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 α-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 α-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 [1], and it also reacts with chlorine, bromine [2], and iodine [3] to give the corresponding halogen silanes and hydrogen halides. Jenkins and Post [2] 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 [4] 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 α-bromopropionate could react with triethylsilane in the absence of aluminium chloride. The compounds were reduced to propene and methyl propionate according to the equations

$$(C_2H_5)_3SiH + BrCH_2 \cdot CH{:}CH_2 \rightarrow (C_2H_5)_3SiBr + CH_3 \cdot CH{:}CH_2 \quad (1)$$

$$(C_2H_5)_3SiH + BrCH_2 \cdot CH_2 \cdot COOCH_3 \rightarrow (C_2H_5)_3SiBr + CH_3 \cdot CH_2 \cdot COOCH_3 \quad (2)$$

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 β-bromopropionate and triethylsilane. 5.8 g (0.05 mole) of triethylsilane and 8.35 g (0.05 mole) of methyl β-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

was added and the excess of iodine was determined with 0.1 *N* sodium thiosulphate. The sample had to be so small that less than half of the iodine was consumed. In this way the following values of the equivalent weight were obtained in different titrations: 118.3, 118.3, 118.9. Calculated for triethylsilane: 116.3.

When determining the amount of triethylsilane in the syntheses described above, a sample of about 0.2 ml was removed for titration. One test was made when the reaction components were mixed, and from this zero value the composition of the mixture could easily be determined at any time by titration.

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1. Price, F. P. *J. Am. Chem. Soc.* **69** (1947) 2600.
2. Jenkins, J. W. and Post, H. W. *J. Org. Chem.* **15** (1950) 556.
3. Deans, D. R. and Eaborn, C. *Research* **5** (1952) 592.
4. Whitmore, F. C., Pietrusza, E. W. and Sommer, L. H. *J. Am. Chem. Soc.* **69** (1947) 2108.

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A Comment on the Ultraviolet Light Absorption Spectrum of Cytochrome c

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The light absorption spectrum of ferrocytochrome c at neutral pH shows an absorption band at 316 mμ [1] in addition to the protein band at 280 mμ, the Soret band, and the bands in visible light. The 316 mμ-band has been interpreted as indicating the presence of a sulphoxide group [2]. This interpretation became unprobable when the six sulphur atoms in cytochrome c could be accounted for (two thioether, two methionine, and two cystine sulphur atoms) [3,4,5]. We have examined the spectra in the near ultraviolet range of the histidine and ammonia ferri and ferro meso-, proto-, and deuteroporphyrins. The results are given in Table 1 and Fig. 1.

Table 1. Wavelengths in mμ of absorption maxima.

Species	Histidine		Ammonia	
	Ox.	Red.	Ox.	Red.
Proto	Shoulder	327	Shoulder	327
Meso	347	322	350	317
Deutero	337	320	340	315

The solutions (20 ml) were 10 μ*M* in the haemin in question, 0.1 *M* in histidine (free base without chloride in phosphate, resulting pH 7.5) or 5 *M* in ammonia. After deaeration with nitrogen reduction was performed with Pt-H_2 under spectroscopic control. The solution was filtered anaerobically and transfered *via* a capillary tube directly to the cuvette (Beckman). This was sealed with a 4 mm rubber square, provided with a capillary outlet. A system of taps permitted the closed system, in-

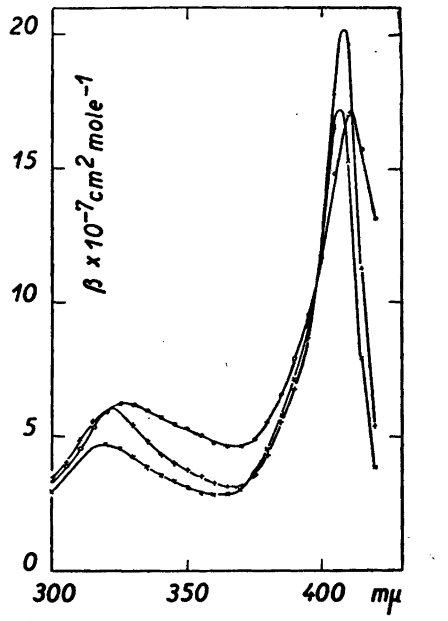

Fig. 1. Absorption spectra of ammonia proto- (○), meso- (+), and deuterohaemochromogens (×).