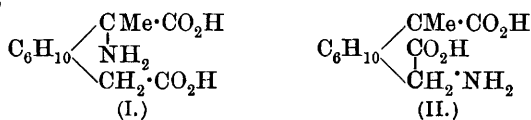


CXIII.—*Condensation Products from Aminopinene-dicarboxylic Acid.*

By WILLIAM GODDEN, B.Sc.

At the conclusion of a paper on the amino-acid derived from pinene (Tilden and Blyther, *Trans.*, 1906, **89**, 1563), it was mentioned that this compound is capable of forming certain condensation products. At the request of Professor Tilden, I undertook the further investigation of the subject, with the following results.

It may be observed that, of the two formulæ possible for this compound,



(Tilden and Burrows, *Trans.*, 1905, **87**, 344), the latter appears to be the more probable, as the acidity of the acid is strongly marked, and when heated it readily evolves carbon dioxide.

An attempt to estimate quantitatively the amount of carbon dioxide produced by heating the acid to the melting point, and absorbing the evolved gas by means of potassium hydroxide, resulted in the collection of 42 parts of carbon dioxide from 229 parts, or one molecular proportion, of the acid. This corresponds therefore with the destruction of one carboxyl group. The residual substance, however, is dark-coloured and viscid, and it has not been found possible to characterise it.

If the acid is heated to fusion for a shorter time, auto-condensation

of the acid seems to occur. A crystalline mass is left on cooling, from which, after removal of the uncrystallisable matter and recrystallisation from alcohol, melts and decomposes at 263° . On analysis, it gave the following results:

Found: C = 58.60, 58.60, 58.40; H = 8.98, 8.40, 8.30; N = 6.34, 6.75.

$C_{11}H_{19}O_4N$ requires C = 57.64; H = 8.30; N = 6.13 per cent.

On comparison of these numbers with those required by the formula of the amino-acid, it will be seen that there is only a slight difference in the carbon. The assumption that two molecules of the acid have interacted with loss of one molecule of water leads to a formula which requires 60.0 per cent. of carbon. The nearest approach to the composition found is provided by a formula which results from the coalescence of three molecules of the acid with loss of one molecule of water. This requires C = 59.1; H = 8.2; and N = 6.2 per cent. On the whole, however, it seems more probable that the substance is merely a kind of salt formed by the union of two or more molecules of the acid in virtue of its amphoteric character, and that, by recrystallisation, the original acid is gradually regenerated. This view is supported by the fact that it gives with sodium hydroxide and dilute copper sulphate solution a bluish-violet coloration practically identical with that which is produced by the original acid.

(1) *Condensation with Glycine.*

Molecular proportions or 5 grams of the amino-acid hydrochloride and 1.4 grams of glycine were mixed together and heated with 30 c.c. of absolute alcohol in a sealed tube at $110-120^{\circ}$ for four hours. No pressure was observed. The clear alcoholic liquid was allowed to evaporate slowly to dryness, and a sticky, white solid separated. This was dissolved in water, neutralised with sodium hydroxide, and shaken with ether. The ether extracted nothing, but from the aqueous solution, on standing, colourless needles, melting at $234-236^{\circ}$, were deposited. On analysis:

Found: N = 9.7, 9.6.

$C_{13}H_{22}O_5N_2$ requires N = 9.8 per cent.

Condensation of one molecule of glycine and one molecule of the amino-acid had thus evidently taken place.

On mixing a hot aqueous solution of the substance with a hot solution of copper acetate, and leaving the mixture to cool, small, bluish-violet needles of the copper hydrogen salt separated. On analysis:

Found: Cu = 10.4, 10.3.

$C_{26}H_{42}O_{10}N_4Cu$ requires Cu = 10.03 per cent.

By suspending the substance in dry ether and passing in dry hydrogen chloride, a *hydrochloride* was produced. This was crystallised from water, and the chlorine estimated by titration with standard nitrate solution.

Found : Cl = 11·6, 11·3.

$C_{13}H_{22}O_5N_2 \cdot HCl$ requires Cl = 11·0 per cent.

(2) *Condensation with Aspartic Acid.*

Molecular proportions or 5 grams of the amino-acid hydrochloride and 2·5 grams of aspartic acid were mixed together and heated with 30 c.c. of absolute alcohol in a sealed tube at 110—120° for four hours. The solution, after being filtered from some deposited aspartic acid, was allowed to evaporate. The crystals obtained were dissolved in water, neutralised with sodium hydroxide, and, on standing, colourless needles were deposited.

Found : N = 7·6, 7·4.

$C_{26}H_{41}O_{10}N_3$ requires N = 7·58 per cent.

The condensation of one molecule of aspartic acid with two molecules of the amino-acid had thus taken place with elimination of two molecules of water.

The residue of unchanged aspartic acid is thus accounted for.

This substance gave a *copper* salt when a hot aqueous solution was mixed with a hot solution of copper acetate. On cooling, bluish-violet needles were deposited.

Found : Cu = 10·34, 10·43.

$C_{26}H_{39}O_{10}N_3Cu$ requires Cu = 10·31 per cent.

Condensation of the amino-acid with benzaldehyde appeared to occur when the two substances were heated together, but the product was uncrystallisable. With anthranilic acid no change seemed to take place.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S. W.