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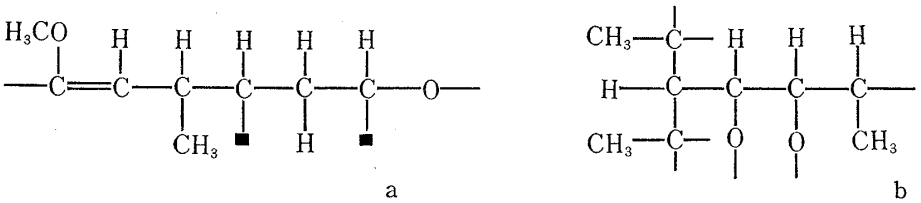
Stereostructure of Picrasin D and E, Simaroubolides of *Picrasma quassioides*

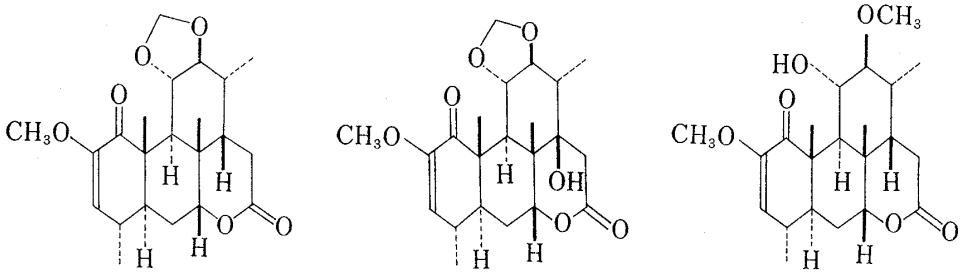
Although the chemical investigations of the bitter principles of the quassia tree, *Picrasma quassioides* BENNETT (=*P. ailanthoides* PLANCHON) (Simaroubaceae), were started as early as the last century[1] but no further result has thereafter been reported, a number of bitter constituents have successively been isolated from the wood of this tree for the last one year, *i.e.* nigakilactone A, B, C,[2] E and F,[3] quassin,[2] and picrasin A,[4] B[5] and C.[6] In continuation of our work, we have further isolated, along with nigakilactone B (III), two new bitters for which the terms picrasin D and E are proposed. We have obtained by means of nuclear magnetic resonance (NMR) technique sufficient evidence to propose formulae I and II for picrasin D and E, respectively, which is described in this communication.

Picrasin D, mp 283.5—285°, has the molecular formula $C_{22}H_{30}O_6$ (M^+ at *m/e* 390 in mass spectrum (MS)). Of the six oxygen atoms, one is involved in an α,β-disubstituted, α,β-unsaturatedcarbonyl in a six- or larger-membered ring (λ_{max} 262 nm, ν_{max} 1704, 1633 cm^{-1}, δ 5.16 ppm, $[\theta]_{335}$ −1030), two in a δ-lactone (ν_{max} 1720 cm^{-1}, δ 4.17 ppm), one in a methoxyl (δ 3.45 ppm), and two in a methylene dioxy ring (δ 5.05, 5.20 ppm (J=1 Hz)). Picrasin D also containstwo secondary methyls (δ 0.88, 0.99 ppm) and two tertiary methyls (δ 1.15, 1.37 ppm) other than the methoxyl. Further analysis of the NMR spectrum with the aid of double resonance experiments has shown the presence of the following partial structures a and b.



a b

■ : denotes a quaternary carbon



I II III

The partial structures thus deduced, together with the previously assigned oxygen functions, have many common features with those of nigakilactone B (III). Furthermore, the NMR parameters for certain hydrogens and optical rotatory dispersion (ORD) and circular dichroism (CD) data of picrasin D agree with those of nigakilactone B (III). These observations have

1) *cf.* C. Wehmer, "Die Pflanzenstoffe," Gustav Fischer, Jena, 1931, p. 643.
2) T. Murae, T. Tsuyuki, T. Nishihama, S. Masuda, and T. Takahashi, *Tetrahedron Letters*, **1969**, 3013.
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) H. Hikino, T. Ohta, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **18**, 219 (1970).
6) H. Hikino, T. Ohta, and T. Takemoto, to be published.

led to the conclusion that picrasin D has the structure I.

Picrasin E, mp 293—295°, has the composition $C_{22}H_{30}O_7$ (M^+ at *m/e* 406 in MS). The functional groups are similar to those of picrasin D. Thus the presence of an α,β-disubstituted, α,β-unsaturated carbonyl in a six- or larger-membered ring (λ_{max} 262 nm, ν_{max} 1700, 1637 cm^{-1}, δ 5.18 ppm, $[\theta]_{342}$ −1070), a δ-lactone (ν_{max} 1715 cm^{-1}, δ 4.74 ppm), a methoxyl (δ 3.46 ppm), a methylene dioxy ring, (δ 5.11, 5.26 ppm (J=1 Hz)), two secondary methyls (δ 0.90, 1.26 ppm) and two tertiary methyls (δ 1.31, 1.46 ppm) are indicated. Analysis of the NMR spectrum has demonstrated that picrasin E also possesses the same part structures (a and b). Further, the chemical shifts and splitting patterns of certain NMR signals and ORD and CD data of picrasin E are in good accord with those of picrasin D, indicating that picrasin E is a derivative of picrasin D.

Picrasin E differs from picrasin D in having one extra tertiary hydroxyl (ν_{max} 3530 cm^{-1}, no carbinyl proton signal), which can only be accommodated as at C-14. This assignment was confirmed by the appearance of signals at δ 2.91 and 3.22 ppm due to a $>C-CH_2-CO-$ moiety, and by the downfield shift (−0.57 ppm) of the C-7 hydrogen signal in comparison with that of picrasin D, the latter fact confirming also the β-orientation of the hydroxyl.[7]

Based on the above evidence, it is concluded that picrasin E is represented by formula II.

From the biogenetic viewpoint, it is assumed that the C-12 methoxyl and the neighboring C-11 hydroxyl of nigakilactone B (III) are subjected to an oxidative cyclization to give picrasin D (I) which on further hydroxylation furnishes picrasin E (II).

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7) W. Stöcklin and T.A. Geisman, *Tetrahedron Letters*, **1968**, 6007.

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A Tetracyclic Compound as a New Coloring Matter of the Reaction of Acetone with 1,3,5-Trinitrobenzene

In a previous paper,[1] the mechanism of the color reaction of acetone with a large amount of 1,3,5-trinitrobenzene (TNB) was discussed by isolating a Meisenheimer type compound[2] (I) and a bicyclic compound[3] (II) as the main coloring matters of the reaction.

In the course of study on the spectral behaviors of I and II, we found that their color intensities much increased as twice when the aqueous solution of I or II was treated with excess

1) K. Kohashi, Y. Ohkura and T. Momose, *Chem. Pharm. Bull.* (Tokyo), **18**, 2151 (1970).
2) M. Kimura, *Yakugaku Zasshi*, **73**, 1219 (1953); R. Foster and C.A. Fyfe, *Rev. Pure and Appl. Chem.*, **16**, 61 (1966).
3) T. Momose, Y. Ohkura and K. Kohashi, *Chem. Pharm. Bull.* (Tokyo), **17**, 858 (1969); R. Foster, M.I. Foreman and M.J. Strauss, *Tetrahedron Letters*, **1968**, 4949; M.I. Foreman, R. Foster and M.J. Strauss, *J. Chem. Soc.* (*C*), **1969**, 2112; M.J. Strauss and H. Schran, *J. Am. Chem. Soc.*, **91**, 3974 (1969); M.J. Strauss, T.C. Jensen, H. Schran and K.O' Conner, *J. Org. Chem.*, **35**, 383 (1970).