Bis(*N,N'*-diethyldiselenocarbamato)copper (II) and bis(*N,N'*-diethyldiselenocarbamato) zinc, reported by Barnard and Woodbridge,[1] were also prepared by the present method. The copper complex (black, m.p. 221°C) was recrystallized from chloroform and the zinc complex (yellow, m.p. 153–154°C) from benzene.

The yields of the complexes were almost quantitative. They were stored in a desiccator, over KOH and under nitrogen, in a cold room.

Bis(O-ethyldiselenocarbonato)nickel(II). Carbon diselenide (0.85 g) was added dropwise to a stirred and ice-cooled solution of potassium hydroxide (0.28 g) in ethanol, kept under nitrogen. This solution was added to a solution of $NiCl_2 \cdot 6H_2O$ (0.59 g) in water, with formation of a red precipitate. This was quickly extracted with chloroform, which on evaporation left black, glistening crystals of the complex.

Bis(N,N'-diethyldiselenocarbamato)nitrosylcobalt(II). Anhydrous cobalt(II) chloride (0.162 g) was dissolved in methanol, previously degassed with nitrogen, and the solution was saturated with nitrogen oxide. Sodium diethyldiselenocarbamate (0.66 g) dissolved in methanol was added to the $CoCl_2$ solution under nitrogen and nitrogen oxide was again passed through the solution. A brown precipitate resulted which was filtered off, washed with cold methanol under nitrogen and recrystallized from chloroform.

Bis(N,N'-diethyldiselenocarbamato)nitrosyliron(II). $FeCl_2 \cdot 4H_2O$ (0.245 g) was dissolved in degassed methanol, and diethyldiselenocarbamate (0.66 g) dissolved in methanol was added under nitrogen, with formation of a red precipitate. On saturation of the solution with nitrogen oxide, a brown precipitate separated. It was filtered off under nitrogen, washed with cold methanol, and crystallized from chloroform.

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Mass Spectrometric and Gas Chromatographic Studies of *N*-Heptafluorobutyryl Derivatives of Peptide Methyl Esters

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The *N*-trifluoroacetyl (*N*-TFA) derivatives of peptide methyl esters have been found useful in the direct mass spectrometric sequence analysis of peptides.[1-3]

It has recently been found by Pollock [4] that the *N*-heptafluorobutyryl (*N*-HFB) derivatives of butyl esters of amino acids have significantly shorter gas chromatographic retention times than the corresponding *N*-TFA derivatives. It was therefore of interest to study the mass spectrometric behaviour of the *N*-HFB derivatives of peptide methyl esters. Two peptide methyl esters, DL-Ala-DL-Phe-OMe and Gly-Gly-Gly-OMe, were acylated using the TFA and HFB anhydrides.[5] The exchange of the trifluoroacetyl for the heptafluorobutyryl group reduced the gas chromatographic retention times on Carbowax 20M columns by approximately 50 %, and considerably lower temperatures were needed for the vapourization of the sample in the direct inlet system of the mass spectrometer. The mass spectra shown on Figs. 1 and 2 show the striking similarity in the fragmentation pattern between the TFA and HFB-derivatives, the only notable difference being that of 100 mass units in the *m/e* of ions containing the *N*-acyl group.

As peptide methyl esters *N*-acylated with long chain acyl groups give excellent mass spectra [6] the mass spectrometric behaviour of peptide esters with higher *N*-perfluoroacyl groups is being studied.

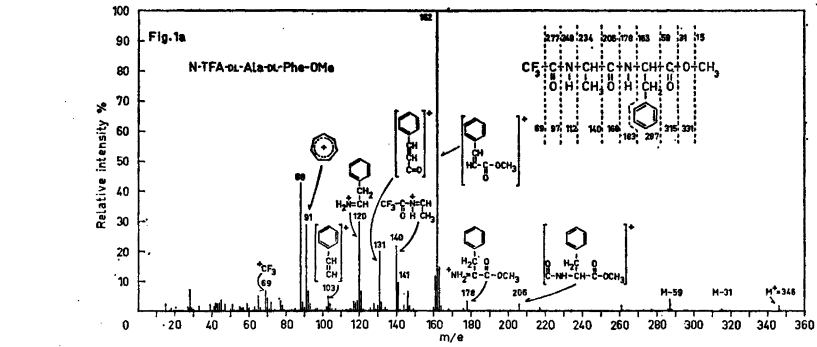
Fig.1a
N-TFA-DL-Ala-DL-Phe-OMe
Relative intensity %
m/e

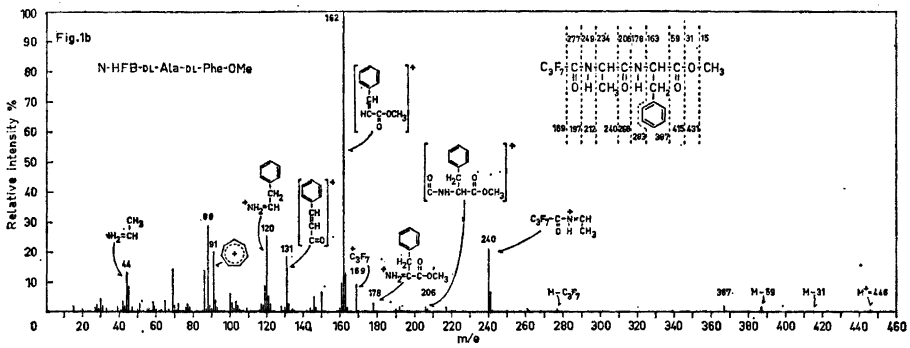
Fig.1b
N-HFB-DL-Ala-DL-Phe-OMe
Relative intensity %
m/e

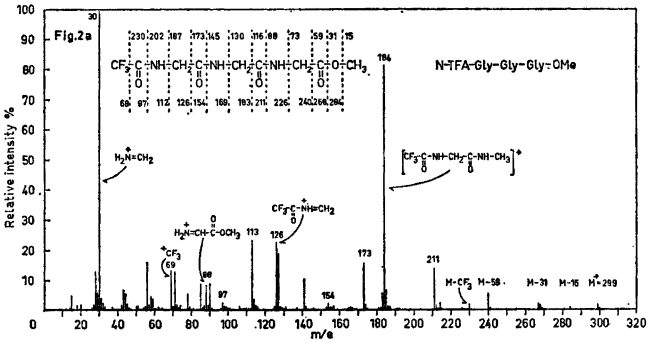
Fig.2a
N-TFA-Gly-Gly-Gly-OMe
Relative intensity %
m/e

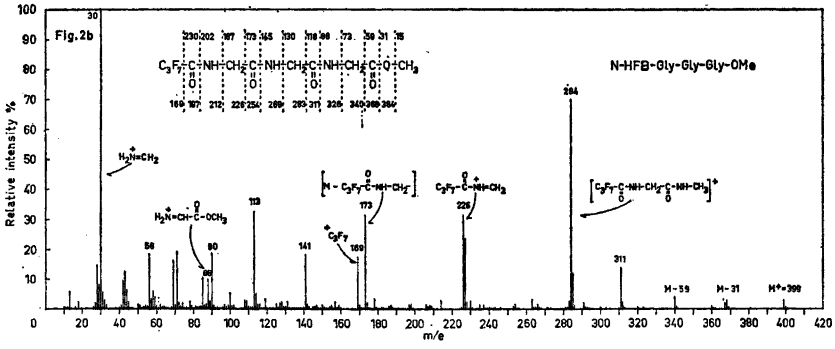
Fig.2b
N-HFB-Gly-Gly-Gly-OMe
Relative intensity %
m/e

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γ-Glutamyl-phenylalanine and γ-L-Glutamyl-L-tyrosine from Seeds of *Aubrietia deltoidea* DC.

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Previous communications from this laboratory reported results obtained during a systematic investigation of the free amino acids in species of Cruciferae.[1] In the course of these investigations the amino acid content in seeds of *Aubrietia deltoidea* DC. was determined by two-dimensional paper chromatography, and a spot was observed which could not be assigned to any amino acid previously identified in species of Cruciferae. The amino acid in question has now been isolated and identified as γ-L-glutamyl-L-tyrosine. In addition γ-glutamyl-phenylalanine has been isolated from the seeds. The latter compound was present in a concentration so small that it was not observed on the original paper chromatogram.

The fraction of acid amino acids from seeds of *A. deltoidea* DC. (1 kg, purchased from I. E. Ohlsen's Enke, Copenhagen) was obtained by traditional methods including defatting with carbon tetrachloride, extraction with methanol:water, isolation of the total amino acid fraction on a strongly acid ion-exchange resin in the acid form with subsequent elution of the amino acids with ammonia, and isolation of the acid amino acids on a strongly basic ion-exchange resin in the acetate form with subsequent elution with acetic acid. Final purification was accomplished by ion-exchange chromatography on a strongly basic ion-exchange resin in the acetate form and by use of small ion-exchange columns and preparative paper chromatography as previously described.[2] Recrystallization from ethanol:water yielded γ-glutamyl-phenylalanine (4 mg, insufficient for the determination of optical rotation) and γ-L-glutamyl-L-tyrosine (101 mg, $[\alpha]_D^{25}$ +26.8° (*c* 1.1, H_2O). Lit. value $[\alpha]_D^{31}$ +25.5° (*c* 4, H_2O).[3] The compounds were identified by comparison with authentic samples [3] by use of infra-red absorption spectra and co-chromatography on paper. Furthermore, acid hydrolysis produced glutamic acid and phenylalanine, respectively tyrosine, as determined by co-chromatography on paper. The complete identity of the infra-red absorption spectrum of the isolated phenylalanine derivative with that of authentic γ-L-glutamyl-L-phenylalanine suggests L- (or more unlikely D-) configuration at both centers.

The presence of γ-glutamyl-tyrosine in seeds of *A. erubescens* Griseb. was established by paper chromatography. Traces of this compound may be present also in seeds of *Berteroa incana* (L.) DC. whereas the two γ-glutamyl derivatives have not been identified in any other species of Cruciferae investigated. A number of other γ-glutamyl derivatives are present in the crucifer *Lunaria annua* L.[1,2]

γ-L-Glutamyl-L-phenylalanine and γ-L-glutamyl-L-tyrosine have been isolated previously from *Glycine max* (soybeans),[3] *Lupinus angustifolius*, and *L. albus*.[4] γ-L-Glutamyl-L-phenylalanine has been isolated also from *Allium cepa* where it occurs together with a number of other γ-glutamyl derivatives.[5]

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