

Citation:

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Chemistry. — "*The double acid from normal- and allo-cinnamic acids*". By A. W. K. DE JONG. (Communicated by Prof. P. VAN ROMBURGH).

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This double acid can be prepared by well known methods, for instance by allowing a solution, saturated at ordinary temperature with respect to both acids, to crystallize slowly, or by dissolving in such a solution equal quantities of the two acids by heat, when on cooling the double acid separates.

It can be readily prepared from normal cinnamic acid as follows. A dilute aqueous solution of sodium cinnamate (10 grm. of cinnamic acid per litre) is exposed to light in open tanks (at Buitenzorg about 3 months suffice for tanks of about 12 litres capacity and 500 cm² surface, with illumination in the fore-noon only). The solution is then evaporated to dryness; the acids are liberated by concentrated hydrochloric acid and are separated from the sodium chloride by hot motor spirit. The petrol solution often gives on cooling crystals of β -cinnamic acid, which on standing pass into the α -variety. After cooling, the solution is exposed to the air in a dish. Generally crystallisation begins soon and well formed, often rhomb-shaped crystals of the double acid separate. On further evaporation of the solution either crystals of allo cinnamic acid are formed, or this acid separates as an oil.

Since there exist two modifications of the normal acid, and three are known of the allo-acid, it would be quite possible that several different double acids should exist.

Now it is not difficult to prepare a solution, saturated with respect to both acids, which is at the same time in equilibrium with one of the three different forms of allo-cinnamic acid. For this purpose a warm concentrated solution of the two acids is prepared and should then be boiled for $\frac{1}{4}$ hour. The flask is plugged with cotton wool, to prevent infection, and the contents are cooled, which causes separation of the double acid, together with melted allo-acid (the temperature here is 25—30°). This solution is in equilibrium with allo-acid of melting point 42°. If the solution is inoculated with allo-cinnamic acid melting at 58° or 68°, it soon crystallizes

and solutions are obtained which are in equilibrium with these two modifications. If these solutions are allowed to evaporate in the air, the double acid separates together with the modification of the allo-cinnamic acid employed for inoculation.

The petrol solution, mentioned above, can also furnish solutions answering the purpose, by inoculation with the desired modifications.

In this way it is easy to make the double acid crystallise in the presence of large crystals of allo-cinnamic acid of melting point 58° or 68°.

By boiling the warm concentrated petrol solution of the two acids for $\frac{1}{4}$ hour, it is possible to obtain by cooling the double acid which separates in the presence of melted acid of m.p. 42°.

The double acids obtained in this manner were analysed according to the method given in *Rec. Trav. chim.* 31, 259, when it was found, that all consisted of equal quantities of the acids, as is seen from the following table. A preliminary experiment with 0.0545 gm. allo- and 0.0510 gm. normal cinnamic acid showed that the 20 c.c. of benzene used dissolved 2.25 c.c. N/10 allo-cinnamic acid as aniline salt.

Double acid	Quantity taken gram.	Titration		Recovered dissolved cinnamic acid gram.	Normal cinnamic acid found	
		15 c.c.	20 c.c.		gram.	%
with allo-, m.p. 42°	0.1040	3.35	4.5	0.0185	0.0520	50
" " " 58°	0.1005	3.1	4.1	0.0245	0.0511	52
" " " 68°	0.1015	3.05	4.1	0.0215	0.0496	49

The various double acids show the same melting intervals; they begin to sinter at about 56° and are fully melted at about 90°¹⁾.

In order to ascertain, whether these varieties of double acids formed in the presence of crystals of allo-cinnamic acid of m.p. 58° and 68°, and in a solution, in equilibrium with the acid of m.p. 42°, were identical, an aqueous solution was prepared saturated at room-temperature with respect to both acids, and in equilibrium with the acid of m.p. 42° (in this case also, when working at

¹⁾ Possibly the triclinic allo-cinnamic acid of ERLIENMEYER *Jun*, with m.p. 80°, is the double acid of normal and allo cinnamic acids *Ber.* 39, 1571 (1906); 40, 662, 663 (1907). Crystallographic measurements were not made on account of the absence of the necessary instruments.

25—30°, the allo-acid was obtained in the melted condition in the presence of the crystals of the double acid).

To portions of this solution crystals of the double acid were added, which, in order to prevent infection by traces of allo-cinnamic acid, had been washed a few times with a little alcohol and then dried between filter paper. If the double acids were different, those which had been formed in the presence of acid of m.p. 58° and 68°, in a solution in equilibrium with the acid of m.p. 42°, should have brought about crystallisation of allo-cinnamic acid melting at 58° or 68° respectively and of the corresponding double acids. The experiment showed, however, that this is not the case; the double acids had no effect whatever on the solution, which proves them to be identical.

Similar experiments were carried out with a petrol solution prepared by boiling for $\frac{1}{4}$ hour a solution from which the double acid and allo-cinnamic acid of m.p. 68° had crystallised, with an adequate quantity of allo-cinnamic acid and the double acid. Next day the solution had not crystallised, but it did so at once on shaking. After standing for a few hours with occasional shaking the experiment with the double acids was carried out, but here also no effect at all was observed. The solution itself was found to crystallise at once on inoculation with allo-cinnamic acid of m.p. 58° and 68°, and to a very large extent, much more than the aqueous solution. It need hardly be pointed out that in these experiments it is necessary to guard against infection.

After the stir created by BILLMANN's well known paper in which he first described the ready inter-conversion of the allo-cinnamic acids and attributed it to trimorphism, various papers have appeared, both from supporters and opponents of his views.¹⁾ The opponents wish to regard the acids as chemical isomerides; thus STOBBE and SCHÖNBURG²⁾ write as the result of their elaborate investigation "dasz die Allo- und Isozimmtsäuren drei chemisch verschiedene Individuen sind."

This conclusion cannot however be correct, since my experiments prove the identity of the double acids of normal and of allo-cinnamic acids, formed in the presence of the allo-acids of m.p. 58° and 68° and in a solution in equilibrium with the acid of m.p. 42°. For if the allo-cinnamic acids were chemically distinct there ought also to be three different double acids with normal cinnamic acid.

¹⁾ For literature references see Ann. 402, 187 (1913).

²⁾ Ann. 402, 258 (1913).

But if we accept BILMANN'S view, the occurrence of one and the same double acid and of three forms of allo-cinnamic acid is intelligible, since it would represent the most stable molecular arrangement, and other arrangements would be very metastable or incapable of existence.

I hope shortly to publish some experiments designed to clear up this contradiction.

Buitenzorg, October 11, 1917.