137. *Acid Salts of Monobasic Organic Acids. Part III.*

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The extent of compound formation which takes place between *r*-mandelic acid and various metal mandelates has already been studied by Ross and Morrison (J., 1933, 1016; J., 1936, 867). In the present investigation similar systems have been studied, active mandelic acid and active metal mandelates being used.

Experimental.

(−)*Mandelic Acid.*—The (−)mandelic acid used was prepared by (*a*) hydrolysis of amygdalin with concentrated hydrochloric acid; (*b*) resolution of *r*-mandelic acid with morphine (McKenzie, J., 1899, **75**, 966; Wood, Chrisman, and Nicholas, J., 1928, 2186), and (*c*) with (−)ephedrine (Roger, J., 1935, 1544). The average value of the specific rotation of the acid in water (1% solution) was $[\alpha]_D^{14°} = -154°$.

Metal Mandelates.—The active mandelates were in most cases prepared in exactly the same manner as the inactive salts, but in dealing with thallous, rubidium, and cæsium mandelates modifications in procedure were introduced which are described below.

The specific rotations of the salts in aqueous solution ($l = 2$) were :

(−)Mandelate.	*c.*	*a.*	*t.*	$[\alpha]_D^{t°}$.
Lithium	1·0	−2·32°	14°	−116°
Sodium	1·037	−2·17	12	−104·6
Potassium	1·017	−1·90	20	− 93·4
Magnesium (hydrated)	1·0	−2·07	14	−103·5
,, (anhydrous)	1·008	−2·28	15	−113·2
Calcium	1·006	−2·24	15	−111·4
Strontium	1·003	−1·19	15	− 95·3
Barium (hydrated)	1·0	−1·64	15	− 81·75
Thallous	1·015	−1·00	14	− 49·26

Thallous (—)*Mandelate*.—This salt was prepared with difficulty. 32·5 G. of (—)mandelic acid, dissolved in 200 c.c. of water, were neutralised with 50 g. of thallous carbonate, but only a gum was produced on attempted crystallisation of the product from aqueous methyl alcohol, although the inactive salt readily crystallised from this solvent: other solvents gave no better results. Finally, a crystalline salt was obtained by the following procedure. 3·25 G. of (—)mandelic acid were melted in a platinum basin at 140°, 5 g. of thallous carbonate added, and the mixture kept for a few minutes at this temperature before being cooled in a desiccator. The solid obtained was used to seed the gum obtained in the previous attempt, and a crystalline non-deliquescent material was formed.

Rubidium and Cæsium (—)*Mandelates*.—The method used for the inactive salts failed to give crystallisable material. Solutions for analysis were prepared by adding appropriate amounts of mandelic acid to weighed amounts of rubidium and cæsium carbonates.

The analytical data for the foregoing salts are included in the table on p. 614.

1. *The System* (—)*Mandelic Acid–Lithium Mandelate–Water*.—The solid phase was separated for analysis by pressing and drying on a porous plate.

Lithium (—)*mandelate.*

Solution.			Solution.			Solution.		
Acid, %.	Salt, %.	Solid phase.	Acid, %.	Salt, %.	Solid phase.	Acid, %.	Salt, %.	Solid phase.
10·1	0·0	Acid	11·9	3·4	1 : 1-Acid salt	6·9	4·0	1 : 1-Acid salt
9·8	0·5	,,	10·6	3·5	,,	5·6	4·0	,,
9·9	0·8	,,	10·8	3·4	,,	2·6	5·6	,,
10·0	1·7	,,	11·0	3·4	,,	1·3	8·6	Normal salt
10·1	2·0	,,	10·6	3·5	,,	1·0	8·5	,,
10·2	2·6	,,	9·9	3·6	,,	0·0	8·6	,,
10·3	3·4	,,	9·2	3·7	,,			

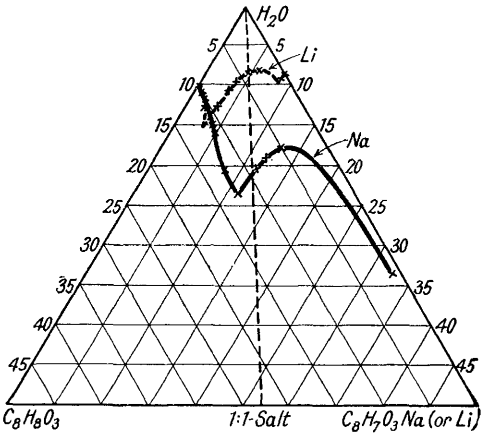
2. *The System* (—)*Mandelic Acid–Sodium Mandelate–Water*.—The solid phase for analysis was dried on a porous plate.

Sodium (—)*mandelate.*

Solution.		Residue.		Solution.		Residue.	
Acid, %.	Salt, %.	Acid, %.	Solid phase.	Acid, %.	Salt, %.	Acid, %.	Solid phase.
10·1	0·0	—	Acid	12·3	11·3	90·9	Acid + 1 : 1-salt
10·0	0·9	—	,,	8·9	11·6	46·5	1 : 1-Acid salt
10·1	1·7	—	,,	7·4	11·9	46·1	,,
11·0	4·3	—	,,	5·1	13·0	—	,,
11·2	5·0	—	,,	0·8	32·6	44·3	,,
12·2	8·5	97·7	,,				

FIG. 1.

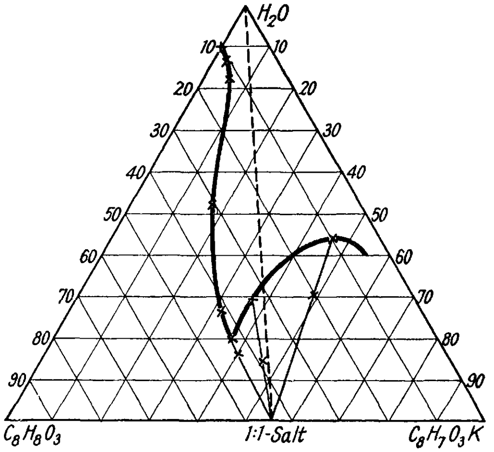
Lithium and sodium mandelates.



Both acid salts stable.

FIG. 2.

Potassium mandelate.



Acid salt stable.

3. *The System* (—)*Mandelic Acid–Potassium Mandelate–Water*.—The solid phase was determined by the residue method.

Potassium (—)mandelate.

Solution.		Residue.		Solid phase.
Acid, %.	Salt, %.	Acid, %.	Salt, %.	
10·1	0·0			Acid
10·1	1·4			,,
10·5	3·2			,,
12·1	6·0			,,
30·9	17·7			,,
39·8	27·2	—	—	Acid + 1 : 1-salt
42·7	37·3	43·6	40·4	1 : 1-Acid salt
34·4	38·5	39·1	46·7	,,
9·7	46·4	20·2	49·6	,,

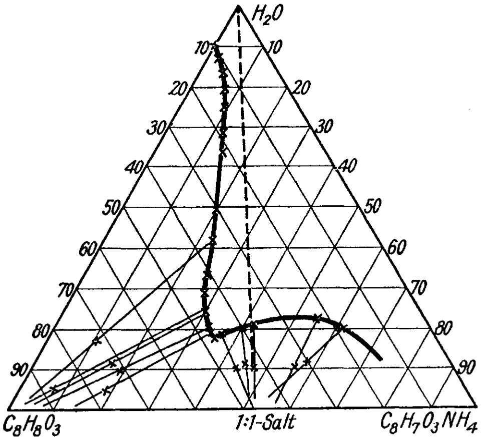
4. *The System (—)Mandelic Acid–Ammonium Mandelate–Water.*— Schreinemakers's residue method was used in the analysis of the solid phase, owing to the very viscous solutions obtained at higher concentrations.

Ammonium (—)mandelate.

Solution.		Residue.		Solid phase.
Acid, %.	Salt, %.	Acid, %.	Salt, %.	
10·1	0·0	—	—	Acid
10·1	2·3	—	—	,,
11·3	5·1	—	—	,,
12·9	7·8	—	—	,,
15·0	10·1	—	—	,,
18·8	13·1	—	—	,,
21·1	15·1	—	—	,,
31·1	19·5	—	—	,,
33·8	22·9	72·7	14·4	,,
39·1	25·9	—	—	,,
40·3	26·4	—	—	,,
41·2	27·4	—	—	,,
44·3	27·6	88·2	7·2	,,
45·8	30·6	71·7	16·5	,,
46·0	30·9	—	—	Acid
46·5	34·0	71·1	17·6	,,
46·8	34·8	76·3	18·4	,,
47·2	35·4	—	—	,,
46·9	36·0	—	—	,,
43·9	36·4	45·9	43·7	1 : 1-Acid salt
38·3	40·2	44·0	44·5	,,
37·0	42·6	42·3	47·1	,,
29·0	48·0	—	—	,,
24·7	51·9	—	—	,,
22·2	55·5	33·6	56·9	,,
19·0	61·0	30·2	57·8	,,
18·7	61·5	—	—	,,

FIG. 3.

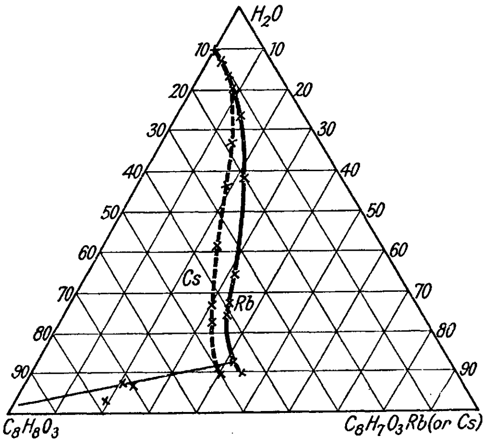
Ammonium mandelate.



Acid salt stable.

FIG. 4.

Rubidium and cæsium mandelates.



No acid salts formed.

5. *The System (—)Mandelic Acid–Rubidium Mandelate–Water.*—Owing to the very viscous nature of the concentrated solutions it was impossible to get points on the curve beyond those shown, and no acid salt was isolated, the solid phase being the acid in every case. The compositions shown are those of the solution.

Rubidium (—)mandelate.

Acid, % ...	10·1	10·0	10·5	11·3	13·0	20·7	26·9	34·2	39·0	41·2	45·3	45·8*	45·5
Salt, % ...	0·0	3·1	6·1	8·7	13·7	21·8	27·9	31·4	33·8	34·3	40·8	41·9*	44·9

* Composition of residue : acid, 71·6; salt, 20·8%.

6. *The System (—)Mandelic Acid–Cæsium Mandelate–Water.*—The same difficulties were encountered in the investigation of this system as in the previous case, and no acid salt was isolated. The results are expressed similarly.

Cæsium (—)mandelate.

Acid, %	10·1	10·3	11·0	12·0	14·5	25·0	34·9	42·8	44·6	49·4*	49·2†
Salt, %	0·0	2·8	5·0	7·1	11·3	19·0	24·3	30·3	32·3	39·4*	42·0†

* Residue: acid, 77·2; salt, 19·3%. † Residue: acid, 69·0; salt, 23·1%.

7. *The System (—)Mandelic Acid–Thallous Mandelate–Water.*—Some of the solutions for analysis were made by mixing appropriate quantities of mandelic acid and thallous carbonate, but later, the crystalline thallous mandelate was used. The composition of the solid phase was determined by the residue method. Some difficulty was experienced at first at high concentrations owing to the separation of two liquid phases. After a few days, however, the lower layer crystallised, and no further trouble was encountered.

Thallous (—)mandelate.

Solution.		Residue.			Solution.		Residue.		
Acid, %.	Salt, %.	Acid, %.	Salt, %.	Solid phase.	Acid, %.	Salt, %.	Acid, %.	Salt, %.	Solid phase.
10·1	0·0	—	—	Acid	18·3*	14·6	24·2	40·2	1 : 1-Acid salt
10·4	2·4	—	—	,,	17·6*	14·6	23·0	33·2	,,
11·2	4·6	—	—	,,	11·3	14·7	—	—	,,
11·4	6·5	—	—	,,	10·0	13·7	17·3	34·2	,,
12·9	9·0	—	—	,,	8·7	13·7	19·4	39·9	,,
15·3	13·7	—	—	,,	7·4	14·1	—	—	,,
16·3	14·3	—	—	,,	5·9	16·2	15·9	36·6	,,
17·8*	16·7	—	—	,,	5·2	17·8	26·3	61·1	,,
19·7*	19·0	—	—	,,	4·5	18·1	15·8	40·6	,,
21·2*	20·8	51·6	14·6	,,	3·1	36·4	17·3	54·6	,,
23·0*	22·0	—	—	,,	3·2	43·7	17·6	57·9	,,
26·3*	27·8	46·3	20·5	,,	3·8	52·2	20·6	62·1	,,
29·2*	28·8	44·6	22·4	,,	5·2	60·1	—	—	,,
19·4	17·0	30·1	21·3	Acid + 1 : 1-salt					

* Metastable points.

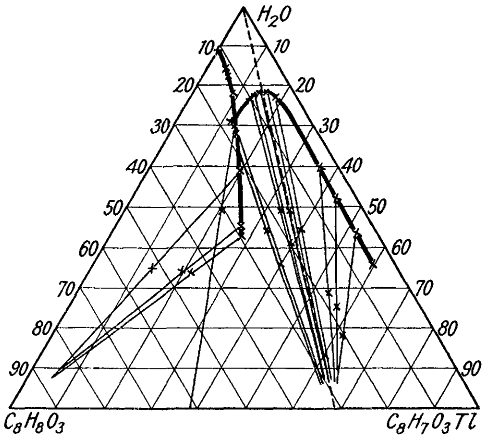
8. *The System (—)Mandelic Acid–Magnesium Mandelate–Water.*—Owing to the slowness with which the systems attained equilibrium, it was necessary to stir them for much longer than usual (40—60 hours). The solubility of the normal salt was found to be 6·08 g. per 100 g. of solution; McKenzie (J., 1899, **75**, 969) found 4·5 g. at 16°, and Findlay and Campbell (J., 1930, 2721) reported 1·96 g. at 25°. In order to confirm the value obtained above, magnesium (—)mandelate was also prepared from equivalent solutions of the ammonium salt and magnesium chloride, being precipitated on boiling. Considerable difficulty was encountered in attempts to determine accurately the composition of the acid salt, because (*a*) the curve is situated almost wholly near the apex of the triangle, and any analytical error is considerably magnified when Schreinemakers's method is applied, (*b*) equilibrium in all systems with magnesium salts is attained very slowly, (*c*) metastable points are found extending into the region where the acid salt is formed. Tie lines coming from the points of intersection of the curve gave solids with 25% and 9·5% of acid in their composition. The acid salt must, therefore, have a composition between these two values. Solids with 18% and 21% acid were obtained from points on the acid salt part of the curve. It appeared likely that the composition of the acid salt for the active mandelic acid was similar to that found for the inactive acid. Solutions of composition corresponding to the centre of the acid salt curve were therefore stirred for 2—3 days with a solid of composition corresponding to this acid salt, and the percentage of acid in the solid did not vary to any considerable extent. Hence, we conclude that the composition of the acid salt in the case of the active acid is almost certainly the same as in that of the inactive acid (17·9% of acid).

Magnesium (—)mandelate.

Solution.			Solution.			Solution.			Solution.		
Acid, %.	Salt, %.	Solid phase.	Acid, %.	Salt, %.	Solid phase.	Acid, %.	Salt, %.	Solid phase.	Acid, %.	Salt, %.	Solid phase.
10·1	0·0	Acid	10·3	4·1	Acid	10·3	4·1	Acid salt	9·9*	6·1	Normal salt
10·0	0·8	,,	10·4*	4·3	,,	10·0	4·2	,,	8·2	5·9	,,
10·1	2·7	,,	10·7*	5·1	,,	9·1	4·4	,,	5·6	5·8	,,
10·4	3·2	,,				8·3	5·6	,,	2·9	5·9	,,
									0·0	6·1	,,

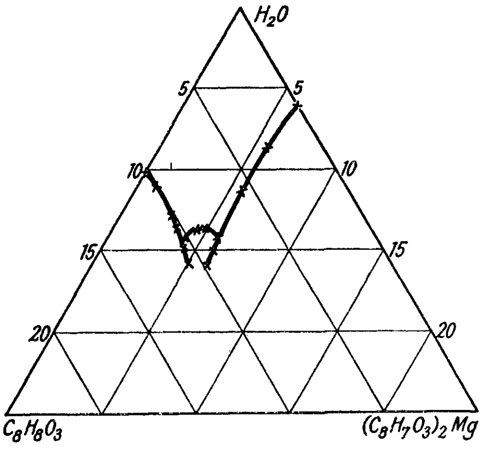
* Metastable points.

FIG. 5.
Thallous mandelate.



Acid salt stable.

FIG. 6.
Magnesium mandelate.



Acid salt unstable.

9. *The System (—)Mandelic Acid–Calcium Mandelate–Water.*—The 1 : 1-salt and the 2 : 1-salt were prepared by crystallising the salt from solutions of (—)mandelic acid. Some difficulty was experienced in freeing the 1 : 1-salt from the mother-liquor and this accounts for the higher percentage of acid found on analysis.

Calcium (—)mandelate.

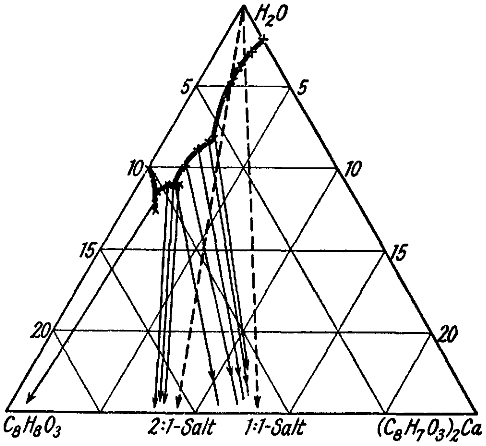
Solution.		Residue.		
Acid, %.	Salt, %.	Acid, %.	Salt, %.	Solid phase.
10·1	0·0	—	—	Acid
10·2	0·5	—	—	,,
10·2	1·0	—	—	,,
10·4	1·1	—	—	,,
10·9	1·2	—	—	,,
11·2	1·4	42·2	5·4	,,
9·6	1·5	64·3	35·7	2 : 1-Acid salt
9·4	1·8	30·0	16·4	,,
9·1	1·9	27·7	14·8	,,
9·2	1·8	29·8	24·2	2 : 1-Salt + 1 : 1-salt
		...		
8·2	2·1	21·4	18·6	1 : 1-Acid salt
7·5	2·0	45·5	54·5	,,
7·0	2·1	49·3	50·7	,,
6·6	2·1	42·8	57·2	,,
6·1	2·2	—	—	,,
5·7	2·6	—	—	1 : 1-Salt + normal salt
4·8	2·3	—	—	Normal salt
3·8	2·2	—	—	,,
2·9	2·1	—	—	,,
2·1	2·2	—	—	,,
1·1	2·2	—	—	,,
0·0	2·3	—	—	,,

10. *The System (—)Mandelic Acid–Strontium Mandelate–Water.*

Strontium (—)mandelate.

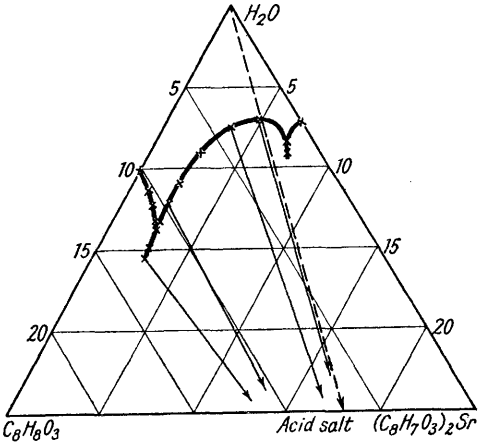
Solution.		Residue.		
Acid, %.	Salt, %.	Acid, %.	Salt, %.	Solid phase.
10·1	0·0	—	—	Acid
10·3	0·9	—	—	,,
10·4	1·8	—	—	,,
10·7	2·4	—	—	,,
12·7	2·6	17·0	16·4	Acid salt
11·2	2·5	—	—	,,
9·8	2·6	30·7	69·3	,,
8·4	2·4	—	—	,,
6·4	2·8	—	—	,,
6·0	2·9	—	—	Acid salt
4·8	3·2	30·3	69·7	,,
2·0	5·0	8·4	20·8	,,
1·2	6·1	—	—	,,
1·3	7·4	—	—	,,
1·6	7·7	—	—	,,
0·8	7·0	—	—	Normal salt
0·0	7·4	—	—	,,

FIG. 7.
Calcium mandelate.



Both acid salts unstable.

FIG. 8.
Strontium mandelate.



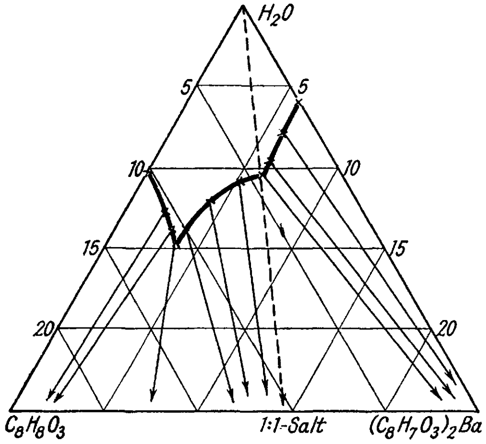
Acid salt stable.

11. *The System (—)Mandelic Acid–Barium Mandelate–Water.*—The residue method was used in the analysis of the solid phase.

Barium (—)mandelate.

Solution.		Residue.			Solution.		Residue.		
Acid, %.	Salt, %.	Acid, %.	Salt, %.	Solid phase.	Acid, %.	Salt, %.	Acid, %.	Salt, %.	Solid phase.
10·1	0·0	—	—	Acid	5·7	5·3	16·0	20·8	Acid salt
10·4	2·3	26·8	1·9	,,	4·1	6·2	10·4	16·3	,,
10·7	3·2	18·6	3·0	,,	4·0	6·3	3·6	15·7	Normal salt
10·9	3·7	26·4	23·0	Acid + acid salt	3·5	6·2	3·6	43·8	,,
10·0	3·7	23·5	33·7	Acid salt	2·0	5·9	1·8	28·3	,,
7·8	4·2	28·1	34·0	,,	0·0	6·0	—	—	,,

FIG. 9.
Barium mandelate.



Acid salt stable.

The analytical data of the various salts are tabulated below.

For univalent metals, a 1 : 1 acid salt is of type $C_8H_8O_3,MC_8H_7O_3$. For bivalent metals, the types of acid salt are as follows: 1 : 1 = $2C_8H_8O_3,M(C_8H_7O_3)_2$; 1 : 2 = $C_8H_8O_3,M(C_8H_7O_3)_2$; 2 : 1 = $4C_8H_8O_3,M(C_8H_7O_3)_2$.

Normal salts (anhydrous).

Metal.	Found, %.	Calc., %.
Li	4·3	4·4
Na	13·1	13·2
K	20·4	20·6
Tl^{I}	57·7	57·5
Mg	7·5	7·5
Ca	11·7	11·7
Sr	22·5	22·5

Acid salts (anhydrous).

		Found, %.		Calc., %.	
Metal.	Type of salt.	Metal.	$C_8H_8O_3$.	Metal.	$C_8H_8O_3$.
Li	1 : 1	2·1	48·8	2·1	49·1
Na	1 : 1	6·8	46·8	7·1	46·6
K	1 : 1	11·2	44·3	11·4	44·4
Tl^{I}	1 : 1	40·3	29·9	40·3	29·95
Ca	1 : 1	—	47·9	—	47·1
,,	2 : 1	4·1	64·1	4·2	64·0
Sr	1 : 2	16·2	28·1	16·2	28·1

Normal salts (hydrated).

	Found, %.		Calc., %.	
	Metal.	H_2O.	Metal.	H_2O.
$Mg(2H_2O)$	6·6	9·5	6·7	9·9
$Ba(\frac{1}{2}H_2O)$	30·6	2·0	30·6	2·0

Acid salt (hydrated), $Ba(C_8H_7O_3)_2,2C_8H_8O_3,\frac{1}{2}H_2O$.

Found, %.			Calc., %.		
Ba.	H_2O.	$C_8H_8O_3$.	Ba.	H_2O.	$C_8H_8O_3$.
18·2	1·3	40·6	18·3	1·2	40·4

No profitable comparison can be made between the inactive and the active mandelates, nor can the effect on the solubility of the acid of the various metal mandelates be studied, until an investigation of the " salting-out " effect of the various metallic ions, now being carried out, has been completed.

SUMMARY.

Solubility curves for the optically active systems (—)mandelic acid–metal mandelates–water at 25° have been investigated in the cases of lithium, sodium, potassium, ammonium, rubidium, cæsium, thallous, magnesium, calcium, strontium, and barium mandelates.

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UNIVERSITY COLLEGE, DUNDEE, UNIVERSITY OF ST. ANDREWS. [*Received, January 29th,* 1937.]