

LXXXVI.—*Resolution of Lactic acid into its Optically Active Components.*

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OF the three known methods of resolving racemoid compounds into their optically active components, the two which depend on the action respectively of micro-organisms and of other active substances have been practised with success in numerous stereochemical investigations in recent times. The third method, on the other hand—spontaneous resolution by crystallisation of the two enantiomorphic forms—does not appear to have been used as a practical means of obtaining optically active compounds, and indeed the phenomenon on which it is based has been but rarely observed to occur. The only instances recorded in the most recent treatise on stereochemistry (Hantzsch, *Grundriss der Stereochemie*, 1893) are the well known cases of certain salts of racemic acid, in which the phenomenon was first noted, and of inactive asparagine, which crystallises always as a mixture of the enantiomorphic forms. E. Fischer has recently shown (*Ber.*, **25**, 1025) that an inactive solution of d.- and l.-gulonic lactones deposits a mixture of the two isomerides, although some of the inactive derivatives made from such a mixture crystallise as true racemoid compounds.

Irrespective of the rarity of its occurrence, the resolution of racemoid compounds by crystallisation possesses a special interest; of the three methods of resolution referred to, it is the only one which is purely chemical in the sense that it is independent, even indirectly, of vital agency, and the phenomenon has, moreover, as has been shown by Van't Hoff (*Ber.*, **19**, 2142) and others, an intimate bearing on problems relating to chemical equilibrium.

The application of the method in question to ordinary inactive lactic acid forms the subject of the present communication, the investigation which is described having been undertaken with the view of discovering a simple means of obtaining the active lactic acids.

In a communication to this Journal (Purdie and Walker, 1892, **61**, 754) on the resolution of inactive lactic acid by crystallisation of the strychnine salts, an active zinc ammonium lactate, of the composition $\text{ZnC}_6\text{H}_{10}\text{O}_6, \text{NH}_4 \cdot \text{C}_3\text{H}_5\text{O}_3, 2\text{H}_2\text{O}$, was described, which is distinguished from most of the other lactates by its habit of crystallising in comparatively large, well-defined forms. It was found to possess in a marked degree the property of forming supersaturated solutions.

Thus, when either of the active zinc lactates was dissolved in an excess of a solution of the corresponding active ammonium lactate, a syrup was obtained on evaporation, from which the salt in question crystallised rapidly when a nucleus of the already formed crystalline salt was added to it. It was also observed that a concentrated solution of inactive ammonium lactate was capable of dissolving large quantities of inactive zinc lactate, a thick syrup being formed, which on dilution, and sometimes on standing, deposited inactive zinc lactate, but that no inactive double salt separated. These observations suggested the idea that possibly the inactive zinc lactate, on being heated in concentrated ammonium lactate solution, was resolved into its active components, and that by altering the conditions of temperature and concentration so as to avoid the recombination of the enantiomorphic forms, the active double salts might be separately crystallised from the supersaturated solution on the addition of the proper nucleus.

The observation referred to regarding the non-formation of an inactive zinc ammonium lactate was erroneous, but the method suggested yielded, nevertheless, after numerous trials, the desired result.

Resolution of Inactive Lactic acid into its Active Constituents.

Preliminary Experiments.—The preliminary experiments which were made were not encouraging. A very concentrated solution of zinc and ammonium lactates was prepared by dissolving with the aid of heat 34 grams of the former salt in a thick syrup of the latter, procured by adding excess of strong ammonia to 36 c.c. of syrupy lactic acid. A nucleus of the active zinc ammonium lactate, which was added, remained undissolved, but it did not induce the desired crystallisation. The syrup gradually solidified to a crystalline mass consisting of tufts of needles, bearing no resemblance to the active double salt. The conditions were varied by carrying out the crystallisation at a low temperature, by adding alcohol to make the solution less syrupy, and by adding lactic acid to distinct acid reaction, but without success. On several occasions, the crystalline splinters which had been added as nuclei seemed to increase a little in size, but they became so soon enveloped with the inactive salt, that it was impossible to be certain of the correctness of the observation. On one occasion, a minute quantity of a granular crystalline powder, differing from the needles and lying round the nuclei, was discernible with the aid of a lens. It was found impossible to separate it from the mass of crystalline inactive salt in which it was imbedded, but these observations led to a continuance of the experiments.

A less concentrated solution was made by dissolving 20 grams of

zinc lactate in the same quantity of ammonium lactate as before, the volume of the solution being 50 c.c. The separation of the inactive salt was slower in this case, but the growth of the active nuclei could not be verified with certainty. A small quantity of this solution, however, which had been placed in a watch glass for a special experiment, with a nucleus of the dextrogyrate double salt, and left exposed to the air for some days, was found to have deposited a thin, transparent film of glassy crystals, which, on examination under the microscope, were seen to bear a close resemblance to the active double salt procured in the strychnine method of separation. After a week, the small quantity of syrup which remained was poured off, the dry crystals, weighing 0.2045 gram, were dissolved in water, and the solution made up to 10 c.c. Polarimetric examination of this in a 200 mm. tube gave the rotation $+7'$. Having, at the time, no lævogyrate salt at my disposal for use as a nucleus, the mother liquor was left to crystallise spontaneously, but it merely deposited needles recognisable as the inactive salt. Crystals and syrup together were therefore dissolved in water. The solution, made up to 10 c.c., showed the rotation $-4'$ in the 200 mm. tube. The solution in the watch glass which yielded the active salt was slightly acid, and of a less syrupy consistency than the solutions which had been previously used, owing to the escape of ammonia and absorption of moisture; the liquid from which it had been taken was, therefore, acidified by the addition of a little dilute lactic acid, heated till clear, and when cool again sown with a trace of powdered dextrogyrate zinc ammonium lactate. In a few days the liquid became turbid, and a deposit consisting of minute, microscopic prisms was formed. The thick, syrupy liquid was poured off as far as possible, and the crystalline paste brought again into solution by the addition of a little water and heating. On standing some days, a thin crust of the same minute, short prisms, formed on the bottom of the crystallising dish, which was, however, soon covered with a much more voluminous deposit of inactive needles. The liquid being poured off, the latter were removed as far as practicable, and the crust which adhered to the bottom of the dish was placed on filter paper. When dry, it weighed 0.83 gram. It was shaken up with rather more than 10 c.c. of water, and filtered into a 200 mm. tube. The solution showed the rotation $+28'$.

The mother liquor from which the crystalline paste had been taken measured 45 c.c. A few c.c. of water having been added to it, it was heated till clear and sown with active salt, but only a thick deposit of inactive salt was obtained. The solution was, therefore, evaporated, and again sown with dextrogyrate salt. The short, minute prisms of the active salt now appeared, but were quickly

followed by the much more abundant growth of inactive needles. 0.79 gram of dry crystals was obtained, a solution of which in 12 c.c. of water showed the rotation +21'.

The mother liquor, on standing a fortnight, deposited 8.4 grams of salt, consisting of radiating groups of much more elongated prisms than those of the active salt; it was found to be quite inactive.

The mother liquor from this deposit was again heated till clear, and sown with a trace of the lævogyrate salt, some of this substance having been meanwhile procured by the resolution of ordinary lactic acid by means of strychnine. The nuclei increased in size, and the liquid became turbid owing to the separation of microscopic prisms exactly resembling the dextrogyrate salt, which in a few days formed a thin layer on the bottom of the dish. None of the radiating groups of inactive salt appeared. 1.75 grams of dry salt was obtained, which nearly all dissolved in 16 c.c. of water, and in a 200 mm. tube gave the rotation -58'.

These experiments afforded proof that the lactic acid had been resolved into its active components by crystallisation of the active zinc ammonium lactate, but the process of resolution was evidently very incomplete, and the tendency of the solutions to deposit one or more inactive salts presented the chief obstacle to the isolation of the active compounds; a series of experiments on a small scale was, therefore, made in order to find conditions of concentration more favourable to the exclusive crystallisation of the latter salts.

In each of the following experiments, 10 c.c. of lactic acid syrup ($d = 1.21$) were taken; strong ammonia was added till a solution was secured which, after being heated during some time, remained distinctly alkaline on cooling; the solution was again heated over the naked flame until it was slightly acid, the zinc lactate being meanwhile dissolved in it, and water added to make it up to the desired volume, and when cool a trace of the powdered dextrogyrate salt was stirred into it. The crystalline deposit which formed was freed from adhering syrup with the aid of a suction pump and washed with dry alcohol, as it was found that the syrup deposited zinc lactate when diluted with water, but remained clear on the addition of alcohol. The washings, having been freed from alcohol by evaporation, were returned to the filtrate, the crystallisation of which, after it had been heated till clear, was again induced by adding a nucleus of the lævogyrate salt. The crystalline deposits were weighed in the air-dried condition, and allowed to remain for 12 hours in 16 c.c. of water, except in a few cases in which the quantity of water used is specially mentioned. The solution was then filtered into the 200 mm. tube and examined with the polarimeter. The weights of zinc lactate used, the volumes of the solutions, also the results of the experiments,

including the weights of the deposits of active salts and the observed angles of rotation under the conditions mentioned, are given briefly below.

Experiment 1.—Zinc lactate, 8 grams; vol., 20 c.c. In 12 hours a pretty large crystalline deposit of the active salt had formed, mixed, however, with tufts of inactive needles: 1st crop, 3.96 grams, in 32 c.c., +14'; 2nd crop, 0.83 gram, -31'.

Experiment 2.—Zinc lactate, 7 grams; vol., 15 c.c. In two days scarcely any crystallisation had occurred; the solution was, therefore, made up with water to 20 c.c.; in 12 hours there was a thick deposit of active salt mixed with tufts of inactive needles: 1st crop, 5.6 grams, in 45 c.c., +9'; the 2nd crop, being very small, was not examined.

Experiment 3.—Zinc lactate, 6 grams; vol., 22 c.c. In a few hours needles of inactive salt appeared in quantity, and in 12 hours there was an abundant deposit, but examination with the microscope showed that there was none of the active salt present. The solution was evaporated to just under 20 c.c.; in 12 hours a deposit of the active salt, mixed with some inactive needles, had formed: 1st crop, 1.94 grams, +29'; 2nd crop, 0.91 gram, -40'.

Experiment 4.—Zinc lactate, 6 grams; vol., 17 c.c. In 12 hours there was an abundant growth of the active salt, and the inactive salt did not appear till the third day: 1st crop, 2 grams, +26'; 2nd crop, 0.54 gram, -28'.

Experiment 5.—Zinc lactate, 5 grams; vol., 20 c.c. In two days inactive salt only had separated; the solution was evaporated to 15 c.c. The crystallisation at this concentration was very slow: 1st crop, after six days, 1.02 grams, +24'; 2nd crop, 0.59 gram, -31'.

Experiment 6.—Zinc lactate, 3 grams, vol., 15 c.c. In four days there was very little crystalline growth; therefore 3 grams more zinc salt were added, and the solution made up with water to 19 c.c. In 12 hours there was a considerable deposit of active salt: 1st crop, 1.37 grams, +24'; 2nd crop, 0.34 gram, in 10 c.c., -30'.

These experiments show that comparatively slight variations in the quantity of water which is present have a marked influence on the nature and quantity of the salt which crystallises from the solution. Dilution beyond a certain limit increases very greatly the quantity of inactive salt which separates, concentration beyond a certain limit practically stops crystallisation altogether, while at intermediate degrees of concentration, both active and inactive salts are deposited, but, by the addition of the proper nucleus, both the enantiomorphic active salts may be made to crystallise from the solution before the inactive salt begins to separate. Thus, when the volume was 15 c.c.,

crystallisation was extremely slow, and the salt which separated was, to a large extent, active. At 22 c.c., crystallisation began at once and was abundant, but the salt was inactive; at 20 c.c., the inactive salt predominated, especially so when the zinc lactate exceeded 6 grams. At concentrations between 15 c.c. and 20 c.c., the crystallisation was fairly rapid, and in its first stages consisted, to a large extent, of active salt.

Experiments on the Larger Scale.—In the following experiment, the proportion of materials was taken which the experiments just described indicated as the most favourable for the desired crystallisation. The quantities used were:—Lactic acid, 200 c.c. (sp. gr. = 1.21); zinc lactate, 120 grams; volume of solution, 360 c.c. The lactic acid was tested and found to be inactive, both in the form of syrup and after it had been diluted to five times its bulk with water and boiled during several hours in a flask fitted with a reflux condenser. The zinc lactate used was also proved to be inactive.

The solution having been prepared in the manner already described, was divided into two portions, A and B, of 150 c.c. each, and three portions, C, D, and E, of 20 c.c. each. To A was added 0.01 gram of the dextrogyrate, to B, 0.01 gram of the lævogyrate zinc ammonium lactate, and to C, 0.01 gram of a mixture of equal parts of the two active salts; to D, 0.01 gram was added of the inactive zinc ammonium lactate crystallising in radiating groups of elongated prisms which had been obtained in a previous experiment, and to E no nucleus was added. The crystalline deposits were treated as already described, and their activity observed by dissolving 2 grams in water and making the solution up to 25 c.c., the length of tube used being 200 mm. After 12 hours, the solution A gave 7.70 grams of crystalline salt, showing a rotation of +50', and B gave 3.11 grams, showing the rotation of -51'. C had crystallised in exactly the same manner as A and B, namely, in isolated, short, microscopic prisms, truncated with characteristic terminal domes, but the salt, 1.72 grams in weight, was entirely different in its behaviour. While 2 grams of the former dissolved readily with slight warming in 25 c.c. of water, the solution remaining clear on standing, a solution of the latter, of the same strength, could be made only by heating to nearly boiling, and it deposited inactive zinc lactate on cooling; the salt remaining in solution was inactive. The salt which had crystallised, was, in fact, a mixture, in equal quantities, of the two active zinc ammonium lactates, which, on the addition of water, formed inactive ammonium lactate and the comparatively insoluble inactive zinc lactate. The solution D had also crystallised in 12 hours, but in a manner quite different from A, B, and C. The deposit consisted of groups of radiating prisms, much more elongated in proportion to their thick-

ness than the prisms of the active salts; it continued to increase in quantity during several days, after which no further growth was perceptible. The solution was left for more than a month, but none of the crystals such as were yielded by A, B, and C were produced. 2 grams dissolved with difficulty in 25 c.c. of water, and the solution, which deposited much inactive zinc lactate on cooling, was found to be inactive. The salt was a zinc ammonium salt of ordinary lactic acid, which was resolved by water into ordinary ammonium and zinc lactates. The solution E, to which no nucleus was added, did not begin to crystallise till the third day, and the deposit which gradually formed was the same inactive salt yielded by the solution D, without any admixture of the active salts. It is thus seen that in a solution such as that used, inactive zinc ammonium lactate, or either of the active salts, can be made to crystallise according to the character of the nucleus used.

In order to obtain some quantity of the active zinc ammonium salts, the solutions A and B were treated alternately with nuclei of the dextrogyrate and lævogyrate salts, and the several crops of crystals weighed and examined with the polarimeter. After five

	Weight.	α .
A.		
1st crop	7.70 grams	+ 50'
2nd "	10.87 "	- 41'
3rd "	2.32 "	- 47'
4th "	4.98 "	+ 52'
5th "	0.78 "	- 57'

B.		
1st crop	3.11 grams	- 51'
2nd "	14.86 "	+ 8'
3rd "	6.24 "	+ 54'
4th "	3.73 "	- 58'
5th "	2.37 "	+ 52'

A and B united.

6th crop	18.45 grams	- 21'
7th "	10.55 "	+ 54'
8th "	16.80 "	- 51'
9th "	11.47 "	+ 58'
10th "	12.77 "	+ 53'
11th "	16.86 "	- 55'
12th "	8.41 "	- 45'

crops had been taken from each, the two solutions were mixed and 20 grams zinc lactate were dissolved in the liquid. A lævo- and a dextro-gyrate crop having been taken out, another 20 grams of zinc lactate were added to the mother liquor, and the process of alternate crystallisation of the oppositely active salts and addition of fresh zinc lactate repeated until seven crops of crystals had been obtained from the united liquids. The results are appended (p. 1149), the numbers given under α being the rotation produced in a 200 mm. tube by solutions containing 8 grams of salt in 100 c.c.

I found, after some practice in later experiments on a still larger scale, that the alternate crystallisation of dextro- and lævo gyrate salt could be conducted with the greatest regularity and certainty, the activity being usually above 50'. It will be observed in the results given above that the signs + and - alternate regularly, except in the 10th and 3rd crops. In the former of these cases, a dextrogyrate nucleus had been added intentionally, but the apparent irregularity of the latter case demands a word of explanation, as it shows that, although the active salts, when present in equal quantities, are not readily deposited unless a nucleus is added, the crystallisation of one of them may begin spontaneously if a large proportion of the other has been previously removed. After removal of the first crops, the mother liquors were left over night, the intention being that they should be heated and sown with the appropriate nuclei in the morning. A great fall of temperature occurred during the night, with the result that heavy deposits formed in both cases. It was expected that the activity of these deposits would be of the same sign as that of the respective first crops, as the solutions had not been filtered clear, and nuclei were, therefore, left in them; to produce the third crops, a lævogyrate nucleus was accordingly added to A, and a dextrogyrate one to B. On subsequent examinations of the second crops, it was found, however, that the signs of activity had become spontaneously reversed, and that the crop from B was only slightly active. The irregularity is easily accounted for. In the case of solution A, the first crop having been comparatively large, the dextrogyrate salt present had been nearly all removed; the further deposition of this salt, therefore, soon ceased, and the spontaneous deposition of the lævogyrate salt occurred. In the case of solution B, the first crop was comparatively small; a considerable quantity of the lævogyrate salt accordingly continued to crystallise, after which the growth of the dextrogyrate salt began, the result being that, in this case, the deposit was a mixture of the two isomerides in nearly equal quantity. In subsequent experiments, with proper precautions, irregularities of the kind indicated were readily avoided. The experiment described yielded in all 56.08 grams of dextrogyrate and 62.88 grams of lævo-

gyrate salt, irrespective of the crops showing the rotations $+8'$ and $-21'$, which were not mixed with the others.

Recrystallisation of the Active Zinc Ammonium Lactates.—Some difficulty was encountered in recrystallising these salts. They crystallise readily from a solution containing an excess of ammonium lactate, but they cannot be satisfactorily crystallised from water. 8 parts of the salt dissolve readily in 100 parts of water, the double salt being, no doubt, to a large extent decomposed into ammonium and zinc lactates; but, as the solution becomes more concentrated by evaporation, it deposits, on cooling, active zinc lactate. The solution of the crystals in water, and the rapid deposition of the zinc salt in the form of needles, is strikingly seen on a slide under the microscope. When the aqueous solution is evaporated to a syrup, its contents solidify rapidly, mostly in the form of the double salt.

After numerous trials, it was found that the salt could be well crystallised by dissolving it in about an equal weight of warm dilute ammonia solution. The salt, under these circumstances, does not undergo the decomposition produced by pure water, and separates, when the solution cools, either spontaneously or on the addition of a nucleus, in large, glassy prisms. The inactive zinc ammonium lactate also dissolves in solution of ammonia without separation of zinc lactate, and the solution deposits an inactive, crystalline, basic salt, containing zinc and ammonia. When a mixture of active and inactive zinc ammonium lactates is crystallised as described, either the active double salt or the inactive basic salt may crystallise first, according as one or the other constituent predominates in the solution. Thus, for instance, in the case of one of the crops of double salt referred to above, which gave only the rotation $-21'$ in an 8 per cent. solution, by recrystallisation from ammonia, 8 grams of inactive salt were first removed, after which, on further standing, 3 grams of active salt were obtained from the solution, giving the rotation $-57'$ under similar conditions. On the other hand, in recrystallising the more active crops of crystals, it was found that the inactive salt was mostly deposited in the later stages of crystallisation.

Composition and Properties of the Active Zinc Ammonium Lactates.

By recrystallising the 56.08 grams of dextrogyrate salt from ammonia solution, three successive crops of crystals were obtained, weighing together 32.10 grams, and possessing the same activity. In the fourth crop, inactive salt, in the form of groups of radiating prisms, could be detected with the lens.

The three crops were mixed and dried in air, and an exact determination of the specific rotation was made, with the following result.

$\alpha = +0.97^\circ$; $l = 200$ mm.; $c = 7.998$; hence

$$[\alpha]_D = \frac{0.97 \times 100}{2 \times 7.998} = +6.06^\circ.$$

The 62.88 grams of lævogyrate salt gave two crops of crystals, weighing together 28.91 grams, and having the same activity; the third crop was considerably less active. A second recrystallisation of the combined first two crops did not raise the activity. An exact determination of the specific rotation gave the following result.

$\alpha = -0.97^\circ$; $l = 200$ mm.; $c = 8.0012$; hence

$$[\alpha]_D = -\frac{0.97 \times 100}{2 \times 8.0012} = -6.06^\circ.$$

The results of analysis show that these compounds are identical with the active zinc ammonium lactates previously obtained from the strychnine salts (*loc. cit.*).

- I. Dextrogyrate salt.—0.635, dried in air, lost 0.0587 in a vacuum, and gave 0.1351 ZnO; 2.2920, similarly dried, gave 0.1026 NH₃.
 II. Lævogyrate salt.—0.4772, dried in air, lost 0.0435 in a vacuum; 0.3965 of the anhydrous salt gave 0.092 ZnO; 2.2362 air-dried salt gave 0.1004 NH₃.

	Calculated for C ₉ H ₁₅ O ₉ ZnNH ₄ ·2H ₂ O.	Found.	
		I.	II.
H ₂ O.....	9.33	9.24	9.12
Zn.....	16.84	17.07	16.92
NH ₄	4.66	4.74	4.75

The active zinc ammonium lactates crystallise in short prisms or plates, exhibiting six, and sometimes eight, prismatic faces and prominent terminal domes. The presence of hemihedral faces could not be detected with certainty; I hope, however, to obtain the crystals sufficiently large and well developed for future exact description. The salts remain unchanged in weight on exposure to the air, but lose their water of crystallisation in a vacuum. As already stated, they are decomposed by water into their constituent simple salts.

When equal quantities of the two salts are mixed together in aqueous solution, inactive zinc lactate is precipitated. 5 c.c. each of 8 per cent. solutions of the dextrogyrate and lævogyrate solutions were mixed; the resulting solution remained clear, but, after a few minutes, a turbidity was perceptible, and in a short time a heavy, crystalline deposit had formed. An estimation of zinc in the crystalline substance, dried in folds of filter paper, gave 22.02 per cent., the calculated number for crystallised inactive zinc lactate being 21.89.

With respect to the specific rotation of the active zinc ammonium lactates, the highest number found for the dextrogyrate salt obtained by crystallising the strychnine salts (*loc. cit.*) was $+6.49$ for a concentration approximating to that used in the present instance. The difference between this number and those quoted above is greater than can be accounted for by errors of experiment, and indicated that the salts prepared by the method here described were not pure. Some of the active double salt was, therefore, made from the active zinc lactate subsequently procured, the purity of which had been proved by polarimetric observations and by analysis. The lævogyrate zinc lactate was dissolved in water; half of the solution was decomposed with sulphuretted hydrogen and filtered; the filtrate, having been neutralised with ammonia, was added to the other half of the solution, and the united liquids were then evaporated to a syrup, from which the double salt crystallised on standing. The following is the result of a determination of the specific rotation of the air-dried salt.

$\alpha = -1.03^\circ$; $l = 200$ mm.; $c = 8.000$; hence

$$[\alpha]_D = -\frac{1.03 \times 100}{2 \times 8} = -6.44^\circ,$$

a number which agrees with that found for the purest specimen of the dextrogyrate salt prepared by the strychnine method. It is true that the zinc lactate prepared from the latter gave a rather low rotation (*loc. cit.*), but I am inclined to attribute this to error of experiment caused by the small quantity of material then at my disposal.

Conversion of the Active Zinc Ammonium Lactates into Zinc Lactates.

To obtain the zinc lactates, the zinc was removed from the double salts by means of sulphuretted hydrogen, and the ammonia was then driven off by boiling the filtered liquids with milk of lime; on treating the filtered solution of the calcium salt with the calculated quantity of sulphuric acid, and subsequently filtering and evaporating, a syrup was obtained which was repeatedly extracted with ether. The acid left on evaporation of the ethereal extract was converted into zinc salt by boiling with water and zinc oxide; the zinc lactate which crystallised from the filtered and evaporated solutions on cooling was analysed and submitted to polarimetric examination.

In the case of the dextrogyrate zinc ammonium lactate, 25 grams of the salt had been used for conversion. The first crop of zinc lactate, amounting to 12 grams, proved to be nearly pure active salt. It was recrystallised and gave a crop of 8 grams of the pure salt. The polarimetric observations made on the hydrated salt, dried in air, are as follows.

1st crop: $\alpha = +0.98^\circ$; $l = 200$ mm.; $c = 7.4665$; hence

$$[\alpha]_D = \frac{0.98 + 100}{2 \times 7.4665} = +6.56^\circ.$$

1st crop, recrystallised: $\alpha = +1.02^\circ$; $l = 200$ mm.; $c = 7.484$;

hence
$$[\alpha]_D = \frac{1.02 \times 100}{2 \times 7.484} = +6.81^\circ.$$

Wislicenus (*Annalen*, **167**, 332) found the specific rotation of zinc sarcosylactate for similar concentration ($c = 7.47$) to be -6.83 .

Of the lævogyrate zinc ammonium lactate, 22 grams were used for conversion into zinc lactate. The first crop of crystals which separated from the solution, weighing 13.9 grams, dried at 105° , consisted of practically pure active salt. Determinations of specific rotation were made both on the anhydrous and hydrated salt, the latter being obtained by recrystallisation of the first crop. The results are as follows.

I. Anhydrous salt: $\alpha = -0.99^\circ$; $l = 200$ mm.; $c = 6.3956$;

hence
$$[\alpha]_D = -\frac{0.99 \times 100}{2 \times 6.3956} = -7.74^\circ.$$

II. Hydrated salt: $\alpha = -1.02^\circ$; $l = 200$ mm.; $c = 7.4685$;

hence
$$[\alpha]_D = -\frac{1.02 \times 100}{2 \times 7.4685} = -6.83^\circ.$$

These numbers are also in accordance with those found by Wislicenus for similar concentrations, namely, for the anhydrous salt, -7.83 ($c = 6.51$), and for the hydrated salt, -6.83 ($c = 7.47$).

The purity of the salts is further confirmed by the results of analysis.

I. Dextrogyrate salt. 0.5662 of the recrystallised 1st crop, dried in air, lost, at 105° , 0.0727 and gave 0.165 ZnO.

II. Lævogyrate salt. 0.5980 of the recrystallised 1st crop, dried in air, lost, at 105° , 0.0768 and gave 0.1735 ZnO.

	Calculated for $C_6H_{10}O_6Zn, 2H_2O$.	Found.	
		I.	II.
H_2O	12.90	12.84	12.84
Zn.....	23.30	23.39	23.28

The inactive zinc lactate used in the experiments was also analysed.

0.5599 of the crystallised salt lost, at 105° , 0.1010 and yielded 0.1548 ZnO. $H_2O = 18.04$; $Zn = 22.19$.

$C_6H_{10}O_6Zn, 3H_2O$ requires $H_2O = 18.18$; $Zn = 21.89$ per cent.

Inactive Zinc Ammonium Lactate.—It has been stated that a solu-

tion used in one of the preliminary experiments, from which a small quantity of active zinc ammonium lactate had been obtained, deposited afterwards on standing a larger quantity (8.4 grams) of an inactive salt crystallising in radiating groups of prisms which were more elongated than those of the active salt. It contained ammonia, and an estimation of zinc in the substance, freed from adhering syrup by means of alcohol and dried in folds of filter paper, gave the number 16.33 per cent. Estimations of zinc and of ammonium in another specimen, similarly obtained, gave the numbers 16.10 per cent. and 4.35 per cent. respectively; the corresponding calculated numbers for a zinc ammonium lactate with 3 mols. H_2O are 16.09 and 4.46. It was found, however, that on further washing the salt with alcohol, the percentage of zinc in it was increased to 16.85, which accords with the composition of a zinc ammonium lactate containing 2 mols. H_2O , namely, 16.84 per cent. Further examination showed, in fact, that the salt undergoes decomposition when left long in contact with alcohol. When the salt is repeatedly washed on a filter and the alcoholic filtrate evaporated, the latter leaves a syrup of ammonium lactate; when put into absolute alcohol, the salt gradually dissolves, and the solution eventually deposits a gelatinous substance, no doubt anhydrous zinc lactate.

The same inactive zinc ammonium lactate was also produced in the solutions designated D and E (p. 1149). The substance in question is, no doubt, the racemoid compound of the active zinc ammonium lactates, of which analyses have been given, and as it was desirable to establish its composition with more certainty than the analytical numbers quoted above afford, some of the salt was specially prepared for the purpose. It is readily procured by using the proportion of materials which has been already indicated as most favourable for the crystallisation of the active salts, namely, lactic acid syrup 10 c.c., zinc lactate 6 grams, volume of solution 18 c.c. If no nucleus of active salt is added, the inactive salt in question crystallises spontaneously. If so much water is added that the volume of the solution much exceeds 20 c.c., zinc lactate is apt to be formed instead of the double salt. In one instance, in which the proportion of water only a little exceeded 20 c.c., it was found, on analysis of the crystalline deposit, that it consisted of pure zinc lactate. For the purpose of analysis, the double salt was thoroughly drained from syrup, very slightly washed with alcohol, and quickly dried in folds of filter paper.

0.4845 lost in a vacuum 0.0650 gram. $H_2O = 13.42$.

0.5688 gave 0.1141 ZnO , and 1.1442 gave 0.0477 NH_3 . $Zn = 16.10$;
 $NH_4 = 4.42$.

Calculated for $C_9H_{15}O_9ZnNH_4 \cdot 2H_2O$, $H_2O = 13.37$; $Zn = 16.09$;
 $NH_4 = 4.46$ per cent.

1156 LACTIC ACID AND ITS OPTICALLY ACTIVE COMPONENTS.

The active and inactive zinc ammonium lactates therefore differ in composition, the former crystallising with 2 mols. H_2O , the latter with 3 mols. H_2O .

There is also a well-marked difference in the properties of the salts. The difference in crystalline habit has been already mentioned. The active salts undergo no change when exposed to the air, but the inactive salt deliquesces, and undergoes decomposition. The former also presents more resistance to the action of alcohol than the latter. The active salts can be crystallised unchanged from dilute ammonia. The inactive salt dissolves in dilute ammonia, like the active salt, but the solution, on standing, deposits a salt in the form of small, transparent prisms which analysis showed to be quite different in composition from the zinc ammonium lactates; it contains ammonia, but deposits zinc oxide when dissolved in water, and estimations of zinc in different preparations of the salt, in the air-dried condition, gave 21.88 and 22.04 per cent., numbers which differ widely from the percentage of zinc in the double salts referred to, and accord with the composition of a substance of the formula $\text{Zn}(\text{C}_3\text{H}_5\text{O}_3)_2, \text{NH}_3, 2\text{H}_2\text{O}$, in which the water of zinc lactate is partially replaced by ammonia. The salt is probably related to the salts prepared by Lutschak (*Ber.*, 5, 30) by passing ammonia gas over anhydrous zinc lactate, to which the formulæ $(\text{C}_3\text{H}_5\text{O}_3)_2\text{Zn}, 2\text{NH}_3$ and $(\text{C}_3\text{H}_5\text{O}_3)_2\text{Zn}, 3\text{NH}_3$ are assigned. My estimations of water and ammonia, however, were not very concordant, and the salt will have to be further examined. The same crystalline salt as that referred to is apparently produced when equal quantities of the oppositely active zinc ammonium lactates are dissolved in ammonia, and when inactive zinc lactate is similarly treated.

The experiments which have been described afford no direct information regarding the so-called "point of transition" of the racemoid and active zinc ammonium lactates, such as is known to exist in the case of the racemates and tartrates. From the fact, however, that at the ordinary temperature the inactive zinc ammonium lactate is deposited spontaneously from the solution, and in much larger quantity than the active salts, it seems probable that the racemoid is the stable form at low temperatures, and that the active salts are formed when the solution is heated, a certain proportion of the latter still remaining in a state of supersaturation in the solution when it has cooled below the point of transition. I propose to continue the study of the resolution of lactic acid by crystallisation of its salts in the hope of throwing further light on this subject.

In working up the residual solutions used in the course of this investigation, I find that by the process described, that is to say, by alternate crystallisation of the oppositely active zinc ammonium lactates and fresh addition of inactive zinc lactate to the exhausted

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mother liquors, it is easy to obtain larger yields of the active salts than those mentioned. It has been shown that salts containing 94 per cent. of active substance can be obtained by recrystallisation of the double salts, and that, by further crystallisation of the active zinc lactates prepared from these, the inactive salt can be eliminated. The method seems, therefore, applicable for procuring the active lactic acids on the large scale, and I propose to make use of it for the preparation of some of the derivatives of these acids, a study of which will be of interest in connection with the subject of the relation of optical activity to chemical composition.

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