

agreed with those of homomethionine sulfoxide. This is the first report on the isolation of L-homomethionine as natural product.

Studies on the biosynthesis of L-homomethionine are now in progress, and it was found that thiomethyl group of L-homomethionine is arisen from methionine. It is probable that L-homomethionine is biosynthesized from α -amino- δ -hydroxyvaleric acid and methyl mercaptan which is derived from methionine. Recently, α -amino- δ -hydroxyvaleric acid has been isolated by Thompson, *et al.*³⁾ from higher plant.

The details of these experiments will be published later.

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3) J. F. Thompson, C. J. Morris, G. E. Hunt : J. Biol. Chem., **239**, 1122 (1964).

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Structure of Digiprolactone

In the preceding communication,¹⁾ the structure of digiprolactone (I), m.p. 149/151°, C₁₁H₁₆O₃, was postulated as I. This report describes confirmatory evidences for this structure.

In order to confirm the structure of the cyclohexane moiety of I, the following degradative reactions were carried out.

Digiprolactone acetate (II) was treated with ozone at -80°, followed by reductive fission of ozonide to give an oxoester (III),²⁾ which was hydrolyzed with sodium carbonate without purification to afford a dihydroxyketone (IV), m.p. 119°, C₉H₁₆O₃, $[\alpha]_D^{24} +22.2^\circ$ (c=1.067, CHCl₃), UV : $\lambda_{\max}^{95\%EtOH} 289\text{ m}\mu$ (log ϵ 1.65), IR $\lambda_{\max}^{Nujol} \mu$: 2.90, 3.08 (OH); 5.88 (C=O). Oxidation of IV with chromic anhydride gave a hydroxydione (V), m.p. 72~72.3°, C₉H₁₄O₃, $[\alpha]_D^{24.5} -13.1^\circ$ (c=1.063, CHCl₃), IR $\lambda_{\max}^{Nujol} \mu$: 3.00 (OH); 5.88 (C=O), which was converted with dil. sulfuric acid to an enedione (VI), UV : $\lambda_{\max}^{95\%EtOH} 238\text{ m}\mu$, IR $\lambda_{\max}^{CCl_4} \mu$: 5.94 (C=O); 6.16 (C=C). Reduction of VI with zinc in acetic acid gave a diketone (VII), m.p. 66°, IR : $\lambda_{\max}^{C^{14}} 5.82\text{ }\mu$ (C=O), which was identified with the authentic sample of 2,6,6-trimethyl-1,4-cyclohexanedione, by mixed melting point determination and comparison of infrared spectra.

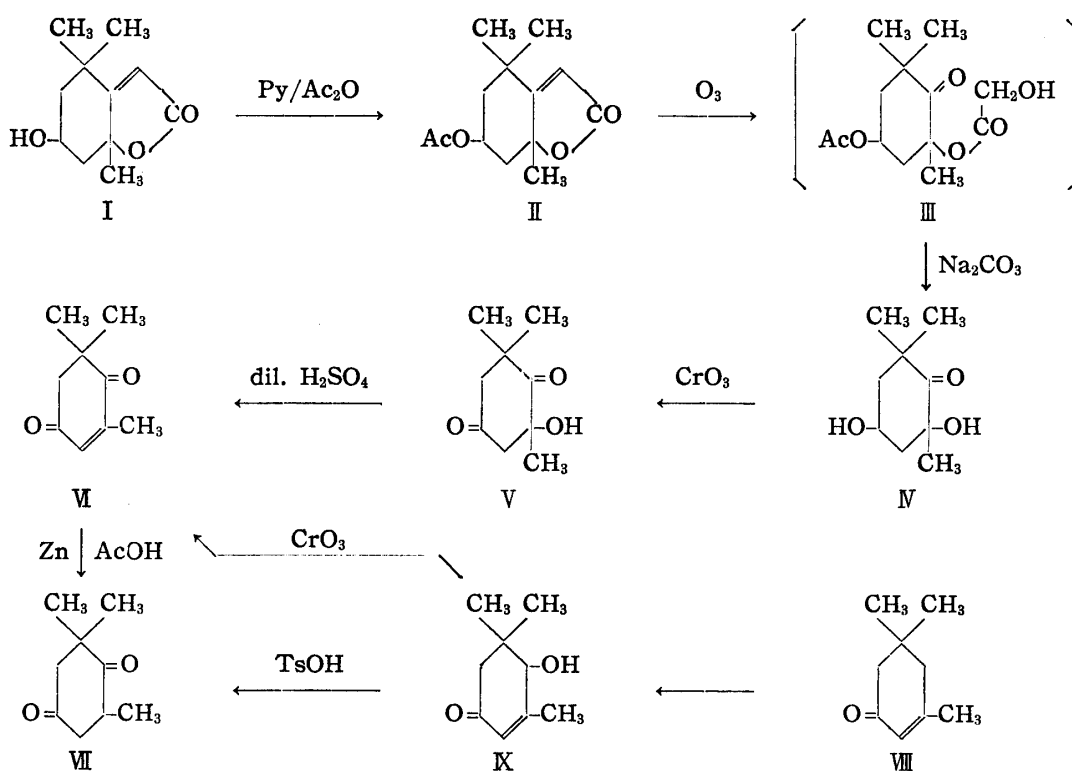
The authentic sample of VII was synthesized from isophorone (VIII) by its conversion to hydroxyisophorone (IX),^{3,4)} followed by the double bond isomerisation with *p*-toluenesulfonic acid to VII. Oxidation of IX with chromic anhydride afforded VI which also gave VII by reduction with zinc in acetic acid.

1) T. Wada, D. Satoh : This Bulletin, **12**, 752 (1964).

2) J. v. Euw, T. Reichstein : Helv. Chim. Acta, **47**, 711 (1964).

3) M. S. Kharasch, E. K. Fields : J. Am. Chem. Soc., **63**, 2308 (1941).

4) O. Isler, *et al.* : Helv. Chim. Acta, **39**, 2041 (1956).



From this result, the structure of digiprolactone was established as 2,4-dihydroxy-2,6,6-trimethyl- $\Delta^{1,2}$ -cyclohexaneacetic acid γ -lactone (I).

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Optical Rotatory Dispersion and Circular Dichroism of Securinine and Allosecurinine

The absolute stereochemistry of securinine has recently been established as I by the chemical and optical rotatory dispersion (ORD) proofs¹⁾ as well as by the X-ray crystallography.²⁾ Since it has been shown that allosecurinine is an epimer of securinine at C_{10a},³⁾ absolute configuration of allosecurinine should be assigned II. The present communication is concerning the ORD and circular dichroism (CD) studies on both alkaloids,

*¹ UV absorption spectra, ORD curves and CD curves were measured with a Hitachi spectrophotometer, a Rudolph automatic recording spectropolarimeter and a Baird-Atomic/Jouan Dichrograph (Model JO-1), respectively.

1) Z. Horii, M. Ikeda, Y. Yamawaki, Y. Tamura, S. Saito, K. Kotera : Tetrahedron, 19, 2101 (1963).

2) S. Imado, M. Shiro, Z. Horii : Chem. & Ind. (London), in press.

3) I. Satoda, M. Murayama, J. Tsuji, E. Yoshii : Tetrahedron letters, 1962, 1199.