Chemistry. — "*The Structure of Truxillic Acids.*" [1]) By A. W. K. DE JONG. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of Sept. 29, 1917).

Up to now the following truxillic acids are known, α, β, γ, δ, ε truxillic acid and β cocaic acid, which belong to two series, because the members of one series cannot be converted to those of the other without previous depolymerisation to cinnamic acid.

The γ acid belongs to the series of the α truxillic acid; it is formed by heating of the α truxillic acid with acetic acid anhydride [2]); the β cocaic acid, which is formed by melting from α truxillic acid with KOH, [3]) belongs to the same series.

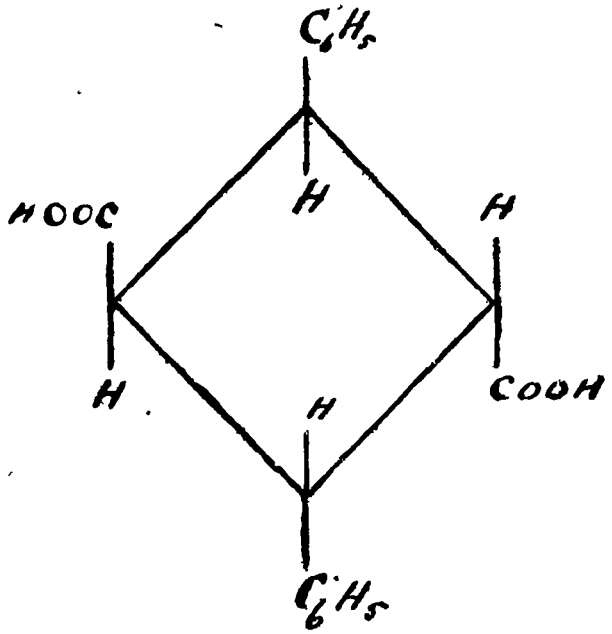
The second series is derived from β truxillic acid, which through melting with KOH passes into δ truxillic acid [4]). The last acid yields ε truxillic acid through heating with acetic acid anhydride; the ε truxillic acid possesses the same melting point as γ truxillic acid; a mixture of the two acids melts, however, about 20° lower, from which the difference of these acids can already appear. Also in the solubility of their salts there are found great differences.

By the formation of α truxillic acid from α normal cinnamic acid [5]) and of β truxillic acid from β normal cinnamic acid [6]) it is known that one of the 4 following structural formulae, corresponding with the 4 different ways in which 2 molecules of cinnamic acid can combine under formation of a tetramethylene ring, belongs to these truxillic acids.

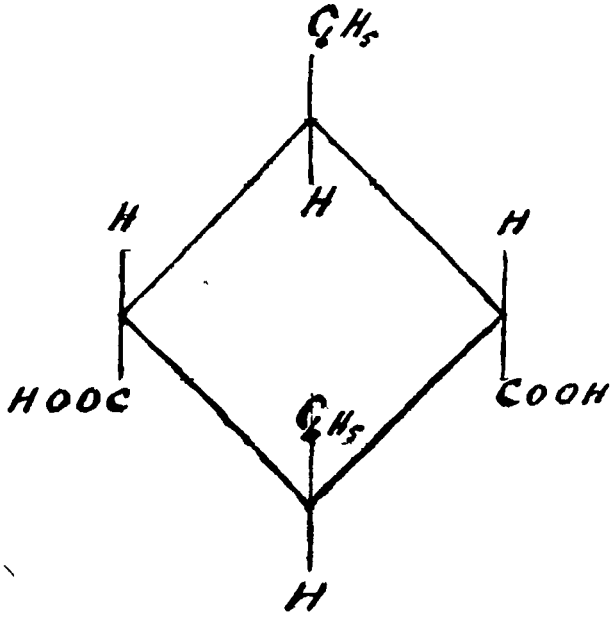
These 4 structural formulae belong to 2 series viz. the two first to one, and the two last to the other series. The members of these series cannot be transformed into each other without previous depolymerisation to cinnamic acid.

We know from LIEBERMANN's researches that β truxillic acid yields benzil [7]) on oxidation with potassium permanganate, from

[1]) Ber. **22**, 2255; Ber. **23**, 2516; Ber. **26**, 834; Ber. **27**, 1410.
[2]) LIEBERMANN, Ber. **22**, 2240.
[3]) HESSE, Ann. **271**, 202.
[4]) LIEBERMANN, Ber. **22**, 2240.
[5]) RUBER, Ber. **35**, 2908.
[6]) These Proc. 1915, Vol. XVIII p. 181.
[7]) Ber. **22**, 2253.



I



II

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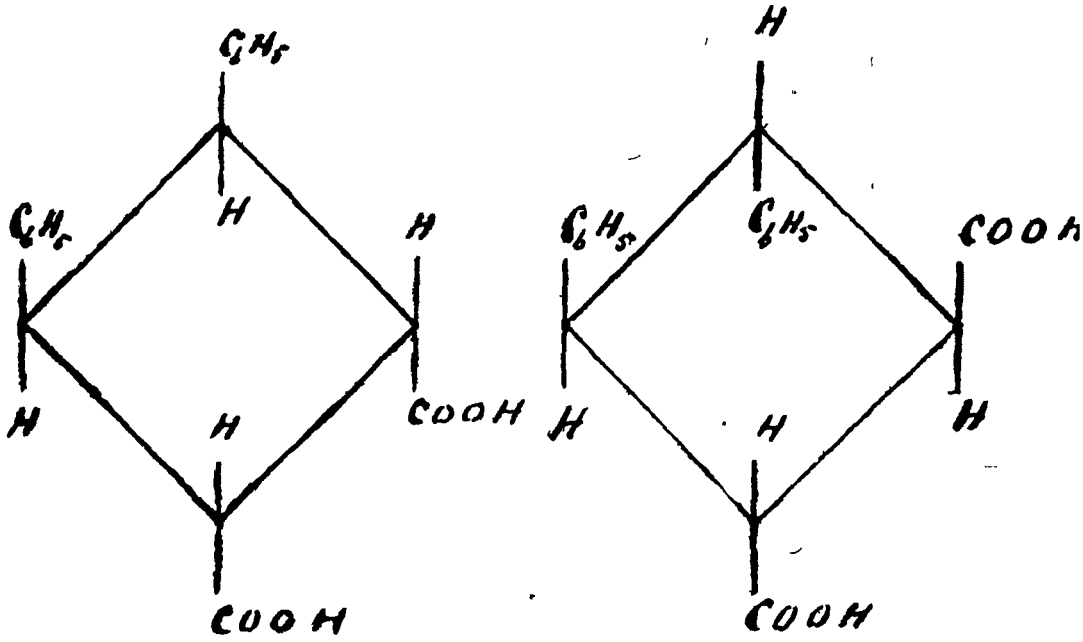


III IV

which it appears that for this acid the C_6H_5-groups must be found at 2 adjacent C-atoms, so that in connection with the formation from normal cinnamic acid one of the formulae III or IV must be assigned to this acid.

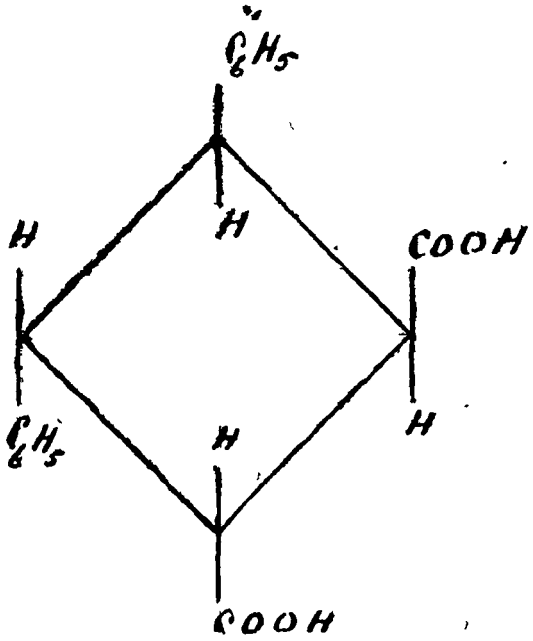
The β truxillic acid forms an internal anhydride [1]), and is not changed into another truxillic acid by heating with acetic acid anhydride [2]). It appears from this that the COOH groups are placed on the same side of the closed-chain of four carbon atoms; hence we must give formula III to the acid.

Through melting with KOH δ truxillic acid is formed from β truxillic acid [3]); this acid cannot have arisen from the former by displacement of one COOH or one C_6H_5 from one side of the ring to the other side, because then in the former case δ truxillic acid with acetic acid anhydride would have to yield β truxillic acid, and in the other case δ truxillic acid would not be changed by heating with acetic acid anhydride, neither of which is conformable to the facts. It must, therefore, be assumed, that 2 groups exchange places at the same time, viz. a C_6H_5 group and a COOH group, because, as is easy to see, the formation of ε truxillic acid from δ

[1]) Ber. 22, 834.
[2]) Id. 2240.
[3]) l. c.

truxillic acid through heating with acetic acid anhydride could not be explained in another way.

These exchanges of place of a C_6H_5- and a COOH-group from one side of the closed-chain to the other side can also take place for the groups of 2 adjacent C-atoms of the four ring, and also of 2 C-atoms placed opposite each other. In one case formula IV is obtained, and in the other case the following formula is valid.



V

This formula is built up from 2 molecules of allo-cinnamic acid.

The δ truxillic acid now is formed from normal cinnamic acid, viz. through the illumination of the stable lead salt of this acid. [1])

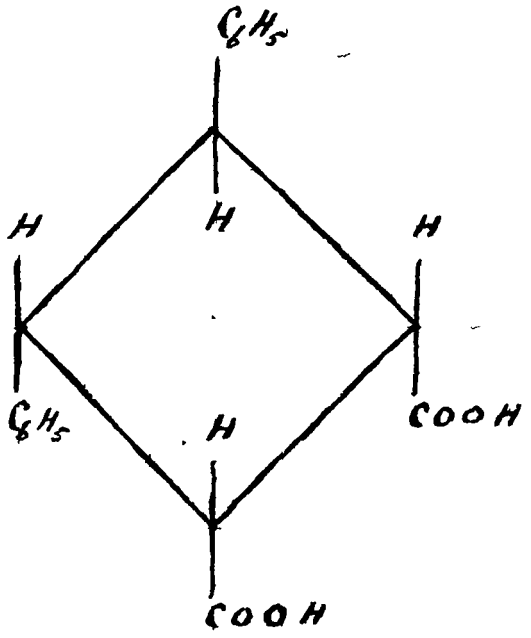
0,466 gr. of cinnamic acid, as lead salt, gave 0,075 gr. of truxillic acid and 0,095 gr. of δ truxillic acid after 27 hours' illumination.

The formula IV must, therefore, be assigned to the δ truxillic acid, whereas the ε truxillic acid possesses the following formula (See form. VI following page).

By heating with hydrochloric acid at 180° and also by melting with KOH it is changed into δ truxillic acid. These two acids are in the same relation to each other as fumaric and maleic acid, ε is the cis-acid, δ the trans-acid.

[1]) Shortly an extensive paper will be published about the action of solar light on cinnamic acid salts.

It is clear that one of the 2 structural formulae I or II must be assigned to the α truxillic acid.



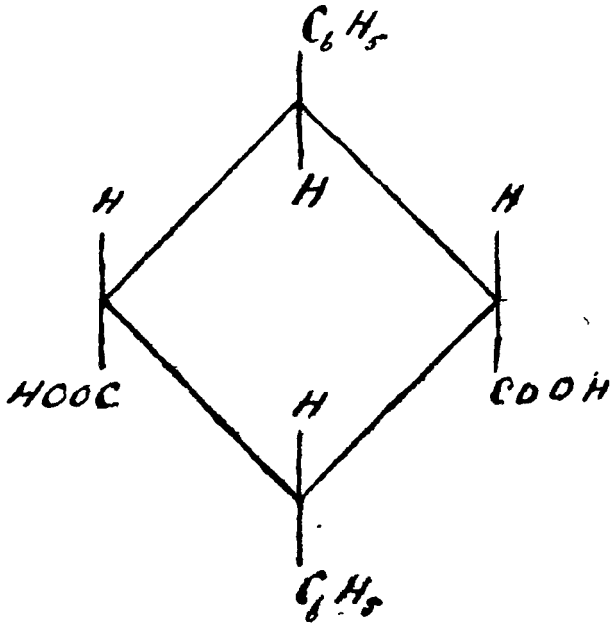
VI

This acid does not give an internal anhydride, [1]) and is converted by heating with acetic acid anhydride into γ truxillic acid, [2]) which acid is again converted into α truxillic acid by heating with hydrochloric acid. [3]) These two acids possess therefore a similar isomerism as the cis- and trans-acids, in which the α truxillic acid possesses the trans-form. In the γ truxillic acid the COOH-groups are on one side of the ring, this not being the case for the α truxillic acid. Accordingly this latter acid must possess formula I, and the γ truxillic acid is formed from the α truxillic acid by displacement of one COOH-group, which causes its structural formula to assume the following form. (See formula VII).

The β cocaic acid arises from α truxillic acid by heating with KOH. [4]) Through heating with acetic acid anhydride it is not changed into another truxillic acid. In this acid the COOH-groups must therefore be situated on one side of the ring, just as in γ truxillic acid. It can however, not have arisen from α truxillic acid by

[1]) Ber. **26**, 834.
[2]) Ber. **22**, 124.
[3]) Ber. **22**, 2245.
[4]) l. c.

displacement of a COOH-group alone, because then it would have to be converted into α truxillic acid by heating with hydrochloric acid, whereas it is not changed by this operation. There must,



VII

therefore, two groups viz. a C_6H_5- and a COOH-group have been displaced from one side of the ring to the other in the formation of β cocaic acid from α truxillic acid. This can take place in two ways, in which in one case formula II arises and in the other case all C_6H_5- and COOH-groups will lie on one side of the ring.

Formula II is built up of 2 molecules of normal cinnamic acid, and the other formula is formed from 2 molecules of allo cinnamic acid. The β cocaic acid was found on illumination of the stable barium salt of normal cinnamic acid together with β truxillic acid.

0,593 gr. of cinnamic acid, as barium salt, yielded 0,168 gr. of β truxillic acid and 0,092 gr. of β cocaic acid after 27 hours' illumination.

It appears therefore from this, that formula II must be assigned to β cocaic acid. Besides it is very improbable that a substance for which the heavy groups are all found on one side of the ring would arise by melting with KOH.

After what has been said about the conversions of the 6 truxillic acids, the following rules may be given.

1. The truxillic acids for which 3 large atom groups are situated on one side of the ring are converted through heating with KOH or HCl to truxillic acids with 2 heavy atom groups on one side.

2. By melting with KOH those forms arise for which the heavy atom groups are situated alternately on one side or on the other of the ring.

3. The truxillic acids for which 2 heavy atom groups are placed on one side of the ring are not changed into another truxillic acid through heating with hydrochloric acid.

In the foregoing exposition it has been assumed that the truxillic acids possess a tetramethylene ring. The proof for this has not yet been furnished; their properties found up to now can very well be reconciled with this conception.

I hope shortly to be able to communicate the results of an investigation in this direction.