Stereostructure of Picrasin A, Simaroubolide of *Picrasma quassioides*

Quite recently, isolation of a number of bitter principles, nigakilactone A, B, and C and quassin by Murae, *et al.*¹⁾ and picrasin B by us,²⁾ from the quassia tree, *Picrasma quassioides* BENNETT (= *P. ailanthoides* PLANCHON) (Simaroubaceae) has been reported. Continuation of our work has led to the further isolation of another bitter for which the name picrasin A is proposed. The present communication provides evidence which indicates that picrasin A has the structure I.

Picrasin A, mp 297—299°, has the composition $C_{26}H_{34}O_8$ (M^+ at m/e 474 in MS). Of the eight oxygen atoms, one is involved in an α,β -disubstituted α,β -unsaturated carbonyl in a six- or larger-membered ring (λ_{max} 271 nm, ν_{max} 1680, 1645 cm^{-1} , δ 5.34 ppm, $[\theta]_{344} -390$), one in a saturated carbonyl (ν_{max} 1720 cm^{-1} , $[\theta]_{306} +3790$), two in a δ -lactone (1733 cm^{-1}), two in a γ -lactone (1775 cm^{-1}), one in a hydroxyl (ν_{max} 3470 cm^{-1}), and one in a methoxyl (δ 3.45 ppm). Picrasin A also contains one secondary methyl (δ 0.89 ppm) and three tertiary methyls (δ 0.94, 0.97, 1.39 ppm) other than the methoxyl. Based on the above evidence, it may be concluded that picrasin A possesses a C_{25} skeleton which consists of three carbocycles and two lactone rings. At this point we have noticed the occurrence in the same simaroubaceous family of the bitter substance, simarolide,^{3,4)} whose structural features are closely related to those of picrasin A. In particular, during the course of structural determination of simarolide, Polonsky³⁾ prepared a diosphenol derivative, deacetyl dehydrosimarolide (II), and such a formula would represent the demethylation product of picrasin A. In fact, deacetyl dehydrosimarolide (II) was easily methylated by diazomethane to furnish a methyl ether which was shown to be identical with picrasin A. Therefore, the stereostructure of picrasin A is represented by formula I.

Picrasin A is thus the second example of the simaroubolides having the C_{25} simarolidane skeleton and may be the precursor of other bitter principles in this plant.

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- 1) T. Murae, T. Tsuyuki, T. Nishihama, S. Masuda, and T. Takahashi, *Tetrahedron Letters*, **1969**, 3013.
- 2) H. Hikino, T. Ohta, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **18**, 219 (1970).
- 3) J. Polonsky, *Proc. Chem. Soc.*, **1964**, 292.
- 4) W.A.C. Brown and G.A. Sim, *Proc. Chem. Soc.*, **1964**, 293.