This investigation was supported by the *Swedish Medical Research Council.*

1. Ågren, G., de Verdier, C-H. and Glomset, J. *Acta Chem. Scand.* **8** (1954) 1570.
2. Ågren, G., de Verdier, C-H. and Glomset, J. *Acta Chem. Scand.* **9** (1954) 1041.
3. Engström, L. and Ågren, G. *Acta Chem. Scand.* **10** (1956) 877.
4. Ågren, G. and de Verdier, C-H. *To be published.*
5. de Verdier, C-H. and Ågren, G. *Acta Chem. Scand.* **12** (1958). *In press.*
6. Ågren, G. *Acta Chem. Scand.* **10** (1956) 152.
7. Leloir, L. F. and Cardini, C. E. in Colowick and Caplan *Methods of Enzymology Vol. III* (1957) 840.
8. Perlmann, G. E. *Advances Protein Chem.* **10** (1955) 1.
9. Di Stefano, V., Neuman, W. F. and Rouser, G. *Arch. Biochem. Biophys.* **47** (1953) 218.

## Mass Spectrometric Studies on Amino Acid and Peptide Derivatives

Carl-Ove Andersson

*Department of Medical Biochemistry, Institute of Medical Chemistry, University of Uppsala, Uppsala, Sweden, and Laboratory for Mass Spectrometry, Kemiska Institutionen I, Karolinska Institutet, Stockholm, Sweden*

In the mass spectrum of a methyl ester of the type $RCH_2COOCH_3$ the most prominent peak is normally found at *m/e* 74 and is due to a rearranged fragment $^1C_3H_6O_2^+$. A prominent peak due to the alkyl fragment $R^+$ is only observed when carbon atom 3 is quaternary. The mass spectrum of the methyl ester of an *α*-amino acid $RCHNH_2COOCH_3$ shows, on the other hand, a very large peak due to the ionized fragment $RCHNH_2^+$. The mass number of this fragment is different for all amino-acids except the isomeric valines and leucines.

The parent peaks are small but in the cases so far examined allow a direct determination of the molecular weight of the esters. A further prominent peak occurs at *m/e* 88 corresponding to the fragment $-CHNH_2COOCH_3^+$.

Although several free amino-acids and simple peptides can be brought into the gas phase without decomposition [2] compounds with the zwitterion structure have been found less suitable for mass spectrometric analysis than compounds in which either the amino group or the carboxyl is protected. It has been found possible to analyze peptides with protected amino- and carboxyl groups. Thus N-trifluoroacetyl-L-alanyl-L-phenylalanine methyl ester [3] gives an excellent mass spectrum with a parent peak at *m/e* 346 (calculated molecular weight 346.3).

The high-mass, high-resolution mass spectrometer thus seems to offer interesting possibilities in the analysis of amino-acids and peptides.

It is intended to extend this work to other amino-acid derivatives and to study the possibility of analyzing mixtures. As carried out at present one analysis requires about 100 micrograms of material.

1. Asselineau, J., Ryhage, R., and Stenhagen, E. *Acta Chem. Scand.* **11** (1957) 196.
2. Gross, D. and Grodsky, G. *J. Am. Chem. Soc.* **77** (1955) 1678.
3. Weygand, F., Geiger, R. and Swodenk, W. *Angew. Chem.* **68** (1956) 307.

## Infrared-spectroscopic Studies on Bile Acids

I. Fischmeister

*Department of Medical Biochemistry, Institute of Medical Chemistry, University of Uppsala, Sweden*

The poor solubility of the bile acids in the nonpolar solvents required for infrared spectroscopy prevents their investigation in solution. We have therefore examined the spectra of the solid substances pressed in potassium bromide pellets. In the case of the bile acid esters which can be examined both in solution and in the solid state, the solid state spectra are found to be more distinct, owing to the fixed positions of the molecules in the crystal.

The spectra are sufficiently specific to allow identification of each bile acid by infrared spectroscopy. They are especially sensitive to the number and position of the hydroxyl groups in the skeleton. This is shown for the series of cholanic acid and its hydroxy derivatives, for coprostanic acid and its 3,7- and 3,7,12-hydroxy derivatives as well as for peptide conjugates of cholanic acid and its hydroxy derivatives with glycine and taurine. The length of the side chain affects not only the $CH_2$-vibrations but also those of the hydroxyl- and carboxyl group, indicating differences in the hydrogen bond pattern and/or different degree of hydrogen bonding in the crystallized compounds with different side chains.