

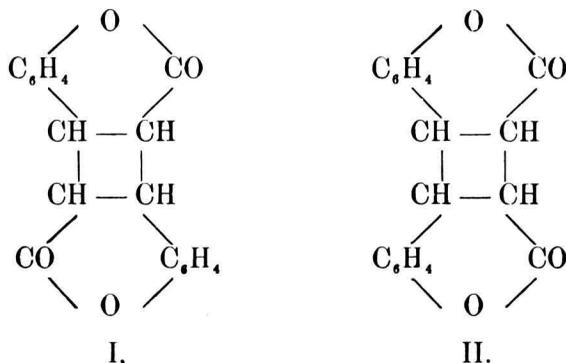
Chemistry. — “*The Biscoumaric Acids*”. By A. W. K. DE JONG.

(Communicated at the meeting of May 27, 1922).

Some time ago ¹⁾ I communicated that the product of illumination of coumarin is not identical with hydrodicoumarin of FITTIG and DYSON, as CLAMICIAN and SILBER had thought, but that it must have another structure, because when treated with alkalis it does not give a mono-basic, but a di-basic acid.

It is natural to suppose that the product of illumination of coumarin is formed from coumarin in the same way as α - and β -truxillic acid are formed from the forms of normal cinnamic acid by the combination with formation of a tetramethylene ring between the doubly bound C-atoms of the two molecules.

As two molecules of normal cinnamic acid can combine in four different ways to a truxillic acid ²⁾ also the combination of two molecules of coumarin will give four different biscoumarins, which will, as the truxillic acids, belong to two series according to the arrangement of the C-atoms with unequal (I) or equal (II) atom-groups next to each other in the tetramethylene ring.



Of both structural formulae two different biscoumarins can exist according to the situation of the coumarinrings on different sides or on the same side of the tetramethylene ring.

¹⁾ These proceedings Vol. XX, 875.

²⁾ These proceedings Vol. XX, 590.

To the product of illumination of coumarin one of these four structural formulae must be assigned.

Also another biscoumarin is known, obtained by KNUT T. STRÖM ¹⁾ by boiling biscoumaric acid, formed by illumination of coumaric acid, with anhydrous acetic acid. This biscoumarin is, as STRÖM already communicated, different from the biscoumarin obtained by illumination of coumarin, nor is it identical with the hydrodicoumarin of FITTIG and DYSON.

The biscoumaric acid of STRÖM is formed from coumaric acid, of which no metastable forms are known till now, in a conformable way as α -truxillic acid of α -normal cinnamic acid, and therefore it is very likely that this biscoumaric acid will have a conformable structure to α -truxillic acid. The properties of this biscoumaric acid known at present are in agreement with this, as will be shown.

The biscoumarin of STRÖM would then possess the structural formula I, the coumarin-rings being situated on different sides of the ring.

To distinguish the different biscoumaric acids I propose to give to these acids similar names as to the truxillic acids, and then the biscoumaric acid of STRÖM must be called α -biscoumaric acid, and its biscoumarin α -biscoumarin. The melting- at the same time decomposition-points of the two substances are the same, viz. 318° (STRÖM stated them to be above 275°); α -biscoumaric acid also changes into its biscoumarin when heated to 250° . The biscoumarin obtained by illumination of coumarin might be different from α -biscoumarin by the position of its coumarin-rings situated, on the same side of the tetramethylene-ring or it might be one of the two other possible biscoumarins indicated by figure II. The first supposition was not very likely, the two biscoumarins showing no change when heated at 210° with the acetic acid anhydride, whilst, when they had only a difference in the situation of the coumarin-rings with respect to the tetramethylene-ring, a change of one into the other was probable. This experiment is, however, not a conclusive proof of a different binding of the coumarin-molecules in the biscoumarins. The best way to decide this is to prepare the acid of the biscoumarin, converting it to the dimethylether, and to try if through heating with the acetic acid anhydride at 210° an anhydride is formed which gives a dimethylether of another biscoumaric acid. If the two coumarin-rings are situated on the same side of the tetramethylene ring, no other biscoumaric acid is formed, whilst

¹⁾ Ber. **37**, 1383.

when they are on different sides, a new biscoumaric acid will be obtained.

The methylation of α -biscoumaric acid by dimethylsulfate gives the dimethylester of the dimethylether crystallized into needles, melting at 133° and sparingly soluble in ether. On boiling with alkalis the dimethylether was obtained melting at 261° — 262° . BERTRAM and KÜRSTEN¹⁾ found the melting point of this substance, obtained by illumination of the methylether of coumaric acid, to be 260 — 262° .

When the dimethylether is heated with the acetic acid anhydride at 210° , the anhydride of the dimethylether of γ -biscoumaric acid was formed, which crystallized in pretty large bright yellow crystals out of the anhydride of acetic acid, melting at 186° — 187° . The dimethylether itself was obtained in fine needles melting at 234° .

When the α -biscoumaric acid is heated with KOH the acid corresponding to β cocaic acid was obtained, which separated in an ether solution by addition of petrolether in rhomb-shaped crystals melting 212° . As it would be strange to give this acid a name connected with coca, I propose to call it ζ -biscoumaric acid. With a similar treatment also the dimethylether of α -biscoumaric acid gave the same acid, which shows that the methylgroups are split off through melting with KOH.

These transformations of the α -biscoumaric acid, respectively the dimethylether, are wholly analogous to these of α -truxillic acid.

The dimethylester of the dimethylether of the biscoumaric acid of the product of illumination of coumarin, for which I propose the name of λ -biscoumaric acid, melts at 112° — 113° ; the dimethylether itself at 134° .

By heating the dimethylether with acetic acid anhydride at 210° and after evaporating the solvent in a glycerine bath at about 130° a brown sirup was obtained, which did not crystallize. The acid obtained by boiling the sirup with alkali crystallizes out of an ether-petrolether solution in fine needles melting at 203° . On account of its resemblance in structure with ϵ truxillic acid I propose to call this substance the dimethylether of ϵ biscoumaric acid. This transformation proves that the coumarin-rings of the illumination product are situated on different sides of the tetramethylene ring and as also α -biscoumarin possesses the same situation of the coumarin-rings and the two substances are different, λ -biscoumarin must have the structure of fig. II and by the removing of a carboxylgroup

¹⁾ Journ. f. pr. Ch. (2) 51, 323.

from one side of the tetramethylene ring to another an *o*-dioxy- ϵ -truxillic acid is formed.

By melting with KOH λ -biscoumaric acid is converted into δ -biscoumaric acid, crystallizing in needles melting at 157°.

I hope to make further communications on other possible transformations of the biscoumaric acids, while it will also be tried to obtain them from the truxillic acids, by which the proposed names and the structural formulae will obtain more security.

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