Chemistry. — A. W. K. de JONG. "*The Truxillic Acids*". (Communicated by Prof. VAN ROMBURGH.)

(Communicated at the meeting of May 3, 1919).

The separation of truxillic acids from cinnamic acid. Since mixtures of cinnamic acid and the truxillic acids are obtained by the action of light on the salts of the former, it was necessary to be in possession of a good method of separation.

Although various attempts have been made to carry out the separation in the wet way, these have so far failed to yield quantitative results. This is partly due to the increased solubility of the truxillic acids in presence of other truxillic acids and especially of cinnamic acid; and partly to the smallness of the quantity of the truxillic acids compared with the cinnamic acid present. With petroleum ether, for example, undoubtedly one of the best solvents for the purpose, no quantitative separation is obtained, since β-cocaic acid and δ-truxillic acid arevery appreciably soluble in proportion to the amount of cinnamic acid present. The same is true in a less degree of the other acids.

The attempt was also made to effect the separation by means of the acid potassium salt, which is difficultly soluble in alcohol. This, however, appeared to be impracticable, since some of the truxillic acids were also precipitated to some extent.

For the present there remains only the sublimation method. This, however, with RIIBER's apparatus proceeds very slowly. For this reason the sublimation was carried out at ordinary pressure in a current of air at 130°. The substance was placed in a little boat, which in its turn was placed in a glass tube. The whole was heated in a sand bath at 130°. Sublimation was continued until the weight of the residue became constant.

Separation of the truxillic acids from each other. The acids were dissolved in the calculated quantity of $N/_{10}$ potassium hydroxide solution on heating. To the solution anhydrous calcium chloride was added, 1.5 grm. for each 10 c. c. of solution. After twenty-four hours the precipitate, which may contain the calcium salts of β-, δ- and ε-truxillic acid, was filtered off and washed with calcium chloride solution (1.5 grm. per 10 c. c.). The acids in the filtrate

were separated by means of hydrochloric acid and ether and then weighed.

They were once more dissolved in the calculated quantity of $N/_{10}$ potassium hydroxide, and calcium chloride (1.5 grm. for each 10 c. c.) again added. After twenty-four hours the precipitate was filtered and washed with a little calcium chloride solution (1.5 grm. in 10 c. c.). The precipitate is added to that first obtained.

Separation of β-, δ-, and ε-truxillic acids. The calcium salts are treated with hydrochloric acid and ether, and the acids dissolved in the calculated quantity of N/10 potassium hydroxide. Twice the volume of water is then added, and as much N/10 barium chloride solution as was used of N/10 potassium hydroxide. After twenty-four hours the precipitate is filtered and washed with water. It consists of the barium salts of β- and ε-truxillic acid. The acids are extracted from the filtrate by means of hydrochloric acid and ether. They are redissolved in N/10 potassium hydroxide. Twice the volume of water is added, and as much N/10 barium chloride as was used of N/10 potassium hydroxide. In this way a little more β- and ε-truxillic acids are obtained as barium salts. The filtrate now obtained yields δ-truxillic acid with hydrochloric acid and ether, which, if necessary, can be purified by recrystallisation from boiling water.

The precipitated barium salts are boiled with water, cooled, and filtered. Hydrochloric acid is added to the filtrate. If a precipitate is formed, the above treatment is repeated until no precipitate is obtained. The filtrates yield ε-truxillic acid on treatment with hydrochlorid acid and ether. This may be purified, if necessary, by recrystallisation from boiling water. The undissolved barium salt gives β-truxillic acid with hydrochloric acid and ether.

Separation of α-, γ-truxillic acids and β-cocaic acid. To the filtrate from the precipitated calcium salts 8.5 grms of anhydrous calcium chloride per 10 c.c. is added. The precipitate is filtered after twenty-four hours and washed with a solution of calcium chloride prepared by dissolving in water as much calcium chloride in grams as there are c.c.'s of water. The acids are extracted from the filtrate, and these are subjected to a similar procedure in order to separate a small quantity of β-cocaic acid as calcium salt. The precipitated calcium salt gives β-cocaic acid, when treated with hydrochloric acid and ether. This may be recrystallised from boiling water if necessary.

The filtrate from the precipitated calcium salt gives α- and γ-truxillic acid with hydrochloric acid and ether. In order to separate these the acid mixture is boiled with water (25 c.c. per 0.1 grm.) with a reflux condenser for half an hour and is then filtered hot.

The residue consists of *α*-truxillic acid. On cooling the filtrate yields *γ*-truxillic acid which, if necessary, may be recrystallised from boiling water.

In order to test the effectiveness of the method of separation a mixture of the six truxillic acids was subjected to the treatment above described with the following result.

	Quantity used grm.	Quantity found grm.	Melting point.	Melting point after recrystallisation from water.
α-truxillic acid	0.119	0.086	270°	—
β „ „	0.100	0.096	202° - 204°	—
γ „ „	0.134	0.099	200° — 215°	220° — 226°
δ „ „	0.106	0.132	gummy	172° — 174°
ε „ „	0.078	0.079	208° — 220°	230°
β-cocaic „	0.106	0.120	165° — 175°	189° — 190°
Total . .	0.643	0.612		

For the sum of the *α*- and the *γ*-acid 0.224 grm. was found.

The method is therefore sufficient for the detection of the truxillic acids in presence of each other. If there are only two truxillic acids in the mixture an almost quantitative separation may be effected.

From the above separation several properties of the truxillic acids may be noted. The following may be added.

β-cocaic acid[1]) forms with cinnamic acid a well crystallised double acid with equal proportions of the components. This is obtained by boiling a petroleum ether solution of cinnamic acid, saturated at the ordinary temperature, with a little *β*-cocaic acid until the latter is dissolved (0.1 grm *β*-cocaic acid in 500 c.c.). On cooling the double acid separates out, frequently only after several days, in long needles, which melt at 139°. The filtrate gives a fresh quantity of double acid whenever 0.1 grm. of each of the acids is dissolved in it by boiling. The composition is determined by sublimation at 130°—140°. The solubility of *γ*-truxillic acid in chloroform is increased in a remarkable degree by the presence of *β*-cocaic acid.

The ammonium salts of the truxillic acids slowly lose their ammonia when their aqueous solutions are evaporated on a water bath and are transformed into the free acids. The ammonium salt of cinnamic acid also possesses this property.

[1]) The acid (m.p. 190°) formerly separated from the acids derived from the coca-alkaloids appears to be *β*-cocaic acid.