XLVII.—*Dehydracetic Acid.*

By W. H. PERKIN, Jun., Ph.D.

DEHYDRACETIC acid was first prepared by Geuther in the year 1866, who obtained it by passing a current of carbonic anhydride over the sodium compound of ethylic acetoacetate. From the analyses of the acid itself and also of its barium and sodium salts, Geuther showed that this new compound was a monobasic acid of the formula $C_8H_8O_4$. He supposed it to be formed by the dehydration of acetic acid, probably thus—

hence the name dehydracetic acid.

Geuther does not appear to have examined this acid further, and it is to Oppenheim and Precht (*Ber.*, **9**, 324) that the first careful study of it is due. These chemists showed that when dehydracetic acid is treated with alkalis it is decomposed into acetone, acetic acid, and carbonic anhydride, thus:—

Besides these products, they obtained by the hydrolysis of dehydracetic acid with baryta-water a small quantity of a crystalline substance very much resembling orcinol, and this led Beilstein to place dehydracetic acid in the aromatic series (*Handbuch der organischen Chemie*, 1527—1528).

Oppenheim and Precht also prepared the methylic and ethylic salts of dehydracetic acid, chlorodehydracetic acid, $C_8H_7ClO_4$, bromodehydracetic acid, $C_8H_7BrO_4$, and by reduction with zinc and hydrochloric acid a new acid of the formula $C_8H_{10}O_3$.

By the action of pentachloride of phosphorus on dehydracetic acid, they obtained a remarkable chloride of the formula $C_8H_6O_2Cl_2$, the formation of which led them to imagine that dehydracetic acid contained two hydroxyl-groups. For this reason they proposed the formula—

as best representing the constitution of this acid.

At the suggestion of Wislicenus, Shibbye (*Dissertation*, Würzburg, 1882, 5), at a later date, repeated the experiments of Oppenheim and Precht on the action of alkalis on dehydracetic acid, and showed that

besides acetone, acetic acid, and carbonic anhydride, considerable quantities of malonic acid were also formed.

As these results were still insufficient to definitely prove the constitution of dehydracetic acid, I thought it would be interesting to carry these experiments further, and wish now to bring before the Society the results I have obtained.

Dehydracetic acid, $C_8H_8O_4$, contains besides the carboxyl-group, two oxygen-atoms, which may either be present as CO, OH, or $C \cdot O \cdot C$.

When treated with hydroxylamine or phenylhydrazine, one oxygen-atom is easily displaced, forming the derivatives $C_7H_8O_3(CNOH)$ and $C_8H_8O_3(N_2H \cdot C_6H_5)$ respectively, a proof that one of the oxygen-atoms is present as CO; but all attempts to displace a second atom by the above groups were fruitless.

Dehydracetic acid does not give an acetyl-compound when treated with acetic anhydride, even after long boiling, and it is therefore clear that the fourth oxygen-atom is not present as hydroxyl, but that it is most probably united by each of its affinities to a different carbon-atom thus: $C \cdot O \cdot C$. This view is borne out by the reduction experiments of Oppenheim and Precht, as also by the behaviour of dehydracetic acid when treated with phosphorus pentachloride. In order to obtain some further clue as to the arrangement of the atoms in this interesting acid, the hydrolysis with alkalis was next very carefully studied.

In a paper on dehydrobenzoylacetic acid (Trans., 1885, 284) it was shown that when this acid is treated with alkalis, the first change which takes place is a quantitative decomposition into 2 mols. of benzoylacetic acid, thus:—

This result is very important for two reasons:—*Firstly*, it shows that the dehydrobenzoylacetic acid is really formed by the splitting off of 2 mols. of water from 2 mols. of benzoylacetic acid; and *secondly*, it proves that the two C_6H_5 -groups are intact in the dehydrobenzoylacetic acid, and that all changes which take place in its formation from benzoylacetic acid must take place within the group $-CO \cdot CH_2 \cdot COOH$. In determining the constitution of dehydracetic acid, it was clearly just as important to determine whether it contained two methyl-groups, in which case the formula proposed by Oppenheim and Precht would be incorrect.

If dehydracetic acid be very carefully hydrolysed with potash, it is possible to isolate an acid, which is without doubt acetoacetic acid; although naturally owing to the instability of the latter no quantita-

tive experiments could be made. From this result, it is legitimate to suppose that this acid, when treated with potash, in a way exactly analogous to dehydrobenzoylactic acid, is first split up into 2 mols. of acetoacetic acid, thus:—

This being the case, it is clear that dehydracetic acid must contain two methyl-groups, in the same way as dehydrobenzoylactic acid contains two phenyl-groups.

The next question is: How is dehydracetic acid formed from 2 mols. of acetoacetic acid?

Dehydracetic acid being a monobasic acid, it naturally follows that one of the carboxyl-groups of one of the molecules of acetoacetic acid must take part in the reaction. Now, as the methyl-groups remain intact, this change can only take place by the condensation of the carboxyl-group of one molecule with the methylene-group of the other molecule, thus:—

In the formation of dehydracetic acid from this intermediate compound, one more molecule of water is split off; the simplest way of effecting this being thus*:—

The most probable formula for dehydracetic acid would therefore be—

In considering how best to obtain evidence in support of this conclusion, it struck me that there was a certain resemblance between this formula and the formula given to cumalinic acid by

* This change is fully discussed in a paper on "Dehydrobenzoylactic Acid" (Trans., 1885, 295—297).

The striking relation of this acid to chelidonic and meconic acids did not occur to me till afterwards.

If the methyl salt of cumalinic acid is treated with ammonia, it is converted, as v. Pechmann has shown in his beautiful researches (*Ber.*, **17**, 2391), into hydroxynicotinic acid, thus:—

It was therefore possible that dehydracetic acid under similar conditions might also yield pyridine-derivatives. The experiment has shown that this is indeed the case.

If methylic dehydracetate is treated with ammonia or aniline, reaction immediately sets in, and pyridine-derivatives are formed, the decomposition being quantitative.

The products formed by the action of ammonia I have prepared but not analysed, as, curiously enough, Haitinger, at the same time as myself, investigated the action of ammonia on dehydracetic acid, and has reserved the further study of these products.

When methylic dehydracetate is warmed with aniline, two substances, $\text{C}_{15}\text{H}_{15}\text{NO}_3$ and $\text{C}_{13}\text{H}_{13}\text{NO}$, are formed, of which the former is undoubtedly the primary product.

The reaction probably takes place in two stages, in a way similar to that shown by v. Pechmann in the case of the cumalinic acid.

During this synthesis, partial hydrolysis of the compound $\text{C}_{15}\text{H}_{15}\text{NO}_3$ and decomposition into carbonic anhydride and the substance $\text{C}_{13}\text{H}_{13}\text{NO}$ takes place. The latter has therefore the constitution—

If the group $\begin{array}{c} \text{CH}-\text{CO}-\text{CH} \\ \parallel \qquad \parallel \\ \text{CH}_3\cdot\text{C}-\text{NH}-\text{C}\cdot\text{CH}_3 \end{array}$ be termed lutidone, it follows

that the primary product of the action of aniline on methylic dehydracetate is methylic phenyllutidinecarboxylate, whereas the substance $\text{C}_{13}\text{H}_{13}\text{NO}$ is phenyllutidone.

A most interesting synthetical proof of the constitution given above to dehydracetic acid has lately been carried out by Conrad and Guthzeit (*Ber.*, 19, 19, and 20, 151 and 154). These chemists found that when the copper salt of ethylic acetoacetate is treated with phosgene, the following decomposition takes place:—

This substance does not appear to exist as such, but spontaneously loses a molecule of water, and is converted into ethylic carboxyldehydracetate thus:—

If this compound is treated with aniline, ethylic phenyllutidone-dicarboxylate is found—

The free acid when heated to 270° is converted into phenyllutidone, a substance identical with that which I obtained by the action of aniline on methylic dehydracetate. This elegant synthesis by Conrad and Guthzeit proves without doubt that dehydracetic acid really has the formula given by me above.

The group pyrone, $\begin{array}{c} \text{CH}-\text{O}-\text{CH} \\ \parallel \qquad \parallel \\ \text{CH}-\text{CO}-\text{CH} \end{array}$ (Haitinger and Zieben, *Monatsh.*,

6, 283), besides being present in dehydracetic acid, is the basis of a number of interesting acids, among them chelidonic acid and meconic acid.

The relation of the most important representatives of this class to one another is clearly seen when their constitutional formulæ are placed side by side, thus:—

Preparation of Dehydracetic Acid.

In preparing dehydracetic acid, Oppenheim and Precht's method, which consists in passing the vapours of ethylic acetoacetate through a tube heated to dull redness, was after a few slight modifications found to give the best results.

The details of this process are the following:—A piece of combustion tube, 50 inches long, and bent about 18 inches from one end to an angle of 120°, is filled up to the bend with small pieces of pumice, and heated in a combustion furnace to dull redness. 200 grams of ethylic acetoacetate are then slowly distilled through this tube, from a distilling flask directly connected to the tube by means of a cork, and the product which comes over is collected in a well-cooled flask placed at the other end of the tube. A dark-brown oil is thus obtained, which on cooling should solidify almost entirely to a mass of crystals of dehydracetic acid. In order to isolate the acid, the crude product is rapidly distilled from a retort, until the temperature rises to 195°, and the residue is then poured into a dish and allowed to solidify. The dark-brown cake formed in this way is next broken up, and digested with an excess of a fairly strong solution of sodic

carbonate and a little animal charcoal for a short time, and filtered hot. The filtrate, on cooling and acidifying with hydrochloric acid, deposits the dehydracetic acid as a slightly brownish-coloured crystalline powder, which, after being collected, well washed, and recrystallised from water is easily obtained pure.

The distillate from the crude dehydracetic acid, boiling below 195°, yields on fractioning a considerable quantity of ethylic acetoacetate, which, when again passed through the tube, gives a further quantity of acid. With a little practice it is easy to obtain by this method from 58—66 grams of pure dehydracetic acid from 200 grams of ethylic acetoacetate. Most of the dehydracetic acid used in this research was obtained from Meister, Lucius, and Brünning, through the kindness of Herr v. Gerichten, and I take this opportunity of thanking these gentlemen for their liberality.

Monobromodehydracetic acid was first obtained by Oppenheim and Precht (*Ber.*, 9, 1101) by treating dehydracetic acid with bromine. As the yield of the brominated acid obtained by this method is small, several experiments were made with the object of improving it. The following modification was found to give good results:—

5 grams of dehydracetic acid are dissolved in about 50 grams of chloroform, a slight excess of bromine, and two or three crystals of iodine added, and the whole warmed in a water-bath at about 50° for a minute or two. As soon as the reaction has once set in, it continues at the ordinary temperature, and is usually finished in about 12 hours. The liquid is then decanted from any crystals which may have separated, and is allowed to evaporate at the ordinary temperatures in an open dish, when a slightly yellowish crystalline mass is left behind, consisting of a mixture of monobromodehydracetic acid and unchanged dehydracetic acid. These two acids may be easily separated by recrystallisation from alcohol, in which the latter is much more easily soluble than the former.

The monobromodehydracetic acid thus obtained is mixed with any crystals which may have separated from the chloroform solution during the preparation, and is purified by two crystallisations from alcohol.

The analysis gave the following numbers:—

0.3258 gram substance gave 0.2458 gram AgBr.

	Found.	Theory. $\text{C}_8\text{H}_7\text{BrO}_4$.
Br	32.11 per cent.	32.38 per cent.

Monobromodehydracetic acid melts at 137° (Oppenheim and Precht give 134°). It is easily soluble in hot alcohol, chloroform, benzene, and light petroleum, but only sparingly in alcohol and light petroleum in the cold.

It crystallises from the hot solution in methyl alcohol, on cooling slowly, in beautiful plates and prisms, having the following forms:—

When the hot solution in methyl alcohol is rapidly cooled, curiously striated four-sided plates (I) are produced, but on slowly crystallising the forms lose the striated appearance and become well developed mostly in the forms II and III.

This interesting compound is the first product of the action of potash on monobromodehydracetic acid, thus:—

To prepare it, pure monobromodehydracetic acid is dissolved in a little alcoholic potash, then mixed with an excess of concentrated alcoholic potash, and the whole allowed to stand 14 days at a temperature of $35-40^{\circ}$. The mass which is at first quite thick, soon becomes more fluid, and at the end of the operation again thick and brownish coloured. In order to isolate the product, water and dilute sulphuric acid are added, when a solid acid separates, which is collected and well washed with water. The mother-liquors, on repeated extraction with ether, give a further quantity of this acid, which is, however, not so pure. The crude product obtained in this way is a mixture of hydroxydehydracetic acid and unchanged monobromodehydracetic acid. These two acids can be easily separated by treatment with chloroform, in which the hydroxy-acid is almost insoluble. The crystalline mass which remains undissolved is then

once recrystallised from dilute alcohol, and thus obtained as a white sandy crystalline precipitate, which, on analysis, gave the following results :—

- I. 0.2381 gram substance gave 0.0947 gram H_2O and 0.4535 gram CO_2 .
 II. 0.2060 gram substance gave 0.0831 gram H_2O and 0.3927 gram CO_2 .

	Found.			Theory.
	I.	II.		$C_8H_8O_5$.
C	51.95	51.99	per cent.	52.17 per cent.
H	4.42	4.48	„	4.35 „
O	43.63	43.53	„	43.47 „

Hydroxydehydracetic acid, when rapidly heated, melts at $250-255^\circ$ with decomposition, if slowly heated, the acid begins to decompose and char at 210° . It is fairly soluble in hot ethyl alcohol and methyl alcohol, but almost insoluble in cold water, chloroform, light petroleum, benzene, and acetone. The hot solutions in alcohol or water deposit the acid on cooling in the form of a heavy sandy precipitate, which when examined under the microscope is found to consist of a mass of small but badly formed four-sided crystals.

The alcoholic or aqueous solution gives an intense violet coloration on the addition of a drop of ferric chloride. When carefully heated in small quantities, this acid sublimes with slight decomposition. Hydroxydehydracetic acid dissolves easily in alkalis. The silver salt appears curiously enough to have the constitution $C_8H_6O_5Ag_2$, which would point to the acid being bibasic. It is intended to further study this interesting acid, and experiments on the subject are already in progress.

In order to prepare this substance, a small quantity of hydroxydehydracetic acid was boiled with an excess of acetic anhydride for two hours, the bulk of the acetic anhydride distilled off, and the clear solution after cooling mixed with water. As soon as the excess of acetic anhydride had been decomposed, the whole was extracted several times with ether, the ethereal solution well washed, and allowed to evaporate at ordinary temperatures. In this way, a colourless crystalline mass was obtained, which, after washing with a little water and drying on a porous plate over sulphuric acid in a vacuum, gave the following numbers on analysis :—

0.2155 gram substance gave 0.0885 gram H_2O and 0.4180 gram CO_2 .

	Found.	Theory. $\text{C}_{10}\text{H}_{10}\text{O}_6$.
C	52.90 per cent.	53.09 per cent.
H	4.56 „	4.42 „
O	42.54 „	42.48 „

This acetate melts at $165-167^\circ$. It is easily soluble in hot alcohol, less so in benzene, chloroform, ether, and bisulphide of carbon. From the hot solution in methyl alcohol, it separates on cooling as a hard sandy mass, which when seen under the microscope is found to consist of beautifully formed crystals, mostly having the following forms:—

When boiled with water or alcohol for any length of time, it is slowly decomposed, hydroxydehydracetic acid being apparently regenerated. The acetate gives no coloration with ferric chloride. When heated in a test-tube, acetic anhydride is split off, and a small quantity of a white sublimate is obtained, which gives a violet coloration with ferric chloride, and consists therefore probably of regenerated hydroxydehydracetic acid.

Dehydracetic acid combines readily with hydroxylamine, if its sodium salt be allowed to remain in contact with a solution of this compound. In a short time, a crystalline substance begins to separate, and after standing for 24 hours the reaction is complete. In order to isolate the product, the solution is slightly acidified with dilute sulphuric acid, and the precipitate thus thrown down is collected, washed with water, and repeatedly recrystallised from alcohol or dilute acetic acid, or light petroleum. In this way, colourless needles are obtained, melting at about $171-173^\circ$ with decomposition.

Analysis:—

0.1874 gram substance gave 0.0812 gram H_2O and 0.3640 gram CO_2 .

0.2261 gram substance gave 15.5 c.c. N, $t = 15^\circ$, bar. = 720 mm.

	Found.	Theory. $C_7H_8O_3NOH$.
C	52.97 per cent.	52.46 per cent.
H	4.81 ,,	4.92 ,,
N	7.60 ,,	7.65 ,,
O	34.62 ,,	34.97 ,,

This substance is formed from dehydracetic acid according to the equation—

This oxime is easily soluble in alcohol, benzene, and acetic acid, but only sparingly in cold light petroleum. The alcoholic solution gives an intense violet coloration with ferric chloride. Odernheimer (*Ber.*, 17, 2087) has also prepared the oxime of dehydracetic acid. In addition to the properties given above, he found that the alcoholic solution was precipitated by silver nitrate, an unstable white precipitate of the silver salt being formed. He also prepared a barium salt by precipitating a neutral solution of the oxime with baric chloride.

The phenylhydrazine-derivative of dehydracetic acid may be prepared in several ways. It was first obtained by treating the sodium salt of dehydracetic acid with a solution of phenylhydrazine acetate, and then acidifying with dilute sulphuric acid, but the easiest way of preparing it is to add an excess of phenylhydrazine to the warm alcoholic solution of dehydracetic acid, and then allowing it to stand. In a short time, a yellow crystalline solid separates out, which after collecting, well washing with alcohol, and recrystallising from alcohol, is easily obtained pure.

Analysis :—

0.2069 gram substance gave 0.1041 gram H_2O and 0.4940 gram CO_2 .

0.2634 gram substance gave 26 c.c. N, $t = 18^\circ$, bar. = 719 mm.

	Found.	Theory. $C_8H_8O_3N_2H \cdot C_6H_5$.
C	65.12 per cent.	65.12 per cent.
H	5.59 ,,	5.42 ,,
N	10.79 ,,	10.85 ,,
O	18.50 ,,	18.61 ,,

This substance is formed from dehydracetic acid according to the equation—

When rapidly heated, it melts at 207° with decomposition, but when slowly heated it begins to decompose at 200° . It is moderately easily soluble in hot benzene, alcohol, and chloroform, but only sparingly in light petroleum. From the hot solution in benzene or alcohol, it crystallises on cooling in beautiful brilliant yellow crystals, which when examined under the microscope are found to have the following forms:—

It dissolves with difficulty in ammonia and sodic carbonate solutions, and is reprecipitated by acids apparently unchanged.

Haitinger (*Ber.*, **18**, 453) suggests that these products of the action of hydroxylamine and phenylhydrazine on dehydracetic acid may have constitutions different from those given above. He thinks it very probable that these basic substances may have acted in the same way as ammonia, producing compounds of the constitution—

This is quite possible, although improbable, and I hope by further experiments to be able to distinguish between these formulæ.

Action of Potash on Dehydracetic Acid.

In the introduction to this paper, I mentioned that the first change which dehydracetic acid underwent when treated with potash was decomposition into 2 mols. of acetoacetic acid, thus:—

The experiments which were made to prove this were conducted in the following way:—

Pure dehydracetic acid was first dissolved in a little dilute alcoholic potash, then an excess of a concentrated alcoholic potash solution added, and the whole allowed to stand for 14 days. The mass soon became brownish coloured and quite thick, but towards the end of the reaction it was again more fluid. The thick stage appears to be brought about by the separation of the potassium salt of dehydracetic acid; this at a later stage gives place to the potassium salt of acetoacetic acid, which is much more soluble.

In order to isolate the product of the reaction, the whole is dissolved in water, acidified with dilute sulphuric acid, and filtered from any unchanged dehydracetic acid which may separate out. The filtrate is then extracted several times with ether, the ethereal solution washed with water, dried over calcic chloride, and evaporated at as low a temperature as possible. A small quantity of dehydracetic acid, which generally crystallises out during this operation, can be easily removed by treating the residue with a small quantity of water and filtering, when the dehydracetic acid remains undissolved. The filtrate which contains the acetoacetic acid gives the characteristic violet coloration on adding ferric chloride. If this solution be extracted with pure ether, a small quantity of a yellowish-coloured oil is obtained, which shows all the reactions of acetoacetic acid. In order to obtain it as pure as possible, it was allowed to stand for some time over sulphuric acid in a vacuum, and then further characterised by distilling with water. In this way, carbonic anhydride was evolved and a distillate obtained, which, when treated with orthonitrobenzaldehyde and dilute soda, gave the indigo reaction very distinctly, thus proving the presence of acetone. The acetoacetic acid had been decomposed into carbonic anhydride and acetone thus:—

The quantity of acetoacetic acid obtained in this way is naturally very small, owing to its instability.

It is an interesting fact that Conrad and Guthzeit (*Ber.*, 20, 152) also obtained a substance by the action of potash on ethylic dimethylpyrnedicarboxylate, which gave a violet coloration with ferric chloride. They consider it probable that in this case acetoacetic acid was also produced by the hydrolysis.

The methylic ether of dehydracetic acid used in the following experiments was prepared by Oppenheim and Precht's method (*Ber.*, 9, 324), that is, by treating the silver salt of dehydr-

acetic acid with methyl iodide, and extracting the product with ether. The yield obtained in this way is far from satisfactory, owing to the difficulty of preparing the silver salt in a pure condition, but up to the present I have not been able to improve on this method, the ordinary methods of etherification with alcohol and hydrochloric acid, &c., being useless in the case of dehydracetic acid. It is, however, very essential, in preparing this methylic salt from the silver salt, to have all the materials scrupulously dry, otherwise no methylic salt at all is obtained.

Methylic dehydracetate melts at 91° , as Oppenheim and Precht have shown. In experimenting with it, I have found it to possess most remarkable properties. It is easily soluble in water, producing a solution which has a decidedly acid reaction to litmus-paper. When treated with potash it is instantly saponified, even in the cold. If a solution of methylic dehydracetate (1 mol.) in pure dry ether is mixed with an ethereal solution of sodic ethylate (1 mol.), a pink sodium compound is precipitated, which, after being collected, well washed with ether, and dried over sulphuric acid in a vacuum, gave the following numbers on analysis :—

I. 0.1440 gram substance gave 0.0476 gram Na_2SO_4 .

II. 0.2414 „ „ 0.0788 „

	Found.		Theory.
	I.	II.	$\text{C}_8\text{H}_6(\text{Na})\text{O}_4\text{CH}_3$.
Na.	10.71	10.60 per cent.	11.27 per cent.

It is possible that this sodium compound has the formula

The hydrogen-atom of the CH -group in methylic dehydracetate may, on account of its position between the ketone-group $-\text{CO}-$ and the ether-group $\equiv\text{C}-\text{O}-\text{C}\equiv$, have an acid character like the hydrogen-atoms of the CH_2 -group in ethylic acetoacetate. It does not appear possible, however, by acting on ethylic or methylic dehydracetate with ethyl iodide to obtain substituted dehydracetic acids (see Shibbye, *Inaugural Dissertation*, Würzburg, 1882, page 12), for this the sodium compound is too unstable. The sodium compound dissolves easily in water, forming a pinkish-coloured solution. On quickly adding acid to this and extracting at once with ether, I once succeeded in obtaining colourless crystals melting at $85-90^{\circ}$, and which consisted probably of impure methylic dehydracetate. On repeating this experiment several times, however, I have

since always obtained an uninviting brownish resin, which resisted all attempts to get it in a crystalline form.

Methylic dehydracetate when treated with aniline is converted almost immediately into methylic phenyllutidonecarboxylate and phenyllutidone, as described in the introduction. In order to effect this change, pure methylic dehydracetate dissolved in a little methyl alcohol, is mixed with about twice its weight of aniline, and warmed gently for about 15 seconds to 50°. An equal bulk of water is then added, and the whole allowed to stand in a cool place for 12 hours. At the end of this time, it is found that a small quantity of a substance crystallising in long, colourless needles has separated. This, after collecting, washing with water, and once recrystallising, is easily obtained pure.

The analysis gave the following numbers:—

0.1472 gram substance gave 0.0775 gram H₂O and 0.3750 gram CO₂.

	Theory. C ₁₅ H ₁₅ NO ₃ .	Found.
C	70.04 per cent.	69.66 per cent.
H	5.83 „	5.69 „

Methylic phenyllutidonecarboxylate is insoluble in sodic carbonate solution. On boiling with alcoholic potash, it is easily saponified, a colourless acid being produced, which has, however, not yet been further examined.

The principal product of the action of aniline on methylic dehydracetate is, however, not methylic phenyllutidonecarboxylate, but a substance which remains dissolved in the mother-liquor after this has crystallised out. If these mother-liquors are evaporated on a water-bath, the solution becomes yellow and yellow, and at last quite deep orange-coloured. This is due to the formation of a colouring matter, and if the evaporation is carried on to dryness, a reddish amorphous mass with a magnificent green lustre remains, which appears to be this colouring matter in an almost pure state. No attempt has been made to isolate and purify this substance, owing to the small amount of material at command.

In order, however, to avoid the formation of this colouring matter, the solution was first acidified with dilute hydrochloric acid, and then

evaporated almost to dryness on a water-bath. The yellow colouring matter does not appear to be formed when acid solutions are employed, the residue left on evaporation being an almost colourless syrup, which did not crystallise after standing for some hours. The whole was therefore rendered slightly alkaline by the addition of potash solution and allowed to stand in a cool place for some hours. After about six hours, a quantity of needle-shaped crystals had separated, which, when collected, washed with a little water, and recrystallised from this solvent, were easily obtained pure.

Analysis:—

0.1392 gram substance gave 0.0833 gram H_2O and 0.4023 gram CO_2 .

	Theory. $\text{C}_{13}\text{H}_{13}\text{NO}$.	Found.
C	78.39 per cent.	78.82 per cent.
H	6.54 „	6.65 „

This substance is *phenyllutidone*.

Phenyllutidone melts at $196-197^\circ$. It is easily soluble in warm water and alcohol, less so in benzene. From the hot solution in water or benzene, it crystallises on cooling in colourless needles. This substance is identical with the phenyllutidone obtained by Conrad and Guthzeit (*Ber.*, **20**, 161), by heating phenyllutidonedicarboxylic acid at 270° . The platinochloride is easily prepared by adding platinum chloride to the solution of phenyllutidone in hydrochloric acid. It is thus obtained as a yellow powder, which crystallises from water in yellow needles; these, when examined under the microscope, are found to have the following forms:—

Analysis:—

0.3017 gram substance gave 0.1080 gram H_2O , 0.4286 gram CO_2 , and 0.0726 gram Pt.

	Theory. (C ₁₃ H ₁₃ NO) ₂ .H ₂ PtCl ₆ .	Found.
C	38·52 per cent.	38·68 per cent.
H	3·46 „	3·97 „
Pt	24·32 „	24·09 „

This platinochloride has also been prepared by Conrad and Guthzeit from their phenyllutidone from phenyllutidonedicarboxylic acid. Both salts were found to be identical, not only in appearance but also in behaviour.

I am at present engaged on further experiments on dehydracetic acid, the results of which I hope to be able to bring before the Society in a short time.