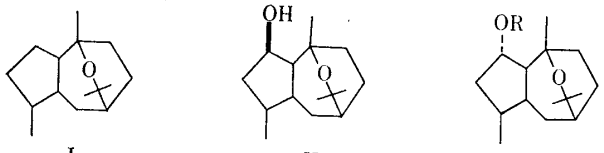

I II III

By the above interconversion, it is revealed that I and II possess the same absolute configuration in every respect, since the relationship between II and III has been established.[4]

The authors would like to express their deep gratitude to Prof. W. A. Ayer, University of Alberta, and Research Laboratories, Takeda Chemical Industries, Ltd., for nuclear magnetic resonance spectra and to Hitachi, Ltd. for mass spectra.

Pharmaceutical Institute,
Faculty of Medicine,
Tohoku University,
Kita-4-bancho, Sendai.

Hiroshi Hikino (ヒキノヒロシ)
Yasuko Hikino (曳野靖子)
Yasuyoshi Takeshita (竹下保義)
Kazuko Shirata (白田和子)
Tsunematsu Takemoto (竹本常松)

January 21, 1963

UDC 547.466.8 : 582.572.2

Isolation of (−) S-Propenyl-L-cysteine from Garlic

Recently, Virtanen, *et al.*[1] reported that the precursor of the lachrymatory factor in onion is S-propenyl-L-cysteine sulfoxide, which is cyclized to cycloalliin when the pH of its solution is raised above 7. From the results they suggested that this compound is the precursor of cycloalliin in onion.

Though cycloalliin is contained much greater than any other amino acids in garlic, the presence of S-propenyl-L-cysteine sulfoxide is obscure, and crushed garlic does not give the lachrymatory effect as such in crushed onion.

During on the studies of the sulfur containing amino acid and the related compound in garlic, the present authors have isolated a new amino acid in crystalline state and confirmed that the crystals are (−) S-propenyl-L-cysteine (CH_3-CH=CH-S-CH_2-CH(NH_2)-COOH), which is assumed to be a precursor of S-propenyl-L-cysteine sulfoxide by the following procedure.

Amino acid fraction of garlic was fractionated by the same method as previously described.[2] The new amino acid was detected in leucine fraction together with methionine and S-propyl-L-cysteine. The leucine fraction was desalted and rechromatographed on a column (3×70 cm.) of Dowex 50×4 equilibrated with 0.05*M* $HCOONH_4$, pH 2.4. Elution of the absorbed amino acids was carried out with $HCOONH_4$ buffers of pH 3.5 to 5.5. The rate of flow through the column was adjusted to 10 ml. per 30 min. and the effluent was collected in 10 ml. fractions. Column fractions 80~83 contained leucine, fractions 86~92 contained methionine and fractions 92~95 contained S-propyl-L-cysteine. Column fractions 104~116 contained the new amino acid free from other

1) A. I. Virtanen, C. G. Spåre : Suomen Kemistilehti, **B34**, 72 (1961).
2) T. Suzuki, M. Sugii, T. Kakimoto, N. Tsuboi : This Bulletin, **9**, 251 (1961).

amino acids. The fractions which contained new amino acid were combined, lyophilized and desalted. The residue obtained was recrystallized from hydrous ethanol to afford fine needles of m.p. 195° (decomp.),*1 $[\alpha]_D^{10}$ −15° (c=0.4, 2*N* HCl). Thirty milligrams of the crystals was obtained from 5 kg. of garlic bulb.

The analytical results of the new amino acid gave the formula of $C_6H_{11}O_2NS$ (Calcd.: C, 44.71; H, 6.83; N, 8.70. Found: C, 44.53; H, 6.93; N, 8.45). The crystals showed Rf values of 0.80 (PhOH-0.08%NH_4OH=4:1) and 0.60 (BuOH-AcOH-H_2O=4:1:2). The crystals gave positive iodoplatinate and ninhydrin reactions. The infrared spectrum of the crystals has a characteristic band of *trans*-1,2-disubstituted olefin at 930 cm^{-1}.[3] By the hydrogenation in the presence of Adams platinum, it was converted into S-propyl-L-cysteine. Oxidized product of the new amino acid by H_2O_2 showed Rf values of 0.62 (PhOH-0.08% NH_4OH=4:1) and 0.30 (BuOH-AcOH-H_2O=4:1:2). When this oxidized product was treated with ammonia, it was converted into cycloalliin, which showed characteristic blue spot with ninhydrin reaction at Rf 0.80 (PhOH-0.08%NH_4OH=4:1) and 0.25 (BuOH-AcOH-H_2O=4:1:2), and these values were quite identical with those of cycloalliin. On the desulfurization with Raney-Ni, the above cyclic compound gave N-isopropyl-L-alanine.

From above results, it was confirmed that the new amino acid isolated is (−) S-propenyl-L-cysteine. If S-propenyl-L-cysteine sulfoxide is a precursor of cycloalliin, it is considered that the sulfoxide is rapidly cyclized into cycloalliin in garlic plant.

Institute for Chemical Research,
University of Kyoto,
Takatsuki, Osaka-Fu.

Michiyasu Sugii (杉井通泰)
Tomoji Suzuki (鈴木友二)

Faculty of Pharmaceutical Sciences,
University of Kyoto,
Yoshida-Konoe-cho,
Sakyo-ku Kyoto.

Shigeharu Nagasawa (長沢滋治)

January 29, 1962

*1 Determined on a micro hot stage.

3) W.E. Truce, M.M. Boudakian: J. Am. Chem. Soc., 78, 2748 (1956).