(characteristic of the styrylamine chromophore in the 13-membered cyclopeptide alkaloids), 290 sh, 280 sh, and 272 sh (tryptophan unit) [5]; MS, *m/z* 587.3116 ([M]$^+$, 6%), 457 (100), 401 (1.5), 400 (1), 374 (1.5), 373 (3), 372 (1), 304 (1), 259 (1), 233 (1.5), 216 (2) 187 (58), 181 (1), 165 (6), 144 (10), 130 (15), 96 (2), 86 (4), 68 (6).

Hydrolysis. Compound **1** (10 mg) was heated in a sealed tube with 1 ml of 6 N HCl for 20 h at 120°. The presence of isoleucine was confirmed by PC comparison with an authentic sample using *n*-BuOH–HOAc–H_2O (4:1:5) with ninhydrin as detection reagent. Compound **1** (10 mg) was heated with $Ba(OH)_2$ (60 mg) in 1 ml H_2O for 24 hr at 120°. The hydrolysate was neutralized with 2 N H_2SO_4, filtered, chromatographed over Whatman No. 1 and sprayed with Ehrlich's reagent [7]. *N,N*-Dimethyltryptophan was detected in the hydrolysate by comparison with an authentic sample.

Partial hydrolysis. Compound **1** (25 mg) was heated at 100° for 5 hr with 6 ml of conc HCl–HOAc–H_2O (1:1:1). The hydrolysis product after prep. TLC with $CHCl_3$–MeOH (50:1) gave one major compound **3** (5 mg) as a colourless amorphous solid; MS: *m/z* 373 ([M]$^+$) 304, 259, 233, 216, 181, 165, 96, 86. **3** on hydrolysis with 6 N HCl in a sealed tube for 20 hr at 120° gave isoleucine (co-PC with an authentic sample).

Repeated CC and prep. TLC of the crude base fraction of *Z. xylopyra* furnished amphibine-H (15 mg), mp 202–204° and nummularine-K (17 mg), mp 235–238°; *Z. jujuba* gave frangufoline (8 mg). The structure of these alkaloids was established by a study of the spectral data, hydrolysis and direct comparison with authentic samples (mmp and co-TLC).

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PICRASIDINE-T, A DIMERIC β-CARBOLINE ALKALOID FROM *PICRASMA QUASSIOIDES**

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Key Word Index—*Picrasma quassioides*; Simaroubaceae; β-carboline; β-carbolinium; dimeric alkaloid; (±)-picrasidine-T.

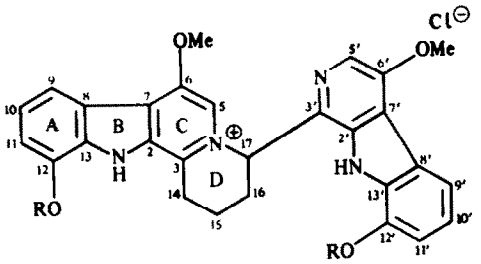
Abstract—A new β-carboline dimeric alkaloid, (±)-picrasidine-T was isolated from the bark of *Picrasma quassioides*. The structure was determined by spectral analysis and chemical evidence.

INTRODUCTION

In our previous studies [1, 2], we obtained three novel β-carboline dimeric alkaloids named (±)-picrasidines F [2], G and S [1] from the root bark of *Picrasma quassioides* Bennet (Japanese name: Nigaki). Structures of the alkaloids were determined as racemic compounds by single crystal X-ray diffraction analysis [2] and spectral analysis [1].

We have recently isolated a new dimeric alkaloid named picrasidine-T from the bark of the plant. This paper deals with its structural elucidation by spectral analysis and chemical evidence of (±)-picrasidine-T hydrochloride (**1**).

*Part 10 in the series 'The alkaloids of *Picrasma quassioides*' For Part 9 see ref. [1].



1 R = H
2 R = Me

RESULTS AND DISCUSSION

A methanol extract of the dry bark of *P. quassioides* was fractionated into picrasidine-T hydrochloride (**1**) by a combination of silica gel CC and preparative medium-pressure liquid chromatography.

(**1**) was obtained as pale yellow needles, $C_{28}H_{24}N_4O_4 \cdot HCl$, $[\alpha]_D^{22}$ 0° (MeOH). Its UV spectrum (EtOH) having absorption maxima at 221, 261, 322, 350, and 390 nm indicated a β-carbolinium chromophore (3). Addition of alkali caused the expected shifts to the absorption of a β-carboline anhydro-base (λ_{max} 231, 257, 281, 340, and 420 nm) [1–4], a UV characteristic similar to that of (±)-picrasidine-S hydrochloride (**2**) [1]. The striking similarity of the UV absorptions between **1** and **2** suggested that they have the same dimeric structure. The ^{1}H NMR spectrum in DMSO-d_6 of **1** showed two three proton singlets at δ3.98 and 4.04 due to the methoxyl groups, two proton singlets at δ9.96 and 10.29 (disappearing on addition of D_2O) due to the hydroxyl groups and two lowest field proton singlets at δ11.84 and 12.83 (disappearing on addition of D_2O) due to the NH protons of indole moieties. Seven aliphatic proton signals in the ^{1}H NMR spectrum of **1**, assigned by double resonance, triple resonance, and ^{1}H–^{1}H shift correlated spectrum (COSY) experiments, revealed the presence of a $-CH_2CH_2CH_2CH-$ grouping. Comparison of the chemical shifts of the aromatic region with that of **2** indicated identical substitute patterns in all cases. The pronounced deshielding of H-5 (δ8.08) compared with H-5′ (δ7.80) indicated that the proton at the C-5 position caused a larger downfield shift than the proton at the C-5′ position due to the neighbouring aromatic quaternary nitrogen atom [1, 2].

In order to determine the location of the two methoxyl groups, NOE experiments were carried out; irradiation of the methoxyl signals at δ3.98 and 4.04 each produced a 20% enhancement of H-5 and H-5′, respectively. Therefore, two methoxyl groups were unambigously placed at the C-6 and C-6′ positions and two hydroxyl groups were placed at C-12 and C-12′ positions; this was supported by a deep purple coloration on reaction with Gibb's reagent.

From these results, the structure of (±)-picrasidine-T hydrocloride is proposed to be formula **1**. Chemical evidence for the structure was obtained by methylation with diazomethane to give synthetic compound **2**. All the spectral data (^{1}H NMR, mass spectrum and IR) of synthetic compound **2** were in good agreement with the natural product **2**.

EXPERIMENTAL

All mps are uncorr. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. Chemical shifts are given as δ (ppm) with TMS as int. std. CC was carried out on silica gel (BW-820 MH, Fuji Devison). Prep. medium-pressure LC was performed on silica gel (CQ-3, Fuji Gel). TLC spots were detected with Dragendorff's reagent or by UV illumination.

Extraction and isolation. Dried bark (7.5 kg) of *P. quassioides* collected at Chiba city, Chiba prefecture in August 1983 was extracted with MeOH (70 l) at 35° for 48 hr. The extract was evapd to dryness and the residue partitioned between H_2O and $CHCl_3$. The $CHCl_3$ soln was dried (Na_2SO_4) and concd to give a $CHCl_3$ sol. fraction (195 g) which was applied to column of silica gel (2 kg) and eluted successively with $CHCl_3$ and MeOH. The fraction (85 g) eluted with $CHCl_3$ was shaken with 3% H_2SO_4, the H_2SO_4 layer basified with 5% Na_2CO_3 and then extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O, dried (Na_2SO_4), then concd to give a basic fraction (9.5 g), which was applied to column packed with silica gel (180 g). The column was eluted successively with $CHCl_3$, 1, 2, 5, 10, 20 and 50% MeOH in $CHCl_3$ and finally MeOH. The fraction (637 mg) eluted with 5% MeOH in $CHCl_3$ was dissolved in MeOH and 10% aq. HCl added. The hydrochloride (630 mg) that pptd was further purified by prep. medium pressure LC on silica gel (24 mmϕ × 360 mm) with 20% MeOH in $CHCl_3$ (1 ml/min) to give (±)-picrasidine-T hydrochloride (**1**, 4 mg).

(±)-Picrasidine-T hydrochloride (**1**). Pale yellow needles (MeOH), mp > 300°, $[\alpha]_D^{22}$ 0° (MeOH; *c* 0.4). UV λ_{max}^{EtOH} nm (log ε):

Table 1. ^{1}H NMR spectral data of compounds **1** and **2**

H	1	2
1	12.83 *s**	12.93 *s**
5	8.08 *s*	8.18 *s*
9	7.77 *dd*[a]	7.83 *dd*[a]
10	7.25 *t*[b]	7.36 *t*[b]
11	7.16 *dd*[a]	7.31 *dd*[a]
14a	3.59 *ddd*[c]	3.62 *ddd*[c]
14b	3.79 *ddd*[d]	3.85 *ddd*[d]
15a	1.85 *ddddd*[e]	1.85 *ddddd*[e]
15b	1.99 *ddddd*[f]	2.23 *ddddd*[f]
16a	2.60 *dddd*[g]	2.60 *dddd*[g]
16b	2.65 *dddd*[h]	2.67 *dddd*[h]
17	6.94 *dd*[i]	7.14 *dd*[i]
1′	11.84 *s**	12.13 *s**
5′	7.80 *s*	7.85 *s*
9′	7.69 *dd*[a]	7.83 *dd*[a]
10′	7.10 *td*[a]	7.25 *t*[b]
11′	7.02 *td*[a]	7.20 *dd*[a]
6-OMe	3.98 *s*	4.01 *s*
6′-OMe	4.04 *s*	4.04 *s*
12-OMe		4.14 *s*
12′-OMe		4.11 *s*
12-OH	9.96 *s**	
12′-OH	10.29 *s**	

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

Coupling constants (Hz): [a] J = 8.0, 1.0; [b] J = 8.0; [c] J = 18.0, 10.0, 8.0; [d] J = 18.0, 7.0, 2.0; [e] J = 15.0, 12.0, 10.0, 7.0, 4.0; [f] J = 15.0, 8.0, 3.0, 2.0, 1.0; [g] J = 16.0, 4.0, 2.0, 1.0; [h] J = 16.0, 12.0, 4.0, 3.0; [i] J = 4.0, 2.0.

* Disappeared with D_2O.

221 (4.25), 261 (4.38), 322 (3.79), 350 (3.54), 390 (3.20). UV $\lambda_{max}^{EtOH+NaOH}$ nm (log ε): 231 (4.26), 257 (4.17), 281 (4.25), 340 (3.68), 420 (3.98). IR ν_{max}^{KBr} cm^{-1}: 3400, 3120, 1615, 1580, 1560, 1540, 1400, 1280, 1110. ^1H NMR: Table 1. FDMS *m/z*: 480 [M − HCl]$^+$. EIMS *m/z* (rel. int.): 480 [(M − HCl)$^+$, 12], 266 (43), 252 (74), 242 (25), 236 (33), 228 (78), 214 (100), 200 (42), 185 (41). Analysis Found: C, 65.11; H, 5.68; N, 10.92% Calcd for $C_{28}H_{24}N_4O_4 \cdot HCl$: C, 65.05; H, 5.65; N, 10.84%.

Methylation of 1. Compound 1 (2 mg) was dissolved in MeOH and methylated with CH_2N_2 at room temp. for 24 hr to give 12,12′-*O*-dimethyl-(±)-picrasidine-T hydrochloride (**2**, 2 mg), mp 215–218° (dec.). EIMS *m/z*: 508 (M − HCl)$^+$. IR ν_{max}^{KBr} cm^{-1}: 3430, 1635, 1587, 1548, 1285, 1145, 1055, 1045. ^1H NMR: Table 1.

The synthetic product was identified by direct comparison (^1H NMR, MS, IR, and mmp) with natural (±)-picrasidine-S hydrochloride (**1**).

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