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Chemistry. — *"The trimorphism of allocinnamic acid."* By Dr. A. W. K. DE JONG, Buitenzorg. (Communicated by Prof. P. VAN ROMBURGH).

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As has already been pointed out in a previous communication, the formation of the same double acid of normal- and allo-cinnamic acid with the different forms of allo-cinnamic acid is in conflict with the view that these forms are chemical isomerides.

STOBBE, the most zealous exponent of this view, has undertaken, in conjunction with SCHÖNBURG[1]), a detailed investigation in which, according to them, it is clearly shown that the allocinnamic acids are chemical isomerides. Their first series of experiments[2]) with the two modifications melting at 68° and 42° respectively led to the following conclusion: "Aus den in diesem Abschnitte beschriebenen 70 Einzelversuchen geht hervor, dass die stabile 68° - Säure und die metastabile 42° - Säure bei Abwesenheit von Keimen unverändert umzukrystallisieren sind; die erstere aber mit Sicherheit nur dann, wenn bei dem Lösungsakte und bei den späteren Vorgängen die Temperatur ihres Schmelzpunktes bzw. des durch das Lösungsmittel erniedrigten Schmelzpunktes nicht erreicht wird, wenn also ein Schmelzen der 68° - Säurekrystalle vermieden wird. Tritt dieses ein, so kann 42° - Säure als Krystallisationsproduct auftreten. Hiernach bewahren also die beiden Säuren in ihren Lösungen bei genau bekannten Bedingungen ihre Individualität. Die Lösungen beider Säuren sind trotz der gleichen Lichtabsorption und trotz der gleichen Leitfähigkeit doch verschieden. Die Allozimtsäure (68°) und die Isozimtsäure (42°) sind zwei chemisch isomere Verbindungen". On page 233 of the same communication this conclusion is extended to the case of the acid melting at 58°.

It appeared to me to be not impossible that the above mentioned investigators had been led astray by the presence of crystal nuclei which, as is only too well known, play a prominent part in the

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[1]) Annalen, **402**, 187 (1914).

[2]) loc. cit. p. 199.

case of these acid forms. This was the more probable, since it is clear from their communication that they had formed no adequate idea of the nuclei in question. Although they mention the "beim Einfüllen der Lösung etwa an den Wandungen entstandenen Keime" [1], they neglect to give sufficient attention to the nuclei which can occur in the solution, and to those which are notoriously present in the air.

Before describing how the experiments of STOBBE and SCHÖNBURG were repeated, it is desirable to discuss the considerations which form the basis of the experimental method adopted.

By "nuclei" are to be understood molecular complexes which remain over from the solid state after solution, and which can be formed in the liquid as a preliminary to crystallisation.

According to the solvent used, nuclei and single molecules, or nuclei, double molecules and single molecules can occur in the solution.

If a solution of one of the forms of allocinnamic acid is prepared, a complete or an incomplete dissociation into single molecules results, according to the temperature and the concentration. The higher the temperature and the smaller the concentration, the more complete is the dissociation. It is thus possible to prepare two kinds of solutions, namely, those which contain only single molecules, and those which, in addition, contain also nuclei. In solvents in which double molecules can occur, a third kind of solution is also possible containing single and double molecules, while a solution with nuclei may also at the same time contain single and double molecules.

While within the solutions equilibria between the different kinds of molecules are established, for which, of course, a longer time is required according as the molecules are more strongly held together, the concentration of the solution is greater, and the temperature lower; equilibria are also established above the solutions between the nuclei, the double-molecules and the single molecules. These equilibria are dependent on the composition of the solution.

It is now sufficiently known from experimental investigation, that the atmospheric nuclei of the forms of allocinnamic acid are very persistent. It follows therefore from this that the equilibrium in the air lags behind variations in the solution. As a consequence nuclei are often still present in the air when the solution consists of single molecules only.

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[1] loc. cit. p. 198.

In the experiments it is therefore especially necessary to exclude the dangerous air-nuclei, and, at the same time, to give the solutions sufficient opportunity to reach the equilibrium condition.

The experiments of STOBBE and SCHÖNBURG were repeated with due regard to these considerations in the following manner. The solutions were prepared some time before the distillation and were kept during this time in the dark. At the same time the solutions were several times transferred to another flask. During this process the air nuclei were got rid of by transferring the solution first of all to a small flask which was filled to the brim, blowing away the air above it, and then pouring it into the new flask. Before use any nuclei still remaining in the air above the solution were removed by filling outside the laboratory a small measuring cylinder to the brim with the solution and blowing away the air over it. The solution was then poured from the cylinder through a glass funnel into a distillation flask (50 c.c. to 100 c.c.). The latter was closed by means of a cork through which passed a glass tube reaching to the middle of the bulb of the flask. A plug of cotton wool was inserted into the glass tube, while a larger plug was tied round the tube externally, fitting into the neck of the flask above the side-tube. Both the flask and the tube with the plugs were heated for several hours beforehand in a steam-heated air oven. In fitting them together care was taken that the fingers did not come into contact with any interior part.

In order to exclude the possibility of accidental inoculation, a rapid current of air saturated with the solvent was drawn through the flask for about five minutes. The air was led in through the tube, so that any atmospheric nuclei present could be carried off through the side-tube. The cork was now raised a little, and, by means of a copper wire, which had been heated red-hot, the larger of the cotton wool plugs was pushed below the side-tube of the flask. The latter was then closed again by the cork.

Since STOBBE and SCHÖNBURG observed that the melting of the 68°- and the 58°-acid, which takes place in petroleum ether and in water at 50° and 40°—42° respectively, must be avoided, as this gives rise to the formation of 42°-acid, it was necessary to drive off the solvent at a temperature not exceeding 35°. At this temperature they found no transformation of the two higher melting forms into the 42°-acid.

When the concentration of the solutions was small, the distillation was generally effected in a partial vacuum, while with more concentrated solutions the solvent was evaporated by means of a

current of dry air at ordinary temperatures (25°—30°). After the distillation and· after the removal of the remainder of the solvent by a dry air current, the flask was closed and placed in ice, whereupon after a longer or shorter time crystallisation began.

The preparation of the allocinnamic acid by subjecting an aqueous solution of sodium or potassium cinnamate (containing about 1 °/₀ acid) to light was somewhat modified, so that a more rapid transformation was attained, and at the same time the unaltered cinnamic acid could easily be used again.

Flat tin-plate vessels were used. In these the solution was set out in the daylight, and the water lost by evaporation was made up daily. After about eight to fourteen days, exposure the solutions were worked up.

In order to separate out the allocinnamic acid the solution was evaporated to about one tenth of its volume and acidified with sulphuric acid when cold. After cooling, the normal cinnamic acid was filtered off, washed, and immediately after drying was used again for the preparation of a new solution. If this acid melts on the water-bath, then allocinnamic acid is still present. This can be extracted by means of hot ligroin. The filtrate was neutralised with alkali, and the solution then evaporated, until crystals began to form. After cooling sulphuric acid was added, which caused the allocinnamic acid to separate out as an oil. This is dissolved in ligroin, and the solution is allowed to crystallise quietly after "seeding" with the 68°- or the 58°-acid as required.

These forms crystallise in large crystals, which even by their appearance and also by their melting points are easily distinguished from the crystals of the double acid of normal and allocinnamic acids, which occurs only in small quantity. In this way almost perfectly colourless crystals are obtained at first which, after recrystallising once from petroleum ether solution, are quite pure. Repetition of the above procedure yields crystals with a pale yellow colour. These may be decolourised in alcoholic solution by means of animal charcoal.

The water solution can afterwards be extracted with ether and yields a further small quantity of impure allocinnamic acid.

The transformation of the 68°-acid into the 58°-acid is easily brought about by boiling the crystals with a little water for a quarter of an hour. The flask is then closed by means of cottonwool, and the boiling continued. On cooling the allocinnamic acid separates out in oily drops which are transformed into the 42°-acid in ice. If the solution with the oily drops is "seeded" with a trace

of the 58°-acid, beautiful needle crystals of this acid are formed on standing.

Experiment gave the following result:

Solutions of the 58°-acid and the 68°-acid in petroleum ether, saturated at 25° (about 0.26 grm. and 0.17 grm. in 5 c.c. respectively) were allowed to stand for eight days in the dark at 25° to 30°. *Without the previous presence of crystals* the solutions gave, on evaporation of the solvent at the ordinary temperature by means of a current of air, a residue which in ice was transformed into the 42°-acid.

After having stood for eight days in the dark, less concentrated solutions of the two acids gave always the 42°-acid. This 42°-acid remained unchanged during the whole period of observation, about one month.

If, however, the solvent was distilled off immediately after the preparation of the solution, it was found impossible to effect the transformation even of a solution containing only 0.05 grm. of either of the two acid forms in 5 c.c., into the 42°-acid. Solutions in petroleum ether which were kept for eight days before distillation *in contact with crystals of one or other of the two higher melting forms*, gave, either during or immediately after the distillation of the solvent, crystals of the acid from which the solution was made.

LIEBERMANN and TRUCKSÄSS [1] succeeded frequently in excluding nuclei of the higher melting acids by filtering the petroleum ether solution and afterwards heating it on a water bath at 35°. In six out of ten experiments with 68°-acid the transformation into the 42°-acid was effected. The same result was obtained with the 58°-acid in two out of four cases.

Experiments were carried out to ascertain if it were not perhaps possible to remove the nuclei more quickly than by a complete dissociation at ordinary temperature. The same procedure was adopted as before to exclude atmospheric nuclei. Heating at 35° was however, omitted. It was found that when solutions, almost saturated at the ordinary temperature and prepared immediately beforehand, were filtered through cotton-wool, ordinary filterpaper, or even through quantitative filterpaper, they yielded the original acids. If the solutions, even those containing crystals, were filtered after standing for twenty four hours, a residue was frequently, though not always, obtained, which yielded crystals of the 42°-acid. The reason for this may be ascribed to an alteration in the size

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[1] Ber. **43**, 411 (1910).

and also in' the number of the nuclei, or possibly in both causes together. The transformation of the nuclei of the 68°- and the 58°-acid in ethyl ether and benzene solutions, saturated at 25°, without crystals, did not take place even after they had stood in the dark for fourteen days. This is very 'probably due to the great concentration of the solutions. At 25° about 4.4 grms. of 58°-acid is soluble in 1.6 grms. of ethylether, and about 4.6 grms. in 2.3 grms. of benzene. The 68°-acid dissolves to the extent of about 6.6 grms. in 3.2 grms. of ethylether and about 4 grms. in 3 grms. of benzene.

An ether solution containing 2 grms. of 68°-acid in 5 c.c. and a benzene solution containing 2.1 grms. of acid in 3.6 grms. of solvent, gave a residue after standing for eight days in the dark which yielded the 42°-acid on crystallisation. After two months, standing in the dark a solution containing 2 grms. of the 58°-acid in 1.6 grms. of ether and a benzene solution with 1.8 grms. of acid in 2.5 grms. of solvent gave also a residue which crystallised out as 42°-acid. An attempt to remove the nuclei from ethylether and benzene solutions, saturated at 25°, by filtration through cotton wool or filter paper was not successful, even when the solutions had been kept for more than ten days free from crystals.

From the foregoing it appears that the transition of the 58°-acid and the 68°-acid into the 42°-form in solution can take place independently of the melting of these forms, and that at 25°—30° they can form solutions which, apart from differences of concentration, are identical, provided that the nuclei are afforded an opportunity for transformation, and that atmospheric nuclei are excluded. When, however, the concentration of the solution is high, as may be the case with ether and benzene solutions, then it is not possible to break up the nuclei, or to remove them by filtration. In this case there exists most probably an equilibrium between the nuclei and the other molecules.

One of the principal arguments of STOBBE and SCHÖNBURG for the chemical isomerism of these acid forms is thus rendered ineffective, while the results are in complete agreement with the assumption of the trimorphism of the allo-cinnamic acids.

In connection with what STOBBE and SCHÖNBURG have communicated regarding the transformation of the 42°-acid and the 58°-acid into the 68°-acid at —14° (ice and salt), it was of importance to investigate if the same change also took place in solution.

Various solvents were used. The most important results were obtained with water, so that these may be detailed first.

An experiment was made with 68°-acid which had been freed

from 68°-acid nuclei by boiling with water. The solution was evaporated down until the acid separated out as an oil at ordinary temperature. This solution gives crystals of 42°-acid on cooling to 0°. The presence of a small quantity of liquid acid indicates at once the occurrence of undesired inoculation.

Small quantities of this solution were introduced into the flasks with the cotton wool plugs.

After filling and drawing air through the flask, the solution was again boiled. After cooling the flasks were placed in a freezing mixture. The temperature of the mixture was in some experiments about —10°, in others about —16°. After twenty-four hours these temperatures were 0° and 5° respectively. (The mixtures were kept in a box packed with hay).

The cooling was continued until transformation had taken place. This point is easily recognised from the more copious crystallisation and also from the form of the crystals. After the ice had melted, the flask was opened, the tube with the plug withdrawn, and the solution carefully poured out so that the crystals as far as possible remained in the flask. The flask was then closed in the usual way, and the few drops of water were removed by means of a stream of dry air at the ordinary temperature. The melting point was then determined.

It was found that, whenever the initial temperature of the mixture was —10°, the 58°-acid was always formed, while, when the initial temperature was —16°, the 58°-acid was formed in nearly as many cases as the 68°-acid. (58°-acid in five experiments and 68°-acid in seven). There is apparently a range of temperature within which the 58°-acid is formed, while at lower temperatures the 68°-acid is obtained.

The transformation at —10° sometimes requires several days; at —16° it is complete after a few hours. In this way a method is given by which one or other of these acid forms may be prepared. Experiments with a solution in petroleum ether of low boiling-point were carried out as follows. A dilute solution of the 68°-acid in petroleum ether was prepared and freed from nuclei at the ordinary temperature. Portions of this solution were introduced into several flasks through which a rapid stream of air was drawn. After the cotton-wool plug had been pushed below the side tube, a large portion of the solvent was distilled off. The solution was then cooled. It was found that, both when the initial temperature was —10° and when it was —16°, the 58°-acid was obtained in several cases, but generally the 68°-acid was formed.

Solutions in benzene prepared in a similar way showed at —10°, a transformation only in exceptional cases. In these cases the 68°-acid was obtained. At —16° after twenty four hours the 68°-acid was always formed.

Further experiments were made by adding a few drops of the solvent to crystals of the 42°-, 58°-, and the-68°-acid contained in the flasks with the cotton wool plugs, in such a way that crystals still remained in the solution. The solvent was introduced into the flasks through the glass tube with the cotton wool plug, the part of the tube projecting beyond the cork having been previously heated in order to prevent infection. It was found that the 58°- and the 68°-acid were unchanged. The 42°-acid was, however, transformed, the same changes being observed as with the solutions.

STOBBE and SCHÖNBURG[1]) assert that the 42°-acid and also the 58°-acid in the solid state are transformed into the 68°-acid on cooling in ice and salt. As the results obtained by me would seem to cast doubt on the correctness of this assertion, the solid substances, after having been carefully dried, were cooled for six days in ice and salt in the flasks with the cotton wool plugs. In the case of the 42°-acid the drying was effected by heating the flask to 80°—90°. It was observed that none of the three acid forms was altered by cooling. As STOBBE and SCHÖNBURG always worked with capillary tubes, a small quantity of the dry acid was introduced into a capillary from the flask. After six days cooling this also showed no change in the melting point. The solid substances are thus unchanged by cooling in this way. If, however, the 42°-acid is moist, transformation can take, place. To this fact the changes of this acid observed by the above investigators are probably due.

It is difficult to understand the transformation of 58°-acid into 68°-acid on cooling, as observed by STOBBE and SCHÖNBURG, unless one assumes that they used only ten capillaries for the cooling of the acid, in which after determined intervals of time the melting-point was taken. In that case the possibility is always present that 42°-acid is formed by the melting, as this takes place more easily in capillaries than would appear from the results of these investigators (p. 239). From the 42°-acid in a moist state the 68°-acid would then be formed.

As a further result of the investigation may be deduced, that there is a great difference between double molecules and nuclei. The transformations which have been described take place only in solu-

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[1]) loc. cit., p. 218, 236.

tions of suitable concentration, while even a chloroform solution which contained 35.4 % by weight of allocinnamic acid, and in which, therefore, double molecules were certainly present, no transformation was observed after six days' cooling. In my opinion the explanation of this is that only solutions containing nuclei can be transformed, and that there exists only one kind of double molecule.

Van der Waals' supposition that double molecules consist merely in the temporary association of the single molecules, is thus rendered more probable. Further investigation is required to clear up this point.

In the nuclei we have thus a determinate arrangement of the molecules. They represent the smallest particles of the substance in the solid condition, the simplest nucleus consisting of two molecules. It is not necessary to assume that the molecules are united at the carboxyl groups in order to explain the existence of different isomerides, since, as I have found, coumarine, which has no carboxyl group in the molecule, occurs also in a metastable form. It appears to me more probable that the reason for the occurrence of isomerides must be sought in the double bond. I hope shortly to return to this point.

Stobbe and Schönburg (p. 200) consider the occurrence of "Lösungsgemische" of the 42°- and the 68°-acid as an argument for the isomerism of these acids. It is clear from what has been said above, that the nuclei in the solution play an important part. The authors have however, interpreted their experiments in a different sense. They supposed that they had found that "In jedem Einzelfalle als Verdampfungsrückstand 68°-Säure erhalten wird nach einem Gesamtzusatz von 2.9—4.1 Proz. 68°-Säure, d. h. waren weniger als 2.9 Proz. 68°-Säure zur 42°-Säurelösung zugesetzt, so schmolz der Verdampfungsrückstand bei 42°; betrug der Zusatz mehr als 4.1° Proz. 68°-Säure, so zeigte der Verdampfungsrückstand den Schmelzp. 68°". They therefore conclude that the distillation residues are to be regarded as mixtures of the 42°-acid and the 68°-acid. On p. 204 they state: "Wenn, wie oben gezeigt worden, die Lösung von der 68°-Säure verschieden von der Lösung der 42°-Säure ist, und wenn nach Zusatz von wenig 68°-Säurelösung zur 42°-Säurelösung ein bei 42° schmelzender Verdampfungsrückstand erhalten wird, so kann dieser nicht reine 42°-Säure (fest) sein. Es muss vielmehr ein Gemisch der beiden isomeren Säuren sein". It is then assumed that solid solutions of these forms exist, and that the crystals are mixed crystals of the 42°-acid and the 68°-acid. It is obvious from what has been said above that this hypothesis is devoid of foundation.

Also on theoretical grounds, from the point of view of the authors, this hypothesis is untenable.

If the 68°-acid and the 42°-acid are *chemically* different, *the "seeding" power of the former must be a property resident in the molecule.* It is therefore impossible to explain why a nucleus of 68°-acid or a trace of this substance is capable in a short time of converting a large quantity of 42°-acid, while, when the molecules of the 68°-acid were distributed in a regular manner among those of the 42°-acid, as must be the case with mixed crystals, no transformation took place until 2.9 % of 68°-acid was present.

Fusion experiments have also led these investigators to assume the existence of solid solutions or mixed crystals. On p. 213 they write : "Ein Teil der eben besprochenen, bei 42° schmelzenden Erstarrungsproducte bleibt jahrelang unverandert, ein anderer Teil verwandelt sich bei Zimmertemperatur, zuweilen schon nach Minuten oder Stunden ohne erkennbare Ursache in 68°-Saure. Diese erstarrten Schmelzen sind also unter einander nicht gleich; sie sind ebenso wie die aus den Lösungsgemischen erhaltenen Verdampfungsruckstände, feste Lösungen oder Mischkristalle mit wechselnden Anteilen 68°-Säure und 42°-Säure [1]). It is not altogether improbable that these transformations could be brought about by one or more atmospheric nuclei which had not been broken up, in cases where no care had been taken to ensure the removal of these A single nucleus remaining in the melt is sufficient to cause transformations of this kind.

On the assumption of the trimorphic nature of allocinnamic acid it might be expected that, when the different forms were melted, the dissociation into single molecules would be more complete according as the time of heating is longer and the temperature higher. This was confirmed by STOBBE and SCHONBURG for the 58°-acid (p. 239) and the 68°-acid (p. 211). In these experiments only 5—7 mgr. was introduced into each capillary. Experiments with 10—50 mgr. of the 68°-acid in larger capillaries showed that even heating for twenty-five minutes at 70° was not sufficient, even in a single case, to bring about a permanent change into the 42°-acid, while on heating 5—7 mgr. of the acid for ten minutes the transformation was effected in four out of ten experiments. The same thing has already been stated by other observers, namely, that large quantities are more difficultly transformable than small quantities.

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[1]) The opinion of STOBBE that a solid solution is the same thing as nuclei in a melt, is certainly by no means always correct. Nuclei are molecule-complexes, and the molecules of the nuclei in different parts of the melt with nuclei are not necessarily uniformly distributed. On the other hand it is precisely in the case of a solid solution or of mixed crystals that we have a uniform distribution of the molecules among themselves.

The presence of nuclei affords an easy explanation of this. Let us suppose, for example, that the dissociation of the 68°-acid is allowed to proceed so far that there are now only two nuclei remaining in 20 mgr. of the substance.

Suppose also that the substance may now be divided into four equal parts. In two parts there are now at the most one nucleus each; in the other two parts there is no nucleus In this way we have, using portions of 5 mgr., 50 % of the substance transformed into 42 -acid under the applied conditions of temperature and heating. If the substance had not been subdivided, then the 20 mgr. with the two nuclei would have been transformed, either immediately or after several hours, into 68°-acid. [1] It is now easy to see that, if the probability of transformation for 5 mgr. is 50 %, it is 25 % for 10 mgr., 12.5 % for 20 mgr., 6.25 % for 40 mgr., etc., that is, the probability of complete transformation with a given temperature and time of heating becomes smaller and smaller as greater quantities of substance are used.

For each experiment Stobbe and Schönburg heated only ten tubes, so that the figures obtained by them are certainly not to be used as mean values. They found, for example, on heating 5—7 mgr. of 68°-acid for 10 minutes at 70° that four tubes out of the ten were transformed. (In the case that one part melted at 42° and another at 68°, complete transformation was not obtained). At 100° also only four of the ten showed a transformation into the 42°-acid. At 70° the mean value was probably somewhat lower. If we assume that the mean for ten minutes' heating at 70° was 40 %, then the probability of the conversion of 0.05 gr. in ten minutes is only 5 %, that is, the conversion should take place in one experiment out of twenty.

In order to investigate if perhaps atmospheric nuclei were in part responsible for the difficulty of the transformation, quantities of the 68°-acid were melted in U-tubes. One limb of these U-tubes was provided with a plug of cottonwool. Through this limb a rapid current of air at 70° was drawn during the time the U-tube was being heated in a water-bath at 70°, in order to drive out the air nuclei through the other limb.

After the heating the other limb was closed by means of a cotton wool plug. Working in this way 1 was as unsuccessful as Stobbe and Schönburg in transforming 0.05 gr. of 68°-acid permanently into 42°-acid by heating for twenty minutes at 70°.

[1] This is the reason for the phenomenon, observed by Stobbe and Schönburg, that in the capillary tubes some portions melted at 42° and others at 68° or 58°.

In this experiment it frequently happened that the melt first crystallised to the 42°-acid and afterwards was transformed back into the 68°-acid. This was also noticed by Stobbe and Schönburg. This phenomenon is therefore not due to atmospheric nuclei, but to nuclei in the liquid.

Although for a permanent transformation into the 42°-acid a complete absence of 68°-acid nuclei is essential, it is, of course, to be understood that a single nucleus of this acid, remaining over on melting the acid, is not necessarily sufficient to cause an immediate transformation of the melt. This may only take place after the lapse of several hours. Moreover, the nuclei vary in size, and the effect produced by the smallest, which is probably built up of only two molecules of allocinnamic acid, is presumably less effective and less rapid than that of nuclei consisting of several molecules.

From the foregoing it appears that the arguments used by Stobbe and Schönburg in support of the chemical isomerism of the allocinnamic acids are fallacious, while the experimental results obtained admit of satisfactory explanation on the assumption of the trimorphism of these acids.

Short summary of the results obtained.

1. An experimental method was worked out and applied by which it is possible to avoid inoculation, to exclude atmospheric nuclei, and to bring about the complete dissociation of those nuclei present in the liquid.

2. With this method it was shown that dilute solutions of the 58°-acid and the 68°-acid give, after removal of the solvent by distillation at ordinary temperature, a residue which is transformed into the 42°-acid.

3. When the concentration of the solutions of the 58°-acid and the 68°-acid is great, as may occur with ether and benzene as solvents, these acids are not transformed into the 42°-acid at ordinary temperatures.

4. The solutions may be transformed by cooling in ice and salt. In this way an aqueous solution containing no nuclei of the 58°-acid or the 68°-acid gives at —10° the 58°-acid and at —16° the 58°-acid or the 68°-acid.

5. In the solid state the acid forms appear to be unaltered after cooling for six days in ice and salt.

6. The arguments of Stobbe and Schönburg in support of the chemical isomerism of these acids are shown to be fallacious. All the results obtained are completely explicable on the assumption that the allocinnamic acids are trimorphous.

Buitenzorg, January 1919.