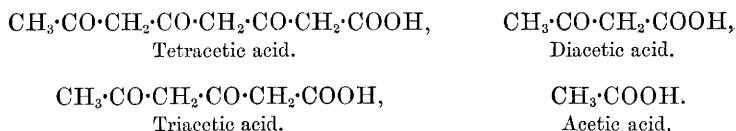


LVI.—*The Lactone of Triacetic Acid.*

By J. NORMAN COLLIE, Ph.D., F.R.S.E., University College, London.

IN a paper which I communicated to this Society some short time ago (this vol., p. 5, 189) on the constitution of dehydracetic acid, I pointed out that if the formula which I proposed for dehydracetic acid were the correct one, it would then be the *δ-lactone of tetracetic acid*. The following list was then given, which was intended to show the connection between the condensed acids formed from acetic acid:—

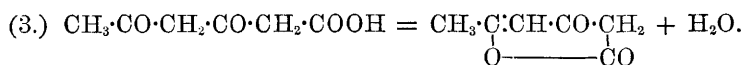
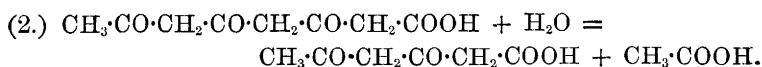
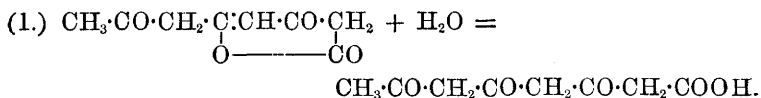


Although no acid corresponding to the triacetic acid or its lactone was then known, still, by analogy, one could predict the possibility of its existence. Since the paper on dehydracetic acid was published, I have been trying in various ways to substantiate by means of experiment the correctness of my views with regard to dehydracetic acid, and although the work on dehydracetic acid itself, is not yet finished, yet I have been able to obtain a new acid from it which seems, without doubt, to be the missing lactone of triacetic acid.

When dehydracetic acid is dissolved in strong sulphuric acid, no reaction takes place, but if the temperature is raised to about  $150^\circ$ , the dehydracetic acid is completely decomposed and a very large portion is converted into acetic acid.

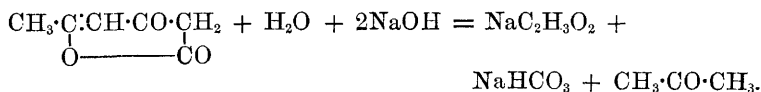
If, however, dehydracetic acid is mixed with sulphuric acid containing about 8—10 per cent. of water, and the mixture kept at  $130$ — $135^\circ$  for a few minutes and then cooled, on pouring it into water a new acid separates in crystals, which, when pure, have a much higher melting point ( $188$ — $189^\circ$ ) than dehydracetic acid.

This new acid is probably the lactone of triacetic acid and is formed according to the following reactions:—

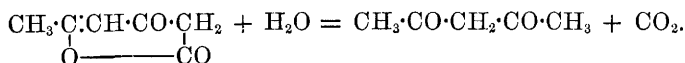


The properties of this new substance are very similar to those of dehydracetic acid. It has an acid reaction with litmus paper, yet it does not seem to form a stable ammonium salt, for its solution in ammonia, when evaporated in a vacuum, leaves a certain amount of free acid uncombined. This ammonium salt is, however, more stable than the corresponding compound of dehydracetic acid.

When warmed with alkalis, complete decomposition occurs, acetic acid, acetone, and carbonic acid being formed:—

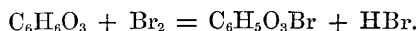


Boiled with water or with acids, it splits into acetylacetone and carbon dioxide:—



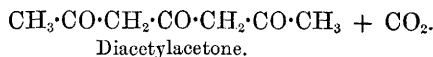
Treated with hydroxylamine, an oxime results, which proves the presence of a carbonyl group.

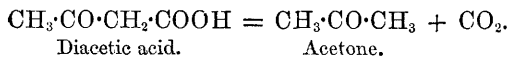
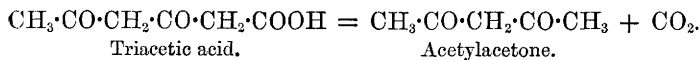
With bromine, a mono-substituted compound is obtained:—



The lactone cannot be distilled, but suffers decomposition when heated to a little above 200°.

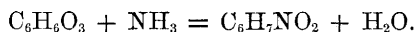
From the above reactions, it seems probable that this substance is the lactone of triacetic acid. The formation of acetylacetone when boiled with acids resembles, in a striking way, the decomposition of diacetic and tetracetic acids when similarly treated:—





In the case of dehydracetic acid, however, the diacetylacetone suffers a further loss of water, and dimethylpyrone is formed.

Lastly, when triacetic lactone is treated with ammonia, and the ammonium salt heated on the water-bath, nearly the whole is converted into a new compound, which contains nitrogen, but which does not give ammonia when boiled with strong caustic soda :—



#### EXPERIMENTAL PART.

##### *Action of 90 per cent. Sulphuric Acid on Dehydracetic Acid.*

50 grams of dehydracetic acid were dissolved in 150 grams of dilute 90 per cent. sulphuric acid. The mixture was then heated in a flask which was immersed in an oil-bath. When the contents of the flask were at a temperature of 130°, a drop was allowed to fall into water; as soon as no crystals formed in the water after the addition of the drop of the mixture, the flask was rapidly cooled, and the contents poured into about 200 c.c. of cold water. The new compound crystallised out at once. It was then recrystallised from hot water; this operation must be done as quickly as possible, for prolonged boiling decomposes the lactone to a considerable extent. By this process a yield of between 80—90 per cent. was obtained.

The new acid is more soluble in water than dehydracetic acid; it is also easily soluble in alcohol or hot acetone. In ether, benzene, chloroform, or light petroleum, it is only sparingly soluble. When pure, it crystallises in long, white needles which melt at 188—189° (corr.). An analysis gave the following numbers :—

- I. 0·3870 gram substance gave 0·8130 gram CO<sub>2</sub> and 0·1730 gram H<sub>2</sub>O.  
 II. 0·3785 gram substance gave 0·7950 gram CO<sub>2</sub> and 0·1650 gram H<sub>2</sub>O.

	Calculated for C <sub>6</sub> H <sub>6</sub> O <sub>3</sub> .	Found.	
		I.	II.
C .....	57·14	57·29	57·28
H .....	4·76	4·96	4·84

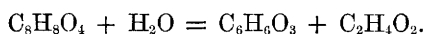
The percentage of carbon and hydrogen is, of course, the same as

that required by dehydracetic acid ( $C_8H_8O_4$ ), and also with other acids of the  $C_{2n}H_{2n}O_n$  series. It was, therefore, necessary to determine the molecular weight. This was done by the Raoult method, and also by the analysis of some of the salts:—

0.5040 gram substance lowered the melting point of 39.55 grams of acetic acid,  $0.38^\circ$ . Molecular weight = 130.

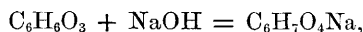
	Calculated for $C_6H_6O_3$ .	Found.
Mol. weight .....	126	130

The new acid has, therefore, been produced by the elimination of acetic acid from tetracetic acid:—



In order to verify whether acetic acid had been formed during the reaction, the mother liquors from an experiment where 20 grams of dehydracetic acid had been used were neutralised with caustic soda, and then evaporated to dryness. The residue was extracted with alcohol, and the sodium acetate thus obtained corresponded to 9 grams of acetic acid, the theoretical amount, according to the above equation being 7 grams. The sodium acetate seemed to be nearly pure, and was characterised by its properties and reactions.

The new acid reddens litmus paper, and produces an effervescence when added to potassium or barium carbonates. It seems to be mono-basic, for 9.415 grams acid took 2.95 grams caustic soda for neutralisation. From the following equation:—



the amount required is 2.98 grams.

The acid when neutralised with ammonia and evaporated in a vacuum over sulphuric acid loses some of its ammonia; it therefore in this respect resembles dehydracetic acid, and is probably not a true acid but a lactone. Most of its salts are soluble in water; even the silver salt can only be precipitated from strong solutions.

*Silver Salt.*—On adding a concentrated solution of either the ammonium or barium salt of the acid to a strong solution of silver nitrate, a granular, white precipitate forms.

- I. 0.4120 gram salt gave 0.1895 gram Ag = 46.00 per cent. Ag.
- II. 0.2235 gram salt gave 0.1035 gram Ag = 46.28 per cent. Ag.
- III. 0.3170 gram salt gave 0.1460 gram Ag = 46.05 per cent. Ag.
- IV. 0.4065 gram salt gave 0.4630 gram  $CO_2$ , 0.0840 gram  $H_2O$ , and 0.1880 gram Ag.

	Calculated for $C_6H_5O_3Ag.$	Found.			
		I.	II.	III.	IV.
C .....	30.90	—	—	—	31.00
H .....	2.14	—	—	—	2.14
Ag .....	46.25	46.00	46.28	46.05	46.25

I, II were precipitated from silver nitrate solution by the ammonium salt.

III, IV were precipitated from silver nitrate solution by the barium salt.

*Potassium Salt.*—The acid was exactly neutralised by potassium carbonate. The solution was evaporated to dryness, and extracted with alcohol. The alcoholic solution on evaporation left a syrup which would only crystallise when the last traces had been evaporated. The salt was therefore again dissolved in dry alcohol, and precipitated by adding dry ether. It was then obtained as a white, crystalline precipitate. This was dried in a vacuum over sulphuric acid and analysed.

0.3450 gram salt gave 0.1850 gram  $K_2SO_4 = 24.03$  per cent. K.

	Calculated for $C_6H_5O_3K.$	Found.
K .....	23.78	24.03

*Barium Salt.*—This salt was prepared both from the hydrate of barium and from the carbonate. The solution of the salt evaporated either over sulphuric acid or on the water-bath dried up to a vitreous mass. It was, however, obtained as a crystalline precipitate by adding dry ether to the alcoholic solution:—

0.3900 gram salt (dried in a vacuum) gave 0.2240 gram  $BaSO_4 = 33.77$  per cent. Ba.

0.4220 gram salt (dried at  $130^\circ$ ) gave 0.2520 gram  $BaSO_4 = 35.11$  per cent. Ba.

	Calculated for		Found.	
	$(C_6H_7O_4)_2Ba.$	$(C_6H_5O_3)_2Ba.$	I.	II.
Ba .....	32.38	35.40	33.77	35.11

Nearly all the metallic salts of the lactone seem to be very soluble, as no precipitates were obtained by using a concentrated solution of the barium salt, and adding it to copper acetate, lead acetate, or mercuric chloride. The lead salt can be obtained by boiling the lactone with lead carbonate. The action is, however, very slow. The solution of the lead salt on evaporation deposits oily drops,

which eventually crystallise. The barium salt of the lactone added to a neutral solution of ferric chloride gives an orange-brown precipitate.

*Action of Bromine on the  $\delta$ -Lactone of Triacetic Acid.*

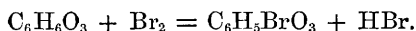
The lactone of triacetic acid reacts with bromine in a manner similar to dehydracetic acid. When the lactone is dissolved in strong acetic acid and bromine is carefully added to the well cooled mixture, after a short time a mono-brominated derivative crystallises out. The new compound is best purified by recrystallisation from acetic acid, and can be obtained in long needles, which turn black at about 200°, and decompose a few degrees higher with evolution of gas.

0.4310 gram substance gave 0.0960 gram H<sub>2</sub>O and 0.5535 gram CO<sub>2</sub>.

0.3015 gram substance gave 0.2805 gram AgBr = 39.59 per cent. Br.

	Calculated for C <sub>6</sub> H <sub>5</sub> BrO <sub>3</sub> .	Found.	
		I.	II.
C .....	35.46	35.02	—
H.....	2.46	2.47	—
Br .....	39.40	—	39.59

The compound has therefore been formed by the substitution of one hydrogen atom in the lactone by bromine :—



The substance possesses acid properties, and forms well defined salts, which are much more easily obtained in the crystalline condition than the corresponding ones of the lactone.

*The Barium Salt.*—This crystallises easily from a concentrated solution in stellate tufts of needles, and seems from its analysis to exist either as a salt of the true bromotriacetic acid or as a salt of the lactone. Some of the salt dried in the air gave the following numbers :—

0.2755 gram salt gave 0.107 gram BaSO<sub>4</sub> = 22.89 per cent. Ba.

2.0040 gram salt lost, in a vacuum over sulphuric acid, 0.0610 gram H<sub>2</sub>O = 3.04 per cent. H<sub>2</sub>O.

	Calculated for (C <sub>6</sub> H <sub>5</sub> BrO <sub>3</sub> ) <sub>2</sub> Ba, H <sub>2</sub> O.	Found.
Ba .....	22.87	22.89
H <sub>2</sub> O .....	3.00	3.04

Another specimen was dried in a vacuum over sulphuric acid:—

0.5655 gram salt gave 0.5200 gram CO<sub>2</sub> and 0.0965 gram H<sub>2</sub>O.  
0.4265 gram salt gave 0.1715 gram BaSO<sub>4</sub> = 23.64 per cent. Ba.

	Calculated for (C <sub>6</sub> H <sub>6</sub> BrO <sub>4</sub> ) <sub>2</sub> Ba.	Found.	
		I.	II.
C .....	24.87	25.07	—
H .....	2.06	1.89	—
Ba.....	23.58	—	23.64

And, lastly, some was dried at 127—130°, when it ceased to lose weight:—

0.4615 gram salt gave 0.1980 gram BaSO<sub>4</sub> = 25.22 per cent. Ba.  
0.3700 gram salt gave 0.1570 gram BaSO<sub>4</sub> = 24.90 per cent. Ba.

	Calculated for (C <sub>6</sub> H <sub>4</sub> BrO <sub>3</sub> ) <sub>2</sub> Ba.	Found.	
		I.	II.
Ba.....	25.13	25.22	24.90

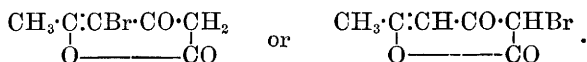
*The Silver Salt.*—This salt can be precipitated as a bulky mass of hair-like needles on adding a solution of the barium salt to silver nitrate. It can be recrystallised from hot water. It was dried in a vacuum and analysed:—

0.2365 gram salt gave 0.1340 gram AgBr = 32.55 per cent. Ag.

Calculated for C<sub>6</sub>H<sub>4</sub>BrO<sub>3</sub>Ag, Ag = 34.61 per cent. Calculated for C<sub>6</sub>H<sub>6</sub>BrO<sub>4</sub>Ag, Ag = 32.72 per cent.

Most of the other metallic salts are extremely soluble in water, as no precipitate could be obtained on adding solutions of lead, copper, or mercury salts. With a neutral solution of ferric chloride, an orange precipitate is obtained.

When the bromine compound is boiled with water, a strong smell of bromacetone is at once produced. From this fact it seems probable that the formula is either



The same decomposition also occurs when a solution of the bromine compound is boiled with dilute sulphuric acid; it can, however, be boiled for some time with caustic soda without any decomposition, the brominated lactone being precipitated unchanged on the addition of an acid.

*Action of Hydroxylamine on the  $\delta$ -Lactone of Triacetic Acid.*

The lactone was dissolved in sodium carbonate solution, and the hydrochloride of hydroxylamine then added, care being taken to have just sufficient carbonate to keep the solution alkaline. The mixture, after being left for 24 hours, was acidified, and the precipitate collected and recrystallised from hot alcohol and water; it forms long needles melting at 230—231° (corr.). Dried over sulphuric acid,

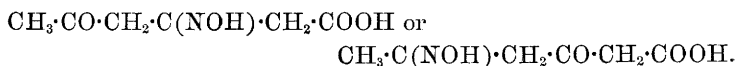
0.5255 gram substance gave 0.9755 gram  $\text{CO}_2$ .\*

0.2520 gram substance gave 0.4665 gram  $\text{CO}_2$  and 0.1385 gram  $\text{H}_2\text{O}$ .

0.3005 gram substance gave 24.8 c.c. N. at 16° and 768 mm. pressure.

	Calculated for $\text{C}_6\text{H}_9\text{NO}_2$ .	Found.		
		I.	II.	III.
C .....	50.35	50.62	50.48	—
H .....	6.29	—	6.10	—
N .....	9.79	—	—	9.73

The compound is therefore probably the oxime of triacetic acid,



With litmus paper it has an acid reaction.

The action of phenylhydrazine on the lactone was also tried, but although combination occurred, the resulting compound did not crystallise at all easily, so the reaction was not pursued farther.

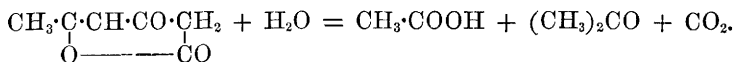
*Action of Concentrated Caustic Soda on the  $\delta$ -Lactone of Triacetic Acid.*

Ten grams of the lactone were boiled for a few minutes with strong caustic soda free from carbonate. The flask in which the mixture was boiled was connected with a reflux condenser. The mixture was then distilled; the distillate, on fractional separation, was found to consist of acetone and water, the acetone being recognised by its boiling point and the crystalline bisulphite compound. The residue containing the excess of caustic soda was neutralised with hydrochloric acid, when considerable effervescence of carbon dioxide occurred. The solution was then evaporated to dryness. The solid residue gave all the tests for acetic acid.

\* The hydrogen determination in this combustion was spoilt, owing to oxides of nitrogen being absorbed in the sulphuric acid bulb.



The  $\delta$ -lactone of triacetic acid therefore decomposes as follows:—



*Action of Heat on the  $\delta$ -Lactone of Triacetic Acid.*

Dehydracetic acid is capable of distillation without much decomposition; it was therefore expected that the lactone of triacetic acid would behave in a similar manner, but such was not found to be the case.

Ten grams were heated in an oil bath to about  $250^\circ$ ; complete decomposition occurred, and 3 grams of a liquid distillate was obtained, a large quantity of carbon dioxide was also evolved, and a considerable residue of charred matter remained in the flask. Nothing could be extracted from the charred residue except a small quantity of crystals, which were not further examined.

The distillate proved to be nearly pure acetylacetone (b. p.  $137-143^\circ$ ).

0.1520 gram substance gave 0.3350 gram  $\text{CO}_2$  and 0.1105 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_5\text{H}_8\text{O}_2$ .	Found.
C .....	60.00	60.10
H .....	8.00	8.07

Some of the characteristic copper salt was also prepared and analysed:—

0.2200 gram salt gave 0.0670 gram  $\text{CuO}$  = 24.28 per cent. Cu.

0.3048 gram salt gave 0.0920 gram  $\text{CuO}$  = 24.06 per cent. Cu.

	Calculated for $(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cu}$ .	Found.	
		I.	II.
Cu .....	24.13	24.28	24.06

*Action of Pentachloride of Phosphorus on the  $\delta$ -Lactone of Triacetic Acid.*

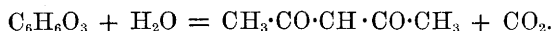
This reaction was looked upon with some interest, because the chloride which ought to be formed should on reduction yield normal hexylic acid. The result of the action of pentachloride of phosphorus was, however, very disappointing. The experiment was made in several different ways, but always with the same result.

At ordinary temperatures no action took place, but, on warming, a

vigorous reaction at once set in, with the invariable result that a dark-coloured mass was produced, which gave with water a magnificent rose-red solution; the bulk of the product of the reaction, however, was a black resin, which was only sparingly soluble in water, and gave a deep reddish-brown solution, which possessed the property of dyeing silk a beautiful salmon-pink. As no pure compounds could be separated from the products of the reaction, and the reaction itself seemed to be one of considerable complexity, the attempt to substitute chlorine for the oxygen atom in the carbonyl group of the lactone was abandoned.

The action of several other reagents was tried on the lactone. Heated with strong sulphuric acid at 200°, evolution of carbon dioxide began, and a small quantity of acetylacetone was produced. On cooling the mixture and pouring it into water, the original lactone crystallised out. If the heat is raised above 200°, the lactone is completely decomposed with evolution of carbon dioxide, sulphur dioxide, and other products, whilst a black charred mass remains in the flask.

With dilute sulphuric acid (25 per cent.), the lactone is at once decomposed. 1·30 grams were boiled with excess of the dilute sulphuric acid; 250 c.c. of carbon dioxide were at once evolved, and at the end of five minutes no further evolution of gas occurred. The residue contained nothing but acetylacetone and the sulphuric acid. The reaction appears, therefore, to be quantitative, and is expressed by the following equation:—



1·30 grams of the lactone of triacetic acid should give about 240 c.c. of carbon dioxide.

The lactone can be evaporated to dryness over the water-bath with strong nitric acid, without much change taking place; on the other hand, if it is first dissolved in strong sulphuric acid and the solution kept cold in a freezing mixture, the addition of a mixture of strong nitric and sulphuric acids causes no evolution of gas, but on pouring the liquid on to powdered ice, a nitro-compound separates as a flocculent precipitate. When recrystallised from glacial acetic acid, this forms yellow crystals melting at 210—212° (corr.).

On analysis:—

0·4045 gram substance gave 29·5 c.c. N at 758 mm. and 15° = 8·51 N.

	Calculated for $\text{C}_6\text{H}_5(\text{NO}_2)\text{O}_3.$	Found.
N .....	8·18	8·51

The lactone when warmed with hydriodic acid seems to be un-

acted on, as only traces of acetylacetone were noticed, and apparently the whole of the lactone could be recovered.

Heated at 100° with acetyl chloride and sodium acetate, it remains unchanged and therefore probably does not contain a hydroxyl group.

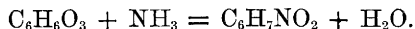
*Action of Heat on the Ammonium Salt of the  $\delta$ -Lactone of Triacetic Acid.*

If the lactone is dissolved in strong aqueous ammonia and the salt heated on the water-bath, a crystalline substance very soon begins to separate, and if the mixture is evaporated to dryness and the residual salt heated to about 100°, the conversion into a new nitrogen compound is very nearly complete. The new compound, recrystallised from alcohol and water, melts at about 315° (330°, corr.); it then rapidly chars. When boiled with strong caustic soda, not a trace of ammonia is evolved. Heated with zinc-dust, it gives the pyrrol reaction with a pine splinter moistened with strong hydrochloric acid.

- I. 0.2060 gram substance gave 0.4315 gram CO<sub>2</sub> and 0.1080 gram H<sub>2</sub>O.  
 II. 0.1980 gram substance gave 0.4160 gram CO<sub>2</sub> and 0.1055 gram H<sub>2</sub>O.  
 III. 0.2630 gram substance gave 26.2 c.c. N at 16° and 760 mm.

	Calculated for C <sub>6</sub> H <sub>7</sub> NO <sub>2</sub> .	Found.		
		I.	II.	III.
C .....	57.60	57.12	57.30	—
H .....	5.60	5.85	5.92	—
N .....	11.20	—	—	11.61

The reaction therefore is a simple one:—



As the investigation of this new nitrogen compound is not yet completed, I shall reserve the results for a future communication.