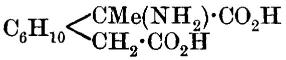
CLVI.—*The Aminodicarboxylic Acid derived from Pinene.*

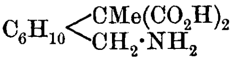
By William Augustus Tilden and Donald Francis Blyther.

By treating pinene *iso*nitrosocyanide with sulphuric acid and hydrolysing the resulting pseudoxime by means of hydrochloric acid, Tilden and Burrows (Trans., 1905, **87**, 344) obtained an amino-acid to which one of the two following formulæ was attributed :



$$\mathrm{C_6H_{10}}\!\left<\begin{matrix}\mathrm{CMe(NH_2)\cdot CO_2H}\\ \mathrm{CH_2\cdot CO_2H}\end{matrix}\right.$$

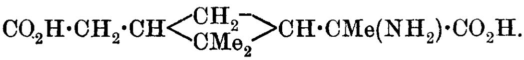
I.



$$\mathrm{C_6H_{10}}\!\left<\begin{matrix}\mathrm{CMe(CO_2H)_2}\\ \mathrm{CH_2\cdot NH_2}\end{matrix}\right.$$

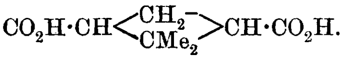
II.

Assuming G. Wagner's formula for pinene (*Ber.*, 1894, **27**, 1651), this compound contains the dimethylated tetramethylene ring to which Baeyer has given the name picean, and formula I must be represented as follows :



$$\mathrm{CO_2H\cdot CH_2\cdot CH}\!\left<\begin{matrix}\mathrm{CH_2}\\ \mathrm{CMe_2}\end{matrix}\right>\!\mathrm{CH\cdot CMe(NH_2)\cdot CO_2H.}$$

The products of the oxidation of this acid should be pinic and ultimately Baeyer's norpic acid (*Ber.*, 1896, **29**, 1910) :



$$\mathrm{CO_2H\cdot CH}\!\left<\begin{matrix}\mathrm{CH_2}\\ \mathrm{CMe_2}\end{matrix}\right>\!\mathrm{CH\cdot CO_2H.}$$

The study of this amino-acid has been again taken up with the object of examining the products of oxidation, but the work is far from complete. The amino-acid hydrochloride when treated with an equivalent quantity of sodium nitrite gave off nitrogen, and the ethereal extract contained a viscid acid substance only sparingly soluble in hot water. The aqueous solution of this acid dissolved lead hydroxide, but the lead and zinc salts could not be made to crystallise. Treated with a 5 per cent. solution of permanganate, rapid oxidation occurred in the cold. The solution, evaporated to a small bulk, acidified, and extracted with ether, gave a viscid substance possessing a peculiar penetrating odour. These experiments will be renewed with larger quantities. In the meantime the following facts concerning the properties of the amino-acid and of some of its compounds may be recorded.

Preparation of the Hydrochloride.

Pinenecarboxylic acid pseudoxime was dissolved in hydrochloric acid in the proportion of 5 grams to 15 c.c. of concentrated acid and 15 c.c. of water, and the solution heated in sealed tubes to 110—120° for four hours. A small quantity of a dark-coloured liquid floated on the solution, and on steam distillation passed over as a colourless oil which has not been further examined. The acid solution separated from this and evaporated on the steam-bath, gave the hydrochloride, which was purified by recrystallisation from dilute hydrochloric acid. The hydrochloride forms long, colourless prisms or plates which are very soluble in water, and were found to contain 13·07 per cent. of chlorine, whilst the formula $C_{11}H_{19}O_4N,HCl$ requires 13·37 per cent.

It decomposes at about 236° with evolution of carbon dioxide, accompanied by an odour resembling that of cymene.

Preparation of the Acid.

A cold aqueous solution of the hydrochloride, triturated with a slight excess of silver carbonate, yielded a solution from which, on evaporation, after removal of excess of silver by means of hydrogen sulphide, the amino-acid was obtained in crystals.

The acid may also be obtained by mixing a solution of the hydrochloride with a solution of sodium carbonate exactly equivalent to the hydrogen chloride it contains. In consequence of its comparatively slight solubility in water, the acid is soon precipitated in a crystalline state.

It crystallises from water or dilute alcohol in colourless prisms which melt at 273° with evolution of carbon dioxide.

Dried at 100° and analysed, it yielded $C = 57·65$; $H = 8·33$; $N = 6·12$.
$C_{11}H_{19}O_4N$ requires $C = 57·61$; $H = 8·36$; $N = 6·13$ per cent.

Nitrate.

The amino-acid dissolves readily in dilute nitric acid, yielding a solution which deposits colourless, radiating needles on evaporation.

The nitrate is very soluble in water, and melts at about 195° with decomposition. It yielded $N = 9{\cdot}68$, $C_{11}H_{19}O_4N,HNO_3$ requiring $N = 9{\cdot}61$ per cent.

Acid Oxalate.

This salt is precipitated when concentrated aqueous solutions of the amino-acid hydrochloride and potassium oxalate are mixed. It crystallises from water in long, colourless prisms which contain one molecule of water of crystallisation and which melt at 279°.

On analysis, the oxalate yielded $C = 45{\cdot}59$; $H = 6{\cdot}66$; $N = 4{\cdot}18$; $H_2O = 5{\cdot}30$.

$C_{11}H_{19}O_4N,H_2C_2O_4,H_2O$ requires $C = 46{\cdot}26$; $H = 6{\cdot}87$; $N = 4{\cdot}16$; $H_2O = 5{\cdot}34$ per cent.

Copper Salt.

A hot dilute aqueous solution of the amino-acid hydrochloride dissolves copper carbonate with effervescence, forming a bluish-violet solution. If excess of copper carbonate is used, the solution must be filtered rapidly, and, on cooling, the copper salt is deposited in brilliant blue prisms which are practically insoluble in water, alcohol, and ether, but soluble in acetic acid, forming a green solution. When heated, the blue salt becomes violet from partial loss of water of crystallisation. At 150°, the salt loses about $3\frac{1}{2}$ molecules of water, but it cannot be rendered anhydrous without decomposition.

Analysed, it yielded $N = 4{\cdot}32$, $Cu = 17{\cdot}46$, and $17{\cdot}30$.

$C_{11}H_{17}O_4NCu,4H_2O$ requires $N = 3{\cdot}87$; $Cu = 17{\cdot}53$ per cent.

Monoethyl Ester Hydrochloride.

This compound is readily formed when hydrogen chloride gas is passed into a solution of the acid hydrochloride in absolute ethyl alcohol. When nearly saturated, colourless plates are deposited which melt at 241° and contain one molecule of water of crystallisation.

Analysed, the ester yielded $N = 4{\cdot}97$; $Cl = 11{\cdot}31$; $H_2O = 5{\cdot}71$.

$C_{13}H_{23}O_4N,HCl,H_2O$ requires $N = 4{\cdot}50$; $Cl = 11{\cdot}37$; $H_2O = 5{\cdot}78$ per cent.

Monoethyl Ester.

The hydrochloride of the ester dissolves readily in cold water. On adding a cold aqueous solution of the calculated amount of sodium carbonate, the free ester crystallises out after a few minutes. Recrystallised from absolute alcohol, it forms slender needles, which retain a molecule of water of crystallisation and melt at 250°.

Analysis gave the following results: $C=56{\cdot}04$; $H=9{\cdot}00$; $H_2O=6{\cdot}59$; $C_{13}H_{23}O_4N,H_2O$ requiring $C=56{\cdot}67$; $H=9{\cdot}16$; $H_2O=6{\cdot}55$ per cent.

Acetyl Derivative of the Acid.

The amino-acid hydrochloride is soluble in a mixture of glacial acetic acid and acetic anhydride, and on heating the solution to a temperature near its boiling point for about five hours acetylation takes place and hydrogen chloride is expelled.

The acetyl compound is deposited on evaporating the solution, and it may be recrystallised from a mixture of glacial acetic acid and ethyl acetate in microscopic, rhombic plates which melt at 223°.

It was found to contain $N=5{\cdot}34$, whilst $C_{13}H_{21}O_5N$ requires $N=5{\cdot}18$ per cent.

This amino-acid and its hydrochloride appear to interact with benzaldehyde and with glycocine when heated with those substances. The products will be examined when more material has been prepared.

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