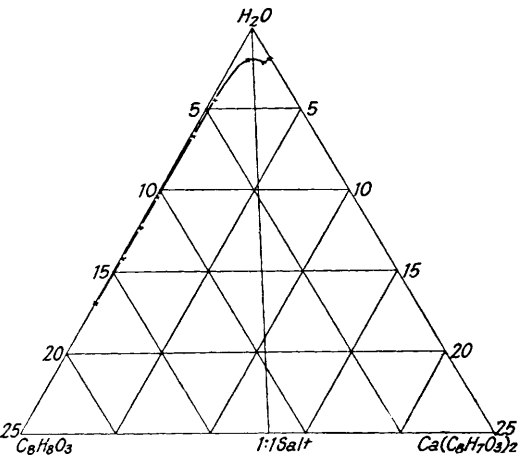


FIG. 7.

the concentration of the calcium salt became too small to be measured accurately by the method used. No further acid salts are to be expected, however. The acid salt is stable in presence of water.

	Found, %.	Calc., %.		Found, %.	Calc., %.
Normal salt	Ca, 11.8	Ca, 11.7	1 : 1 Salt	Ca, 6.1; $C_8H_8O_3$ , 47.2	Ca, 6.2; $C_8H_8O_3$ , 47.1

#### SUMMARY.

The solubility curves of the optically inactive systems mandelic acid-metal mandelate-water have been examined at 25° for the following mandelates: potassium, sodium, lithium, barium, calcium. The following acid salts have been isolated:  $[K(C_8H_7O_3)_4]H_3$ ;  $[K(C_8H_7O_3)_3]H_2$ ;  $[K(C_8H_7O_3)_2]H$ ;  $[Na(C_8H_7O_3)_4]H_3$ ;  $[Na(C_8H_7O_3)_2]H$ ;  $[Li(C_8H_7O_3)_2]H$ ;  $[Ba(C_8H_7O_3)_4]H_2 \cdot H_2O$ ;  $[Sr(C_8H_7O_3)_4]H_2$ ;  $[Ca(C_8H_7O_3)_4]H_2$ .

The above method of representation of the acid salts has been shown to be the most satisfactory.

The extent of compound formation in solution is shown to be related to the electrode potential of the metal. The influence of hydration, due to its small ionic size, explains the anomalous position of lithium.

UNIVERSITY COLLEGE, DUNDEE.  
UNIVERSITY OF ST. ANDREWS.

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