

*Citation:*

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We may also represent the isovolumetric reaction by (21), then the coefficients will have another value. As at the reaction from right to left heat can as well be given out as absorbed, the equilibrium  $F + F' + F''$  can, therefore, starting from  $r$  go as well towards higher as towards lower temperatures.

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(To be continued).

**Chemistry.** -- "Action of Sunlight on the Cinnamic Acids". By Dr. A. W. K. DE JONG. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of March 27, 1915).

Some time ago <sup>1)</sup> I communicated that *allo*-cinnamic acid is converted in sunlight into  $\alpha$ -,  $\beta$ -truxillic acid and normal cinnamic acid.

In a communication as to this photo-action in the Recueil <sup>2)</sup> I drew, in connexion with the progressive change of the transformation and also because the addition of normal cinnamic to the *allo*-acid increased the quantity of  $\beta$ -truxillic acid, the conclusion that  $\beta$ -truxillic acid was formed by the combination of one molecule of *allo*-acid with one molecule of normal acid.

For a further study of  $\beta$ -truxillic acid it was of great importance to possess larger quantities of the same.

The preparation may take place from the split off coca acids, or from the *allo*-cinnamic acid that has been affected by sunlight.

The first process is tedious and, from a comparatively large quantity of split off acids, it yields but a small amount of  $\beta$ -truxillic acid.

In connexion herewith, attention may be called to the fact that commercial cinnamic acid may often contain not unappreciable quantities of  $\beta$ -truxillic acid which very likely has got into it in the preparation of the cinnamic acid from the above coca acids (both acids possess calcium salts sparingly soluble in water). For instance, a product called Ac. cinnamylicum puriss. D. Ap. V. contained 1.8% and another labelled Ac. cinnamylicum synth. puriss 3% of  $\beta$ -truxillic acid, whilst in the Ac. cinnamylicum purum of the same works occurred a trace. The  $\beta$ -truxillic acid, being the stronger acid, may be readily separated from the cinnamic acid by dilute aqueous sodium hydroxide.

<sup>1)</sup> Proc. 14, 100 (1911).

<sup>2)</sup> R. 31, 258 (1912).

The second way of preparing  $\beta$ -truxillic acid did, however, not seem difficult, if only a sufficient quantity of *allocinnamic* acid were at disposal.

Owing to the researches of STOERMER<sup>1)</sup> to whom belongs the credit of having found an easy method for the preparation of the *allo*-form of cinnamic acid and its derivatives, it was possible to prepare the *allo*-acid from cinnamic acid with the aid of sunlight. A solution of sodium cinnamate was exposed daily in large bottles to sunlight and after a few months the *allocinnamic* acid was isolated in the usual manner as the aniline salt. In this manner, I came, in a short time, in possession of a fairly large quantity of *allocinnamic* acid.

As the conditions, in which the most advantageous formation of  $\beta$ -truxillic acid takes place, were not yet known, it was first of all ascertained what influence can be exerted by different factors.

For these experiments I used porcelain dishes. The *allocinnamic* acid was dissolved and by evaporating the liquid and moving the dish thus allowing it to spread all over the sides of the dish, the distribution of the acid over the surface was made as even as possible. The exposure to light took place simultaneously and for the same length of time.

After the end of the exposure the product was treated as follows.

The acids were dissolved in dilute ammonia and this solution was precipitated with barium chloride. After 24 hours the precipitate was collected, washed and the  $\beta$ -truxillic acid liberated by means of hydrochloric acid. The filtrate from the barium salt was acidified with hydrochloric acid, the precipitate collected, washed and dried. By heating with benzine the cinnamic acid was separated from the  $\alpha$ -truxillic acid.

It was found that the fusion of the *allocinnamic* acid (which readily takes place in sunlight) was prejudicial to the formation of  $\beta$ -truxillic acid as it causes the acid to collect in droplets. Hence, in the other experiments the dishes were kept cold by allowing them to float upon water.

The size of the surface over which the acid was distributed also exerted an influence, which will be readily understood, as a small surface receives in the same time less light than a large one.

Also in sunlight, in the same time, more  $\beta$ -truxillic acid was formed than in diffused daylight.

The covering with a glass plate impeded the formation of  $\beta$ -truxillic acid.

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<sup>1)</sup> Ber. 42, 4865 (1909) 44, 637 (1911).

The transformation was very much favoured by repeatedly interrupting the illumination and redissolving and recrystallising the mass.

The addition of benzoic acid,  $\alpha$ - or  $\beta$ -truxillic acid to the *allo*-cinnamic acid ( $\frac{1}{2}$  gram *alloacid* + 1 gram of the other acids) was found to be injurious, whereas the admixture with cinnamic acid was very advantageous. From half a gram of *allocinnamic acid* alone, 0.264 gram of  $\beta$ -truxillic acid was formed, whilst this quantity of *alloacid* when mixed with one gram of *n*-cinnamic acid had yielded 0.707 gram of  $\beta$ -truxillic acid.

This result is, therefore, quite in harmony with what was found previously.

This increased yield of  $\beta$ -truxillic acid on adding normal cinnamic acid to the *alloacid* was formerly explained by me by assuming that  $\beta$ -truxillic acid might be formed from one molecule of *alloacid* and one molecule of normal cinnamic acid. It is, however, obvious that we should observe the same thing when *n*-cinnamic acid itself was transformed into  $\beta$ -truxillic acid and when the *alloacid* formed  $\beta$ -truxillic acid indirectly over the *n*-cinnamic acid.

Up to the present, however, the transformation of *n*-cinnamic acid into  $\beta$ -truxillic acid has not been observed. RIBER<sup>1)</sup>, CIAMICIAN and SILBER<sup>2)</sup> and also myself when following RIBER's plan of illumination, could not demonstrate a formation of  $\beta$ -truxillic acid from *n*-cinnamic acid.

In order, however, to be able to make a choice of these two explanations, the following experiment was made.

On three dishes (diameter 18 cm.) of equal size and shape were distributed in the manner directed 1 gram of *alloacid*, 1 gram of *n*-cinnamic acid and  $\frac{1}{2}$  gram of *alloacid* +  $\frac{1}{2}$  gram of *n*-cinnamic acid, respectively. The illumination took place for two hours in sunlight; after each half hour, however, the acids were redissolved and recrystallised. The following quantities of  $\alpha$ - and  $\beta$ -truxillic acid were found to have formed.

	$\alpha$	$\beta$
1 gr. of <i>allocinnamic acid</i>	trace	0.073
1 gr. „ cinnamic acid	0.117 <sup>3)</sup>	0.498
$\frac{1}{2}$ gr. „ <i>allo</i> - + 1 gr. normal cinnamic acid	0.013	0.193

<sup>1)</sup> Ber. **35**, 2908 (1902).

<sup>2)</sup> Ber. **35**, 4128 (1902), **46**, 1564 (1913).

<sup>3)</sup> The transformation of *n*-cinnamic acid into  $\alpha$ -truxillic acid was first noticed by J. BERTRAM and KÜRSTEN [Journ. f. prakt. Chemie **51**, 324 (1896) and Ber. **28** IV, 387 (1896)].

A second experiment similarly conducted gave a concordant result. Hence, it appears that

- a. normal cinnamic acid can yield  $\alpha$ - as well as  $\beta$ -truxillic acid,
- b. the formation of  $\beta$ -truxillic acid takes place not primarily but secondarily over the normal acid,
- c.  $\beta$ -truxillic acid is not formed by the union of 1 molecule of normal and one molecule of *allocinnamic* acid as was supposed formerly.

It was still required to ascertain the reason why the *modus operandi* applied by RUBER did not give  $\beta$ -truxillic acid.

According to this method the powdered cinnamic acid is spread out in a thin layer on a sheet of paper and placed in a photographic frame.

From the results of the following experiment it will be seen that the finely divided state of the cinnamic acid obstructs the formation of  $\beta$ -truxillic acid.

On sheets of paper were plotted surfaces of equal size. These sheets were placed on enfleurage frames and on each marked space were spread out 1 gram of cinnamic acid powdered or crystallised. After about an hour's exposure to light, both the powders and the crystals were treated as stated in the following survey. In all, the exposure occupied 5 hours.

	With glass covering		Without glass covering	
	$\alpha$	$\beta$	$\alpha$	$\beta$
Powdered	0.364	nihil	0.650	nihil
„ mixing	0.260	„	0.705	„
Crystallised in porcelain dish and removed by scraping	0.120	0.044	0.321	0.150
Same, after being recrystallised in the same manner each hour	0.061	0.088	0.221	0.176

The glass used as covering and derived from photographic plates was not of uniform quality, hence the results obtained with glass covering are not mutually comparable.

The powdered cinnamic acid, both with and without glass covering, has always yielded  $\alpha$ -truxillic acid only. From the crystals  $\alpha$ - and  $\beta$ -truxillic acid have formed in both cases.

I hope, shortly, to revert to this remarkable transformation.