think that also these experiments are confirmatory of the hypothesis
that the action of pepsin is not determined by the H-ion-concentration
alone, but principally by the condition of the substratum and in the
first place by the swelling.

Of course the experiments with protein-solutions have to be continued
and extended to other acids and here also the influence of salts has
to be studied.

It is perhaps hardly necessary to add that other enzymes have to be
subjected to similar observations. The curve representing the viscosity
and consequently also the swelling as a function of p_H is strikingly
analogous to the curve representing the action of many hydrolitic
enzymes as a function of p_H; as with trypsin and also with ptyalin [1]).
We are, therefore, inclined to believe that with these enzymes also
the condition of the substrata plays a prominent part.

Chemistry. — "*The action of sun-light on the cinnamic acids.*"
By Dr. A. W. K. DE JONG.

(Communicated in the meeting of September 25, 1915).

For the continued research of α- and β-"Storax" cinnamic acid it
was necessary to possess a method by which large quantities of the
α-acid can be readily converted into the β-acid.

The rapid evaporation of an alcoholic solution spread in a thin
layer on glass plates certainly provides the means of preparing the
β-acid on a small scale, but in this manner one is obliged to always
work with small quantities of solution, as otherwise crystals of the
α-acid soon occur beside those of the β-acid.

According to ERLENMEYER Jun.[2]) the β-acid is formed in the
following ways[3]).

α-"Storax" cinnamic acid is dissolved in as little ether as possible
and precipitated with petroleum ether. If the ethereal solution is not
sufficiently concentrated α-acid only, or else a mixture of the two
acids, is formed.

A warm solution of the α-acid in dilute (75°/$_0$) alcohol deposits
on cooling the β-acid.

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[1]) Vide VAN TRIGT and RINGER's publication in the Proceedings of the meeting
of Nov. 30, 1912, Vol. XXI. Part. 1, p. 858 (1912).

[2]) Ber **39**, 1581 et seq (1906).

[3]) In what manner LEHMANN has prepared the β-acid, I have not been able
to trace as the original literature is not obtainable in Java.

As a third method he mentions that on heating the α-acid above its melting point the β-acid is formed [1].

The first two methods, however, do not always give the desired result, according to ERLENMEYER. He writes [2]: "In anderen Fallen gelingt die Umwandlung aus noch unbekannten Gründen selbst bei öfterer Wiederholung nicht."

The third method given by him is not correct. Both the solidified melt and the sublimate gave, on being illuminated, α-truxillic acid only.

After various experiments I observed that the β-acid is most conveniently prepared by pouring an alcoholic solution of α-cinnamic acid, saturated at the ordinary temperature, in a large quantity of water with stirring. On being illuminated this product always yielded β-truxillic acid only.

β-cinnamic acid may be also obtained by allowing warm solutions of cinnamic acid to crystallise. In this case the crystals are mostly visible with the naked eye and the change into the α-acid can also be traced.

If, however, we make a saturated aqueous solution at boiling heat, filter the same rapidly through cottonwool and filter off the crystallisations at intervals, the succeeding fractions appear to be different. The fraction depositing at a high temperature yields α-cinnamic acid, whereas at a lower temperature β-cinnamic acid crystallises (as proved by illuminating).

Benzine and petroleum are very suitable liquids for readily tracing the transformation of the cinnamic acids. If we wish to prepare the β-acid in this manner we must take care that the solution is not too concentrated as otherwise plate-like crystals of α-cinnamic acid will appear. The best thing is to cool locally (for instance the bottom of the flask) a warm and not too strong benzene solution. Splendid needles united in feathers are then formed. On these being left undisturbed the crystals are seen to partly vanish, plate-like crystals are formed and a few of the needles although retaining their original shape are seen to become transformed into a series of adjacent plates which convey the impression that they were tacked with the original needles.

The lower the boiling point of the benzene and the greater the concentration the more rapidly we notice the appearance of the plates in addition to the little feathers.

As to the transformation of the β-"Storax" cinnamic acid into the α-acid, ERLENMEYER also reports the following particulars.

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[1] See also: Bioch. Zeitschr. **34**, 356. (1911).

[2] Ber. **42**, 509. (1909).

In dilute (75 %) alcoholic solution the transformation takes place slowly and spontaneously and only at the end of 14 days has the greater part of the β-acid disappeared[1].

On repeated recrystallisation from ether or dissolving in absolute alcohol, the β-acid is generally converted into the α-acid. In some cases, however, it will remain unchanged for weeks. "Wie es scheint spielt auch bei diesen Umwandlungen die Belichtung eine wichtige Rolle, die aber noch der Aufklärung bedarf[2]". This last remark looks to me as if he has occasionally mistaken the crystals. Here, where the temperature is generally 10—20° higher, the transformation of β-cinnamic acid in water, benzene or alcohol proceeded very rapidly in a few days.

In a dry state and at the ordinary temperature the α-cinnamic acid keeps unchanged for a very long time. The fine powder obtained by pouring an alcoholic solution of cinnamic acid into water is but very slowly converted even after an addition of β-cinnamic acid. A specimen that had been mixed with 1 % of cinnamic acid after being kept in the dark for over a month gave, on illuminating 0.5 gram during one morning, 0.09 gram of α-acid and 0.10 gram of β-truxillic acid.

On heating, however, the β-cinnamic acid, even without previous fusion, is changed very rapidly into α-cinnamic acid. The higher the temperature, the more rapidly the transformation.

From all these data it thus appears that at the ordinary and also at a higher temperature the α-cinnamic acid is the stable modification and that the β-acid, for this temperature range, is always metastable.

From the ready change of the β-cinnamic acid into the α-acid it may be explained that concentrated solutions, which commence to crystallise at a higher temperature than the dilute ones, give α-cinnamic acid, whereas from dilute solutions which crystallise at a lower temperature, β-crystals are deposited.

We have already stated previously with a few words that — considering it has been generally found in the case of the organic acids that in some solvents (benzene, chloroform etc.) they occur at great concentration, almost exclusively, and at low concentrations still partially, as double molecules — we must also assume that in the solid condition at least double molecules occur.

According to BECKMANN[3] the formula of the double molecule in a general form would be as follows:

[1] Ber. 39, 1583. (1906).
[2] Ber. 42, 509 (1909).
[3] Z. f. ph. Ch. 6, 469. (1890).

$$R-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R$$
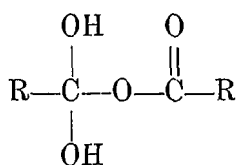
An objection to this formula is that two hydroxyl-groups are found at one C-atom which is not possible because water would then be readily split off.

The following formula appears to me to agree better with the data. As is well-known alcohols have the power to form large molecular compounds in the said solvents but only in concentrated solutions, whereas the dilute solution contains single molecules. Hence, we must assume that, in the acids, two causes are at work, which by themselves are not capable of producing the effect, namely the hydroxyl- and the CO-groups.
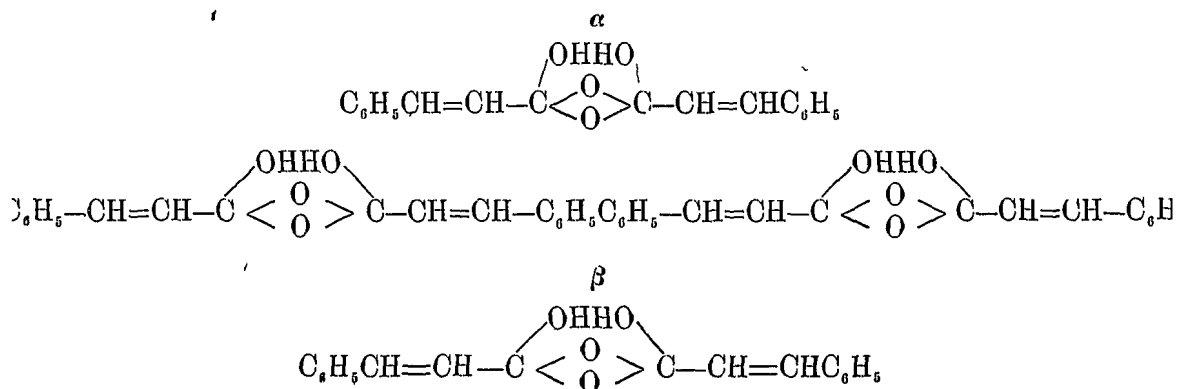
As the manner in which the OH-groups react on each other cannot be properly represented in the formula as yet, the double molecule might be represented as follows:

$$R-C\underset{\displaystyle O}{\overset{\displaystyle OHHO}{<\underset{\displaystyle O}{\overset{\displaystyle O}{}}>}}C-R.$$
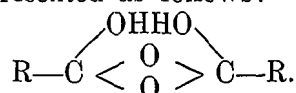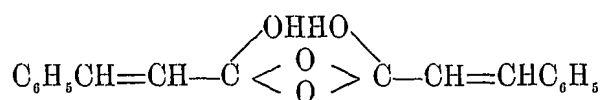
For our purpose, however, it is for the moment of less importance what idea one entertains as to the double molecule; it is certain, however, that in the case of acids we generally notice that they combine by means of their carboxyl-groups.
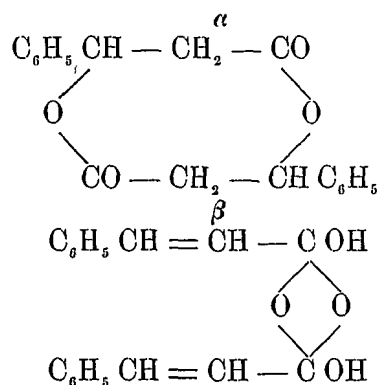
In the case of acids possessing two bonds in their molecule it is very probable that on the transition of the liquid state into the solid one, the attraction of the two bonds may direct the molecules

Supposing the difference between α- and β-cinnamic acid to consist solely in a difference of position of the double molecules in the "Raumgitter" we might then arrive to the following schema which elucidates the transformation of the acids into α- and β-truxillic acid.

$$\alpha$$

$$C_6H_5CH=CH-C\underset{\displaystyle O}{\overset{\displaystyle OHHO}{<\underset{\displaystyle O}{\overset{\displaystyle O}{}}>}}C-CH=CHC_6H_6$$

$$C_6H_5-CH=CH-C\underset{\displaystyle O}{\overset{\displaystyle OHHO}{<\underset{\displaystyle O}{\overset{\displaystyle O}{}}>}}C-CH=CH-C_6H_5C_6H_5-CH=CH-C\underset{\displaystyle O}{\overset{\displaystyle OHHO}{<\underset{\displaystyle O}{\overset{\displaystyle O}{}}>}}C-CH=CH-C_6H$$

$$\beta$$

$$C_6H_5CH=CH-C\underset{\displaystyle O}{\overset{\displaystyle OHHO}{<\underset{\displaystyle O}{\overset{\displaystyle O}{}}>}}C-CH=CHC_6H_5$$

$$C_6H_5CH{=}CH{-}C \underset{O}{\overset{OHHO}{<}} \overset{O}{\underset{O}{}} \overset{}{>} C{-}CH{=}CHC_6H_5$$

Also when we assume that on solidifying a change in structure of the double molecule takes place and that the formation of the truxillic acids occurs in the double molecule itself and not between two double molecules it is possible to give structural formulae for α- and β-cinnamic acid.

$$
\begin{array}{c}
\overset{a}{} \\
C_6H_5\,CH - CH_2 - CO \\
\diagup \qquad\qquad \diagdown \\
O \qquad\qquad\qquad O \\
\diagdown \qquad\qquad \diagup \\
CO - CH_2 - CH\,C_6H_5 \\
\overset{\beta}{} \\
C_6H_5\,CH = CH - C\,OH \\
\diagup\diagdown \\
O \quad O \\
\diagdown\diagup \\
C_6H_5\,CH = CH - C\,OH
\end{array}
$$

In the first representation it is not evident why the structure of
should make the acid more stable than that of β; in the second representation this is, however, better visible, although a lactide of the formula α will also not possess much stability. Yet there are some facts which lead us to believe that the lactide formula is a very probable one.

An argument in favour of this formula is furnished by the following experiments.

The cinnamates, namely the acid potassium-, the normal potassium-, the calcium- and the barium salt have on exposure to light, in the solid condition always yielded β-truxillic acid only and not in one instance α-truxillic acid, although their preparation had been modified in different ways. The result was the same whether we started from α- or from β-cinnamic acid; the temperature also made no difference.

No salts can, therefore, be derived from the α-acid.

If the difference between the α- and the β-cinnamic acid consisted merely in the position of the molecules in the "Raumgitter" it would be rather strange (when the α-arrangement is the more stable one) that this grouping does not occur in the salts. If for the α-cinnamic acid the lactide form is accepted, the non-existence of salts speaks for itself.

We might argue that in the salts no double molecule need occur, or else that these molecules possess a somewhat different structure; for the acid potassium salt, however, this does not do because the

acid molecule must, as in the case of the acids, be combined to the potassium salt molecule, as the acid is very strongly combined and cannot be extracted by ether from the solid powdered salt, as has already been stated by ERLENMEYER [1].

The a-cinnamic acid would then be the lactide of β-phenylhydracrylic acid.

It is known that the a-oxyacids on being heated in a vacuum are converted into lactides; β-oxyacids on heating give unsaturated acids with elimination of water, whereas γ- and δ-oxyacids very readily form lactones.

From this it appears that, as a rule, the substances possessing a carboxyl- and a hydroxyl-group, always have a greater tendency to split off water between these two groups, whether this takes place between the groups of one molecule, or whether the reaction proceeds between two molecules.

Only the β-oxyacids apparently make an exception.

The β-phenylhydracrylic acid, for instance, on being slowly heated breaks up at $180°$ into cinnamic acid and water according to the equation:

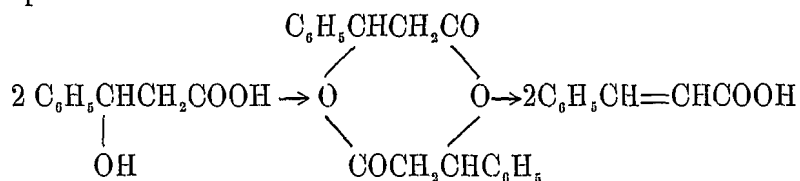$$C_6H_5CHCH_2COOH \rightarrow C_6H_5CH=CHCOOH + H_2O.$$
$$\underset{OH}{|}$$
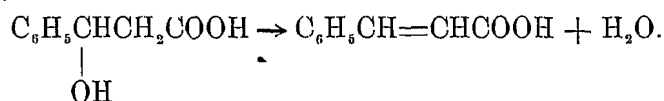
With substances possessing no carboxylgroup this elimination of water does not take place readily, as will appear from the following examples:

$(CH_3)_2 C_6H_3CH (OH) CH_2CH_2CH_3$ boils at $270°$ [2].

$CH_3CH(OH)C_6H_2 (CH_3)_3$ boils at $248°$ [3].

$C_6H_5CH_2CH (OH) C_6H_5$ melts at $62°$ and distils unchanged [4].

Non-aromatic secondary alcohols also generally boil unchanged [5]. If, however, we assume that from the β-phenylhydracrylic acid a lactide is first formed, this ready elimination of water becomes comprehensible.

$$2\ C_6H_5CHCH_2COOH \rightarrow \overset{\displaystyle C_6H_5CHCH_2CO}{\underset{\displaystyle COCH_2CHC_6H_5}{\diagup\quad\diagdown}} \overset{O}{\underset{O}{\quad}} \rightarrow 2C_6H_5CH=CHCOOH$$
$$\underset{OH}{|}$$

The transformation of other β-oxyacids, on heating, may be supposed to take place in a corresponding manner.

[1] Ber. 42, 515 (1909).
[2] BEILSTEIN II, p. 1067.
[3] Ber. 31, 1008 (1898).
[4] Ann. 155, 63 (1870).
[5] C. 1901 I, p 623.