XXI.—*Salts of Glyceric acid, Active and Inactive; Influence of Metals on the Specific Rotation of Active Acids.*

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It has been shown by one of us (Percy Frankland and Frew, Trans., 1891, **59**, 81 and 96) that by fermenting a suitable solution of calcium glycerate with the *Bacillus ethaceticus*, about one half of the salt undergoes decomposition with formation of ethyl alcohol, acetic and formic acids, traces of succinic acid, together with gaseous products, whilst the other half which remains undecomposed is found to have a powerful lævorotatory effect on a beam of polarised light. On preparing the glyceric acid from this lævorotatory calcium salt, it was found, on the other hand, to be dextrorotatory. The activity of the acid, however, is subject to great variation, according to the treatment which its aqueous solution has received; thus, if it is much concentrated on the water bath, the dextrorotation becomes smaller and smaller, and by long-continued heating it is actually exchanged for a powerful lævorotation. These phenomena are perfectly similar to those which had been previously observed by Wislicenus (*Annalen*, **167**, 332) in his classical researches on the isomeric lactic acids, and is explicable on the assumption of there being a certain amount of anhydride formation even in aqueous solution, the anhydride being powerfully lævorotatory, whilst the acid is less strongly dextrorotatory.

Preparation of Active Glyceric acid.

We have not materially modified the method of preparation described in the previous communication; it has successfully served us for obtaining very considerable quantities (several hundred grams) of the active calcium salt, which is readily purified in consequence of the ease with which it is obtained in large crystals; these, which are sometimes upwards of half an inch in length, and beautifully lustrous, have been examined and described by Mr. Tutton (Trans., 1891, **59**, 233) as monoclinic prisms exhibiting hemihedral faces.

From the calcium salt, the acid is readily obtainable by precipitating the calcium with the theoretical quantity of oxalic acid, and its solution should invariably be carefully sterilised if it is to be kept for any length of time, as it is otherwise liable to become infested with fungoid growths.

From the acid, we have prepared the salts of the more important.

metals, and have determined the composition, rotatory power, and solubility of these salts, as well as of their inactive isomers.

Calcium Glycerate.

(a.) *Inactive.*—In the previous communication, we have shown that this salt has the composition $(C_3H_5O_4)_2Ca + 2H_2O$.

The water of crystallisation is only partially lost at $105-110^\circ$, the salt on drying until constant at that temperature losing only 5.61 per cent., whilst the loss corresponding to 1 mol. H_2O is 6.29 per cent. This salt has already been very fully described by Debus (*Annalen*, **106**, 87), in his classical paper on the preparation of glyceric acid.

Notwithstanding repeated efforts, we have been unable to obtain this salt in any other than an indistinctly crystalline form, in which respect it contrasts most strikingly with its brilliantly crystalline isomer.

Its solubility was determined in two experiments; 100 parts by weight of water at 20° dissolved:—

I	4.37 parts	$(C_3H_5O_4)_2Ca + 2H_2O$
II	4.42 „	„
Mean	4.40 „	„
or, 3.85 parts of the anhydrous salt.		

(b.) *Active.*—A fresh preparation, different from that referred to in the previous communication, yielded the following results:—

- I. 0.234 gram of salt gave 0.1115 gram $CaSO_4 = 14.01$ per cent. Ca.
 II. 0.3705 gram of salt gave 0.1770 gram $CaSO_4 = 14.05$ per cent. Ca.

The rotation was also determined on this new specimen:—

1. Concentration = 10 per cent. solution. Temperature, 17.5° .
 Rotation, -2.3° .
 2. Concentration = 10 per cent. solution. Temperature, 17.0° .
 Rotation, -2.3° .

$$[\alpha]_D = \begin{cases} (1) -11.59^\circ \\ (2) -11.59 \end{cases}$$

Repeated on the former preparation, it was found to be:—

$$[\alpha]_D = \begin{cases} (1) -11.84^\circ \\ (2) -11.61 \end{cases}$$

$$\text{Mean } [\alpha]_D = -11.66^\circ \text{ } (-13.34 \text{ for the anhydrous salt}).$$

The solubility was determined in two experiments; 100 parts by weight of water at 20° dissolved:—

I	10·61 parts	(C ₃ H ₅ O ₄) ₂ Ca + 2H ₂ O,
II	10·71	„ „
Mean	10·66	„ „
or 9·32 parts of the anhydrous salt.		

Thus the active calcium glycerate is more than twice as soluble as the inactive variety.

Barium Glycerate.

(a.) *Inactive.*—On evaporating a solution of the inactive barium glycerate and allowing it to stand, a crystalline mass was obtained, which was only pressed between filter-paper for analysis.

The barium was determined in two experiments:—

- I. 0·2765 gram of salt yielded 0·1815 gram BaSO₄ = 38·59 per cent. Ba.
- II. 0·3235 gram of salt yielded 0·2120 gram BaSO₄ = 38·51 per cent. Ba.

This corresponds to Ba(C₃H₅O₄)₂ + $\frac{1}{2}$ H₂O, which requires 38·49 per cent. Ba.

The solubility was determined with the following results:—

100 parts by weight of water at 20° dissolved:—

I	6·56 parts of	Ba(C ₃ H ₅ O ₄) ₂ + $\frac{1}{2}$ H ₂ O,
II	6·97	„ „ „
Mean	6·77	„ „ „
or, 6·60 parts of the anhydrous salt.		

(b.) *Active.*—On evaporating a solution of the active barium glycerate, a syrupy mass was obtained, which would not solidify in desiccator; it was therefore dissolved in a small volume of water, and to this a large volume of methylated spirit was added; the barium salt separated as a white gummy mass, and this, after three or four days' contact with the alcohol, became transformed into an indistinctly crystalline solid, which could be pulverised and pressed between filter-paper for analysis.

Three barium determinations of the air-dried salt were made:—

- I. 0·238 gram of barium salt yielded 0·146 gram BaSO₄ = 36·05 per cent. Ba.
- II. 0·241 gram of barium salt yielded 0·148 gram BaSO₄ = 36·10 per cent. Ba.

III. 0.1805 gram of barium salt yielded 0.1105 gram BaSO_4 = 36.01 per cent. Ba; mean = 36.05 per cent. Ba.
 $\text{Ba}(\text{C}_3\text{H}_5\text{O}_4)_2 + 2\text{H}_2\text{O}$ requires 35.77 per cent. Ba.

The salt was also dried at 130° until constant, and then submitted to analysis:—

0.134 gram of barium salt yielded 0.0895 gram BaSO_4 = 39.27 per cent. Ba.
 $\text{Ba}(\text{C}_3\text{H}_5\text{O}_4)_2$ requires 39.48 per cent. Ba.

The activity of the barium salt was determined, with the following results:—

2 grams of the air-dried salt were dissolved in water and made up to 20 c.c.; a rotation of -1.8° was observed in the 198.4 mm. tube at 12° , a second experiment giving precisely the same result. From this the specific rotation follows:—

$$[\alpha]_D = \frac{100 \times 1.8}{1.984 \times 10} = -9.07^\circ \quad (-10.01^\circ \text{ for the anhydrous salt}).$$

The solubility was also determined in two experiments; 100 parts by weight of water at 20° dissolved:—

I	55.59 parts of $\text{Ba}(\text{C}_3\text{H}_5\text{O}_4)_2 + 2\text{H}_2\text{O}$,
II	55.10 " " "
Mean.....	55.35 " " "
	or 50.15 parts of the anhydrous salt.

Thus the lævorotatory barium glycerate is about eight times as soluble as the inactive variety, and crystallises with 2 mols. H_2O , whilst the latter has only $\frac{1}{2}$ mol. H_2O .

Strontium Glycerate.

(a.) *Inactive.*—This was prepared for analysis in the same way as the inactive barium glycerate. Three strontium determinations were made on the air-dried salt:—

- I. 0.2295 gram of strontium salt yielded 0.138 gram SrSO_4 = 28.67 per cent. Sr.
- II. 0.234 gram of strontium salt yielded 0.140 gram SrSO_4 = 28.55 gram per cent. Sr.
- III. 0.2005 gram of strontium salt yielded 0.1205 gram SrSO_4 = 28.68 per cent. Sr.

Another strontium determination was made on some of the salt after it had remained for some time in the vacuum desiccator:—

IV. 0.190 gram of strontium salt yielded 0.1145 gram $\text{SrSO}_4 = 28.74$ per cent. Sr; mean = 28.66 per cent.

This corresponds to $\text{Sr}(\text{C}_3\text{H}_5\text{O}_4)_2 + \frac{1}{2}\text{H}_2\text{O}$, which requires 28.57 per cent. Sr.

Two determinations of its solubility were made with the following results; 100 parts of water by weight at 20° dissolved:—

I	6.57 parts	$\text{Sr}(\text{C}_3\text{H}_5\text{O}_4)_2 + \frac{1}{2}\text{H}_2\text{O}$,
II	6.15	„ „ „
Mean.....	6.36	„ „ „
	or 6.17 parts of the anhydrous salt.	

(b.) *Active*.—The active strontium salt was obtained in a solid, crystalline state, by making use of the same artifice as was employed in the case of the active barium salt. It was pulverised and repeatedly pressed between filter-paper for analysis, but as the salt is very deliquescent, it entailed very considerable loss of material.

One strontium determination was made:—

0.3275 gram of strontium salt yielded 0.1705 gram $\text{SrSO}_4 = 24.84$ per cent. Sr,

which corresponds to $\text{Sr}(\text{C}_3\text{H}_5\text{O}_4)_2 + 3\text{H}_2\text{O}$, requiring 24.91 per cent. Sr.

A second preparation of this salt was made, the syrupy mass being this time left in contact with the large excess of methylated spirit for eight weeks; the resulting solid was then placed in a vacuum desiccator for two weeks, and afterwards for three weeks in an ordinary one. With this, the following results were obtained on analysis:—

I. 0.2717 gram of strontium salt yielded 0.1575 gram $\text{SrSO}_4 = 27.66$ per cent. Sr.

II. 0.4100 gram of strontium salt yielded 0.2365 gram $\text{SrSO}_4 = 27.52$ per cent. Sr.

This corresponds to $\text{Sr}(\text{C}_3\text{H}_5\text{O}_4)_2 + \text{H}_2\text{O}$, requiring 27.76 per cent. Sr.

Thus, the active strontium salt appears to crystallise, in the first instance, with 3 mols. H_2O , two of which are easily parted with, as in the method of desiccation employed in the second preparation.

The rotation was separately determined on each of these preparations of the salt.

Thus, with $(\text{C}_3\text{H}_5\text{O}_4)_2\text{Sr} + 3\text{H}_2\text{O}$, a 10 per cent. solution gave a rotation of -2.0° in the 198.4 mm. tube at 15° :—

$$[\alpha]_D = \frac{100 \times -2}{1.984 \times 10} = -10.08^\circ;$$

this corresponds to $[\alpha]_D = -11.91^\circ$ for the anhydrous salt.

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The rotation of the salt with 1 mol. of water $(C_3H_5O_4)_2Sr + H_2O$, in a 10 per cent. solution at 19° was -2.3° , and thus :—

$$[\alpha]_D = \frac{100 \times -2.3}{1.984 \times 10} = -11.59^\circ,$$

corresponding to $[\alpha]_D = -12.29^\circ$ for the anhydrous salt.

The exact determination of the solubility was unfortunately lost through an accident, but we have ascertained that 100 parts by weight of water at 20° dissolve about 300 parts of the salt.

The active strontium salt is thus enormously more soluble than the inactive, and also much more soluble than either the active barium or calcium salts.

Lithium Glycerate.

(a.) *Inactive.*—The solution of glyceric acid was boiled for one hour with excess of lithium carbonate, filtered, and evaporated to dryness on the water-bath. The residue was dried for three hours at 100° , and then extracted with strong methylated spirit in a Soxhlet's apparatus to separate it from lithium carbonate. The earlier alcoholic extract deposited small crystals of a prismatic form, whilst the later extract gave crystals having more the appearance of plates; the two portions were collected and treated separately. The salt, before analysis, was placed for five to six weeks in the vacuum desiccator, after which it was no longer deliquescent.

Lithium determinations were made in each of the specimens obtained as above :—

Specimen No. 1.

I. 0.2445 gram Li salt yielded 0.120 gram $Li_2SO_4 = 6.25$ per cent. Li.

II. 0.328 gram Li salt yielded 0.1555 gram $Li_2SO_4 = 6.04$ per cent. Li.

Specimen No. 2.

I. 0.3165 gram Li salt yielded 0.155 gram $Li_2SO_4 = 6.23$ per cent. Li.

II. 0.292 gram Li salt yielded 0.144 gram $Li_2SO_4 = 6.28$ per cent. Li.

III. 0.2075 gram Li salt yielded 0.103 gram $Li_2SO_4 = 6.31$ per cent. Li,

showing that both specimens were anhydrous lithium glycerate, $C_3H_5O_4Li$, containing 6.25 per cent. Li.

It is, however, probable that the salt only becomes anhydrous in the desiccator, for the crystals lost their transparency during desiccation.

Owing to the exceedingly soluble nature of this salt, and the small quantity available, its solubility could not be determined.

(b.) *Active*.—The active salt was prepared in the same way as the inactive, and on evaporating its solution it was deposited in beautiful, radiating, acicular crystals, which could not be further examined in consequence of their rapid deliquescence. The salt was purified by alcohol, as described for the inactive variety above, and finally placed in the vacuum desiccator before analysis; it was then no longer deliquescent.

The lithium determinations gave the following results:—

- I. 0.2562 gram Li salt yielded 0.127 gram $\text{Li}_2\text{SO}_4 = 6.31$ per cent. Li.
- II. 0.222 gram Li salt yielded 0.1095 gram $\text{Li}_2\text{SO}_4 = 6.28$ per cent. Li,

corresponding to the anhydrous salt, $\text{C}_3\text{H}_5\text{O}_4\text{Li}$, which contains 6.25 per cent. Li.

Examined with the polarimeter, a 10 per cent. solution of the salt gave a rotation of -4.1° at 11° , from which the specific rotation follows:—

$$[\alpha]_D = \frac{100 \times -4.1}{1.984 \times 10} = -20.66^\circ.$$

Sodium Glycerate.

(a.) *Inactive*.—This salt was prepared by adding the calculated amount of standard sodium hydrate to a solution of glyceric acid, and evaporating, when a thick syrup was obtained, which refused to crystallise even after remaining three weeks in the vacuum desiccator, nor was the application of a freezing mixture more successful.

(b.) *Active*.—The active sodium glycerate was similarly prepared, and also refused to crystallise in the vacuum desiccator, although kept there for several weeks. The attempt to crystallise it had almost been abandoned when, after it had been exposed to the air of the laboratory for about an hour, it was found to be crystallising in silky needles, radiating from a centre of dust on the surface of the syrup (similar exposure to dust did not induce the inactive salt to crystallise). The whole mass ultimately became crystalline, after which it was broken up and pressed between filter-paper for analysis, a process which entailed much loss, as the salt is very deliquescent.

A sodium determination gave the following result:—

0.2040 gram of sodium salt yielded 0.1075 gram $\text{Na}_2\text{SO}_4 = 17.07$ per cent. Na,

which corresponds to $\text{C}_3\text{H}_5\text{O}_4\text{Na} + \frac{1}{2}\text{H}_2\text{O}$, requiring 16.79 per cent. Na.

Another portion of the sodium salt, dried for two or three days in a vacuum desiccator before analysis, yielded the following figures:—

0.275 gram of sodium salt gave 0.1515 gram $\text{Na}_2\text{SO}_4 = 17.85$ per cent. Na.

Another portion was dried at 130° before analysis, and this gave the following result:—

0.2045 gram of sodium salt yielded 0.1135 gram $\text{Na}_2\text{SO}_4 = 17.98$ per cent. Na.

Both of the latter determinations correspond to the anhydrous salt, $\text{C}_3\text{H}_5\text{O}_4\text{Na}$, which contains 17.98 per cent. Na.

The anhydrous salt, examined in 10 per cent. solution in the polarimeter, gave a rotation of -3.2° at 12° , which leads to the specific rotation

$$[\alpha]_D = \frac{100 \times -3.2}{1.984 \times 10} = -16.13^\circ.$$

Potassium Glycerate.

(a.) *Inactive.*—Owing to the non-crystallisable character of the normal salt, only hydrogen potassium glycerate was prepared. The solution, on evaporation, showed no signs of crystallisation, but after being placed for a week in the desiccator, a beautifully crystalline, but highly deliquescent, product was obtained. One portion was submitted to immediate analysis, with the following results:—

I. 0.3505 gram of potassium salt yielded 0.1235 gram $\text{K}_2\text{SO}_4 = 15.81$ per cent. K.

II. 0.3530 gram of potassium salt yielded 0.1220 gram $\text{K}_2\text{SO}_4 = 15.50$ per cent. K.

Another portion was dried in the vacuum desiccator and then analysed:—

I. 0.4720 gram of potassium salt yielded 0.1660 gram $\text{K}_2\text{SO}_4 = 15.76$ per cent. K.

II. 0.4795 gram of potassium salt yielded 0.1680 gram $\text{K}_2\text{SO}_4 = 15.70$ per cent. K;

in both cases the figures correspond to the anhydrous acid salt, $\text{C}_3\text{H}_5\text{O}_4\text{K}$, which contains 15.60 per cent. K.

This salt, corresponding in chemical composition and physical properties, was also prepared by Debus (*loc. cit.*).

(b.) *Active*.—Neither the normal nor acid salt could be obtained in a crystalline state; hence only the rotation of these salts in solution was studied.

1. A solution containing 11.635 per cent. of normal salt, $C_3H_5O_4K$, gave a rotation of -3.8° at 18° , from which follows

$$[\alpha]_D = \frac{100 \times -3.8}{1.984 \times 11.635} = -16.46^\circ.$$

2. A solution containing 9.778 per cent. of normal salt, $C_3H_5O_4K$, gave a rotation of -3.09° at 16.5° , corresponding to

$$[\alpha]_D = \frac{100 \times -3.09}{1.984 \times 9.778} = -15.93^\circ.$$

3. A solution containing 11.8336 per cent. of normal salt, $C_3H_5O_4K$, gave a rotation of -3.9 at 17° , corresponding to

$$[\alpha]_D = \frac{100 \times -3.9}{1.984 \times 11.8336} = -16.61^\circ.$$

Mean of the three results for about 10 per cent. solution of $C_3H_5O_4K$ —

$$[\alpha]_D = -16.33^\circ.$$

A solution of the acid salt was prepared by dividing a solution of glyceric acid into two equal parts, neutralising the one with caustic potash, and then mixing with the other part. The two following observations were made:—

1. A solution containing 10.359 per cent. of $C_3H_5O_4K, C_3H_6O_4$ gave a rotation of -1.9° at 18° , from which

$$[\alpha]_D = \frac{100 \times -1.9}{1.984 \times 10.359} = -9.24^\circ.$$

2. A solution containing 17.605 per cent. of $C_3H_5O_4K, C_3H_6O_4$ gave a rotation of -3.15° at 18° , from which

$$[\alpha]_D = \frac{100 \times -3.15}{1.984 \times 17.605} = -9.02^\circ.$$

This rotation of the acid salt is the same as if only the normal portion of the molecule had been present in the solution; thus, in the first of the two above experiments, the 10.359 grams of acid salt contain 5.9668 grams of normal salt, from which

$$[\alpha]_D = \frac{100 \times -1.9}{1.984 \times 5.9668} = -16.05^\circ,$$

which is in the closest possible agreement with the specific rotation actually found for the normal salt.

Ammonium Glycerate.

(a.) *Inactive.*—Ammonium hydrate was added to a solution of glyceric acid until neutral, the liquid was concentrated, and whilst still neutral was transferred to the vacuum desiccator, in which further evaporation and ultimate crystallisation took place. The crystals were deliquescent.

The ammonia was determined by distillation with sodium hydrate into seminormal sulphuric acid:—

I gave 10·98 per cent. N; II gave 11·12 per cent. N; III gave 10·92 per cent. N,

corresponding to the normal anhydrous salt, $C_3H_5O_4 \cdot NH_4$, which contains 11·38 per cent. N.

This salt is also described by Debus (*loc. cit.*).

(b.) *Active.*—The active ammonium salt was only experimented with in solution. A solution of active glyceric acid was exactly neutralised with ammonia and made up to volume, the ammonia and rotation being determined in aliquot parts. The following determinations of the rotation were made:—

1. A solution containing 10·61 grams $C_3H_5O_4 \cdot NH_4$ in 100 c.c. gave a rotation of $-3\cdot8^\circ$ at 20° , which leads to the specific rotation

$$[\alpha]_D = \frac{100 \times -3\cdot8}{1\cdot984 \times 10\cdot61} = -18\cdot05^\circ.$$

2. The same solution, diluted to one-half the above strength, gave exactly the same specific rotation $-18\cdot05^\circ$.
3. A solution containing 2·898 grams $C_3H_5O_4 \cdot NH_4$ in 100 c.c. gave a rotation of $-1\cdot1^\circ$ at 14° , from which the specific rotation is calculated,

$$[\alpha]_D = \frac{100 \times -1\cdot1}{1\cdot984 \times 2\cdot898} = -19\cdot13^\circ.$$

4. A solution containing 1·796 gram $C_3H_5O_4 \cdot NH_4$ in 100 c.c. gave a rotation of $-0\cdot7^\circ$ at 16° , from which

$$[\alpha]_D = \frac{100 \times -0\cdot7}{1\cdot984 \times 1\cdot7836} = -19\cdot78^\circ.$$

From these results it would appear that the rotation increases with the degree of dilution, but a more extensive series of experiments would be necessary to demonstrate this fully.

Magnesium Glycerate.

(a.) *Inactive*.—The solution was evaporated down until crystallisation took place, and the crystals, which consist of extremely small needles, were pressed between filter-paper for analysis.

The magnesium determinations gave the following results:—

- I. 0.7040 gram of magnesium salt yielded 0.336 gram $\text{MgSO}_4 = 9.55$ per cent. Mg.
 II. 0.4410 gram of magnesium salt yielded 0.212 gram $\text{MgSO}_4 = 9.61$ per cent. Mg,

corresponding to $(\text{C}_3\text{H}_5\text{O}_4)_2\text{Mg} + \text{H}_2\text{O}$, which contains 9.52 per cent. Mg.

The solubility also was determined with the following result; 100 parts by weight of water at 20° dissolved:—

I	24.54 parts	$(\text{C}_3\text{H}_5\text{O}_4)_2\text{Mg} + \text{H}_2\text{O}$
II	24.51	„ „ „
Mean.....	24.53	„ „ „
	or 22.78 parts of the anhydrous salt.	

(b.) *Active*.—The solution of this salt on evaporation formed a syrup which became crystalline on standing for two days. It was dried for analysis by pressing between filter-paper.

The magnesium determinations gave the following results:—

- I. 0.3315 gram of magnesium salt yielded 0.1575 gram $\text{MgSO}_4 = 9.50$ per cent. Mg.
 II. 0.4292 gram of magnesium salt yielded 0.2030 gram $\text{MgSO}_4 = 9.46$ per cent. Mg,

corresponding to $(\text{C}_3\text{H}_5\text{O}_4)_2\text{Mg} + \text{H}_2\text{O}$, which contains 9.52 per cent. Mg.

The determination of its solubility gave the following result; 100 parts by weight of water at 20° dissolved:—

46.36 parts $(\text{C}_3\text{H}_5\text{O}_4)_2\text{Mg} + \text{H}_2\text{O}$,
 or 43.05 parts of the anhydrous salt.

Thus the solubility is nearly twice as great as that of the inactive salt.

Examined in a 10 per cent. solution, the hydrated salt gave a rotation of -3.7° at 19° , leading to the specific rotation

$$[\alpha]_D = \frac{100 \times -3.7}{1.984 \times 10} = -18.65^\circ \text{ } (-20.08^\circ \text{ for the anhydrous salt}).$$

Zinc Glycerate.

(a.) *Inactive*.—The preparation of the salt for analysis was carried out in the same manner as already described for the magnesium salt. The crystals are seen under the microscope to be rhombic plates grouped together in little tufts. The zinc determinations gave the following results:—

- I. 0.7561 gram of zinc salt gave 0.2093 gram $\text{ZnO} = 22.23$ per cent. Zn.
 II. 0.7106 gram of zinc salt gave 0.1956 gram $\text{ZnO} = 22.11$ per cent. Zn.
 III. 0.7941 gram of zinc salt gave 0.2195 gram $\text{ZnO} = 22.20$ per cent. Zn.

corresponding to $(\text{C}_3\text{H}_5\text{O}_4)_2\text{Zn} + \text{H}_2\text{O}$, which contains 22.26 per cent. Zn.

This is the same as the zinc salt prepared by Debus (*loc. cit.*).

The solubility was determined, with the result that 100 parts by weight of water at 20° dissolved:—

I	4.19 parts	$(\text{C}_3\text{H}_5\text{O}_4)_2\text{Zn} + \text{H}_2\text{O}$
II	4.01 "	" "
Mean.....	4.10 "	" "
or 3.87 parts of the anhydrous salt.		

(b.) *Active*.—This was similarly prepared; the crystals, consisting of delicate needles radiating from a centre, were pressed between filter-paper for analysis. The zinc determinations gave the following results:—

- (1). 0.2980 gram of zinc salt yielded 0.0825 gram $\text{ZnO} = 22.25$ per cent. Zn.
 (2). 0.4030 gram of zinc salt yielded 0.1105 gram $\text{ZnO} = 22.03$ per cent. Zn,

corresponding to $(\text{C}_3\text{H}_5\text{O}_4)_2\text{Zn} + \text{H}_2\text{O}$, containing 22.26 per cent. Zn.

The solubility was determined, with the result that 100 parts by weight of water at 20° dissolved:—

41.58 parts $(\text{C}_3\text{H}_5\text{O}_4)_2\text{Zn} + \text{H}_2\text{O}$,
 or 39.03 parts of the anhydrous salt,

so that the solubility of the active is about 10 times as great as that of the inactive salt.

Examined in 10 per cent. solution at 16° , a rotation of -4.4° was observed, leading to the specific rotation

$$[\alpha]_D = \frac{100 \times -4.4}{1.984 \times 10} = -22.18^\circ (-23.63^\circ \text{ for the anhydrous salt}).$$

Cadmium Glycerate.

(a.) *Inactive*.—This was prepared similarly to the zinc and magnesium salts already described. It separates from solutions in rosettes of tabular crystals, apparently hexagonal plates.

The cadmium determinations gave the following results:—

- I. 0.5535 gram of cadmium salt yielded 0.3285 gram $\text{CdSO}_4 = 31.92$ per cent. Cd.
- II. 0.4225 gram of cadmium salt yielded 0.2490 gram $\text{CdSO}_4 = 31.74$ per cent. Cd.
- III. 0.5220 gram of cadmium salt yielded 0.3085 gram $\text{CdSO}_4 = 31.82$ per cent. Cd,

corresponding to $(\text{C}_3\text{H}_5\text{O}_4)_2\text{Cd} + 1\frac{1}{2}\text{H}_2\text{O}$, which contains 32.09 per cent. Cd.

The determination of the solubility gave the following results; 100 parts by weight of water at 20° dissolved:—

I	4.87	parts	$(\text{C}_3\text{H}_5\text{O}_4)_2\text{Cd} + 1\frac{1}{2}\text{H}_2\text{O}$
II	4.72	„	„
Mean.....	4.80	„	„
or 4.43 parts of the anhydrous salt.			

(b.) *Active*.—The solution of this salt on evaporation yielded a syrup which refused to crystallise, so it was dissolved up in a small quantity of water and precipitated with alcohol as a sticky mass, which, on remaining in contact with the alcohol, became hard and crystalline in about three days. It was pressed between filter-paper for analysis.

The cadmium determinations gave the following figures:—

- I. 0.2430 gram of cadmium salt yielded 0.1435 gram $\text{CdSO}_4 = 31.81$ per cent. Cd.
- II. 0.2543 gram of cadmium salt yielded 0.1510 gram $\text{CdSO}_4 = 31.97$ per cent. Cd,

corresponding to $(\text{C}_3\text{H}_5\text{O}_4)_2\text{Cd} + 1\frac{1}{2}\text{H}_2\text{O}$, which contains 32.09 per cent. Cd.

Thus both inactive and active cadmium glycerate form the same hydrated salt with $1\frac{1}{2}$ mols. of water.

The solubility is about 20 times as great as that of the inactive salt, thus, 100 parts by weight of water at 20° dissolved:—

92 parts $(\text{C}_3\text{H}_5\text{O}_4)_2\text{Cd} + 1\frac{1}{2}\text{H}_2\text{O}$,
or 85 parts of the anhydrous salt.

Examined in 10 per cent. solution at 19°, a rotation of -2.8 was observed, corresponding to a specific rotation of

$$[\alpha]_D = \frac{100 \times -2.8}{1.984 \times 10} = -14.11^\circ \text{ } (-15.29^\circ \text{ for the anhydrous salt}).$$

Silver Glycerate.

Only the active salt was prepared. It was obtained by placing an excess of silver oxide in contact with a solution of the active glyceric acid for several hours, frequently shaking, and gently heating to about 40°. The liquid was filtered, and the filtrate allowed to evaporate in the vacuum desiccator; a brownish-yellow syrup was left, which, on standing for more than a month, formed feathery needles radiating from nuclei resembling in appearance those of the sodium salt. The salt, which even in the dry state is lemon-coloured, yields a very dark brown solution, apparently through decomposition, and on this account, unfortunately, no determination of the optical activity could be made.

The salt was pressed between filter-paper for analysis, and the following silver determinations obtained with it:—

I. 0.3055 gram of silver salt yielded 0.197 gram $\text{AgCl} = 48.51$ per cent. Ag.

II. 0.2255 gram of silver salt yielded 0.145 gram $\text{AgCl} = 48.38$ per cent. Ag,

corresponding to $(\text{C}_3\text{H}_5\text{O}_4)\text{Ag} + \frac{1}{2}\text{H}_2\text{O}$, which contains 48.65 per cent. Ag.

Thus the silver and sodium salts both crystallise also with the same amount of water.

In the following table (p. 310), we have recorded the chemical composition and solubility, when that could be determined, of each of the glycerates, inactive and active, submitted to analysis.

This table shows that, in every case in which the solubility has been determined, the solubility of the active salt is greater, and in some cases enormously greater, than that of the inactive salt of the same metal. The "homologous" metals for which the data are most complete are calcium, strontium, and barium on the one hand, and magnesium, zinc, and cadmium on the other. In the case of the inactive salts, strontium is more soluble than calcium, and barium slightly more soluble than strontium, whilst of the active salts, barium is much more soluble than calcium, and strontium* probably

* Unfortunately, through an accident, the determination of the solubility of the active strontium salt was lost, but we have ascertained that about 300 parts of the salt dissolve in 100 parts of water at 20°.

Glycerates.	Chemical composition.	Solubility of crystalline salt in 100 parts of water at 20° C.	Solubility of anhydrous salt in 100 parts of water at 20° C.
Lithium (inactive)	$\text{LiC}_3\text{H}_5\text{O}_4$	—	—
„ (active)	—	—	—
Ammonium (inactive) ..	$\text{NH}_4\text{C}_3\text{H}_5\text{O}_4$	—	—
„ (active)	—	—	—
Sodium (inactive)	—	—	—
„ (active)	$\text{NaC}_3\text{H}_5\text{O}_4 + \frac{1}{2}\text{H}_2\text{O}$	—	—
Magnesium (inactive) ..	$\text{Mg}(\text{C}_3\text{H}_5\text{O}_4)_2 + \text{H}_2\text{O}$	24.53	22.78
„ (active)	—	46.36	43.05
Potassium (inactive) ...	—	—	—
„ (active)	—	—	—
„ acid (inactive)	$\text{KC}_3\text{H}_5\text{O}_4, \text{C}_3\text{H}_6\text{O}_4$	—	—
„ „ (active) ..	—	—	—
Calcium (inactive)	$\text{Ca}(\text{C}_3\text{H}_5\text{O}_4)_2 + 2\text{H}_2\text{O}$	4.4	3.85
„ (active)	—	10.66	9.32
Zinc (inactive)	$\text{Zn}(\text{C}_3\text{H}_5\text{O}_4)_2 + \text{H}_2\text{O}$	4.10	3.87
„ (active)	$\text{Zn}(\text{C}_3\text{H}_5\text{O}_4)_2 + \text{H}_2\text{O}$	41.58	39.03
Strontium (inactive) . . .	$\text{Sr}(\text{C}_3\text{H}_5\text{O}_4)_2 + \frac{1}{2}\text{H}_2\text{O}$	6.36	6.17
„ (active)	$\text{Sr}(\text{C}_3\text{H}_5\text{O}_4)_2 + 3\text{H}_2\text{O}$	very soluble	indeed
Silver (active)	$\text{AgC}_3\text{H}_5\text{O}_4 + \frac{1}{2}\text{H}_2\text{O}$	—	—
Cadmium (inactive) . . .	$\text{Cd}(\text{C}_3\text{H}_5\text{O}_4)_2 + 1\frac{1}{2}\text{H}_2\text{O}$	4.80	4.43
„ (active)	—	92.0	85.0
Barium (inactive)	$\text{Ba}(\text{C}_3\text{H}_5\text{O}_4)_2 + \frac{1}{2}\text{H}_2\text{O}$	6.77	6.60
„ (active)	$\text{Ba}(\text{C}_3\text{H}_5\text{O}_4)_2 + 2\text{H}_2\text{O}$	55.35	50.15

much more soluble than either. There is a similar relationship between the amounts of water of crystallisation; the inactive and active calcium salts contain the same amount (2 mols.) of water of crystallisation, and there is comparatively little difference in their solubilities; the inactive barium and strontium salts contain the same amount ($\frac{1}{2}$ mol.) of water of crystallisation and are almost identical in solubility; the active barium salt contains much more water of crystallisation (2 mols.) than the inactive, and is much more soluble; the active strontium salt has an even larger amount of water of crystallisation (3 mols.) than the inactive, and is enormously more soluble. In the magnesium, zinc, and cadmium sub-group, on the other hand, the inactive and active zinc salts are less soluble than the corresponding salts of magnesium and cadmium, the magnesium inactive and the cadmium active being the most soluble. The magnesium inactive and active contain the same water of crystallisation (1 mol.) and differ comparatively little in their solubility; the cadmium inactive and active salts contain also the same water ($1\frac{1}{2}$ mols.), but the active is enormously the more soluble; similarly, the active and inactive zinc salts contain the same water of crystallisation (1 mol.), but the active is, notwithstanding, much the more soluble.

Glycerate.	Formula.	Concentration (percentage).	Observed rotation for D line in 1·984 dm. tube.	Specific rotation, $[\alpha]_D$.		Molecular rotation of anhydrous salt, $M \times \frac{[\alpha]_D}{100}$.	Specific rotation of glyceric acid ($C_3H_5O_4$).
				Salt as analysed.	Anhydrous salt.		
Lithium	$LiC_3H_5O_4$	10	-4·1°	—	-20·66°	-23·14°	-21·83°
Sodium	$NaC_3H_5O_4 + \frac{1}{2}H_2O$	10	-3·2	—	-16·13	-20·65	-19·48
Potassium	$KC_3H_5O_4$	11·635	-3·8	—	-16·46	-23·70	-22·36
„ (acid)	$KC_3H_5O_4, C_3H_5O_4$	10·359	-1·9	—	-9·24	-23·10	-10·90
Ammonium	$NH_4 \cdot C_3H_5O_4$	10·610	-3·8	—	-18·03	-22·20	-20·94
Calcium	$Ca(C_3H_5O_4)_2 + 2H_2O$	10	-2·3	-11·66°	-13·34	-33·35	-15·73
Strontium	$Sr(C_3H_5O_4)_2 + 3H_2O$	10	-2·0	-10·08	-11·91	-35·44	-16·72
Barium	$Ba(C_3H_5O_4)_2 + 2H_2O$	10	-1·8	-9·07	-10·01	-31·73	-16·38
Magnesium	$Mg(C_3H_5O_4)_2 + H_2O$	10	-3·7	-18·65	-20·08	-46·99	-22·16
„ Zinc	$Zn(C_3H_5O_4)_2 + H_2O$	10	-4·4	-22·18	-23·63	-65·05	-30·69
„ Cadmium	$Cd(C_3H_5O_4)_2 + 1\frac{1}{2}H_2O$	10	-2·8	-14·11	-15·29	-49·23	-23·22

In the table (p. 311), we have recorded the activities of the several salts experimented with, together with their molecular rotations and the specific rotation of the glyceric acid as deduced from the rotations of the individual salts.

The figures which are of chief importance in the above table are those in the last column, which indicate the optical activity of the glyceric acid as calculated from the optical activities of the several salts. From these figures it is at once apparent that the specific rotation of the glyceric acid is subject to great variations according to the particular metals which have replaced its hydrogen; broadly speaking, its activity is greatest when the hydrogen is replaced by the metals of the magnesium group, least when replaced by the metals of the alkaline earths, and intermediate when the alkaline metals are introduced. The dependence of the activity of the acid on the metal introduced is perhaps most forcibly brought out by the optical behaviour of the normal and acid potassium salts; thus the molecular rotation of both these salts is almost identical, which means that the molecule of glyceric acid which the acid salt contains exercises practically no influence on its rotation; the rotation of a solution of the acid salt is, in fact, the same as that which is observed if only such a quantity of normal salt is in solution as is present in the acid salt itself.

That the optical activity of the glyceric acid is influenced by the particular metal replacing its hydrogen was indeed already shown by one of us in the original communication (*Trans.*, 1891, **59**, 96), for the activity of the salts is both much greater in degree than that of the glyceric acid from which they are derived, and also opposite in direction.

That the optical activity of an active substance is altered by introducing different inactive substances is quite out of harmony with the more recent views which have been expressed on this subject. Thus Ostwald (*Lehrb. der allgemeinen Chemie*, Leipzig, p. 498, 1891) states, "Both the compounds of active bases with inactive acids, as well as those of active acids with inactive bases, are subject to the simple law that the molecular rotation of the salts in somewhat dilute solution is independent of the nature of the inactive part." This law, which is due to Oudemans, is based on observations made with the monacid alkaloids, which yield the same molecular rotation irrespective of the acid with which they are combined, and again from similar observations which have been made with the salts of active acids, thus for

	K.	Na.	Am.
Podocarpic acid..	134°	133°	130°

SALTS OF GLYCERIC ACID, ACTIVE AND INACTIVE. 313

	K.	Na.	Am.	Ba.	Sr.	Ca.	Mg.
Quinic acid.....	48·6°	48·9°	47·9°	46·8	48·7°	48·4	47·9°
Cholalic acid...	28·0°	27·0°					
	LiHT.	AmHT.	NaHT.	KHT.			
Tartaric acid (acid salts).....	28·5°	28·5°	27·5°	28·3°			
	Li ₂ .	Am ₂ .	Na ₂ .	K ₂ .			Mg.
Tartaric acid (normal salts).....	38·6°	42·9°	39·9°	43·0°			41·2°
	(NH ₄)Na.	(NH ₄)K.	NaK.				
Tartaric acid (normal salts).....	41·2°	42·6°	41·6°				
	Li ₂ .	Mg.	Am ₂ .	Ca.	Na ₂ .	K ₂ .	Ba.
Camphoric acid (normal salts)..	37·5°	39·5°	38·4°	39·1°	36·0°	36·1°	36·5°

Amongst these acids we must distinguish between those the rotation of which is less, and those the rotation of which is greater than that of their salts. Thus tartaric acid has a much smaller rotation than its salts, quinic acid a slightly smaller rotation than its salts, whilst the rotations of cholalic and camphoric acids are much greater than those of their salts. The rotation of podocarpic acid is almost exactly the same, but if anything slightly greater than that of its salts; Beilstein gives it as $[\alpha]_D = +136^\circ$.

It is obvious that we should not necessarily expect the phenomena exhibited by camphoric and cholalic acids to resemble those to which glyceric acid gives rise, inasmuch as the relationship of their optical properties to those of their salts is so entirely different from the relationship subsisting between glyceric acid and its salts.

In the case of tartaric acid, however, analogy to glyceric acid in this respect might reasonably be expected, and, indeed, it will be found that such analogy does exist as far as the salts of tartaric acid have been investigated; but in the case of tartaric acid, only the lithium, sodium, ammonium, potassium, and magnesium salts are available for comparison. Thus the specific rotation of the tartaric and glyceric acids respectively deduced from these salts is as follows:—

	Li.	Am.	Na.	K.	Mg.
Tartrates (normal)	38·6°	42·9°	39·9°	43·0°	41·2°
Glycerates	21·8°	20·9°	19·5°	22·4°	22·2°

In both series the activity culminates in the potassium salt, the activity of the ammonium salt being also greater than that of the sodium salt; however, the differences within this series are so small

that we cannot attribute any great importance to them without making a more exhaustive investigation of the individual salts, so that the effect of dilution may be more taken into account, and this we propose doing later.

If then the above had been the only salts of glyceric acid examined, the results would have fully substantiated the law which has been enunciated by Oudemans, but it is impossible to harmonise with this law the rotations either of the glycerates of the alkaline earths or of zinc, the former giving values for the specific rotation of glyceric acid very much below, and the latter very much in excess of, the values obtained from the alkali salts. The cadmium salt, on the other hand, gives a value for the specific rotation of glyceric acid which is somewhat above that derived from the magnesium, but much below that calculated from the zinc, salt.

It should be pointed out, indeed, that the rotations of the tartrates themselves do not altogether support Oudemans' law, since the rotation of tartar emetic is altogether anomalous, giving a value for the specific rotation of tartaric acid enormously greater than that which is calculated from the other salts of tartaric acid. This anomaly, which occurs also in the case of ammonium antimonyl malate, is duly recognised by Oudemans himself, although he does not attempt to give any explanation of the circumstance beyond remarking that the peculiarity must be attributed to the antimony of the antimonyl group. This is practically a renunciation of the validity of the law which he has himself formulated.

The phenomena exhibited by the salts of quinic acid, which have been so carefully investigated by Oudemans, are also enlisted by him in support of his generalisation, but a careful examination of his figures shows that these salts display the same optical relationships in miniature as are met with on an exaggerated scale in the case of the glycerates.

Thus, after giving the mean specific rotation of quinic acid calculated from the rotations of its salts as below,

$[\alpha]_D$ for $C_7H_{12}O_6$,			
From K	salt		48·8°
„ Na	„		48·9
„ Am	„		47·9
„ Ba	„		46·6
„ Sr	„		48·7
„ Ca	„		48·7
„ Mg	„		47·8
„ Zn	„		51·0
	Mean.....		48·5

he says that "the difference between the values obtained and this mean are in general very small; only the values obtained with the zinc salt and the barium salt sensibly deviate from it. Probably these differences must be attributed to divers disturbing influences, such as the influence of concentration, errors of observation, impurity of the salts employed, &c."

It will be observed that these deviations from the mean are the same in kind as those of the zinc and barium salts of glyceric acid, although much less in degree.

In the case of lactic acid, however, the parallelism, as far as it goes, is complete, but the data unfortunately are most scanty. Thus Wislicenus (*Annalen*, 167, 332) determined the rotations of the calcium and zinc salts of sarcolactic acid with the following results:—

Salt.	Percentage concentration for anhydrous salt.	Specific rotation of anhydrous salt, $[\alpha]_D$.	Molecular rotation, $M \times [\alpha]_D$. 100	Specific rotation of sarcolactic acid (calculated), $C_3H_6O_3$.
$Zn(C_3H_5O_3)_2 + H_2O$	13.98	-7.30°	-17.76°	-9.87°
	9.60	7.29	17.74	9.85
	6.51	7.83	19.05	10.58
	5.36	8.49	20.66	11.48
	4.75	8.43	20.51	11.39
	4.58	8.73	21.24	11.80
$Ca(C_3H_5O_3)_2 + 9H_2O$	5.35	-5.25	-11.45	-6.36

From the above it will be seen that not only is the specific rotation deduced for lactic acid very much greater in the case of the zinc salt than in that of the calcium salt, but the ratio between the two values is almost identical with the ratio between the corresponding values for glyceric acid. Thus selecting, of course, the rotations for the same concentration in the case of the zinc and calcium lactates, we have

$$\frac{\text{Specific rotation of lactic acid deduced from zinc lactate}}{\text{Specific rotation of lactic acid deduced from calcium lactate}} = \frac{11.48}{6.36} = 1.805,$$

whilst for zinc and calcium glycerates we find—

$$\frac{\text{Specific rotation of glyceric acid deduced from zinc glycerate}}{\text{Specific rotation of glyceric acid deduced from calcium glycerate}} = \frac{30.69}{15.73} = 1.951.$$

The coincidence is as close as could be anticipated when it is borne in mind that the concentration for which this comparison is made in the case of the lactates (5.36 per cent.) is only about one-half as great as that (10 per cent.) for which it has been made in the case of the glycerates. We purpose shortly making a fuller examination of these remarkable relationships in the case of the lactates, for which further information is urgently demanded.

Turning again to the table of glycerate rotations on p. 311, it would appear that there are no less than four values for the specific rotation of glyceric acid deducible from its metallic compounds; the lowest is that derived from the acid potassium salt, the second that from the salts of the alkaline earths, the third that from the alkaline salts, as well as the salts of magnesium and cadmium, whilst the fourth and highest value is that calculated from the zinc salt. These values are approximately in the ratio of 1 : 1.5 : 2 : 3.

It is further worthy of remark that in the case of the alkaline and magnesium salts the specific rotation of the glyceric acid is approximately one-half of that of tartaric acid deduced from the same salts, whilst in the case of the zinc and calcium salts the specific rotation of lactic acid appears to be about one-third of that deduced for glyceric acid when combined with the same metals.

It thus appears that the influence of different metals on an active acid is at any rate well marked in the case of those acids which have a lower specific rotation than their salts; thus, in the case of quinic acid, the influence of the metal on the activity, although distinct, is not nearly so pronounced as in that of glyceric and lactic acids; but it is just in the case of glyceric and lactic acids that the rotations of the salts are so much greater than the rotations of the free acids, whilst in the case of quinic acid the free acid has a rotation but slightly inferior to that of its salts. Tartaric acid, the rotation of which is also much increased in its salts, has not had the optical properties of the latter sufficiently investigated to throw light on this point, the determinations being limited to the salts of the alkalis and magnesium, but the remarkable rotation of tartar emetic, already referred to, clearly points to the powerful influence of some metals on the specific rotation of this acid also. As regards camphoric acid, in which the rotation of the acid is much greater than that of its salts, the data are insufficient to determine whether the activity of the acid is influenced by the nature of the metal introduced; it is worthy of remark that in Hartmann's figures, given above (see p. 313), there is some evidence of the values being in the inverse order to that which holds good in the case of the glycerates, tartrates, and quimates, but the differences in these values for the

salts in question are so small that much stress cannot at present be laid upon them.

In conclusion, we may refer to the advanced and beautiful theory of M. Philippe Guye (*Arch. des Sci. Phys. et Natur.*, 1891, **26**, 97—369) that the degree of rotation of active substances is dependent on the extent of the dissymmetry of their molecules, as measured by the inequality of the masses of the four groups attached to the asymmetric carbon atom. This theory, which serves to account for the relationship between the rotations of such a large number of substances, fails signally, as admitted by Guye himself, in the case of the aqueous solutions of the simplest active acids and their salts, namely, lactic and glyceric acids and their salts. Thus, formulating these acids as below,

Lactic acid.

Glyceric acid.

it is obvious that in each case their salts should rotate the plane of polarisation in the same direction as the parent acid, inasmuch as the displacement by metals of the hydrogen in the COOH group has the effect of still further weighting the heaviest of the four groups, yet as a matter of fact in the case of both acids the sign of the rotation is opposite to that of their salts. Not only is the theory inadequate to explain the relationship between the rotations of these acids and their salts, but the relationship between the rotations of the salts themselves is out of harmony with it; thus, taking the salts of glyceric acid with the monad metals, the specific rotation of the lithium salt should be the lowest, and that of the potassium salt the highest; again, in the case of the glycerates of the dyad metals, the rotation of the magnesium salt should be lowest and that of the barium salt the highest, but, as a matter of fact, none of these predictions is actually verified. Indeed, in the present uncertain state of our knowledge concerning the phenomena of solution, these peculiarities do not appear to admit of any satisfactory explanation, but they may at some future time be of great importance in throwing light on the complex problems of solution itself.

We do not at present propose drawing any conclusions from the relationships between the rotations which we have established, as we purpose making a more detailed investigation of these phenomena, in which the effect of concentration will have to be further tested. The results, however, as far as they go, appear to lend support to and to extend the views on multiple rotation which have been expressed by Mulder (*Zeitschr. f. Chem.*, 1868, 58), Krecke (*J. pr. Chem.*, 1872, **5**, 6), Landolt (*Ber.*, 1873, **6**, 1073), and T. Thomsen (*Ber.*, 1880, 2168, 2264, 2269; 1881, 29, 134, 203, 807, 1647), but subsequently controverted by Landolt (*Ber.*, 1881, 296, 1048) and Oudemans (*Rec. Trav. Chim.*, 1885).

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