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PICRASINOSIDE-A, A NOVEL QUASSINOID GLUCOSIDE FROM *PICRASMA AILANTHOIDES* PLANCHON

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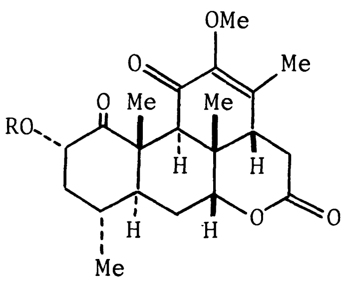
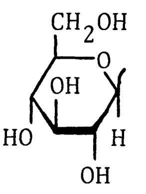
A novel quassinoid glucoside picrasinoside-A was isolated from *Picrasma ailanthoides* PLANCHON and the structure was established from spectral data, chemical transformations into picrasin B and quassin, and enzyme hydrolysis. The aglycon picrasin B showed a significant clastogenic activity in cell cultures of Don lung cells of Chinese hamster.

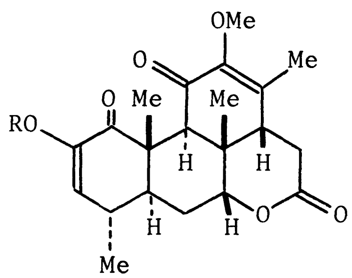
An earlier investigation of the bitter principles of the *Picrasma ailanthoides* PLANCHON (= *P. quassioides* BENNETT) has led to the isolation of twenty or more quassinoids by Murae *et al.*[1] and by Hikono *et al.*[2] However, they have not isolated any quassinoid glycosides in the plant. Lee *et al.* have isolated antileukemic quassinoid glycosides, bruceoside-A and -B [3] from *Brucea javanica* and bruceantinoside -A and -B [4] from *Brucea antidysenterica*. These facts suggest that *P. ailanthoides* might also contain quassinoid glycosides. We now report the isolation and the structural elucidation of a novel quassinoid glucoside picrasinoside-A (1) from bark extract of *P. ailanthoides*.



R

1 

2 H



R

3 H

4 Me

The fresh barks (500 g) of *P. ailanthoides*, collected at the hill in the suburbs of Hiroshima-city in May of 1981, were extracted with methanol at room temperature. Nonpolar substances in the methanol extract were removed by hexane extraction to give a residue. Careful column chromatography of the residue on Sephadex LH 20 eluting with methanol gave an amorphous compound (11 g). Rechromatography of the amorphous compound on silica gel eluting with a mixed solvent of chloroform - methanol - water (50 : 14 : 3, v/v, lower layer = solvent A) followed by preparative TLC and HPLC has led to the isolation of a colorless amorphous compound (1, 37 mg) which gave one spot (R_f 0.25) on TLC using solvent A: mp 166 °C; $[\alpha]_D^{24}$ - 54°

(c 0.4 in pyridine); ν_{max}^{nujol} 3350, 1080, and 1050 cm^{-1} (OH); negative for silver mirror test. The structural elucidation of 1 was performed as follows.

A solution of 1 (23 mg) in 3N sulfuric acid - methanol - 1-butanol (1 : 2 : 1, v/v, 20 *ml*) was stirred at 90 °C for 17 h and then extracted with ethyl acetate. The ethyl acetate extract was subjected to preparative TLC (solvent A) and then preparative HPLC to yield a colorless amorphous compound (9.5 mg) which gave one spot (R_f 0.67) on TLC using solvent A and a single peak on GC (OV-17, 2 %, 2.6 mm ID x 2.4 m, 280 °C, t_R 12.3 min). The IR spectrum of the compound showed a hydroxyl band at 3480 cm^{-1}, δ-lactone bands at 1740 and 1230 cm^{-1}, a cyclohexanone band at 1720 cm^{-1}, cyclohexenone bands at 1685 and 1645 cm^{-1}. The ^{1}HNMR spectrum showed two tertiary methyl signals at δ 1.21 (s) and 1.46 (s), one secondary methyl at δ 0.93 (d, J = 6 Hz), one methoxyl at δ 3.63 (s), one methyl on a C=C double bond at δ 1.91 (s), and one proton on the oxygen bearing carbon at δ 4.27 (m). The mass spectrum showed a molecular ion peak at *m/z* 376 ($C_{21}H_{28}O_6$) as a base peak. These data coincided with those of picrasin B (2, = nigakilactone I).[2)]

The aglycon 2 was further converted to quassin (4, = nigakilactone D)[1)] in the following way. The compound 2 (9.0 mg) was oxidized with Jones reagent[5)] at 0 °C for 4 h and the reaction product was isolated by silica gel CC and preparative HPLC as colorless crystals (3, 5.8 mg) which gave one spot (R_f 0.4) on TLC using a mixed solvent of ethyl acetate - ether (1 : 1, v/v): mp 125 °C; *m/z* 374 (100 %, M^+, $C_{21}H_{26}O_6$). The compound 3 (5.3 mg) was methylated with diazomethane in the usual manner and the product was purified by HPLC to give colorless crystals (1.7 mg) whose IR and mass spectra [*m/z* 388 (M^+, $C_{22}H_{30}O_6$)] coincided with those of 4.[1)]

Furthermore, when compound 1 (2.6 mg) was hydrolyzed at 37 °C with β-glucosidase in acetate buffer (pH 5.0) for two weeks and the product was extracted with chloroform the aglycon was obtained as colorless crystals. It was identified as 2 by comparison of the data of TLC, GC, and GC-MS (*m/z* 376) with those of the authentic sample. The aqueous layer was treated with Amberlite IR-120 and Amberlite IRA-410 for removal of the acetate buffer to give a colorless paste which was identified as a mixture of α- and β-D-glucose by comparison of retention times in GC of trimethylsilylated products (OV-17, 140 °C → 170 °C, 1 °C/min, t_R 12.7 and 18.0 min) with those of the authentic samples.

The aglycon 2 induced significant chromosomal aberrations in cell cultures of Don lung cells of Chinese hamster (39 % at 12 h after treatment at a concentration of 25 μg/*ml* for 1 h).

References

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