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Received October 2, 1971

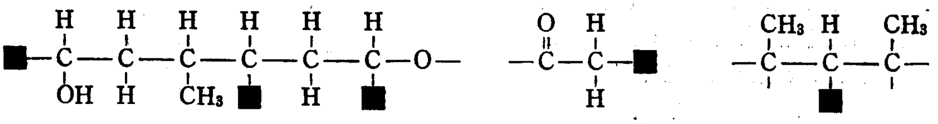
[Chem. Pharm. Bull.
19(12)2651–2652(1971)]

UDC 547.991.02 : 581.192.582.752.1

Stereostructure of Picrasin G, Simaroubolide of *Picrasma quassioides*

Knowledge of the bitter principles of the quassia tree, *Picrasma quassioides* Bennett (Simaroubaceae) has been fairly accumulated during the past few years.[1–10] We have further isolated another new bitter which is now named picrasin G. In the present communication, we wish to provide evidence that picrasin G is represented by formula I.

Picrasin G has the composition $C_{21}H_{28}O_7$ (M^+ at m/e 392 in mass spectrum). Of the seven oxygen atoms, one is involved in a secondary hydroxyl next to a carbonyl (ν_{max} 3440 cm^{-1}, δ 4.84 ppm, formation of a monoacetate (δ 2.12, 5.87 ppm), consumption of periodate), one in an unconjugated ketone in a six- or larger-membered ring (ν_{max} 1710 cm^{-1}), one in an α,β,β-trisubstituted, conjugated ketone in a six- or larger-membered ring (λ_{max} 252 nm, ν_{max} 1685, 1630 cm^{-1}, $[\theta]_{329}$ -5420), two in a δ-lactone (ν_{max} 1722 cm^{-1}, δ 4.62 ppm), one in a methoxyl (δ 3.62 ppm), and the remaining one in a tertiary hydroxyl (ν_{max} 3440 cm^{-1}, no carbinyl hydrogen signal). Picrasin G also contains a secondary methyl (δ 0.92 ppm), two tertiary methyls (δ 1.12, 1.45 ppm), and a vinyl methyl (δ 1.90 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. The partial structures so arrived at, along with the previously assigned oxygen functions, have many features in common with those of picrasin B (V). Furthermore, the NMR parameters for certain hydrogens of picrasin G are in good agreement with those of picrasin B (V), indicating that picrasin G is similar in structure to picrasin B.



$$\blacksquare-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-\underset{\blacksquare}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{\blacksquare}{\overset{H}{C}}-O- \qquad -\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{H}{C}}-\blacksquare \qquad -\overset{CH_3}{C}-\underset{\blacksquare}{\overset{H}{C}}-\overset{CH_3}{C}-$$

■ denotes a quaternary carbon

Picrasin G differs from picrasin B in having one extra tertiary hydroxyl. This difference is reflected in the NMR spectra of both the substances, where the C-15 methylene hydrogens

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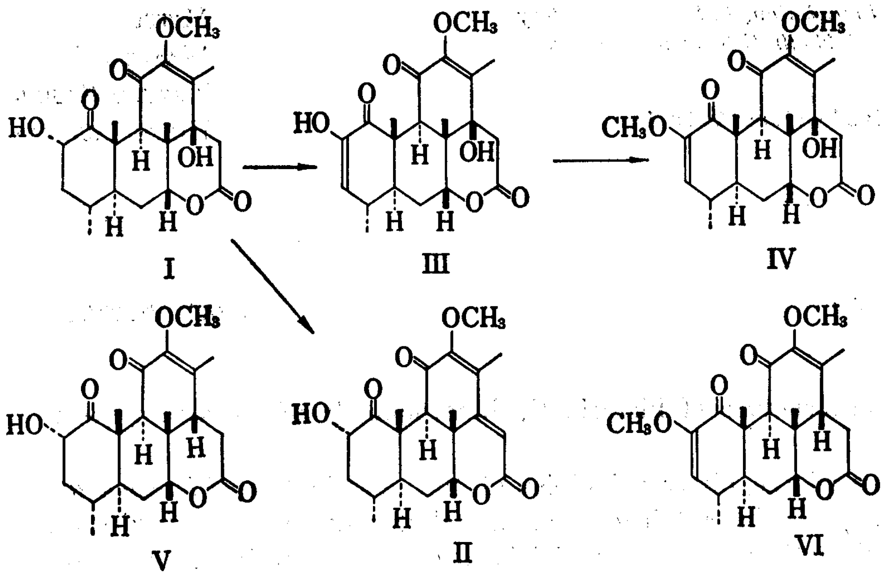

in picrasin G appear as a singlet at 3.00 ppm, showing no coupling with other hydrogens, a fact which demonstrates the hydroxyl group to be located at C-14. The paramagnetic shift of 0.40 ppm for the C-7 hydrogen signal of picrasin G as compared with that of picrasin B is also consistent with the presence of the C-14 hydroxyl group in the β-orientation.[11] From the accumulated data, it is suggested that picrasin G is represented by formula I, a supposition that was confirmed as follows.

Treatment of picrasin G with thionyl chloride in pyridine gave anhydropicrasin G (II), mp 196—199°, whose UV absorption (λ_{max} 302 nm (ε 8960), 225 nm (ε 7640)) indicates that the conjugated chromophore has been extended. In the NMR spectrum of the anhydro-derivative (II), the C-15 methylene hydrogen signals found in the spectrum of picrasin G are absent and, instead, a singlet for an α-hydrogen in an α,β-unsaturated carbonyl is observed (δ 6.04 ppm). Picrasin G on bismuth trioxide oxidation afforded dehydropicrasin G (III), which was methylated with diazomethane to give dehydropicrasin G methyl ether (IV), whose spectral properties are consistent with the expectation that the methyl ether (IV) is the 14β-hydroxy-derivative of quassin (VI).

Based on the above evidence, it is concluded that picrasin G has the stereostructure I.

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

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Received September 16, 1971

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[11] W. Stöcklin and T.A. Geisman, *Tetrahedron Letters*, **1968**, 6007.