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PICRASINOL D, A NEW QUASSINOID FROM THE STEM WOOD OF *PICRASMA AILANTHOIDES*

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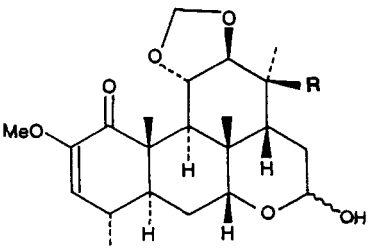
ABSTRACT.—A new quassinoid, picrasinol D [**1**], was isolated from the stem wood of *Picrasma ailanthoides*. The structure was elucidated by spectral evidence and chemical transformation.

More than 20 quassinoids (aglycones) have been isolated by Murae *et al.* (1–6) and Hikino *et al.* (7) from *Picrasma ailanthoides* Planchon (Simaroubaceae). We have isolated eight new quassinoid glucosides, picrasinosides A–H, and three new quassinoid hemiacetals, picrasinols A, B, and C, from the stem bark of *P. ailanthoides* (8–10). Further study on the stem wood of this plant has led to the isolation of a new quassinoid, picrasinol D [**1**]. This report deals with the isolation and structure elucidation of this compound.

The new compound [**1**] was obtained as an amorphous solid. Its ir spectrum showed the presence of hydroxyl (3450 cm^{-1}) and α,β-unsaturated carbonyl (1695 cm^{-1}) groups. The uv spectrum of **1** exhibited maximal absorption at 256 nm due to a conjugated enone system. Compound **1** was inferred as being a new quassinoid, because its ir and ^{1}H-nmr spectra did not coincide with those of any of the known quassinoids, and it was named picrasinol D.

Picrasinol D [**1**] had the molecular formula $C_{22}H_{32}O_7$ as determined by hreims. The ^{13}C-nmr signals (Table 1) observed for C-1 to C-12, C-14, C-15, and the methylenedioxy moiety in **1** were nearly identical with those of **2** (8). However, the ^{13}C-nmr signals for C-13 and Me-13 of **1** were found at lower field than those of **2**. Chemical shift values (ppm) for the C-13 and Me-13 signals were 40.8 and 11.1, respectively. The DEPT spectra of **1** and **2** showed that the C-13 of **1** is a quaternary carbon, whereas C-13 of **2** is a methine carbon.

The ^{1}H-nmr signals of **1** (Table 2) were similar to those of **2** except for those of Me-8 and Me-13. The Me-8 and Me-13 signals of **1** appeared at lower field by 0.21 and 0.46 ppm each, respectively, compared to analogous signals for **2**. On the other hand, the ^{1}H- and ^{13}C-nmr signals of **1** coincided with those of **3** (11), except for the signals at H-16 and C-16, as shown in Tables 1 and 2. These findings, therefore, suggested that **1** has a hydroxyl group at C-13. Additionally,



1 R=OH, **2** R=H

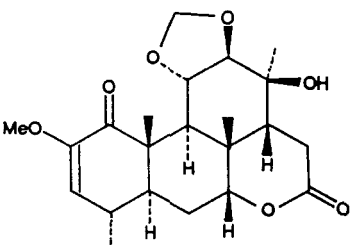


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TABLE 1. ^{13}C-Nmr Spectra of Compounds **1–3**.[a]

Carbon	Compound		
	1	**2**	**3**
C-1	199.0 (C=O)	198.7 (C=O)	198.1 (C=O)
C-2	149.3 (C)	148.2 (C)	149.0 (C)
OMe-2	54.8 (CH_3)	54.8 (CH_3)	54.9 (CH_3)
C-3	115.2 (CH)	115.3 (C)	115.5 (C)
C-4	32.3 (CH)	32.2 (CH)	32.0 (CH)
Me-4	19.4 (CH_3)	19.4 (CH_3)	19.2 (CH_3)
C-5	44.5 (CH)	44.3 (CH)	43.4 (CH)
C-6	26.3 (CH_2)	26.4 (CH_2)	25.8 (CH_2)
C-7	78.3 (CH)	79.1 (CH)	81.7 (CH)
C-8	40.0 (C)	39.0 (C)	38.7 (C)
C-9	38.6 (CH)	37.2 (CH)	38.2 (CH)
C-10	47.6 (C)	47.4 (C)	47.2 (C)
Me-10	13.4 (CH_3)	13.1 (CH_3)	13.3 (CH_3)
C-11	76.1 (CH)	78.3 (CH)	75.4 (CH)
C-12	85.4 (CH)	83.3 (CH)	84.4 (CH)
C-13	74.3 (C)	33.5 (C)	73.9 (C)
Me-13	26.1 (CH_3)	15.0 (CH_3)	24.0 (CH_3)
C-14	54.3 (CH)	48.5 (CH)	51.3 (CH)
C-15	31.3 (CH_2)	31.1 (CH_2)	31.0 (CH_2)
C-16	91.4 (CH)	93.1 (CH)	170.4 (C=O)
-OCH_2O-	95.7 (CH_2)	95.5 (CH_2)	95.9 (CH_2)

[a]Values are in ppm. Measured at 125.7 MHz in C_5D_5N.

the molecular formula of **1** obtained from hreims indicated that **1** has one more oxygen atom than **2**.

Oxidation of **1** with Jones reagent in Me_2CO afforded a lactone compound whose ir and ^{1}H-nmr spectral data and hplc retention time were identical with those of **3**. From an analysis of all of the above data, the structure of the isolate from *P. ailanthoides* was proposed as **1**.

The structure of **1** was also confirmed by CH long-range correlations in the HMBC nmr spectrum, which showed the following correlations: the methyl protons at δ 3.49 (OMe-2) with the carbon at δ 149.3 (C-2); the methyl protons at δ 0.99 (Me-4) with the carbons at δ 32.3 (C-4) and δ 44.5 (C-5); the olefinic proton at δ 5.20 (H-3) with the carbons at δ 199.0 (C-1) and δ 44.5 (C-5); the methyl protons at δ 1.76 (Me-8) with the carbon at δ 78.3 (C-7); the methyl protons at δ 1.51 (Me-13) with the carbon at δ 54.3 (C-14); the methine proton at δ 3.30 (H-9) with the carbons at δ 199.0 (C-1), δ 40.0 (C-8), δ 76.1 (C-11), and δ 85.4 (C-12); the methine proton at δ 2.53 (H-14) with the carbons at δ 40.0 (C-8) and δ 31.3 (C-15); the methyl protons at δ 1.54 (Me-10) with the carbons at δ 199.0 (C-1) and δ 47.6 (C-10); and the methine proton at δ 3.86 (H-12) with the carbon at δ 76.1 (C-11).

The relative stereochemistry of **1** was confirmed by nOe correlations that were observed between Me-4 and H-4, Me-4 and H-5, Me-8 and H-7, Me-8 and H-14, Me-10 and H-11, Me-10 and H-4, Me-10 and Me-8, H-7 and H-14, H-9 and H-12, and H-12 and Me-13. Thus, the relative stereochemistry of **1** was determined as shown in Figure 1.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mps were determined on an MRK air bath-type melting point apparatus and were uncorrected. Specific rotations were observed on a Jasco DIP-370 polarimeter (cell length=0.1 dm). Ir and uv spectra were recorded on a Jasco IR-810 spectrometer and a Hitachi 320-S spectrometer, respectively. Nmr spectra were recorded on a Varian URX-500 spectrometer (499.8 MHz for ^{1}H and 127.5 MHz for

TABLE 2. ^{1}H-Nmr Spectra of Compounds **1–3**.[a]

Proton	Compound		
	1[b]	**2**[b]	**3**[c]
OMe-2	3.49 s	3.48 s	3.49 s
H-3	5.20 d (2)	5.21 d (2)	5.20 d (2.2)
H-4	2.31 m	2.15 m	2.18 m
Me-4	0.99 d (6.5)	0.93 d (6.5)	0.88 d (6.8)
H-5	2.20 m	[d]	2.20 br s
H-7	3.44 br s	3.37 br s	4.27 br s
Me-8	1.76 s	1.09 s	1.72 s
H-9	3.30 d (11.5)	3.19 d (11)	2.99 d (11)
Me-10	1.54 s	1.42 s	1.50 s
H-11	4.44 dd (11.5,9)	3.66 dd (11,10)	4.20 dd (11,10)
H-12	3.86 d (9)	3.56 d (10)	3.69 d (10)
Me-13	1.51 s	1.05 d (6.5)	1.49 s
H-14	2.53 t (9.5)	[d]	2.12 t (11)
H-16	5.66 br s	[d]	—
$-OCH_2O-$	5.15 br s	5.11 s	5.18 br s
	5.36 br s	5.26 s	5.39 br s

[a]Values are δ ppm. Coupling constants in Hz in parentheses.
[b]Measured at 500 MHz in C_5D_5N.
[c]Measured at 200 MHz in C_5D_5N.
[d]Not assignable.

^{13}C) and a Varian XL-200 spectrometer (200 MHz for ^{1}H) in C_5N_5N, using TMS as an internal standard. Mass spectra (eims, hreims) were recorded on a Hitachi M-80 spectrometer. Si gel (Merck, type 60, 70–230 mesh) was used for cc. Precoated Si gel plates (Merck 60 F_{254} of 0.25-mm thickness) were used for analytical tlc and plates of 1-mm and 2-mm thickness were used for prep. tlc. Analytical hplc was performed on a Tosoh liquid chromatograph equipped with a detector at 245 nm and a reversed-phase column (TSK-gel ODS-80T_M), using a mixed solvent of MeOH/H_2O. Prep. hplc was carried out with the same solvent system using reversed-phase columns (Dynamax-60A and Lichrosorb RP-60).

PLANT MATERIAL.—The stems of *P. ailanthoides* were procured and identified by Professor K. Kondo, Laboratory of Plant Chromosome and Gene Stock, Faculty of Science, Hiroshima University. A voucher specimen (No. 8201) has been deposited in the Department of Interdisciplinary Studies of Natural Environment, Hiroshima University.

EXTRACTION AND ISOLATION.—Half-dried stems of *P. ailanthoides* were separated into bark and wood. The wood (40 kg) was cut into small chips and soaked in MeOH (90 liters) at room temperature for two weeks. The fatty substances in the MeOH extract were removed by extraction

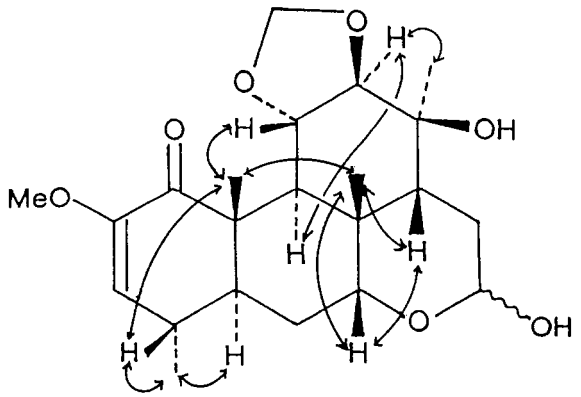

FIGURE 1. NOe correlations for **1**.

with hexane (2×), and the material used for this investigation was obtained by $CHCl_3$ extraction (3×) as a brown resinous substance (143 g) (9). The resinous substance (100 g) was chromatographed on a Si gel column eluted with a mixed solvent of $CHCl_3$-MeOH-H_2O (50:14:3, lower layer) and MeOH to afford 31 fractions. Tlc and hplc analysis of all these fractions indicated that fractions 5–11 contained quassinoid compounds.

Fraction 11 (1.91 g) was subjected to prep. hplc [Dynamax-60A, MeOH-H_2O (1:1)] to afford 10 fractions. The fifth fraction contained quassinoid **1** as the major component. Careful repeated prep. hplc [Lichrosorb RP-18, MeOH-H_2O (1:1)] of the fraction led to the isolation of picrasinol D [**1**] (49.3 mg, 0.00017%).

Picrasinol D [**1**].—Colorless amorphous solid: mp 138–140°; $[\alpha]^{21}D$ +38.2° (c=0.17, EtOH); uv λ max 255 (ε 4140) nm; ir (KBr) ν max 3450 (OH), 1695 (α,β-unsaturated C=O), 1625 (C=C) cm^{-1}; ^{13}C-nmr data, see Table 1; ^1H-nmr data, see Table 2; hreims *m/z* found $[M]^+$ 408.2154 (calcd for $C_{22}H_{32}O_7$, 408.2147).

Oxidation of picrasinol D [**1**].—Picrasinol D [**1**] (5.0 mg, 0.012 mM) was dissolved in Me_2CO (10 ml). Jones reagent (1 ml, 2.7 mM) in Me_2CO (10 ml) was added dropwise to the solution stirring at 0°. The solution was stirred at 25° for 2 h, after which EtOH (0.2 ml) and H_2O (10 ml) were added. The resulting solution was extracted with $CHCl_3$ (5 ml) three times. The $CHCl_3$ solution was washed with H_2O, dried over $MgSO_4$, and evaporated. Purification of the crude product by prep. hplc [Lichrosorb RP-18, MeOH-H_2O (1:1)] afforded compound **3** (3.6 mg, 72% yield).

Compound **3**.—Colorless amorphous solid: mp 260–262°; ir (KBr) ν max 3375 (OH), 1710 (δ-lactone C=O), 1705 (α,β-unsaturated C=O), 1630 (C=C) cm^{-1}; ^1H nmr (200 MHz, C_5D_5N) δ 0.88 (3H, d, J=7.0 Hz, Me-4), 1.49 (6H, s, Me-10 and Me-13), 1.72 (3H, s), 3.49 (3H, s, OMe-2), 5.20 (1H, d, J=2.0 Hz, H-3), 5.18 (1H, s, -OCH_2O-), 5.39 (1H, s, -OCH_2O-); eims *m/z* $[M]^+$ 406 (100).

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