UDC 547.466.8.05:582.572.2

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

S-Allyl-L-cysteine sulfoxide (alliin) was isolated by Stoll and Seebeck[1] from garlic (*Allium sativum*). The presence of alliin suggests the possibility that S-allyl-L-cysteine, which is assumed to be a precursor of alliin, should be present in garlic, but its presence has not been reported in any literature. In recent times, this compound was isolated in crystalline form from garlic in a following manner.

Tracer technique was successfully used for the detection of S-containing amino acids of garlic, as reported in the previous communication.[2] On the autoradiogram of amino acid fraction, which was extracted from garlic after 24 hours' feeding of sulfate[^{35}S], an unusual spot at Rf 0.80 (PhOH-0.08% $NH_4OH = 8:2$) and 0.50 (BuOH-AcOH-$H_2O = 5:1:4$) appeared on the paper chromatogram. The Rf values of this compound were quite identical with those of synthesized S-allyl-L-cysteine. The radioactive spot was extracted and treated with hydrogen peroxide and the oxidized radioactive product gave Rf values of 0.68 (PhOH-0.08% NH_4OH) and 0.22 (BuOH-AcOH-H_2O) which were identical with those of synthesized alliin. These results suggest that the compound should be S-allyl-L-cysteine. However, detection of this compound on the paper chromatogram by Ninhydrin and chloroplatinic acid reagents was difficult, since the content of this compound was low and always contaminated with Ninhydrin-active compound such as phenylalanine.

To isolate the new compound in large quantities, neutral amino acid fraction was adsorbed on a column of Dowex-50 ×4 buffered at pH 2.40 with 0.05*M* ammonium formate buffer. The amino acids adsorbed on the resin were fractionated with 0.2*M* ammonium formate buffer (pH 3.15). The fractions containing the new amino acid were contaminated with an unidentified amino acid of Rf 0.11 with a solvent system of BuOH-AcOH-H_2O. The two amino acids were separated from each other by a cellulose-powder column chromatography, eluted with a mixture of butanol, acetic acid, and water (5:1:4). The isolated new amino acid was purified by crystallization from hydrous ethanol and approximately 50 mg. of fine scales, m.p. 218° (decomp.), $[\alpha]_D^{20}$ −8.7°, was obtained from 5 kg. of garlic. On oxidation with hydrogen peroxide, the new amino acid easily converted to alliin. The elementary composition of the isolated amino acid corresponded to the formula $C_6H_{11}O_2NS$ (Calcd: C, 44.74; H, 6.83; O, 19.87; N, 8,70; S, 19.87. Found: C, 44.37; H, 6.88; O, 19.94; N, 8.65; S, 19.77). The new amino acid was found to be identical with the synthesized S-allyl-L-cysteine with respect to infrared spectrum, melting point, and Rf values on paper chromatogram. From these results, it is certain that the new amino acid is (−)S-allyl-L-cysteine.

Morris and Thompson[3] had revealed the presence of S-methylcysteine sulfoxide in several Cruciferae, but they could not prove the presence of S-methylcysteine in the same plant. From these facts, they thought that either methylcysteine is rapidly converted to the sulfoxide or the sulfoxide is not formed in the plant by oxidation of S-methylcysteine but formed by another route. While Thompson, *et al.*[4] isolated S-methylcysteine from beans, they could not isolated its sulfoxide.

The present experimental result is the first example for the occurrence of S-alkylcysteine and its sulfoxide in the same plant. This is an interesting evidence for the study of biosynthesis of alliin in garlic.

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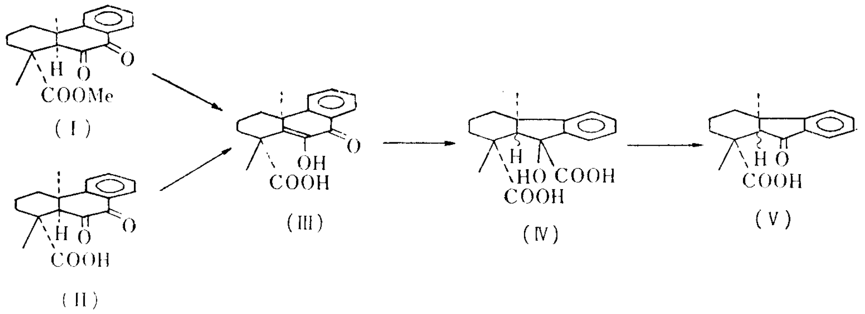
Transformation of Abietic Acid to the Hydrofluorene Derivatives*1

Interest in the biosynthetical correlation[1] between resin acids and gibberellins,[2,3]*2 the plant growth-promoting substance obtained from *Gibberella fujikuroi*,[4] prompted the present work on the transformation of abietic acid to the hexahydrofluorene derivative, which is a skeleton of gibberellins. Recent work on the same reaction by Grove and Riley accelerated the publication of the result of this work obtained to date.



Methyl 9,10-dioxo-deisopropyl-allodehydroabietate[5] (I) and 9,10-dioxo-deisopropyl-allodehydroabietic acid (II), yellow prisms, m.p. 147~149°(decomp.) (*Anal.* Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.18; H, 6.44), obtained from abietic acid, gave the same α,β-keto-enol (III), colorless prisms, m.p. 133~134°(decomp.), from methanol with addition of water, which gives violet color with ferric chloride; $[\alpha]_D^{8.5}$ −34.1°(EtOH); UV λ_{max}^{EtOH} mμ(log ε): 259.5(3.928), 304.5(3.931). IR ν_{max}^{KBr} cm^{-1}: 1709, 1633, 1598 (*Anal.* Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.29; H, 6.44) by treatments with alkaline solution such as 8.5% methanolic potassium hydroxide solution at room temperature for 2 days, 8.5% potassium hydroxide solution in a boiling water bath for a few minutes, or 20% potassium hydroxide solution in a boiling water bath for 2 hours.

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*1 This communication will be published in detail as Diterpenoids (I) by this author.

*2 Gibberellin A_3 was named gibberellic acid by the ICI research group.

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