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Chemistry. — "*The heterocinnamic acids of ERLÉNMEYER Jr.*" By
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(Communicated by Prof. P. VAN ROMBURGH.)

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Besides the storax cinnamic acids there are, according to ERLÉNMEYER Jr., two other normal cinnamic acids, the heterocinnamic acids, which were separated from synthetic cinnamic acid.

ERLÉNMEYER asserts that the difference between storax- and heterocinnamic acid consists solely in the different mode of crystallisation of these acids from ether. He says: ¹⁾ "Wie ich schon in der ersten Abhandlung erwähnt habe, steht bei der Bearbeitung der Zimtsäuren als einziges brauchbares Unterscheidungsmerkmal die verschiedene Krystallisationsart der Storaxzimtsäure und der synthetischen Zimtsäure aus Aether zur Verfügung. Mit Hilfe dieses allerdings ungewöhnlichen Unterscheidungsmittels gelang es, zu zeigen, dass die synthetische Zimtsäure nach verschiedenen mitgetheilten Methoden in zwei unter einander und von der synthetischen Säure verschiedene Säuren, die Storaxsäure und die Heterosäure, zerlegt werden kann, welche bei der Analyse einen Unterschied in der Zusammensetzung nicht erkennen liessen," while on page 502, loc. cit., he writes: "Begnügt man sich damit, beide Säuren aus Wasser zu krystallisieren und die Schmelzpunkte zu bestimmen, so wird man keinen so wesentlichen Unterschied wahrnehmen, dass die Annahme einer prinzipiellen Verschiedenheit berechtigt erschiene. Ganz anders aber, wenn man die beiden Säuren in Aether löst und diese Lösungen langsam verdunsten lässt. Aus der aetherischen Lösung der Storaxsäure erhält man so ohne Muhe wasserklare, dicktaflige, gut ausgebildete Krystalle, welche mehrere Zentimeter gross und über 2 mm. dick werden können; aus der aetherischen Lösung der reinen synthetischen Zimtsäure dagegen krystallisieren unter genau den gleichen Bedingungen Aggregate von über einander geschichteten, mit einander verwachsenen, äusserst dünnen Lamellen, welche meist keine geradlinigen Umgrenzungslinien erkennen lassen." "An demselben Thermometer beobachtet, schmilzt

¹⁾ Ber. 42, 2649.

die synthetische Säure bei 132—133°, die Storaxsäure bei 134—135°. 1)''

It was shown by RIBER and GOLDSCHMIDT 2) that the differences between the synthetic and storaxcinnamic acid observed by ERLÉNMEYER, can easily be attributed to impurities in the synthetic acid, since the mode of crystallisation of cinnamic acid is strongly influenced by traces of other acids such as chlor- or nitro-cinnamic acids. They found that commercial synthetic cinnamic acid contained chlor-cinnamic acid as an impurity.

To this ERLÉNMEYER 3) answered that even synthetic cinnamic acid prepared from pure, well crystallised storaxcinnamic acid by dissolving in alkali, oxidising with permanganate to benzaldehyde, and then from this preparing the acid by the PERKIN synthesis, exhibits the same peculiar crystalline form.

In spite of this answer, a study of ERLÉNMEYER's papers leads to the conclusion that heterocinnamic acid is not a pure substance, and that the difference from ordinary cinnamic acid found by him must be referred to some impurity.

According to ERLÉNMEYER 4) both synthetic and heterocinnamic acids can be transformed, although with a 10% loss, into storaxcinnamic acid by heating their colourless aqueous solutions with animal charcoal. Also repeated sublimation 5) brings about the transformation of heterocinnamic into storaxcinnamic acid. He also succeeded by fractional precipitation 6) of the sodium salt of synthetic cinnamic acid in easily separating 90% as storaxcinnamic acid, whereas synthetic cinnamic acid should consist of storaxcinnamic acid to the amount of 50%. 7) He says then: 8)

„Da die Heterozimtsäure, trotz der Gewinnung von Storaxzimtsäure aus ihr, in ihren Eigenschaften unverändert bleibt, kann man nicht anders annehmen, als dass bei dem fortgesetzten Fraktionierungsverfahren ein allmählicher Uebergang von Hetero- in Storaxzimtsäure stattfindet“.

In his detailed papers no indication is given of the method which he used for the preparation of pure cinnamic acid for his investi-

1) Further particulars of the crystalline forms are given in Biochem. Zeitschr. 34, 366 and in Ber. 42, 507.

2) Ber. 43, 453.

3) Ber. 43, 955.

4) Ber. 43, 1076.

5) Ber. 42, 2658.

6) Bioch. Zeitschr. 34, 423.

7) Bioch. Zeitschr. 34, 425.

8) Ibidem 424.

gations. Evidently he assumes that well crystallised storaxcinnamic acid¹⁾ can contain not even minimal amounts of impurities. Here, however, it is a question of traces of impurity, seeing that so small a quantity as 1% of p-chlorocinnamic acid can so influence the crystallisation of storaxcinnamic acid that it shows a perfect resemblance to the synthetic acid,²⁾ while only 0.3% of o-nitrocinnamic acid was necessary to produce the same effect.³⁾ If the impurity occurs in smaller amount, it is possible that its effect on the crystalline form is not observed. The reason why ERLÉNMEYER was always able to prepare so-called synthetic cinnamic acid from cinnamic acid derived from various sources must thus be looked for in the impurity of the materials used. Whether or not this impurity was the same in all cases may for the present be left out of consideration. It must, however, have been a substance which on oxidation gives an aldehyde from which by the PERKIN reaction a substituted cinnamic acid is formed. In the oxidation with permanganate the benzaldehyde has relatively the better chance of being oxidised to benzoic acid than the aldehyde impurity, which occurs only in traces, since, the vapour present being generally unsaturated with respect to the latter, the impurity is more quickly removed from the liquid reaction mixture. The amount of the impurity in the benzaldehyde will thus be greater than in the cinnamic acid originally used. In the PERKIN synthesis, according to the researches of ERLÉNMEYER himself, the aldehyde impurity is more completely transformed into the substituted cinnamic acid than the benzaldehyde, since the cinnamic acid obtained was the so-called synthetic acid, while fine crystals of storaxcinnamic acid were deposited from the residual benzaldehyde. The cumulative result of these circumstances should be that the amount of the impurity is increased, and its effect in modifying the crystalline form rendered perceptible.

It seemed to me thus necessary to ascertain whether synthetic cinnamic acid can in fact be prepared from pure cinnamic acid in the way indicated by ERLÉNMEYER, and if the product has the properties observed by him.

Preparation of pure cinnamic acid.

As raw material the ethereal oil extracted from the roots of *Alpinia malaccensis* was used. This consists, according to the researches

1) Ber. 43, 957. He speaks here of "25 gr. der als einheitlich anerkannten Storaxzimtsäure".

2) RIBBER and GOLDSCHMIDT Ber. 43, 460 and Biochem. Zeitschr. 34, 406.

3) Ber. 43, 461.

of VAN ROMBURGH,¹⁾ mostly of the methyl ester of cinnamic acid. ERLLENMEYER²⁾ states that on treatment with ether the cinnamic acid prepared from *Alpinia* gave crystals on the sides of the beaker which resembled the synthetic acid, while on the bottom beautiful crystals of α -storaxcinnamic acid were formed.

The ethereal oil was saponified, the solution extracted three times with light petroleum, and the acid precipitated, filtered, and washed. On oxidation with potassium permanganate the mixture foamed up vigorously so that the distillation had to be continually interrupted in order to avoid frothing over, although the flask was sufficiently large. For this reason the yield was very poor. In order to purify it, the acid was therefore dissolved by heating in sodium carbonate solution. On cooling the solution was extracted three times with light petroleum, and the acid again precipitated. This product gave no frothing on oxidation with potassium permanganate. Cinnamic acid prepared by the PERKIN synthesis separates out, according to ERLLENMEYER³⁾, after treatment with ether in characteristically developed crystals of α -cinnamic acid, which exhibited no perceptible difference from the original acid.

The cinnamic acid was then dissolved in caustic soda solution in just sufficient quantity of the latter, so that 1 gr. of the 9 gr. acid present remained unneutralised⁴⁾. The solution was then well boiled, and the acid separated completely by shaking after cooling. From solution in ether the acid crystallised in large flat plates which differed from the original acid in their size and thinness. Heterocinnamic acid, which, according to ERLLENMEYER, should result from this procedure, was not obtained. The crystals did not correspond with those of the so-called synthetic cinnamic acid, since the edges were straight and the angles well formed. They approximated closely to them, however, and showed also iridescence.

The possibility was not excluded that the difference from the naturally occurring acid was due to an impurity in the cinnamic acid used. For this reason I have subjected the substance to different processes of purification, which may be briefly indicated in the following.

Purification of the methylester by crystallisation.

For this purpose more than 5 kilos of the ethereal oil were taken

¹⁾ These Proceedings, April 1898.

²⁾ Ber. **39**, 1581.

³⁾ Biochem Zeitschr. **34**, 406. In place of beakers ERLLENMEYER used flasks.

⁴⁾ Ber. **42**, 519.

from which, merely by allowing to stand, a large portion of the ester separated out in crystals. It was purified by melting and by allowing it to recrystallise slowly at the prevailing temperature (about 25—30°). The portion which still remained liquid after 24 hours was removed by draining. This procedure was repeated until the ester solidified entirely within 24 hours. Its melting point measured on an Anschütz thermometer placed in the substance was 34° (a trace of water was present).

From 28 gr. of this ester a yield of 7.7 gr. of benzaldehyde was obtained, which gave 4.25 gr. of cinnamic acid, while more than 3 gr. of benzaldehyde were separated which had not taken part in the reaction¹⁾. Only 17% of the quantity of cinnamic acid used is thus recovered as synthetic product. The synthetic acid was recrystallised from boiling water to free it from a small amount of brown impurity. On treatment with ether well developed crystals of α -cinnamic acid were obtained with straight edges and sharp angles. The product, like the acid previously obtained, showed none of the properties which ERLÉNMEYER ascribes to the so-called synthetic cinnamic acid.

16 gr. of synthetic product were then prepared from the ester by ERLÉNMEYER'S method, and from this 1 gr. was separated by dissolving in an insufficient quantity of a boiling solution of caustic soda. This last product crystallized from ether in thin transparent superposed glittering plates showing iridescence. Of these several had curved edges. From benzene solution large thin plates with partly curved edges separated out which under the influence of light gave α -truxillic acid. On cooling the hot petrol solution locally small curved needles were obtained, which on exposure to light were transformed into β -truxillic acid. The properties of the first portion agree with those of synthetic cinnamic acid as given by ERLÉNMEYER, whereas, according to the method of preparation, heterocinnamic acid should have resulted.

That in this case so-called synthetic cinnamic acid was obtained, while the original oil treated in the same way gave a product in which these properties were not yet fully developed, must probably be attributed to the quantities of the cinnamic acid used, 9 gr. and 16 gr., from which the first fractions were prepared.

It may also be pointed out that so-called synthetic cinnamic acid apparently occurs in two forms, an α - and a β -form. This fact is not mentioned by ERLÉNMEYER.

¹⁾ These figures are the means of eight preparations.

A further purification of the ester by crystallisation was undertaken. A large vessel full of water was placed in a hay box. When the ester was placed in the water its temperature was 36° and after 24 hours, 32°. After repeated crystallisations the melting point of the ester was 34°.8—34°.9. The determination was made by heating the ester in a testtube provided with an air-jacket in a bath at 45°. A thermometer reading to $\frac{1}{20}$ of a degree was placed in the substance and the readings plotted on a curve.

The following temperatures are given as the melting-point of this ester: 33°¹⁾, 36°²⁾ near 36°³⁾, 34°⁴⁾, while SCHIMMEL and Co. found 36° for the ester from Wartara-oil, and 34°–35° for their own preparations⁵⁾. From this ester 16.5 gr. synthetic cinnamic acid was prepared according to ERLÉNMEYER. The first portion separated from the solution of the sodium salt; about 1 gr., was found on testing with ether to be ERLÉNMEYER's synthetic cinnamic acid.

Purification of cinnamic acid by crystallisation from water.

200 gr. cinnamic acid prepared from the roots of *Alpinia Malaccensis*, was dissolved by boiling in about 16 litres of water. On the following day the crystallised acid was filtered off and again dissolved in 16 litres of water. This procedure was repeated ten times. The quantity of cinnamic acid had then been reduced to about 40 gr. 20 gr. of this product was then recrystallised four times from water and from the final product synthetic cinnamic acid was prepared by the method indicated by ERLÉNMEYER.

From 17 gr. of the synthetic acid the first fraction, about 1 gr., was separated and was deposited from ether in well formed thin plates of cinnamic acid. These were larger and thinner than those given by the original acid and were to some extent superposed. Curved edges were not shown. The substance was thus not identical with so-called synthetic cinnamic acid according to ERLÉNMEYER.

Purification of cinnamic acid by crystallisation from 96 % alcohol.

860 gr. cinnamic acid, separated from the ethereal oil was dissolved in 1720 c.c. hot alcohol, and after filtration the solution was made to crystallise by cooling and stirring. In this way a mass of

1) ANSCHÜTZ and KINNICUTT, Ber. 11, 1220.

2) WEGER, Ann. 221, 74.

3) VAN ROMBURGH, l. c.

4) ULTÉE, Mededeeling v. h. Alg. Proefstation at Salatiga II, N^o. 45.

5) GILDEMEISTER and HOFFMANN, Die aeth. Oele, 2e Aufl. I, 522.

very small crystals was obtained, which, when filtered off and washed with alcohol, gave 241 gr. of cinnamic acid. The product was recrystallized once more in the same way. The synthetic acid prepared from this gave a first fraction of 1 gr. from 13.5 gr., which was unmistakably ERLÉNMEYER'S so-called synthetic acid.

It appears therefore from this investigation that the heterocinnamic acids of ERLÉNMEYER JR. are not obtained by the method described by him from pure cinnamic acid. Their formation is to be ascribed to an impurity in the cinnamic acid which he used.

The heterocinnamic acids are therefore not pure chemical compounds.

A remark on the reaction of BEILSTEIN may be made here. ERLÉNMEYER makes the following statement:¹⁾ "Es mag hier darauf hingewiesen werden, dass selbst die best krystallisierte Storaxzimtsäure, welche bei der Prüfung mit Soda und Salpeter sich chlorfrei erweist, mit der Kupferoxydperle in der Flamme des Bunsen-Brenners erhitzt, dieser eine intensiv grüne Färbung zu verleihen vermag."

I have also found that cinnamic acid, by whatever method it was purified, always gave BEILSTEIN'S reaction, although only faintly.

The methyl ester, even the unpurified substance, gave no coloured flame reaction when heated with copper oxide. The copper salt is, however, quickly formed by heating cinnamic acid and copperoxide, and the same salt, prepared from an alkaline solution of the ammonium salt by precipitation with copper sulphate, gave the reaction more distinctly than the free acid.

According to ERLÉNMEYER JR., pure copper carbonate also gives the reaction. Possibly the BEILSTEIN reaction is more sensitive for acids than for neutral substances or altogether inapplicable in the case of most acids. In the meantime no conclusion can be arrived at since the possibility of the presence of impurity, even in small quantity, in the cinnamic acid used by me is not excluded.

Buitenzorg, August 1918.

¹⁾ Ber. 43, 956 note.