tohogenol must be represented by the formulation (I) (serratan-3β,14β,21α-triol). In accordance with this consideration, dehydration of tohogenol diacetate (II) and reacetylation of the resulting partly hydrolysed product quantitatively yielded serratenediol diacetate (V) (IR comparison).

The other triterpenoid, tohogeninol, was isolated as its triacetate (IV), m.p. 256~258°, $[\alpha]_D$ +118° (c=1.01, $CHCl_3$), $C_{36}H_{58}O_7$, NMR : $-\overset{|}{\underset{|}{C}}-CH_3$ 9.13 (9H), 9.09 (3H), 9.02 τ (6H); -O-CO-$\underline{CH_3}$ 7.95 τ (9H); $-\overset{|}{\underset{|}{C}}-C\underline{H_2}$-OAc 5.76 τ (AB quartet J=12 c.p.s., δ_{AB}=18 c.p.s.); $>C\underline{H}$-OAc 5.43 τ (2H, multiplet). Alkaline hydrolyis of the triacetate gave the tetra-ol, tohogeninol (III), m.p. 311~312°, $C_{30}H_{52}O_4$.

The saturated nature of the compound was shown by its negative test to tetranitromethane and by the absence of a vinylic proton in the nuclear magnetic resonance spectrum of the triacetate. The infrared spectrum of the triacetate (IV) in Nujol mull indicated, besides the ester absorption at 1724 cm^{-1} and 1250 cm^{-1}, the strong hydroxyl absorptoin at 3497 cm^{-1}, thus accounting for the four oxygen functions in tohogeninol as one primary, two secondary and one tertiary hydroxyl groups. Treatment of the triacetate with 3% alcoholic hydrochloric acid and reacetylation of the product, as described in tohogenol, resulted, in excellent yield, an anhydro-compound, m.p. 247~249°, completely indentical with serratriol (serrat-14-en-3β,21α,24-triol) triacetate (VI)*2 (mixed m.p., IR and TLC comparisons). Hence, on analogy with tohogenol, the structure (III) was advanced to tohogeninol.

The biosynthetic problem whether these saturated alcohols are the products by hydration of the corresponding unsaturated compounds or they are intermediates of the serratene derivatives from α-onocerin analogs may be interesting to investigate.

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*2 The structure of serratriol will be reported in a separate paper in preparation.

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Thermal Decomposition of Azidoformate with the Retention of Configuration

It was reported very recently by Smolinsky, *et al.*[1] that the thermal decomposition of *S*(+)-2-methylbutyl azidoformate (*S*(+)-II) prepared from *S*(−)-2-methyl-1-butanol (*S*(−)-I) led to the formation of 4-ethyl-4-methyl-2-oxazolidinone ((+)-III), $[\alpha]_D^{25}$ +0.354° (C_2H_5OH), which was hydrolysed with alkali to give (+)-2-amino-2-methyl-1-butanol ((+)-IV), $[\alpha]_D^{25}$ +3.39° (C_2H_5OH).

From the suggested reaction mechanism and the fact that III thus obtained showed the optical activity, this nitrene insertion reaction was assumed to proceed with retention

1) G. Smolinsky, B. I. Feuer : J. Am. Chem. Soc., 86, 3085 (1964).

of configuration at the asymmetric carbon atom. However the absolute configurations of III and IV were not established, and moreover the extent of optical purity of both compounds obtained was not shown because of the unsuccessful resolution of the racemic III. Therefore, it had not been proved with certainty whether or not this reaction occurred evidently with retention of configuration and further, even though it may do so, the extent of optical retention had not been shown at all.

The present authors have clearly established the absolute configuration of (−)isovealin ((−)-V) as *R*-configuration[2]. This study prompted us to investigate the correlation of optically active III and IV with *R*(−)-V in order to examine the Smolinsky's proposal.

The chemical correlation of optically active III and IV with *R*(−)-V was examined under the sequence shown in Chart 1. Esterification of *R*(−)-isovaline (*R*(−)-V), $[\alpha]_D^{12}$ −5.4°(c=2.03, H_2O) (46% optically pure),[3] obtained by the method of Akabori, *et al.*[4] yielded isovaline ester hydrochloride (VI) which was reduced with sodium borohydride in ethanol[5] to give *R*(+)-isovalinol (*R*(+)-IV), $[\alpha]_D^{15}$ +1.2°(c=7.21, C_2H_5OH). A reflux of *R*(+)-IV with diethyl carbonate in the presence of sodium methylate[6] for 4.5 hr. gave *R*(+)-oxazolidinone (*R*(+)-III), viscous oil, $[\alpha]_D^{12}$ +1.0°(c=5.92, C_2H_5OH) in 67% yield. A reflux of *R*(+)-III with sodium acetate in acetic anhydride[6] for 3 hr. gave *R*(−)-3-acetyl-4-ethyl-4-methyl-2-oxazolidinone (*R*(−)-VII) in 87% yield, white crystals, m.p. 56~

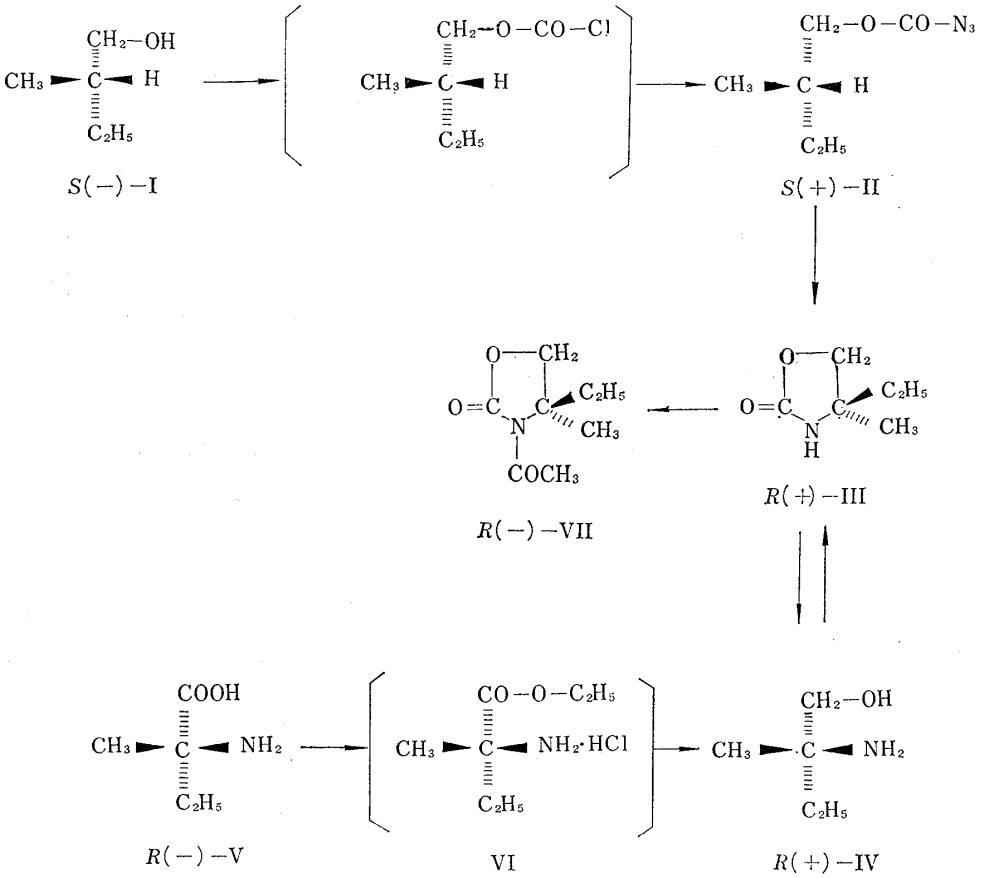


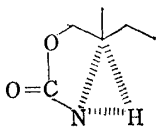
Chart 1.

2) S. Yamada, K. Achiwa : This Bulletin, **12**, 1525 (1964).
3) The optically pure *S*(+)-isovaline, $[\alpha]_D^{16}$ +11.8°(c=0.886, H_2O). (S. Terashima, K. Achiwa, S. Yamada: This Bulletin, in press.)
4) S. Akabori, T. Ikenaka, K. Matsumoto : Nippon Kagaku Kaishi, **73**, 112 (1952).
5) H. Seki, K. Koga, H. Matsuo, T. Oki, I. Matsuo, S. Yamada : This Bulletin, in press,
6) A. H. Homeyer : U. S. Pat., 2,399,118 (1946).

61°,[7] $[\alpha]_D^{12}$ −6.9° (c=2.06, C_2H_5OH). *Anal.* Calcd. for $C_8H_{13}O_3N$: C, 56.12; H, 7.65; N, 8.18. Found : C, 56.11; H, 7.71; N, 8.22. IR ν_{max}^{KBr} cm^{-1} : 1769 (2-oxazolidinone >C=O), 1706 (amide >C=O).

On the other hand, *S*(+)-2-methylbutyl azidoformate (*S*(+)-II), α_D^{11} +4.59° (*l* ldm., neat) was prepared from commercially available *S*(−)-2-methyl-1-butanol (*S*(−)-I) (α_D^{10} −4.18° (*l* ldm., neat), 87% optically pure) in 64% yield according to the method of Smolinsky, *et al.*[1] The thermal decomposition of *S*(+)-II in diphenyl ether at 190~210°[8] followed by the purification by chromatography on alumina, subsequent distillation under the reduced pressure and column chromatography on silicic acid afforded (+)-III, $[\alpha]_D^8$ +2.0° (c=11.1, C_2H_5OH), infrared spectrum of which was superimposable with that of DL-III in neat. This oxazolidinone ((+)-III) was submitted to N-acetylation under the similar procedure discribed above to yield (−)-VII, white crystals, m.p. 72.5~74°,[9] $[\alpha]_D^8$ −10.8° (c=1.83, C_2H_5OH). *Anal.* Calcd. for $C_8H_{13}O_3N$: C, 56.12; H, 7.65; N, 8.18. Found : C, 56.18; H, 7.61; N, 8.02. Infrared spectrum (in $CHCl_3$) of this compound was identical with that of *R*(−)-VII prepared from *R*(−)-isovaline.

In our reaction, that is, thermal decomposition of azidoformate II in solution phase, it is concluded clearly that the nitrene insertion reaction proceeded with retention of configuration, and the extent of retention percent of this reaction resulted in nearly 100% retention based on the calculation of optical purity of the starting materials, I and V. It is also shown that the reaction in vapour phase decomposition reported by Smolinsky, *et al.*[1] also took place with retention of configuration. These facts suggest that the intermediate of nitrene insertion reaction of this type may be shown as VIII, although other reaction mechanism cannot be definitely ruled out. Since our finding showed that this reaction proceeds with full retention of configuration, this type of reactions would have a high potentiality to utilize for the synthesis from optically active $\overset{*}{\text{C}}$-H bond to $\overset{*}{\text{C}}$-N bond. The scope and detailed mechanism of this reaction are under investigation.



VIII

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7) DL-VII has m.p. 49.5~51.5°. The IR spectrum of DL-VII in solid state is essentially superimposable with that of (−)-VII.
8) G. Smolinsky : J. Am. Chem. Soc., 83, 2489 (1961).
9) The mixed melting point of this sample with *R*(−)-VII obtained from *R*(−)-V was shown to be 61~69°.

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UDC 547.466.1.07:581.19:582.287.238

Synthesis of Tricholomic Acid, a Flycidal Amino Acid. I.

In 1964 Takemoto, *et al.*[1] isolated a flycidal constituent "tricholomic acid" from *Tricholoma muscarium* KAWAMURA, an edible mushroom in the northern part of Japan.

1) T. Takemoto, T. Nakajima : J. Pharm. Soc. Japan, 84, 1183 (1964).