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Chemistry. — “Action of sun-light on the cinnamic acids”. By
Dr. A. W. K. DE JONG.

The continued investigation has shown that the peculiar behaviour of cinnamic acid in the solid condition under the influence of sun-light must be attributed to the ease with which it passes into the metastable form. This metastable condition has been described first by O. LEHMANN¹⁾ in 1885. ERLLENMEYER Jr. has communicated a very lengthy investigation as to the existence of different forms of cinnamic acid in the Ber. D. Ch. G. and further in the Biochem. Zeitschr. He comes to the conclusion that of the normal cinnamic acid there exist four different modifications, namely α - and β -Storax cinnamic acid and α - and β -Hetero cinnamic acid. Cinnamic acid derived from plants consists of Storax cinnamic acid with but 0,5% of the Hetero-acid whilst synthetic cinnamic acid is a mixture of about equal parts of those acids. On heating their aqueous or dilute-alcoholic solutions the α -acids are converted into the β -acids. In Ber. 39 p. 1581, Ber. 42 p. 509 and Biochem. Zeitschr. 34 p. 355 some further conversions of the α - into the β -acids, and the reverse phenomenon, are communicated. The cinnamic acid used in my experiments was Storax cinnamic acid (probably derived from hydrolysed coca-acids; see previous communication) as it was deposited from alcohol in the well-formed, thick prismatic crystals of Storax cinnamic acid (in Ber. 42, p. 504 are found the photographs of the various forms). On repeatedly recrystallising from warm 95% alcohol which took place in the said experiments the α -Storax cinnamic acid is converted more or less into the β -acid. This mixture when illuminated always yielded α - and β -truxillic acid. The transformation into β -acid was much promoted, because after dissolving the cinnamic acid in alcohol the solution was made to evaporate rapidly by the shaking of the dish. For it was noticed that when an alcoholic solution of α -Storax cinnamic acid is poured on to a glass plate and the alcohol allowed to evaporate rapidly by blowing, only crystals of β -Storax cinnamic acid are formed. These crystals when illuminated gave only β -truxillic acid whereas the prismatic crystals of the α -Storax cinnamic acid gave only α -truxillic acid. The crushing of the crystals caused no change in the action of the light.

From the research is thus shown that α -Storax cinnamic acid gives α -truxillic acid when illuminated in the solid condition, whilst under the same circumstances, β -truxillic acid is formed from the β -Storax acid.

¹⁾ Ber. 43, 461 (1910); GRAHAM OTTO's Lehrbuch der Chemie Bd. I, 3e Abth., p. 57.

As to the connexion existing between α - and β -Storax cinnamic acid, nothing is as yet known with certainty.

The occurrence of differently crystallised forms of a substance may be generally attributed to polymerism, isomerism or polymorphism.

In the first case the one form is a polymeride of the other and thus possesses a double or multiple molecular weight, in the second case the molecular weight is the same but the structure of the molecule is different, whereas in the latter case where the difference exists only in the solid condition and disappears both in the liquid and the gas the arrangement of the molecules in the "Raumgitter" is accepted by some as the cause of the difference whilst others think that in this case also, a chemical difference between the solid forms is very probable¹⁾.

There has been no lack of efforts to determine the connexion between the different forms of the cinnamic acids.

According to ERLLENMEYER Jr.²⁾ there exist eight forms of cinnamic acid, namely four of the normal and four having as type *allocinnamic acid*. The first four appertain to each other two and two and according to ERLLENMEYER, these pairs should exhibit differences in the benzene nucleus.

Among the four *alloacids* we find mentioned, in addition to the three known acids, also a triclinic cinnamic acid, which he noticed a few times during his research, but of which the mode of formation is as yet quite obscure. ERLLENMEYER sees in the different crystallised forms different chemical substances and endeavours to explain this case of isomerism.

I cannot find his effort, which he himself wishes to be looked upon as a *sketch*, a very happy one.

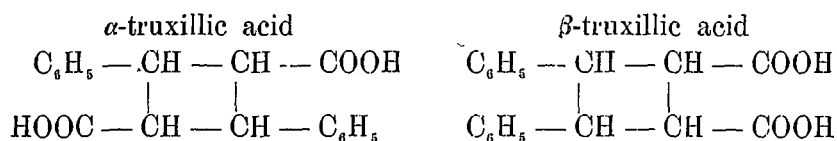
He reverts to the antiquated idea where the properties of a double bond are explained by the presence of a single bond and free affinities or as some express it, unoccupied affinity positions. Then, he assumes that on turning one of the two carbon tetrahedrons, between which the double bond exists, three different metastable forms can occur dependent on the different position of the groups on the one carbon tetrahedron in regard to that of the other one. In this manner he arrives at six different forms all capable of occurring in left- and right-handed modifications. Three thereof belong to the type of the *normal cinnamic acid* and three to that of the *alloacid*.

¹⁾ O. LEHMAN writes in "Die neue Welt der flüssigen Kristalle" 1911 p. 81: "daraus folgt aber lediglich, dass diese chemischen Methoden nicht ausreichend sind, jede Verschiedenheit der Moleküle zu entdecken und dass man polymorphe Modifikationen nicht ohne weiteres als chemisch identisch betrachten darf."

²⁾ Biochem. Zeitschrift **35**, 149 (1911) and following.

Opposed to this stands the view of BILLMANN¹⁾ that the differences of the *alloacids* must be attributed to trimorphism whereas RUIBER and GOLDSCHMIDT²⁾ consider the occurrence of α - and β -Storax cinnamic acid as a typical case of dimorphism.

The changes which α - and β -Storax cinnamic acid suffer in sunlight afford us a view on the difference existing between these acids in the solid condition. The polymerisation products of these acids are, as we noticed, α - and β -truxillic acid to which are attributed the following formulae as being the most likely :



As to the position of the groups with regard to the plane of the \perp -ring not much is known; in the case of β -truxillic acid the probability is that the COOH groups are found at the same side.

From these structural formulae it is plainly perceptible that one molecule of these truxillic acids is generated from two molecules of cinnamic acid and that the different manner in which the combination takes place gives rise to the occurrence of two truxillic acids.

Hence it must be assumed that there exists between α - and β -truxillic acid such a difference that the first, by the action of light, renders possible only a bond such as occurs in α -truxillic acid, whereas the β -Storax cinnamic acid must be such that only the binding as present in β -truxillic acid can take place exclusively.

A different placing of the groups in the molecule in regard to each other, which ERIENMEYER suggests to explain the difference between α - and β -cinnamic acid cannot avail us as even then for each formula the linking of two molecules can always take place in such a manner that both α - and β -truxillic acid can form.

If, however, we assume that the position of the molecules in the crystals is different for the two acids, a different bond due to the action of light might be coupled with this. The different behaviour of the acids might then be looked for in a different arrangement of the molecules in the "Raumgitter".

The following hypothesis may also be proposed. As is well known³⁾, most probably all organic acids dissolved in hydroxyl-free solvents possess double molecules. Hence there is a great probability that in

¹⁾ Ber. **42**, 184 (1909). Ber. **43**, 569 (1910).

²⁾ Ber. **43**, 461 (1910).

³⁾ VAN 'T HOFF, Vorlesungen über theoretische und physikalische Chemie, zweites Heft, pg. 52.

the solid condition at least double molecules occur. The difference between α - and β -cinnamic acid might then have its origin in the manner in which the single molecules are placed in the double molecule.

The difference between these two assumptions consists in this that the first admits of a difference in the solid condition only, whereas the second renders possible a difference for the solution also.

A further investigation will have to decide which representation is in harmony with the facts. I hope to revert to this in detail, shortly.

Physics. — “*Some Remarks on the Osmotic Pressure*”. By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of May 29, 1915).

With much interest I read Prof. EHRENFEST's paper [in the Proceedings of this Academy (April 1915)] on the kinetic interpretation of the osmotic pressure.

However, I can concur neither with the deeper ground of his interesting considerations, nor with the “Remarks” that are added to them, which in some respect may be considered as resulting from the foregoing considerations.

Prof. EHRENFEST knows that I feel a special interest in the osmotic pressure and its correct interpretation, so that he will no doubt excuse me if I once more return to it.

I will therefore briefly summarize my objections, already set forth in different papers¹⁾, in a number of Theses.

THESES I. The results of a kinetic theory must necessarily be in accordance with the established results of Thermodynamics.

If the results of the kinetic theory differ from those of Thermodynamics, the kinetic theory in question is not valid.

THESES II. Through the equating of the molecular thermodynamic potentials of the water in the solution and of the pure water outside it [there exists namely only thermodynamic equilibrium between the “water” on either side of the membrane, as this is supposed to be permeable only to water] the thermodynamic theory leads to²⁾

¹⁾ See particularly: Sechs Vorträge (1906), p. 17—36, and These Proc. of June 1906, p. 53 et seq. Also Zeitschr. f. physik. Ch. 64, p. 629 et seq. (1908).

²⁾ I gave this simple derivation already in 1894 (Zeitschr. f. physik. Ch. 15, p. 463 et seq.).