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### Structure of Kessane

The sesquiterpenoid oxide, kessane, has newly been isolated from several kinds of Japanese valerian roots.<sup>1,2)</sup> In the present communication the authors wish to propose structure (I) for kessane on the basis of the following experimental evidences.

Kessane (I) is a colorless liquid,  $\text{C}_{15}\text{H}_{26}\text{O}^{*1}$ , b.p.<sub>6</sub> 110~112°,  $d_4^{25}$  0.970,  $n_D^{25}$  1.491,  $[\alpha]_D$  -7.2° ( $\text{CHCl}_3$ ), whose infrared spectrum (liquid) exhibited no band associated with hydroxyl or carbonyl group and a band at 1095  $\text{cm}^{-1}$  which could be assigned to an ether bridge. The nuclear magnetic resonance spectrum of I showed a doublet (3H) at 9.23  $\tau$  ( $\tau=6.0$  c.p.s) due to the methyl group in  $\text{CH}_3\text{-CH}<$  type and two singlets at 8.98  $\tau$  (3H) and 8.82  $\tau$  (6H) attributed to the methyl groups in  $\text{CH}_3\text{-C}<\text{O-}$  type. In the mass spectrum of I, there were the molecular ion peak at  $m/e$  222, but no other dominant peaks at the heavy end which would be useful for structural elucidation. Although the prominent peaks at  $m/e$  126 and below were less indicative of the structure, they were present in that of  $\alpha$ -kessyl alcohol (II)<sup>3)</sup> without exception, and thus both ion spectra or lower  $m/e$  bore a striking resemblance. Dehydrogenation of I with palladium-carbon or sulfur gave S-guaiazulene, characterized as its 1,3,5-trinitrobenzene adduct, m.p. 147~149°. All these data permitted the hypothesis that I might be the desoxy-compound of II.

In an attempt to find support for this hypothesis by synthesis, 2-*epi*- $\alpha$ -kessyl alcohol (III; R=H)<sup>4)</sup> was converted with tosyl chloride in pyridine to the corresponding tosylate (III; R=Ts),  $\text{C}_{22}\text{H}_{32}\text{O}_4\text{S}$ , m.p. 96~97°, infrared bands (KBr) at 1602, 1355, 1172 (tosylate)  $\text{cm}^{-1}$ , which by reduction with lithiumaluminium hydride furnished I,  $\text{C}_{15}\text{H}_{26}\text{O}$ , b.p.<sub>5</sub> 105°,  $d_D^{25}$  0.969,  $n_D^{25}$  1.492,  $[\alpha]_D$  -4.9° ( $\text{CHCl}_3$ ), together with small amount of III (R=H). The identity was established by gas chromatography, infrared spectrum, and nuclear magnetic resonance spectrum.

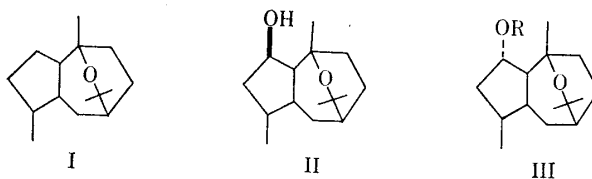
\*1 All analytical values are in good agreement with molecular formulae shown. Melting points and boiling points are uncorrected. NMR spectra were measured at 60 Mc. in  $\text{CCl}_4$  vs.  $\text{Me}_4\text{Si}$  as internal reference.

1) H. Hikino, Y. Hikino, H. Kato, Y. Takeshita, T. Takemoto: *Yakugaku Zasshi*, 83, 219 (1963).

2) H. Hikino, Y. Hikino, Y. Takeshita, Y. Isurugi, T. Takemoto: *Ibid.*, (1963). in press and references cited therein

3) cf. J. Simonsen, P. de Mayo: "The Terpenes," V 564 (1957), Cambridge University Press, London,

4) unpublished data.



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.<sup>4)</sup>

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### Isolation of (–) S-Propenyl-L-cysteine from Garlic

Recently, Virtanen, *et al.*<sup>1)</sup> 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 ( $\text{CH}_3\text{-CH=CH-S-CH}_2\text{-CH(NH}_2\text{)-COOH}$ ), 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.<sup>2)</sup> 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 0.05M  $\text{HCOONH}_4$ , pH 2.4. Elution of the absorbed amino acids was carried out with  $\text{HCOONH}_4$  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. Späre : Suomen Kemistilehti, **B34**, 72 (1961).

2) T. Suzuki, M. Sugii, T. Kakimoto, N. Tsuboi : This Bulletin, **9**, 251 (1961).