

INFRARED SPECTRA OF SOME DERIVATIVES OF METHIONINE

By

Kikunoshin NAKAMURA and Hisashi ARIYAMA

*Department of Living Science, Faculty of Agriculture,
Tohoku University, Sendai, Japan*

(Received October 24, 1958)

There are numerous published observations on the infrared absorption of amino acids and their derivatives. On methionine itself and its derivatives, however, a few spectroscopic studies in infrared range have been reported.

Bellamy (1) illustrated an absorption chart of methionine in his monograph but no interpretation of the absorption bands in details was represented. Cymerman and Willis (2) noted that a weak but characteristic absorption occurred at 688 cm^{-1} and assigned it to sulfur-carbon linkage in methionine. Recently Micheel and Schlepplinghoff (3) reported some absorptions in the curve of *N*-acetyl methionine for characterizing or analytical use.

In the present paper, the authors deal with some charts of the infrared absorption of derivatives of methionine in biological interest, i. e. *s*-methyl methionine sulfonium chloride and two specimens of the iodide. In addition to these sulfonium compounds, infrared absorption curves of *N*-carbobenzoxy methionine, *N*-benzoyl methionine, and trimethyl sulfonium iodide which was given as a degradation product of methyl sulfonium salt of *N*-substituted methionine, are also drawn.

Experimental

Preparation of methionine derivatives ... *s*-Methylmethionine sulfonium iodide was prepared by two different procedures. The first method followed the procedure reported by Atkinson and Poppelsdorf (5). The resulted salt by this method, melted at 170°C (uncorr. decomp.) after three times recrystallizations. The yield was 55–56 per cent. *Anal.* Calcd. for $\text{C}_6\text{H}_{14}\text{O}_2\text{NSI}$: N, 4.81. Found: N, 4.40 by micro-Kjeldahl method. Another procedure may be regarded as a slight modification of the first one. The reaction was carried out in a small autoclave made of stainless steel with *Teflon*-packing, at 100°C for two hours. The crystalline product obtained showed m. p. $150\text{--}151^{\circ}\text{C}$ (uncorr. decomp.), which stood very close to the melting point which was previously reported by

others (5), (6). These two specimens with different melting points were common in their reaction with chloroplatinic acid and with phosphotungstic acid. These two salts also showed the same R_f value on paper chromatogram (R_f 0.13 in the solvent system of the upper layer of BuOH-AcOH-H₂O 4:1:5. Sprayed ninhydrin and chloroplatinic acid).

s-Methyl methionine sulfonium chloride was prepared from the corresponding iodide, according to McRorie *et al.* (4). Resulted matter was recrystallized from aqueous alcohol. The crystal was recognized to be pure on paper chromatogram (R_f 0.12 in the BuOH-AcOH-H₂O mixture. Sprayed ninhydrin and chloroplatinic acid). M. p. 135°C (uncorr. decomp.).

N-Carbobenzoxy methionine was synthesized in the Schotten-Baumann reaction (7). The synthesis of N-benzoyl methionine was done following the method reported by Windus and Marvel (8).

Trimethyl sulfonium iodide was obtained when N-carbobenzoxy or benzyl methionine was autoclaved with methyl iodide. The obtained crystal flashly decomposed at 212°C without bubbling or browning.

This substance makes precipitation with chloroplatinic acid or phosphotungstic acid.

DL-Methionine of guaranteed quality was obtained from the Minophagen Pharmaceutical Co., Tokyo.

Spectrophotometry ... All of the spectra were run on the Parkin-Elmer model-21 Infrared Spectrophotometer, using a sodium chloride prism in potassium bromide disc method.

Result and Discussion

Spectra of methionine and its derivatives are illustrated in Fig. 1-7. These curves of methionine and its derivatives represent a characteristic pattern of amino acids, namely, very strong absorption band assigned to be ionized

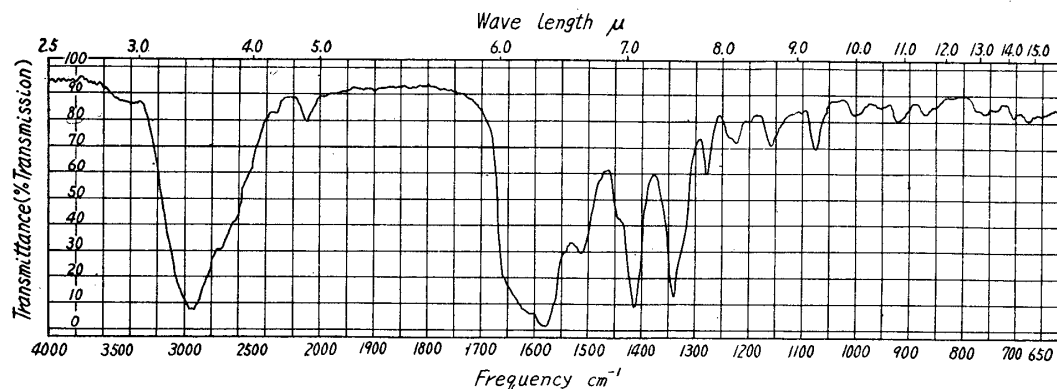


Fig. 1. Infrared spectrum of DL-methionine.

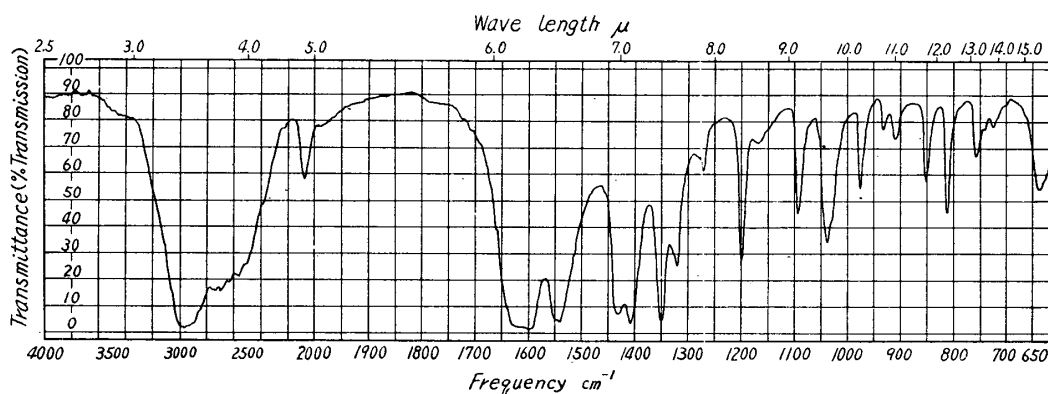


Fig. 2. Infrared spectrum of *S*-methyl methionine sulfonium chloride.

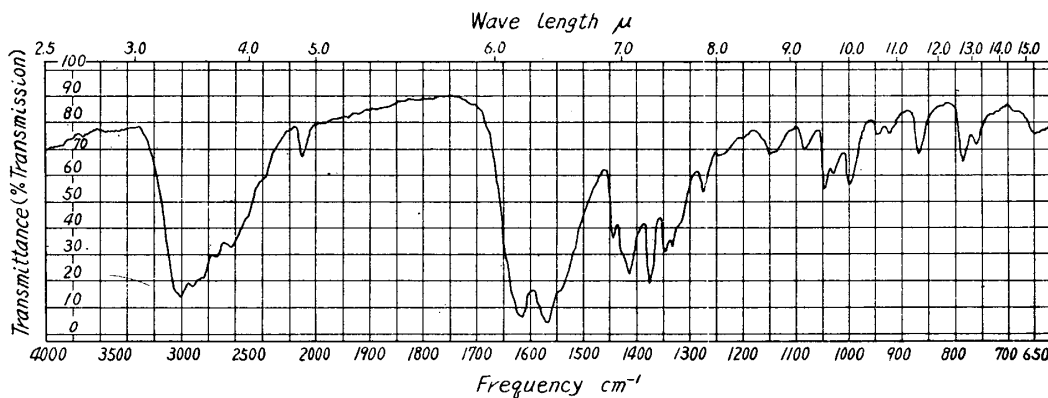


Fig. 3. Infrared spectrum of *S*-methyl methionine sulfonium iodide. m.p. 170°C

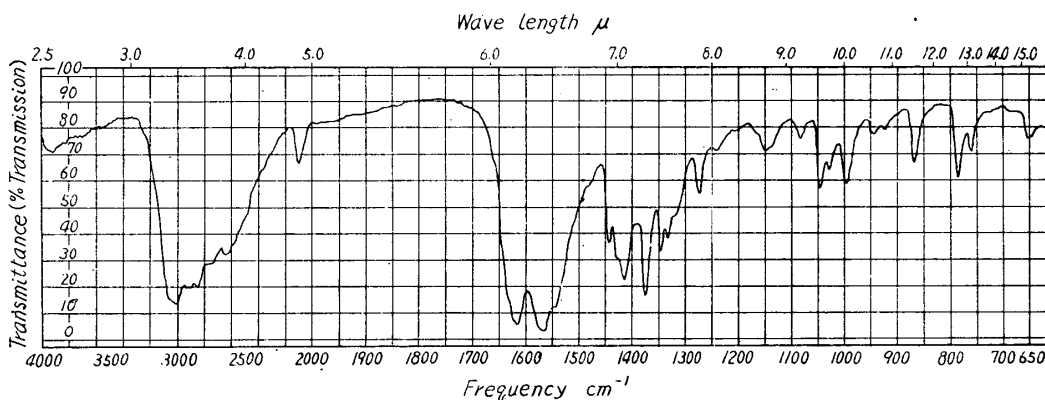


Fig. 4. Infrared spectrum of *S*-methyl methionine sulfonium iodide. m.p. 150.5~151°C

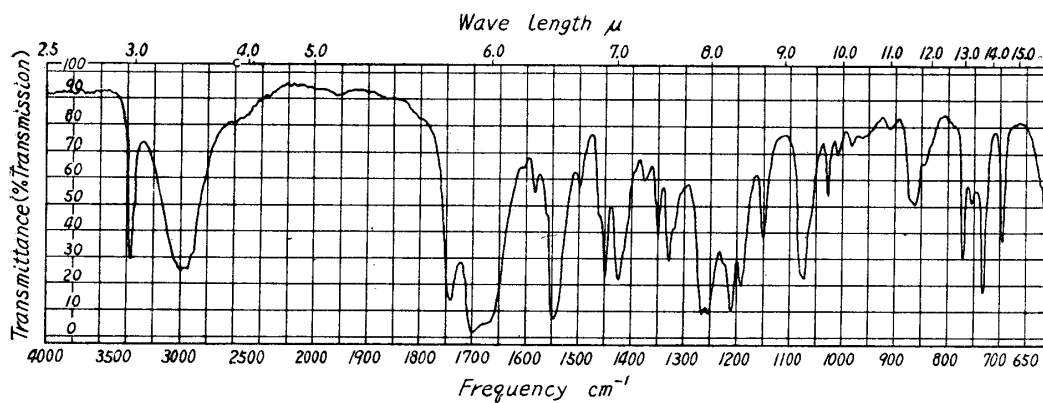
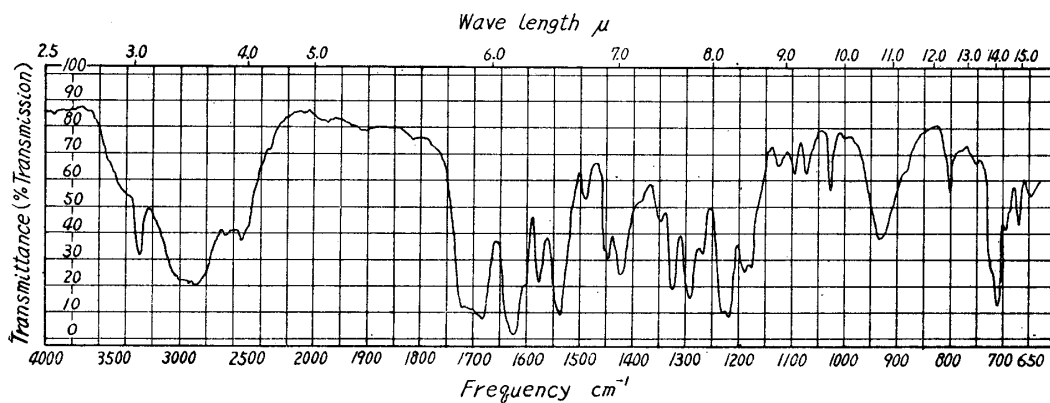
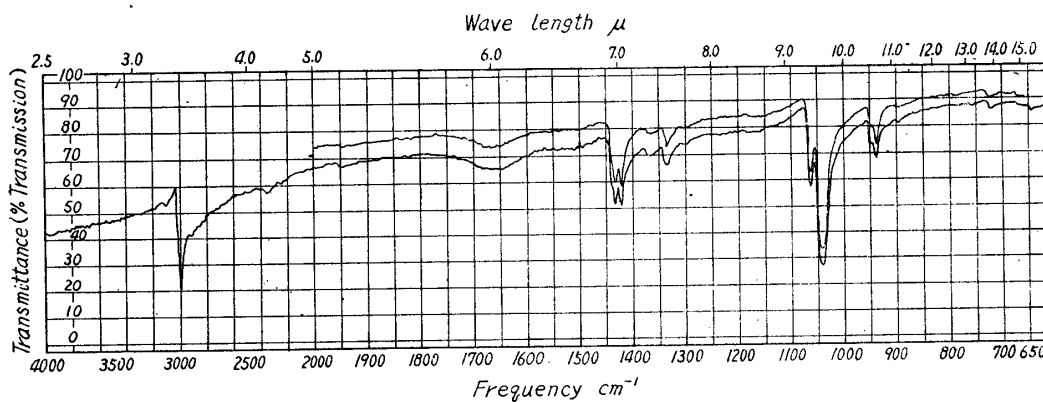
Fig. 5. Infrared spectrum of *N*-carbobenzoxy methionine.Fig. 6. Infrared spectrum of *N*-benzoyl methionine.

Fig. 7. Infrared spectrum of Trimethyl sulfonium iodide.

carboxyl group, which occurs at about 1600 cm^{-1} . Strong absorptions responsible for the ionized amino group or amide linkage are also detectable. The methionine derivatives which are covered on α -amino group with carbobenzoxy or benzoyl radical, show a series of absorptions assigned to *out-of-plane* vibration of aromatic ring in the lower wave number range (below *ca.* 800 cm^{-1}). It may be a notable fact that a weak but very specific absorption which occurs at 2100 cm^{-1} in the spectra of methionine and methionine sulfonium salts is disappeared, and instead of this absorption, an adsorption band of medium strength and with very sharp cut is found, when the α -amino group is covered (*vid.* Fig. 5 and 6. *ca.* 3400^{-1} cm).

The strong absorptions in trimethyl sulfonium iodide should be associated with methyl radicals in the molecule and their mutual interaction.

Summary

Methionine and its derivatives, i. e. *s*-methyl methionine sulfonium chloride, two specimens of *s*-methyl methionine sulfonium iodide with different melting points, *N*-carbobenzoxy methionine, *N*-benzoyl methionine and trimethyl sulfonium iodide were investigated infrared spectrophotometrically.

Acknowledgement: The authors wish to acknowledge their indebtedness to Prof. Dr. Fujise and the members of his laboratory for their cooperation in the synthesis of the above mentioned compounds. The infrared absorption spectrophotometry was carried out by Mr. Ikegami in the Chemical Research Institute of Non-aqueous Solutions of Tohoku University to whom our thanks are due.

References

- 1) Bellamy, L. J. (1954). *The Infra Red Spectra of Complex Molecules*: The chart p. 240, Methuen & Wiley, (London & New York).
- 2) Cymerman, J. and J.B. Willis (1951). *J. Chem. Soc.*, 1332.
- 3) Micheel, F. and B. Schlepplinghoff (1955). *Chem. Ber.*, **88**, 763.
- 4) McRorie, R.A. *et al.* (1954). *J. Biol. Chem.*, **211**, 489.
- 5) Atkinson, R.O. and F. Poppelsdorf (1951). *J. Chem. Soc.*, 1378.
- 6) Toennies, G. and J.J. Kolb (1945). *J. Am. Chem. Soc.*, **67**, 849.
- 7) Decker, C.A. and J.S. Furton (1948). *J. Biol. Chem.*, **173**, 371. *cf.* *Org. Syn.* **23**, 13.
- 8) Windus, W. and G.S. Marvel (1931). *J. Am. Chem. Soc.*, **53**, 3493. *Addendum*. A Complete bibliography of infrared spectra of methionine and its derivatives is found in Clark, C. and M. Chianta (1957). *Ann. N.Y. Acad. Sci.*, **69**, 218.