

CO<sub>2</sub> nor NH<sub>3</sub> from II, the latter being ninhydrin-positive only on paper, which may be due to some kind of decomposition. However, substance II gives no positive reaction for the secondary amino group as does I. Both I and II are neutral on paper electrophoresis.

The study of these compounds is continued and the experiments and results will be published in detail elsewhere. There is, however, now evidence for the structures proposed for I and II.

The following *R<sub>F</sub>*-values were found:

Lactone of	Phenol- H <sub>2</sub> O-NH <sub>3</sub>	BuOH- AcOH-H <sub>2</sub> O
homoserine	0.95	0.35
Unknown I	0.82	0.24
Unknown II	0.66	0.33
Alanine	0.62	0.27
Homoserine	0.57	0.23

When investigating other specimens of the family *Liliaceae*, substance I could be found only in *Convallaria majalis*, *Polygonatum giganteum*, *P. multiflorum*, *Smilacina stellata* and *Majanthemum bifolium*, but not *e. g.* in *Paris quadrifolia*. From a taxonomical point of view this result is very interesting.

We wish to express our deeply felt gratitude to Mr. Andreas Rosenberg, Uppsala for taking the infrared spectra.

1. Giri, K. V. and Nagabhushanan, A. *Naturwiss.* **39** (1952) 548.
2. Wendt, G. *Ber.* **75** (1942) 425.

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## New Aminodicarboxylic Acids and Corresponding $\alpha$ -Keto Acids in *Phyllitis scolopendrium*

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In a paper by Virtanen and Alfthan<sup>1</sup> the appearance of two new  $\alpha$ -keto acids and the corresponding  $\alpha$ -amino acids in a fern (*Phyllitis scolopendrium*) was reported.

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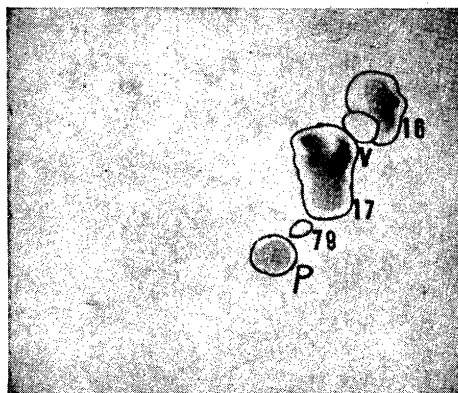


Fig. 1. Two-dimensional paper chromatogram (butanol-acetic acid and phenol-NH<sub>3</sub>) of acidic amino acids in *Phyllitis scolopendrium*. 16 = asp. V = unknown amino acid, 17 = glu, 79 =  $\gamma$ -methylglutamic acid, P = unknown amino acid.

ted. These amino acids formed the spots V and P on a two-dimensional paper chromatogram (butanol-acetic acid and phenol-NH<sub>3</sub>). Both acids were found to be acidic. We have isolated these amino acids and established their chemical nature. At

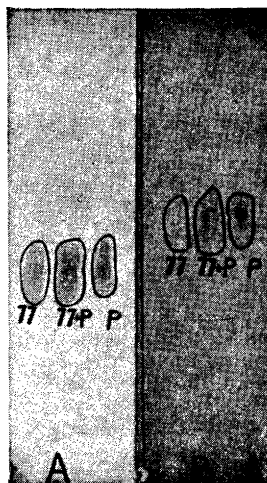


Fig. 2. One-dimensional paper chromatograms of P, synth.  $\gamma$ -methylglutamic acid (77), and a mixture of both. A: butanol-acetic acid, B: phenol-NH<sub>3</sub>.

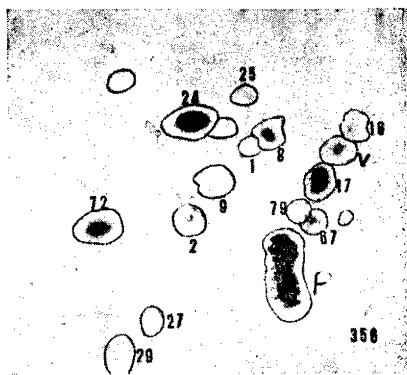


Fig. 3. Two-dimensional paper chromatogram of free amino acids in *Phyllitis*. 67 =  $\alpha$ -aminoadipic acid (added), 79 = methyleneglutamic acid, P = unknown amino acid.

the same time the structure of the corresponding keto acids has been established.

The amino acids were isolated using our earlier method. A 70% ethanol extract of the plants was run through an Amberlite IR-120 column, and the amino acids remaining in the column were eluted with 1 N ammonia. Acidic amino acids were separated from the neutral and basic ones in an Amberlite IR-45 column. The acidic amino acids were eluted from the column with 0.4 N hydrochloric acid. The solution was evaporated *in vacuo* to a very small volume. This solution contained aspartic acid, the amino acid V, glutamic acid,  $\gamma$ -methyleneglutamic acid, and the amino acid P (Fig. 1). The acids were separated from each other on the paper chromatogram using butanol-acetic acid as solvent. The separation of P from other amino acids was relatively easy, but the separation of V from aspartic acid and glutamic acid proved to be difficult.

The amino acid P travels with the same velocity as  $\gamma$ -methylglutamic acid (synthetic preparation) when either butanol-acetic acid or phenol-NH<sub>3</sub> are used as solvents (Fig. 2). Analysis of the amino acid P: C 44.88; H 6.87. Calc. for C<sub>6</sub>H<sub>11</sub>O<sub>4</sub>N: C 44.72;

H 6.83; N 8.69. The substance did not contain any OH group.  $\alpha$ -Aminoadipic acid travels both with butanol-acetic acid and phenol-NH<sub>3</sub> more slowly than its isomer  $\gamma$ -methylglutamic acid or P (Fig. 3). On the basis of both chromatographic and elementary analysis the amino acid P is  $\gamma$ -methylglutamic acid, HOOC-CH(CH<sub>3</sub>)-CH<sub>2</sub>-CHNH<sub>2</sub>-COOH.

When still working on the purification and structure of the amino acid V, we were informed by Dr. F. C. Steward that from the *Adiantum* fern he had isolated a small amount of an amino acid which proved to be identical with synthetic  $\gamma$ -methyl- $\gamma$ -hydroxyglutamic acid. A small amount of this synthetic acid which Dr. Steward sent in his letter was, according to paper chromatographic analysis, found to be identical also with our amino acid. For the present we have not investigated our acid V more closely chemically. As it is probable that hydroxy- $\alpha$ -aminoadipic acid should travel with the solvents used with about the same velocity as its isomer  $\gamma$ -methyl- $\gamma$ -hydroxyglutamic acid a later control of the amino acid V is still needed.

On the basis of the results related above the  $\alpha$ -keto acids which Virtanen and Alfthan reduced to the corresponding amino acids seem to have the following structure:  $\gamma$ -methyl- $\alpha$ -ketoglutaric acid, HOOC-CH(CH<sub>3</sub>)-CH<sub>2</sub>-CO-COOH, and  $\gamma$ -methyl- $\gamma$ -hydroxy- $\alpha$ -ketoglutaric acid, HOOC-C(CH<sub>3</sub>)(OH)-CH<sub>2</sub>-CO-COOH.

*Correction:* In the paper by Virtanen and Alfthan<sup>1</sup>, p. 189, "acidic OH-containing amino acid P and — — — of another amino acid V" should according to the manuscript be: acidic amino acid P and — — — of another OH-containing amino acid V.

We are indebted to Dr. L. Fowden, London, for a sample of synthetic  $\gamma$ -methylglutamic acid, and to Dr. F. C. Steward, New York, for  $\gamma$ -methyl- $\gamma$ -hydroxyglutamic acid.

1. Virtanen, A. I. and Alfthan, M. *Acta Chem. Scand.* **9** (1955) 188.

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