

## A New $\alpha$ -Aminodicarboxylic Acid, $\alpha$ -Aminopimelic Acid, in Green Plants

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When investigating free amino acids in green plants we have found an amino acid in the 70% alcohol extract of *Asplenium septentrionale*, which on two-dimensional chromatograms (butanol-acetic acid and phenol-NH<sub>3</sub>) gives a spot X the location of which appears from Fig. 1.

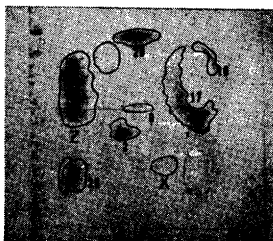


Fig. 1. Hydrolyzed alcohol extract from *Asplenium septentrionale*. Solvents: butanol-acetic acid and phenol-NH<sub>3</sub>. 2 = Ala, 9 = Thr, 16 = Asp, 17 = Glu, 23 = Orn, 29 =  $\gamma$ -aminobutyric acid, X = new aminodicarboxylic acid, Z = unknown neutral amino acid formed through hydrolysis from an acidic amino acid.

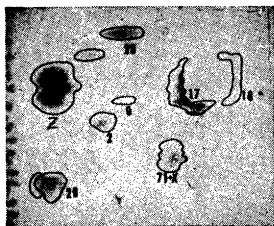


Fig. 2. As Fig. 1, but  $\alpha$ -aminopimelic acid added to alcohol extract. 71 + X = synth.  $\alpha$ -aminopimelic acid + the new aminodicarboxylic acid.



Fig. 3. One-dimensional chromatogram from a not hydrolyzed alcohol extract from *Asplenium septentrionale*. Solvent: butanol + acetic acid. 71 = synth.  $\alpha$ -aminopimelic acid (control), X = the new aminodicarboxylic acid.

Paper electrophoresis shows that this amino acid is acidic. On the basis of the location of the spot on the chromatogram it can be suggested that the amino acid in question is  $\alpha$ -aminopimelic acid. This amino acid has not earlier been found in any organisms as far as we know.

$\alpha$ -Aminopimelic acid, synthesized by Mr. M. Alfthan in this laboratory, travels exactly to the same place as our unknown amino acid on the chromatogram (Fig. 2).



Fig. 4. As Fig. 3.  $\alpha$ -Aminopimelic acid added to alcohol extract (left), no addition (right). 71 + X = synth.  $\alpha$ -aminopimelic acid + the new aminodicarboxylic acid, X = the new aminodicarboxylic acid. 17 = Glu + an unknown compound, which by hydrolysis gives an unknown neutral amino acid Z (cf. Figs. 1 and 2.)

When acidic amino acids are separated from the neutral and basic ones by an ion exchange treatment (Amberlite IR 4B) of the alcohol extract of *Asplenium*, and an one-dimensional chromatogram is made from the fractions obtained, using butanol-acetic acid as solvent, the unknown amino acid and  $\alpha$ -aminopimelic acid cannot be separated from each other, even if the run is continued until the spots are at the lower end of a long paper strip (Figs. 3 and 4).

From chromatographic and paper electrophoretic runs we conclude that the new amino acid in *Asplenium septentrionale* is  $\alpha$ -aminopimelic acid. The difficulty in obtaining enough of plant material has so far prevented us from isolating the acid in pure form. We think, however, that there is a good reason to publish these results while waiting for more plant material.

Later on one of us (V) will give an account of another new acidic amino acid found in different species of *Asplenium*.

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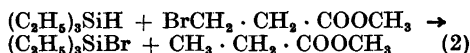
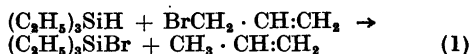
## Reactions between Triethylsilane and Some Organic Bromides

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It is well known that hydrogen bonded to silicon in alkyl-, and arylsilanes can be hydrolysed to silanols in concentrated alcoholic potassium hydroxide solution with the evolution of hydrogen<sup>1</sup>, and it also reacts with chlorine, bromine<sup>2</sup>, and iodine<sup>3</sup> to give the corresponding halogen silanes and hydrogen halides. Jenkins and Post<sup>2</sup> investigated the reactions of triethylsilane and tribenzylsilane with benzoyl chloride, benzoyl bromide and some derivatives of these compounds. Reductions to aldehydes were observed except in a few cases. Whitmore, Pietrusza, and Sommer<sup>4</sup> reported that in the presence of aluminium chloride hexyl chloride reacted with triethylsilane yielding triethylchlorosilane and hexane.

During work on organic silicon hydrides, I found that the bromine in allyl bromide and methyl  $\alpha$ -bromopropionate could react with triethylsilane in the absence of aluminium chloride. The compounds were reduced to propene and methyl propionate according to the equations



The reactions were followed by iodine titration of the remaining triethylsilane. (See below). It does not seem likely that other reactions than those given by the formulae, *e. g.* splitting off hydrogen bromide, had occurred, because the reaction products were isolated in amounts which roughly corresponded to those calculated from the titrations. For *n*-propyl bromide the reaction was very slow.

It is not unlikely that reactions of the type described here may be extended to preparative methods.

*Experimental.* All syntheses were carried out on a steam bath in an atmosphere of dry nitrogen.

*Allyl bromide and triethylsilane.* 5.8 g (0.05 mole) of triethylsilane and 6.1 g (0.05 mole) of allyl bromide were refluxed. After 15 hours the silane was completely (97 %) transformed into triethylbromosilane as determined by iodine titration. The reaction mixture was distilled to yield 8.2 g of triethylbromosilane, b.p. 50–51° (11 mm). The equivalent weight was determined by alkali titration. Found 195.1; Calc. 195.2. According to eq. (1) a gas was evolved during the synthesis which decolorized bromine water.

*Methyl  $\beta$ -bromopropionate and triethylsilane.* 5.8 g (0.05 mole) of triethylsilane and 8.35 g (0.05 mole) of methyl  $\beta$ -bromopropionate were heated together. After 20 hours 40 %, and after 44 hours 50 % of the initial amount of the silane, had reacted. Distillation yielded 1.5 g of methyl propionate, b. p. 80–81°.

*n-Propylbromide and triethylsilane.* 0.025 mole of each was refluxed on the steam bath. After 22 hours about 10 % of the triethylsilane had reacted.

*Determination of triethylsilane by iodine titration* can be performed in the following way: Into 50 ml of ethyl alcohol and 40 ml of 0.1 N iodine solution (containing potassium iodide) 50–70 mg of triethylsilane was introduced. After two hours 10 ml of 5 N hydrochloric acid