At present stage, it is difficult to solve whether this hypotensive substance is an artifact or not. However, it is probable that ammonia and some intermediates which belong to fatty acid degradation process are responsible for its formation.

Details of isolation, chemical properties, determination of chemical structure, synthesis and pharmacological activity of this compound will be reported later.

Faculty of Pharmaceutical Sciences,
Tokushima University
Shomachi 1-chome, Tokushima

HIROAKI TSUKATANI
TAKAFUMI ITAMI
TOSHIKAZU AWAJI
KENKICHI TAKAUCHI

Received July 3, 1971

[Chem. Pharm. Bull.
19(10)2203-2204(1971)]

UDC 547.991.02 : 581.192 : 582.752.1

Stereostructure of Picrasin F, Simaroubolide of *Picrasma quassioides*

The Chemistry of the bitter principles of the quassia tree, *Picrasma quassioides* BENNETT (= *P. ailanthoides* PLANCHON) (Simaroubaceae) has made rapid advances during the past few years.¹⁻⁸⁾ We have recently isolated another new bitter which is now designated as picrasin F. In this communication, evidence to propose formula I for picrasin F is described.

Picrasin F, mp 282—283°, has the molecular formula C₂₂H₃₀O₈ (M⁺ at *m/e* 422 in mass spectrum). Of the eight oxygen atoms, one is involved in an α,β -disubstituted, α,β -unsaturated carbonyl in a six- or larger-membered ring ($\lambda_{\max}$ 262 nm, $\nu_{\max}$ 1709, 1630 cm⁻¹, δ 5.21 ppm, $[\theta]_{340}$ -950), two in a δ -lactone ($\nu_{\max}$ 1720 cm⁻¹, δ 4.67 ppm), one in a methoxyl (δ 3.48 ppm) and two in a methylene dioxy ring (δ 5.18, 5.37 ppm ($J=1$ Hz)). Since picrasin F shows infrared (IR) absorption for hydroxyls ($\nu_{\max}$ 3475 cm⁻¹) but exhibits no NMR signal for a carbinyl hydrogen, the remaining two oxygens may be present as tertiary hydroxyls. Picrasin F also contains a secondary methyl (δ 0.89 ppm) and three tertiary methyls (δ 1.50, 1.54, 1.62 ppm) other than the methoxyl. Further analysis of the nuclear magnetic resonance (NMR) spectrum with the aid of double resonance experiments has demonstrated the presence of the following partial structures. Inter alia, intramolecular nuclear Overhauser effects were found between the C-11 hydrogen and the C-8 methyl hydrogens and between one of the C-15 hydrogens and the C-13 methyl hydrogens.

■ : denotes a quaternary carbon

- 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) T. Murae, T. Ikeda, T. Tsuyuki, T. Nishihama, and T. Takahashi, *Bull. Chem. Soc. Japan*, **43**, 969 (1970).
- 4) H. Hikino, T. Ohta, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **18**, 1082 (1970).
- 5) T. Murae, T. Ikeda, T. Tsuyuki, T. Nishihama, and T. Takahashi, *Bull. Chem. Soc. Japan*, **43**, 3021 (1970).
- 6) T. Murae, T. Ikeda, T. Tsuyuki, T. Nishihama, and T. Takahashi, *Chem. Pharm. Bull.* (Tokyo), **18**, 2590 (1970).
- 7) H. Hikino, T. Ohta, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **19**, 212 (1971).
- 8) H. Hikino, T. Ohta, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **99**, 2211 (1971).

The partial structures thus deduced, along with the previously assigned oxygen functions, have many common features with those of picrasin D (II) and picrasin E (III),⁷⁾ indicating that picrasin F is similar in structure to picrasin D and E. In support of this supposition, the NMR parameters for certain hydrogens and optical rotatory dispersion (ORD) and circular dichroism (CD) data of picrasin F are in agreement with those of picrasin D and E.

Picrasin F differs from picrasin E in having one extra oxygen which can only be accommodated as a tertiary hydroxyl at C-13 by the following data that 1) the C-12 hydrogen signal in the NMR spectrum appears as a doublet showing coupling only with the C-11 hydrogen and 2) the C-13 methyl hydrogen signal occurs as a singlet at a deshielded position (δ 1.54 ppm). The nuclear Overhauser effect between one of the C-15 hydrogens and the C-13 methyl hydrogens indicates the α -configuration of the C-13 methyl group.

Accumulated data has led to the conclusion that picrasin F has the stereostructure I.

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

Pharmaceutical Institute,
Tohoku University
Aoba-yama, Sendai

HIROSHI HIKINO
TOMIHISA OHTA
TSUNEMATSU TAKEMOTO

Received July 5, 1971

[Chem. Pharm. Bull.]
19(10):2204-2207 (1971)

UDC 547.852.3.04 : 547.68.057

Photochemistry. V.¹⁾ Photocyclization of 3,4,6-Tri- and 3,4,5,6-Tetraphenylpyridazines. Formation of 1,2-Diazapolyarenes

In a previous paper, we have reported²⁾ that an irradiation of 3,4,5,6-tetraphenylpyridazine 1-oxide resulted in the rearrangement of the oxygen atom of N-oxide group, followed by elimination of the nitrogen molecule to form tetraphenylfuran, *cis*- and *trans*-dibenzoylstilbene, and $\Delta^{3,6}$ -bicycloheptadienone derivative.

The present paper deals with the photolyses of polyphenylpyridazines lacking N-oxide groups. Interestingly, as the result, the oxidative cyclization among substituent phenyl groups occurred to form various kinds of 1,2-diazapolyarenes.

- 1) Part IV: T. Tsuchiya, H. Arai, H. Kawamura, and H. Igeta, *Chem. Pharm. Bull.* (Tokyo), in press.
- 2) T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron Letters*, 1971, 2579.