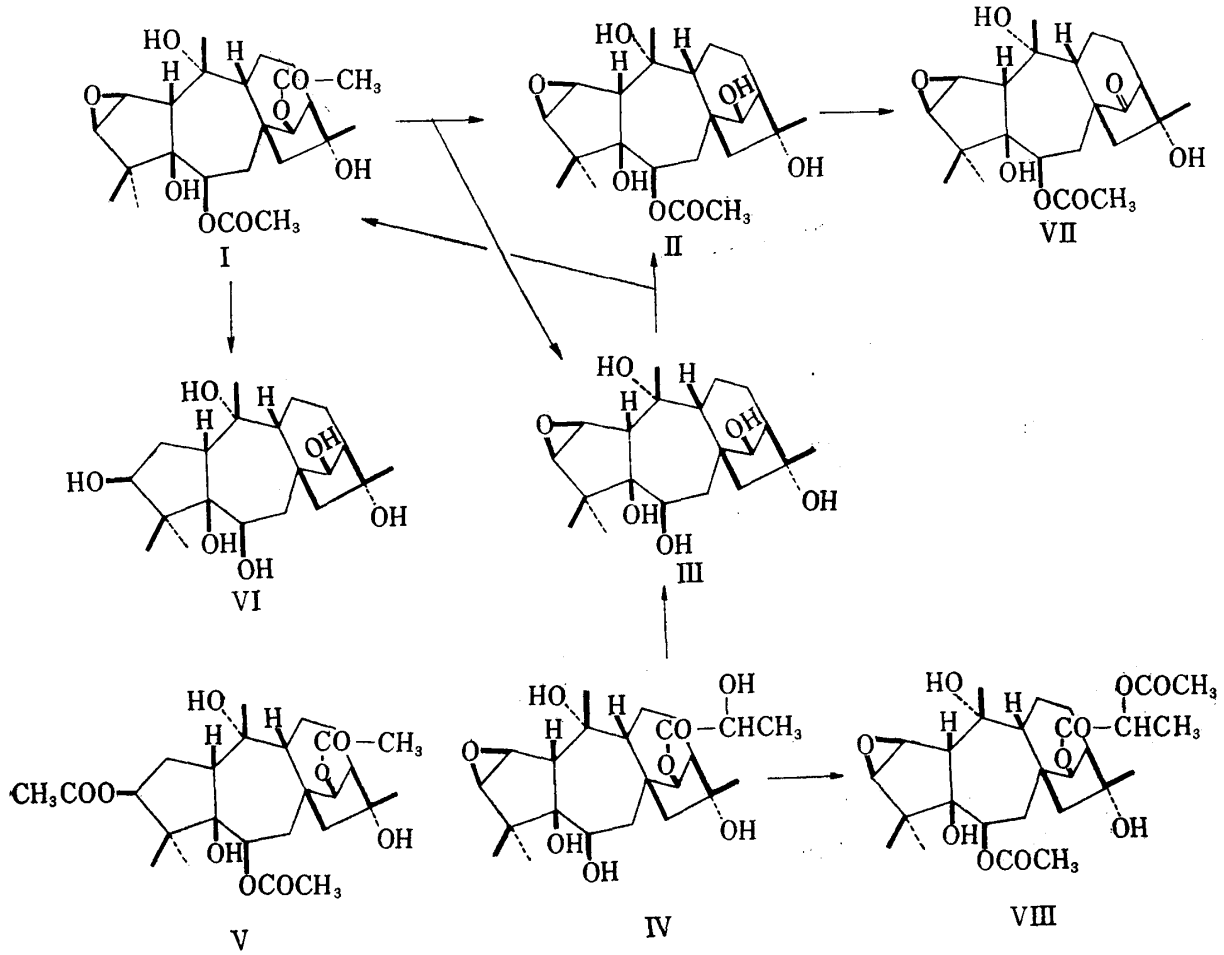
[Chem. Pharm. Bull. 17(5)1078—1079(1969)] UDC 581.19 : 547.597.02 : 582.912.4 : 615.322.011.4

Stereostructure of Rhodojaponin I, II, and III, Toxins of *Rhododendron japonicum*, and of Asebotoxin III, Toxin of *Pieris japonica*

In 1932 Kinoshita reported the isolation of a bitter toxin, rhodojaponin, from *Rhododendron japonicum* SURINGER (Ericaceae), a famous poisonous tree in Japan.[1] However, the structure has remained unknown.

Our reinvestigation on the toxic principles of the flowers of this tree has resulted in the isolation of rhodojaponin along with two other new diterpenoids. Since these three toxins are related each other as described below, we propose the names rhodojaponin I, II, and III (R-I, R-II, and R-III) for them.[2]



R-I, $C_{24}H_{36}O_8$, mp 248.5—250°, was shown by the IR and NMR spectra to have two tertiary methyls (0.87 and 1.22 ppm), two tertiary methyls on hydroxyl-carrying carbons (1.31 and 1.49 ppm), hydroxyls (3530, 3480, and 3400 cm^{-1}), and two secondary acetoxyls (1737, 1250 cm^{-1}, 2.04, 2.24, 4.70, and 5.62 ppm), these functional groups being consistent with those of grayanotoxin III triacetate (V). However, the absence of the signals attributed to the C-3 acetoxyl group in the spectrum of grayanotoxin III triacetate (V), and instead the presence of a pair of signals at 3.84 and 3.21 ppm which constitute an AB part of an ABX system

1) K. Kinoshita, *Nippon Kagaku Kaishi*, 53, 865 (1932).
2) Prof. Kinoshita has approved this proposal.

(J_{AB}=3, J_{AX}=1, and J_{BX}=0 Hz) and, therefore, ascribable to two hydrogens on vicinal carbons bearing oxygen functions, is observed. The accumulated spectral data together with the molecular formula led to the assumption that R-I may probably be formulated as I. R-I was then reduced with lithium aluminum hydride to furnish the reduction product which was found identical with grayanotoxin III (VI), establishing the stereostructure of R-I as represented by formula I.

R-I on hydrolysis afforded the monoacetate, mp 294.5—296°, and the alcohol, mp 285—287°, which were identified as the natural R-II and R-III, respectively. This finding has shown that R-III has the stereostructure III.

When R-III was acetylated, R-II and R-I were obtained. Chromic acid oxidation of R-II gave the cyclopentanone (VII), ν_{max} 1730 cm^{-1}, a fact which has established R-II to be R-III 6-acetate (II).

On the other hand, we have recently reported the isolation and structural elucidation of two new toxic diterpenoids, asebotoxin I and II, from the flowers of *Pieris japonica* D. Don (Ericaceae), another famous poisonous tree in Japan.[3] In continuation of our work on the analysis of the toxic constituents of the flowers, we have further isolated a novel diterpenoid for which the term asebotoxin III (A-III) is given.

A-III, $C_{23}H_{36}O_8$, mp 258—260°, gave on acetylation the diacetate (VIII). The NMR spectrum of the acetate (VIII) is quite similar to that of R-I except that the signal due to the O-acetyl group in the latter is replaced by the signals due to an O-acetyllactoyl group in the former. A-III was then hydrolyzed to give the delactoyl-derivative, which was identified as R-III, and lactic acid. Since the C-14 hydrogen signal in the NMR spectrum of A-III occurs at a lower-field region (6.23 ppm), indicating the C-14 hydroxyl to be esterified, the stereostructure of A-III has been established as being as shown in formula IV.

Acknowledgement Thanks are due to Analytical Laboratory, Department of Chemistry, this University, for the NMR spectra.

Pharmaceutical Institute,
Tohoku University,
Aobayama, Sendai

Hiroshi Hikino
Kunio Ito
Tomihisa Ohta
Tsunematsu Takemoto

Received February 13 1969

3) H. Hikino, K. Ito, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **17**, 854 (1969).