The effects of three thioureas on the nitrosamine formation are shown in Fig. 1. Thiocyanate ion exhibited essentially no catalytic effect under the conditions. The accelerating effect of tetramethylthiourea was considerably larger than that of thiourea, while the effect of *N*,*N'*-dimethylthiourea was very small. These results suggest that some factors other than nucleophilicity are also important for a potential catalyst to be effective in the reaction. Detailed kinetic studies to confirm these factors are in progress.

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The Revised Stereostructure of Patrinoside X-Ray Crystallographic Analysis

The configuration at C-8 position of patrinoside, isolated from *Patrinia scabiosaefolia* FISCHER (Valerianaceae) was revised as *S* configuration by X-ray crystallographic analysis. The absolute configurations of the other carbon atoms are also confirmed as 1*S*, 5*S*, 7*S* and 9*S* (**1**).

Keywords——patrinoside; absolute configuration; X-ray crystallographic analysis; direct method; orthorhombic; *Patrinia scabiosaefolia* FISCHER; Valerianaceae

In the preceding communication, we reported the structure of patrinoside isolated from the root and rhizome of *Patrinia scabiosaefolia* FISCHER (Valerianaceae) and its stereochemistry at C-8 position was suggested as the *R* configuration (formula **2**) by the chemical and spectral studies.[1]

However, on the basis of biogenetic considerations, it has been felt that the C-8 configuration of patrinoside should be reinvestigated. Recently, Jensen *et al.* reported the isolation of the iridoid glycosides from *Viburunum opulus* (Caprifoliaceae), which possess the similar aglycones to that of patrinoside and they proposed the stereochemistry at C-8 position of these glycosides as β-hydroxymethyl and α-hydroxyl groups.[2] Thus, in order to establish the absolute configuration of C-8 position of patrinoside, its single crystal was subjected to X-ray crystallographic analysis by the direct method.

Pure patrinoside was obtained as colorless prisms by recrystallization from H_2O, mp 97—98°, $[\alpha]_D^{25}$ $-45.4°$ ($c=1.63$, MeOH), IR ν_{max}^{KBr} cm^{-1}: 3370, 1740, 1660, *Anal.* Calcd. for $C_{21}H_{34}O_{11}\cdot H_2O$: C, 52.49; H, 7.55. Found: C, 52.44; H, 7.50. The crystals are orthorhombic, space group $P2_12_12_1$ with $a=28.150(10)$, $b=9.651(4)$, $c=9.267(4)$ Å, $U=2517.6$ Å^3, $D_x=1.266$ $g\cdot cm^{-3}$, $Z=4$. The intensity data were measured by a Philips four-circle diffractmeter using graphite monochromated Cu Kα radiation. The 2647 independent reflections were used for the structure determination. The absolute configuration was assigned by taking

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1) H. Taguchi and T. Endo, *Chem. Pharm. Bull.* (Tokyo), **22**, 1935 (1974).
2) K. Bock, S.R. Jensen, B.J. Nielsen, and V. Norn, *Phytochem.*, **17**, 753 (1978).

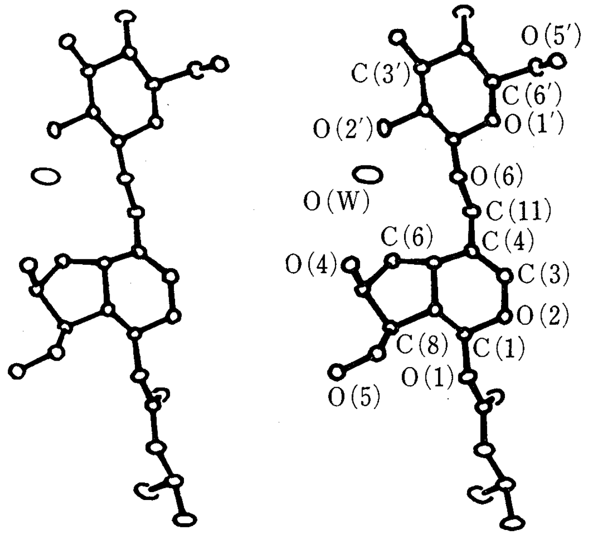
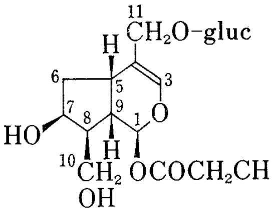


Fig. 1. A Stereoscopic View of **1**

This is drawn by the plotter program ORTEP (C.K. Johnson, 1965, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenessee). O(W): oxygen of water.



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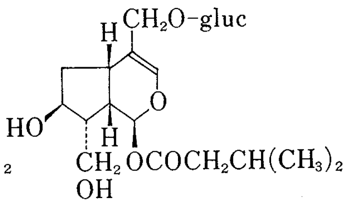

2

Chart 1

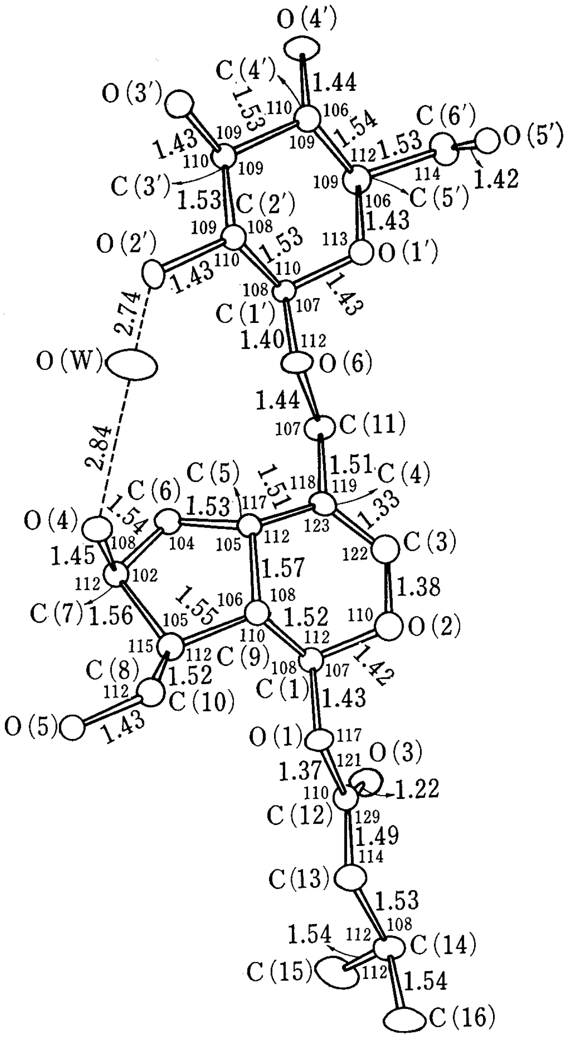

Fig. 2. Bond Lengths (Å) and Angles (°) of **1**

that of β-D-glucose. Final R value was 0.072 without hydrogen atoms. The bond lengths and angles lie in the normal ranges. The configuration of each carbon atom is proved as 1*S*, 5*S*, 7*S*, 8*S* and 9*S* as shown in Figs. 1 and 2. The stereostructure of patrinoside is, thus, expressed as formula **1**.

Within the crystal, an intramolecular hydrogen bond between the secondary hydroxyl groups at C-2′ and C-7 (axial) is formed *via* water oxygen atom O(W).

Chemical reactions of patrinoside based on a revised structure are now under progress in our laboratory.[1]

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