Phytochemistry, Vol. 27, No. 9, pp. 3029–3030, 1988.
Printed in Great Britain.

0031–9422/88 $3.00 + 0.00

PICRASIDINE-U, DIMERIC ALKALOID FROM *PICRASMA QUASSIOIDES**

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(*Received* 22 *December* 1987)

Key Word Index—*Picrasma quassioides*; Simaroubaceae; canthin-5,6-dione; β-carboline; alkaloid; picrasidine-U.

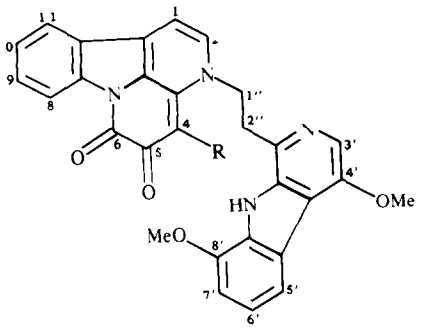
Abstract—A new canthin-5,6-dione and β-carboline dimeric alkaloid, picrasidine-U was isolated from the root wood of *Picrasma quassioides*. The structure was determined by spectral analysis and chemical evidence.

INTRODUCTION

In our previous studies [2, 3], we obtained two novel canthin-5,6-dione and β-carboline dimeric alkaloid named picrasidines-M **(2)** and N **(3)** from the root bark and root wood of *Picrasma quassioides* Bennet. We have recently isolated a new canthin-5,6-dione and β-carboline dimeric alkaloid named picrasidine-U from the root wood of the plant. This paper deals with its structural elucidation by spectral analysis and chemical evidence.

RESULTS AND DISCUSSION

A methanol extract of dry root wood of *P. quassioides* was fractionated into picrasidine-U **(1)** by a combination of silica gel CC and prep. TLC. Compound **(1)** was obtained as red needles, $C_{30}H_{24}N_4O_5$. Its IR spectrum showed amino absorption band at 3450 cm^{-1} and carbonyl absorption band at 1678 cm^{-1}. Its UV spectrum (EtOH) showed absorption maxima at 221, 286, 344, 472 and 500 nm and addition of acid caused the expected shifts to the absorption bands of canthin-5,6-dione alkaloids [2, 3]. The UV spectrum was similar to that of picrasidine-M **(2)** [2]. The striking similarity of UV absorption between **1** and **2** suggested that they have the same dimeric structure. The ^1H NMR spectrum of **1** showed three singlets at δ3.89, 3.95 and 4.08 (each 3H, *s*) assigned methoxyl signals, A_2X_2 pattern signals at δ3.73 and 5.16 (each 2H, *t*, $J = 7.0$ Hz) attributable to a CH_2CH_2 group, and the lowest field proton signal at δ11.48 (disappearing on addition of D_2O) due to the NH proton of an indole moiety (Table 1). Comparison of the chemical shift values of the aromatic region with that of **2** indicated identical substitution patterns, except the C-4 position of canthin-5,6-dione moiety, which lacked the proton, a methoxyl group being replaced at this position. Thus, picrasidine-U is composed the 4-methoxycanthin-5,6-dione and 4,8-dimethoxy-β-carboline subunits linked through N(3) and C(1′) with CH_2CH_2 group. Chemical evidence for the structure was obtained as follows. The cleavage of N(3)–C(1″) bond of **1** with acetic anhydride gave 5-acetoxy-4-methoxycanthin-6-one **(3)** and 4,8-dimethoxy-1-vinyl-β-carboline **(4)**. All the spectral data for **3** and **4** were in good agreement with those of corresponding authentic samples [4, 5]. From these results, the structure of picrasidine-U was determined as formula **1.**



1 R = OMe
2 R = H

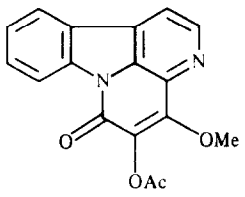
Table 1. ^1H NMR Spectral data of compounds **1** and **2**

H	1	2
1	7.36 (*d*, $J = 6.9$)	7.34 (*d*, $J = 6.9$)
2	7.85 (*d*, $J = 6.9$)	7.87 (*d*, $J = 6.9$)
4	————	6.15 (*s*)
8	8.47 (*dd*, 8.0, 1.0)	8.47 (*dd*, $J = 8.2$, 1.5)
9	7.68 (*td*, 8.0, 1.0)	7.68 (*td*, $J = 8.2$, 1.5)
10	7.51 (*td*, 8.0, 1.0)	7.52 (*td*, $J = 8.2$, 1.5)
11	8.14 (*dd*, 8.0, 1.0)	8.15 (*dd*, $J = 8.2$, 1.5)
3′	7.96 (*s*)	7.99 (*s*)
5′	7.77 (*d*, $J = 7.8$)	7.76 (*d*, $J = 7.9$)
6′	7.16 (*t*, $J = 7.8$)	7.15 (*t*, $J = 7.9$)
1″	5.16 (*t*, $J = 7.0$)	4.77 (*t*, $J = 7.1$)
2″	3.73 (*t*, $J = 7.0$)	3.72 (*t*, $J = 7.1$)
NH(9″)	11.48 (*s*)*	11.42 (*s*)*
4-OMe	3.89 (*s*)	
4′-OMe	4.08 (*s*)	4.08 (*s*)
8′-OMe	3.95 (*s*)	3.97 (*s*)

Spectra were measured at 400 MHz in DMSO-d_6 with TMS as internal reference. Coupling constants in Hz.

*Disappearing an addition of D_2O.

*Part 11 in the series 'The alkaloids of *Picrasma quassioides*'. For Part 10 see ref. [1].



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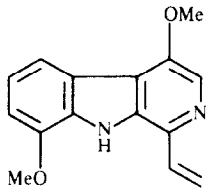

4

EXPERIMENTAL

Mps: uncorr. ^{1}H NMR spectra were recorded at 400 MHz. Chemical shifts are given as δ(ppm) with TMS as int. standard. CC was carried out on silica gel (BW-820 MH, Fuji Devison). Prep. TLC was performed on silica (60 GF_{256}, Merck). TLC spots were detected with Dragendorff's reagent or by UV illumination.

Extraction and isolation. Dried root wood (30 kg) of *Picrasma quassioides* collected at Chiba city, Chiba prefecture, August, 1983, was extracted with MeOH (100 l) at 40° for 48 hr. The extract was evapd to dryness and the residue partitioned between $CHCl_3$ and H_2O. The $CHCl_3$ soln was dried and concd to give a $CHCl_3$ fraction (250 g) which was applied to a column of silica gel (2 kg) and eluted successively with $CHCl_3$, $CHCl_3$–MeOH (19:1, 9:1, 4:1 and 1:1) and MeOH. The $CHCl_3$–MeOH (9:1) fraction was repeatedly chromatographed on silica gel and further purified by prep. TLC on silica gel to give picrasidine-U (4 mg).

Picrasidine-U (**1**). Red needles (MeOH), mp 199–200° (dec.). UV λ_{max}^{EtOH} nm (log ε): 221 (4.73), 286 (4.19), 344 (3.93), 472 (3.87), 500 (3.83). UV $\lambda_{max}^{EtOH+HCl}$ nm (log ε): 248 (4.57), 316 (4.09), 374 (3.83), 492 (3.57), 500 (3.38). UV $\lambda_{max}^{EtOH+NaOH}$ nm (log ε): 221 (4.73), 286 (4.19), 344 (3.93), 472 (3.87), 500 (3.83). IR ν_{max}^{KBr} cm^{-1}: 3450, 1678, 1638, 1536, 1498, 1444, 1408, 1338, 1312, 1280, 1112, 1060. ^{1}H NMR: Table 1. FDMS *m/z* 543 (M^+ + Na), 520 (M^+), 266, 254. EIMS *m/z* (rel. int.): 266 (20), 254 (100), 239 (30), 237 (11), 225 (11), 224 (35), 211 (14), 168 (17), 140 (11). Analysis, found: C, 69.12; H, 4.69; N, 10.88%. Calcd for C, 69.22; H, 4.65; N, 10.76%.

Reaction of **1** *with acetic anhydride.* A soln of **1** (3 mg) was refluxed for 2 hr. The reaction mixture of **1** was poured into ice H_2O, basified with 5% Na_2SO_3 soln and extracted with $CHCl_3$. The $CHCl_3$ soln was dried over Na_2SO_4 and concd to give a mixture of **3** and **4**, which was separated by prep. TLC to give **3** (1 mg) and **4** (1 mg). Compound **3**, colourless needles, mp 200–202°. MS *m/z*: 266 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1762, 1675, 1602, 1200. ^{1}H NMR (400 MHz, DMSO-d_6): 2.40 (3H, *s*, 5-OAc), 4.44 (3H, *s*, 4-OMe), 7.72 (1H, *dd*, J = 8.1, 1.0 Hz, H9), 7.56 (1H, *td*, J = 8.1, 1.0 Hz, H10), 8.31 (1H, *d*, J = 5.1 Hz, H1), 8.32 (1H, *dd*, J = 8.1, 1.0 Hz, H11), 8.43 (1H, *dd*, J = 8.1, 1.0 Hz, H8), 8.86 (1H, *d*, J = 5.1 Hz, H2). Compound **4**, pale yellow prisms, mp 157–158°. MS *m/z*: 254 (M^+). IR ν_{max}^{KBr} cm^{-1}: 3440, 1630, 1575, 1290, 1270, 1050. ^{1}H NMR (100 MHz, $CDCl_3$): 3.92 (3H, *s*, 8-OMe), 4.08 (3H, *s*, 4-OMe), 5.40, 6.22, 7.15 (each 1H, AMX-system, J_{AM} = 17.5, J_{AX} = 11.0 and J_{MX} = 2.0 Hz, –CH=CH_2), 6.87 (1H, *d*, J = 8.0 Hz, H7), 7.15 (1H, *t*, J = 8.0 Hz, H6), 7.86 (1H, *d*, J = 8.0 Hz, H5), 8.03 (1H, *s*, H3). Compounds **3** and **4** were identified by direct comparison (TLC, IR, ^{1}H NMR and mmp) with those of corresponding authentic samples.

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