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Studies on the Alkaloids of *Picrasma quassioides* BENNET. VIII.[1) X-Ray Crystal Structure Analysis of Picrasidine-F

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The structure and absolute configuration of picrasidine F, which was isolated from the root bark of *Picrasma quassioides* BENNET, has been confirmed by an X-ray crystal structure analysis of its hydrochloride (**1**).

Keywords——17 (*R*)-picrasidine F; 17 (*S*)-picrasidine F; dimeric *β*-carboline alkaloid; X-ray crystal structure analysis; *Picrasma quassioides*; Simaroubaceae; root bark

In our previous studies we elucidated the structures of six novel dimeric alkaloids from *Picrasma quassioides* BENNET (Japanese name "Nigaki"; Simaroubaceae).[1) In a continuation of our work on the structural elucidation of alkaloids, we have recently isolated a novel dimeric *β*-carboline alkaloid, named picrasidine F, from the root bark of the plant. This paper deals with the structural elucidation by spectroscopic and X-ray crystal structure analyses of (±) picrasidine F hydrochloride (**1**).

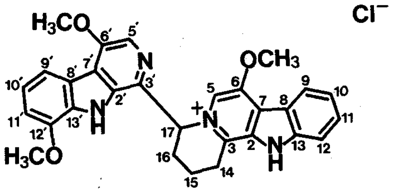

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Chart 1

Results and Discussion

Structural Elucidation

A methanol extract of the root bark of *Picrasma quassioides* was subjected to column chromatography on silica gel to give picrasidine F as an optically inactive compound.

(±) Picrasidine F hydrochloride (**1**) was obtained as colorless plates, mp 265—267 °C (dec.). The ultraviolet (UV) spectrum, having absorption maxima at 252, 282 (shoulder), 310, 347, and 372 nm, indicated the presence of the *β*-carbolinium chromophore.[2) Addition of alkali caused the expected shift to the absorption of the *β*-carboline anhydro-base (λ_{max} 242, 278, 334, and 402 nm).[2) The field-desorption mass spectral (FD-MS) data [m/z 478, $(M-HCl)^+$] and elemental analysis proved the molecular formula to be $C_{29}H_{26}N_4O_3 \cdot HCl$. The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum indicated the presence of 29 carbons; seven aliphatic carbons ($CH_3 \times 3$, $CH_2 \times 3$, and $CH \times 1$) and twenty-two aromatic carbons ($=CH \times 9$ and $=C \times 13$). The proton nuclear magnetic resonance (^{1}H-NMR)

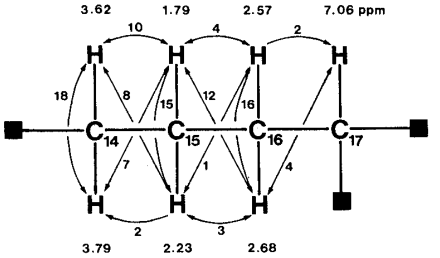
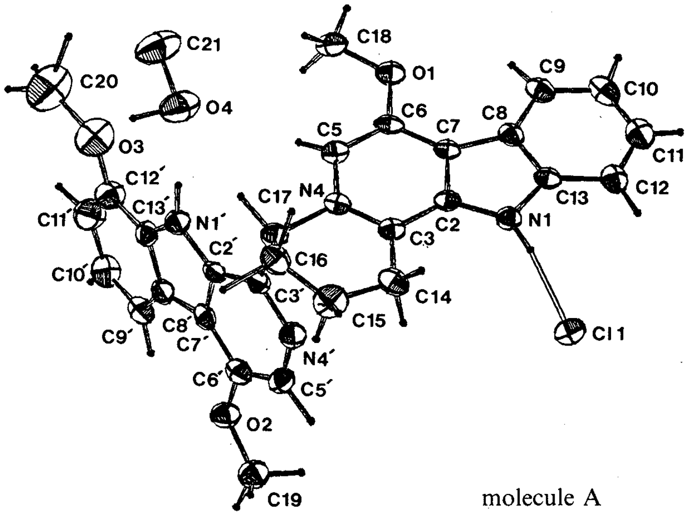
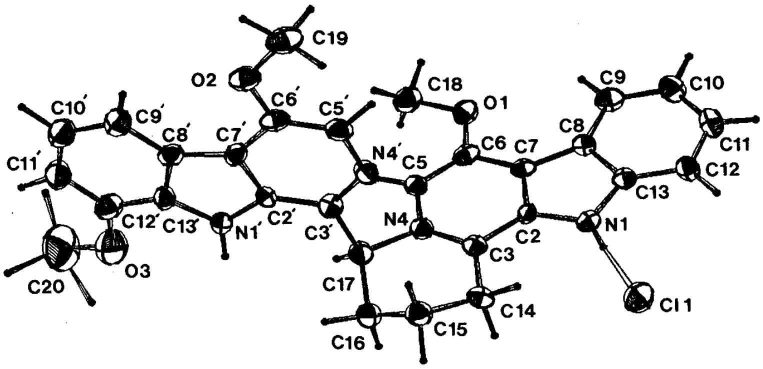


Fig. 1. Partial Structure (**2**) and ^{1}H-NMR Spectral Data

Chemical shifts δ (ppm) and coupling constants (Hz).



molecule A



molecule B

Fig. 2. ORTEP Drawing of Picrasidine F Hydrochloride (**1**)

spectrum showed three methoxyl signals at δ 3.99, 4.03, and 4.08 and seven aliphatic proton signals at δ 1.79, 2.23, 2.57, 2.68, 3.62, 3.79, and 7.06. Extensive ^{1}H-NMR spin decoupling experiments on **1** led to the assignment of the proton resonances and coupling patterns of the partial structure **2** as shown in Fig. 1. Seven aromatic protons on the A-rings were observed at δ 7.18, 7.23, 7.43, 7.75, 7.81, 7.87, and 8.30, while two singlet aromatic protons on the C-rings were observed at δ 7.83 and 8.11, and two signals of NH protons were observed at δ 11.92 and 12.32 (disappeared on addition of deuterium oxide).

All these data indicated that picrasidine F hydrochloride (**1**) is a dimeric alkaloid having the β-carbolinium and β-carboline structures and containing the partial structure **2**.

Hence, **1** was subjected to X-ray crystal structure analysis, which confirmed the structure and the presence of methanol of crystallization in the crystal lattice. Picrasidine-F hydrochloride (**1**) crystallized in the triclinic system, $P\bar{1}$ with $a=15.628$ (7), $b=15.104$ (7), $c=$

TABLE I. ^{1}H-NMR Spectral Data[a] for Picrasidine-F Hydrochloride (**1**)

Proton	δ	Proton	δ
1-H	12.32 (s)[b,c]	16-Hb	2.68 (dddd, $J=16, 12, 4, 3$ Hz)
5-H	8.11 (s)	17-H	7.06 (dd, $J=4, 2$ Hz)
9-H	8.30 (dd, $J=8, 1$ Hz)	1′-H	11.92 (s)[b,c]
10-H	7.43 (td, $J=8, 1$ Hz)	5′-H	7.83 (s)
11-H	7.75 (td, $J=8, 1$ Hz)	9′-H	7.81 (dd, $J=8, 1$ Hz)
12-H	7.87 (dd, $J=8, 1$ Hz)	10′-H	7.23 (t, $J=8$ Hz)
14-Ha	3.62 (ddd, $J=18, 10, 8$ Hz)	11′-H	7.18 (dd, $J=8, 1$ Hz)
14-Hb	3.79 (ddd, $J=18, 7, 2$ Hz)	6-OCH$_3$	3.99 (s)[d]
15-Ha	1.79 (ddddd, $J=15, 12, 10, 7, 4$ Hz)	6′-OCH$_3$	4.03 (s)[d]
15-Hb	2.23 (ddddd, $J=15, 8, 3, 2, 1$ Hz)	12′-OCH$_3$	4.08 (s)[d]
16-Ha	2.57 (dddd, $J=16, 4, 2, 1$ Hz)		

a) The spectrum was measured in DMSO-d_6 at 60 °C. *b*) Disappeared on addition of D$_2$O. *c*, *d*) May be interchanged.

TABLE II. Fractional Atomic Co-ordinates (×10^4) with Estimated Standard Deviations in Parentheses for Molecule A of Picrasidine-F Hydrochloride (**1**)

Atom	*x*	*y*	*z*
C(2)	3269 (6)	4431 (6)	5858 (8)
C(3)	2329 (6)	3756 (6)	4987 (7)
C(5)	2565 (6)	4485 (7)	3936 (8)
C(6)	3475 (6)	5153 (6)	4792 (8)
C(7)	3846 (6)	5117 (6)	5775 (7)
C(8)	4741 (6)	5663 (6)	6817 (8)
C(9)	5620 (6)	6431 (7)	7233 (9)
C(10)	6350 (6)	6764 (7)	8283 (9)
C(11)	6243 (7)	6357 (8)	8921 (9)
C(12)	5404 (6)	5598 (7)	8547 (8)
C(13)	4663 (6)	5261 (6)	7465 (7)
C(14)	1701 (6)	3097 (8)	5153 (9)
C(15)	676 (7)	2580 (9)	4292 (10)
C(16)	369 (7)	2894 (8)	3477 (9)
C(17)	1068 (6)	3015 (7)	2999 (8)
C(18)	1170 (5)	1692 (6)	983 (7)
C(3′)	1194 (6)	1953 (6)	2074 (8)
C(5′)	1463 (7)	286 (7)	1590 (8)
C(6′)	1451 (6)	−6 (7)	512 (8)
C(7′)	1323 (5)	700 (7)	183 (8)
C(8′)	1347 (6)	705 (7)	−791 (8)
C(9′)	1550 (6)	18 (7)	−1781 (8)
C(10′)	1608 (7)	348 (9)	−2493 (9)
C(11′)	1430 (8)	1330 (9)	−2250 (10)
C(12′)	1218 (7)	1988 (8)	−1293 (9)
C(13′)	1183 (6)	1686 (7)	−561 (7)
C(18)	3602 (7)	5997 (8)	3829 (9)
C(19)	1581 (7)	−1802 (8)	−104 (9)
C(20)	1701 (6)	3097 (8)	5153 (9)
C(21)	4394 (6)	688 (6)	6688 (7)
N(1)	3752 (5)	4513 (5)	6879 (6)
N(4)	2030 (5)	3802 (5)	4048 (6)
N(1′)	1067 (5)	2264 (6)	500 (6)
N(4′)	1351 (5)	1273 (6)	2375 (7)
O(1)	4031 (4)	5883 (5)	4769 (6)

TABLE II. (continued)

Atom	x	y	z
O(2)	1544 (4)	−995 (5)	−330 (6)
O(3)	1031 (6)	2980 (7)	−1008 (8)
O(4)	871 (6)	4441 (6)	1736 (8)
H(1)	3566 (69)	4227 (82)	7319 (91)
H(5)	2264 (42)	4421 (49)	3320 (55)
H(9)	5569 (45)	6625 (53)	6727 (59)
H(10)	6919 (66)	7298 (78)	8456 (87)
H(11)	6666 (61)	6605 (72)	9601 (80)
H(12)	5291 (113)	5255 (134)	8943 (148)
H(14A)	1628 (53)	3589 (62)	5998 (70)
H(14B)	1895 (69)	2376 (81)	4884 (91)
H(15A)	119 (78)	2651 (92)	4825 (103)
H(15B)	580 (65)	1802 (77)	3682 (86)
H(16A)	−367 (71)	2168 (83)	2552 (94)
H(16B)	449 (84)	3863 (98)	4217 (110)
H(17)	842 (58)	3461 (69)	2637 (77)
H(1′)	1022 (61)	2954 (71)	874 (80)
H(5′)	1563 (53)	−190 (62)	1933 (70)
H(9′)	1606 (60)	−704 (71)	−1952 (80)
H(10′)	1808 (82)	−122 (96)	−3245 (108)
H(11′)	1410 (62)	1527 (73)	−2855 (82)
H(18A)	3435 (70)	5319 (81)	2990 (92)
H(18B)	2957 (47)	6128 (54)	3750 (61)
H(18C)	4108 (66)	6610 (78)	4082 (87)
H(19A)	1595 (91)	−2613 (107)	−890 (120)
H(19B)	2165 (61)	−1550 (72)	642 (80)
H(19C)	1083 (45)	−1951 (52)	110 (58)
H(20A)	1115 (133)	4518 (158)	−938 (177)
H(20B)	1329 (95)	3532 (110)	−2370 (123)
H(20C)	889 (42)	3054 (49)	−2855 (55)
Cl(1)	3270 (2)	3282 (2)	7905 (2)

TABLE III. Fractional Atomic Co-ordinates ($\times 10^4$) with Estimated Standard Deviations in Parentheses for Molecule B of Picrasidine-F Hydrochloride (1)

Atom	x	y	z
C(2)	6777 (5)	2996 (6)	11746 (7)
C(3)	6437 (5)	3095 (6)	10799 (7)
C(5)	4970 (5)	1786 (6)	10070 (7)
C(6)	5299 (6)	1683 (7)	10993 (8)
C(7)	6237 (5)	2291 (6)	11840 (7)
C(8)	6838 (5)	2371 (6)	12870 (7)
C(9)	6726 (6)	1851 (7)	13414 (8)
C(10)	7507 (7)	2125 (8)	14409 (8)
C(11)	8374 (6)	2911 (8)	14889 (7)
C(12)	8494 (6)	3440 (7)	14392 (8)
C(13)	7737 (6)	3151 (6)	13377 (7)
C(14)	7033 (6)	3891 (7)	10747 (8)
C(15)	6684 (7)	3641 (7)	9501 (8)
C(16)	5620 (7)	3404 (7)	9018 (8)
C(17)	1581 (7)	−1802 (8)	−104 (9)
C(2′)	4394 (6)	688 (6)	6688 (7)

TABLE III. (continued)

Atom	x	y	z
C(3′)	5121 (6)	1311 (7)	7855 (7)
C(5′)	5877 (6)	4 (7)	7134 (8)
C(6′)	5201 (6)	−628 (7)	5961 (8)
C(7′)	4407 (6)	−296 (6)	5704 (7)
C(8′)	3538 (6)	−747 (7)	4674 (7)
C(9′)	3135 (7)	−1711 (8)	3460 (8)
C(10′)	2213 (7)	−1916 (8)	2718 (9)
C(11′)	1715 (7)	−1196 (8)	3133 (9)
C(12′)	2115 (6)	−252 (7)	4300 (9)
C(13′)	3023 (6)	−19 (7)	5064 (7)
C(18)	3804 (6)	415 (8)	10284 (9)
C(19)	6002 (8)	−1964 (8)	5245 (10)
C(20)	660 (10)	206 (14)	4212 (16)
N(1)	7672 (4)	3533 (5)	12686 (6)
N(4)	5544 (4)	2473 (5)	10012 (6)
N(1′)	3538 (5)	850 (5)	6271 (6)
N(4′)	5847 (5)	955 (6)	8049 (6)
O(1)	4795 (4)	1021 (5)	11139 (5)
O(2)	5218 (4)	−1581 (5)	4998 (6)
O(3)	1703 (6)	505 (7)	4821 (8)
H(1)	8172 (40)	4001 (47)	12799 (53)
H(5)	4366 (49)	1402 (57)	9470 (65)
H(9)	6149 (71)	1334 (83)	13032 (93)
H(10)	7449 (61)	1724 (71)	14740 (79)
H(11)	8867 (65)	3181 (77)	15650 (85)
H(12)	9081 (49)	3991 (57)	14768 (64)
H(14A)	7718 (53)	3906 (62)	11089 (70)
H(14B)	7006 (71)	4668 (83)	11336 (92)
H(15A)	6852 (70)	3024 (82)	8950 (91)
H(15B)	6998 (60)	4381 (71)	9604 (79)
H(16A)	5314 (56)	3152 (66)	8146 (74)
H(16B)	5388 (66)	4063 (77)	9609 (87)
H(17)	4442 (50)	2370 (58)	8766 (65)
H(1′)	3360 (54)	1461 (63)	6651 (71)
H(5′)	6480 (59)	−223 (69)	7387 (78)
H(9′)	3498 (70)	−2175 (82)	3215 (91)
H(10′)	1916 (75)	−2671 (88)	1794 (99)
H(11′)	1043 (63)	−1225 (75)	2700 (84)
H(18A)	3411 (59)	833 (69)	10508 (77)
H(18B)	3708 (54)	−49 (63)	9416 (70)
H(18C)	3681 (58)	−105 (68)	10530 (77)
H(19A)	5901 (73)	−2240 (87)	5798 (97)
H(19B)	6733 (62)	−1324 (73)	5775 (82)
H(19C)	5785 (66)	−2633 (77)	4282 (87)
H(20A)	586 (119)	1433 (141)	5305 (159)
H(20B)	588 (116)	149 (139)	3052 (156)
H(20C)	165 (153)	−1449 (178)	3552 (202)
Cl(1)	9466 (18)	4871 (22)	12872 (26)

14.473 (8) Å, $\alpha = 122.68$ (4), $\beta = 107.66$ (5), $\gamma = 95.55$ (5) °, and $Z = 2$. We measured 4225 unique reflections having $F_o > 3\sigma(F_o)$ on a Rigaku AFC-6 diffractometer using graphite monochromated MoK_α radiation. The scanning was done by the ω–2θ scanning method at a speed of 4°/min in 2θ in the range up to $2\theta = 50°$. The structure was solved by the direct method using the

Table IV. Bond Lengths (Å) of Picrasidine-F Hydrochloride (**1**), with Standard Deviations in Parentheses

Atom 1		Atom 2	Moelcule A	Molecule B
N(1)	–	C(2)	1.3788 (8)	1.3697 (14)
C(2)	–	C(3)	1.4069 (15)	1.4096 (9)
C(3)	–	C(7)	1.3841 (15)	1.3859 (16)
C(3)	–	N(4)	1.3251 (8)	1.3383 (15)
C(3)	–	C(14)	1.4984 (16)	1.4903 (18)
N(4)	–	C(5)	1.3596 (14)	1.3727 (16)
N(4)	–	C(17)	1.5007 (15)	1.5174 (9)
C(5)	–	C(6)	1.3765 (17)	1.3717 (10)
C(6)	–	C(7)	1.3904 (9)	1.3968 (16)
C(6)	–	O(1)	1.3566 (15)	1.3578 (14)
C(7)	–	C(8)	1.4326 (14)	1.4385 (10)
C(8)	–	C(9)	1.4091 (19)	1.4253 (13)
C(8)	–	C(13)	1.4233 (12)	1.3894 (18)
C(9)	–	C(10)	1.3887 (14)	1.3707 (14)
C(10)	–	C(11)	1.3974 (14)	1.3955 (22)
C(11)	–	C(12)	1.3671 (20)	1.3904 (15)
C(12)	–	C(13)	1.3791 (12)	1.4062 (13)
C(13)	–	N(1)	1.3825 (16)	1.3953 (10)
C(14)	–	C(15)	1.5234 (17)	1.4923 (13)
C(15)	–	C(16)	1.5135 (14)	1.4657 (23)
C(16)	–	C(17)	1.5393 (17)	1.5053 (18)
C(17)	–	C(3′)	1.5014 (11)	1.5187 (12)
N(1′)	–	C(2′)	1.3956 (12)	1.3680 (16)
C(2′)	–	C(3′)	1.3940 (10)	1.3928 (16)
C(2′)	–	C(7′)	1.4064 (11)	1.4181 (12)
C(3′)	–	N(4′)	1.3207 (13)	1.3300 (16)
N(4′)	–	C(5′)	1.3485 (11)	1.3749 (12)
C(5′)	–	C(6′)	1.3711 (12)	1.3671 (17)
C(6′)	–	C(7′)	1.4028 (14)	1.3901 (18)
C(6′)	–	O(2)	1.3712 (10)	1.3878 (11)
C(7′)	–	C(8′)	1.4240 (10)	1.4244 (18)
C(8′)	–	C(9′)	1.4123 (10)	1.4027 (15)
C(8′)	–	C(13′)	1.3985 (13)	1.4015 (15)
C(9′)	–	C(10′)	1.3932 (15)	1.3849 (22)
C(10′)	–	C(11′)	1.3755 (17)	1.4062 (20)
C(11′)	–	C(12′)	1.3662 (11)	1.3690 (18)
C(12′)	–	C(13′)	1.3747 (12)	1.3740 (20)
C(12′)	–	O(3)	1.3413 (14)	1.4110 (17)
C(13′)	–	N(1′)	1.3756 (8)	1.3809 (13)
O(1)	–	C(18)	1.4531 (9)	1.4332 (17)
C(2)	–	C(19)	1.4347 (15)	1.4246 (17)
O(3)	–	C(20)	1.4806 (16)	1.6829 (33)

structure determination program package MULTAN[3] provided with the diffractometer. The structure was refined by block-diagonal least-squares methods to an *R* value of 0.0797. The ORTEP drawing of the solved structure of **1** is shown in Fig. 2.[4] The final positional parameters are given in Tables II and III, bond lengths and bond angles are listed in Tables IV and V along with their standard deviations, and selected torsion angles are summarized in Table VI. The two independent molecules A and B in the crystal lattice are the enantiomorphs (Fig. 2). These results show that the absolute configurations at C-17 of molecules A and B are *R* and *S*-configurations, respectively. As given in Table VI, the six-membered ring of **1** possesses torsion angles of +45.4, −61.3, +50.6, −24.1, +10.1, and −21.3° for molecule A

Table V. Bond Angles (°) for Picrasidine-F Hydrochloride (**1**), with Standard Deviations in Parentheses

Atom 1		Atom 2		Atom 3	Moelcule A	Molecule B
C(13)	–	N(1)	–	C(2)	109.09 (8)	107.64 (9)
N(1)	–	C(2)	–	C(3)	127.29 (9)	126.95 (11)
N(1)	–	C(2)	–	C(7)	109.48 (9)	110.02 (7)
C(3)	–	C(2)	–	C(7)	123.21 (6)	123.02 (10)
C(2)	–	C(3)	–	N(4)	114.35 (10)	115.33 (10)
C(2)	–	C(3)	–	C(14)	121.68 (6)	121.67 (10)
N(4)	–	C(3)	–	C(14)	123.89 (10)	122.90 (7)
C(3)	–	N(4)	–	C(5)	125.28 (10)	123.96 (6)
C(3)	–	N(4)	–	C(17)	120.92 (9)	119.19 (9)
C(5)	–	N(4)	–	C(17)	113.51 (6)	116.76 (9)
N(4)	–	C(5)	–	C(6)	120.67 (7)	120.65 (11)
C(5)	–	C(6)	–	C(7)	117.46 (10)	118.49 (11)
C(5)	–	C(6)	–	O(1)	125.87 (7)	123.96 (11)
C(7)	–	C(6)	–	O(1)	116.65 (10)	117.50 (6)
C(6)	–	C(7)	–	C(8)	134.05 (11)	134.87 (10)
C(6)	–	C(7)	–	C(2)	118.96 (10)	118.49 (7)
C(8)	–	C(7)	–	C(2)	106.98 (7)	106.64 (10)
C(7)	–	C(8)	–	C(9)	134.77 (7)	133.94 (12)
C(7)	–	C(8)	–	C(13)	106.83 (10)	106.58 (8)
C(9)	–	C(8)	–	C(13)	118.38 (8)	119.43 (9)
C(8)	–	C(9)	–	C(10)	117.86 (9)	117.89 (13)
C(9)	–	C(10)	–	C(11)	121.88 (13)	121.19 (10)
C(10)	–	C(11)	–	C(12)	121.32 (10)	123.05 (9)
C(11)	–	C(12)	–	C(13)	117.69 (8)	115.07 (12)
C(12)	–	C(13)	–	N(1)	129.63 (9)	127.54 (11)
C(12)	–	C(13)	–	C(8)	122.80 (11)	123.34 (9)
C(8)	–	C(13)	–	N(1)	107.57 (7)	109.11 (8)
C(3)	–	C(14)	–	C(15)	113.85 (6)	116.75 (12)
C(14)	–	C(15)	–	C(16)	107.82 (10)	116.40 (12)
C(15)	–	C(16)	–	C(17)	111.62 (10)	114.62 (10)
C(16)	–	C(17)	–	N(4)	111.46 (6)	109.54 (8)
C(16)	–	C(17)	–	C(3′)	112.90 (10)	116.83 (9)
N(4)	–	C(17)	–	C(3′)	107.67 (9)	108.78 (7)
C(13′)	–	N(1′)	–	C(2′)	108.43 (7)	108.88 (8)
N(1′)	–	C(2′)	–	C(3′)	129.51 (7)	131.78 (8)
N(1′)	–	C(2′)	–	C(7′)	107.63 (6)	107.92 (10)
C(13′)	–	C(2′)	–	C(7′)	122.81 (8)	120.20 (11)
C(2′)	–	C(3′)	–	N(4′)	118.62 (7)	120.70 (8)
N(4′)	–	C(3′)	–	C(17)	119.74 (7)	115.80 (10)
C(2′)	–	C(3′)	–	C(17)	121.61 (8)	123.49 (10)
C(3′)	–	N(4′)	–	C(5′)	120.36 (7)	120.04 (10)
N(4′)	–	C(5′)	–	C(6′)	123.81 (9)	121.48 (12)
C(5′)	–	C(6′)	–	C(7′)	118.26 (8)	120.29 (9)
C(5′)	–	C(6′)	–	O(2)	125.70 (9)	124.47 (11)
C(7′)	–	C(6′)	–	O(2)	116.03 (7)	115.23 (10)
C(6′)	–	C(7′)	–	C(8′)	135.80 (7)	134.96 (9)
C(6′)	–	C(7′)	–	C(2′)	116.06 (7)	117.20 (10)
C(8′)	–	C(7′)	–	C(2′)	108.00 (8)	107.78 (10)
C(7′)	–	C(8′)	–	C(9′)	134.53 (9)	134.31 (11)
C(7′)	–	C(8′)	–	C(13′)	106.17 (6)	105.67 (9)
C(9′)	–	C(8′)	–	C(13′)	119.28 (8)	119.84 (12)
C(8′)	–	C(9′)	–	C(10′)	117.73 (10)	118.58 (11)
C(9′)	–	C(10′)	–	C(11′)	121.68 (8)	120.40 (12)
C(10′)	–	C(11′)	–	C(12′)	120.44 (9)	120.75 (15)

Table V. (continued)

Atom 1		Atom 2		Atom 3	Molecule A	Molecule B
C(11′)	-	C(12′)	-	C(13′)	119.77 (10)	119.41 (12)
C(11′)	-	C(12′)	-	O(3)	126.36 (9)	123.23 (14)
C(13′)	-	C(12′)	-	O(3)	113.87 (7)	117.36 (11)
C(12′)	-	C(13′)	-	N(1′)	129.07 (8)	129.15 (10)
C(12′)	-	C(13′)	-	C(8′)	121.04 (7)	120.99 (10)
N(1′)	-	C(13′)	-	C(8′)	109.77 (7)	109.70 (11)
C(6)	-	O(1)	-	C(18)	116.98 (9)	116.73 (7)
C(6′)	-	O(2)	-	C(19)	117.13 (7)	117.96 (10)
C(12′)	-	O(3)	-	C(20)	118.50 (8)	121.36 (12)

Table VI. Torsion Angles (°) in the Six-Membered Ring of Picrasidine-F Hydrochloride (**1**)

Atom 1		Atom 2		Atom 3		Atom 4	Moelcule A	Molecule B
C(3)	-	C(14)	-	C(15)	-	C(16)	45.436	−7.872
C(14)	-	C(15)	-	C(16)	-	C(17)	−61.333	38.580
C(15)	-	C(16)	-	C(17)	-	N(4)	50.609	−53.004
C(16)	-	C(17)	-	N(4)	-	C(3)	−24.062	39.173
C(17)	-	N(4)	-	C(3)	-	C(14)	10.110	−10.200
N(4)	-	C(3)	-	C(14)	-	C(15)	−21.339	−6.800

and −7.9, −38.6, −53.0, +39.2, −10.2, and −6.8° for molecule B at C(3)–C(14)–C(15)–C(16), C(14)–C(15)–C(16)–C(17), C(15)–C(16)–C(17)–N(4), C(16)–C(17)–N(4)–C(3), C(17)–N(4)–C(3)–C(14), and N(4)–C(3)–C(14)–C(15), respectively. These torsion angles and a Dreiding model examination approximate to the framework corresponding to the six-membered rings of molecules A and B being in half-chair form.

Experimental

The melting point was determined on a Yanagimoto micromelting point apparatus and is uncorrected. The UV and infrared (IR) spectra were recorded with Hitachi 340 and Hitachi 260-30 spectrophotometers, respectively. The ^{1}H- and ^{13}C-NMR spectra were recorded with a JEOL JNM-GX-400 (^{1}H-NMR at 400 MHz and ^{13}C at 100 MHz) spectrometer. Chemical shifts are given on the δ scale (ppm) with tetramethylsilane as an internal standard and coupling constants are given in Hz. The following abbreviations are used: s = singlet, d = doublet, dd = double doublet, t = triplet, td = triplet of doublets, q = quartet, and sh = shoulder. FD-MS and electron ionization (EI) MS were measured with a JEOL JMS-DX-300 mass spectrometer. Column chromatography was carried out on a silica gel (BW-820MH, Fuji Devision Co., Ltd.) Semi-pressure preparative chromatography was performed on a silica gel (24 × 360 mm) column. Thin-layer chromatography was performed on Silica gel 60 GF$_{254}$ (Merck) and spots were detected with Dragendorff's reagent or by UV illumination.

Extraction and Isolation——Dried root (5.5 kg) of *Picrasma quassioides* collected at Funabashi city, Chiba prefecture, in August 1984, were extracted with MeOH (72 l) at 40 °C for 48 h. The extract was evaporated to dryness and the residue was partitioned between water and $CHCl_3$. The $CHCl_3$ solution was dried over Na_2SO_4 and concentrated to give a $CHCl_3$-soluble fraction (530 g), which was applied to a column of silica gel (1.5 kg) and eluted successively with $CHCl_3$, $CHCl_3$–MeOH (99 : 1, 49 : 1, 19 : 1, 9 : 1, 1 : 1), and MeOH. The $CHCl_3$–MeOH (19 : 1) fraction (15 g) was repeatedly chromatographed on silica gel to afford the crude alkaloid fraction (3.2 g). The crude fraction was dissolved in MeOH, and 10% HCl solution was added. The hydrochloric salt that precipitated was further purified by semi-pressure preparative chromatography on a silica gel (24 × 360 mm) with $CHCl_3$–MeOH (19 : 1) as an eluent (1 ml/min) to give picrasidine F hydrochloride (15 mg).

(±)-Picrasidine-F Hydrochloride (1)——Colorless plates (MeOH), mp 265—267 °C (dec.). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 252 (4.29), 282 (sh, 3.60), 310 (3.65), 347 (3.42), 372 (3.20). UV $\lambda_{\max}^{\mathrm{EtOH+NaOH}}$ nm (log ε): 242 (4.08), 278 (4.24), 334 (3.57), 402 (3.03). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3420, 3390, 3150, 2950, 1630, 1582, 1548, 1490, 1400, 1288, 1150, 760. ^{1}H-NMR: see

Table I. ^{13}C-NMR (δ in DMSO-d_6 at 60 °C): 13.4 (t), 24.5 (t), 27.2 (t), 55.6 (q), 56.0 (q), 57.3 (q), 64.6 (d), 107.8 (d), 112.4 (d), 115.1 (d), 116.9 (s), 117.9 (d), 118.5 (d), 119.4 (s), 120.0 (d), 120.2 (d), 120.9 (s), 121.2 (s), 123.7 (d), 129.6 (d), 129.9 (s), 132.5 (s), 133.8 (s), 134.8 (s), 137.7 (s), 142.0 (s), 145.6 (s), 150.2 (s), 150.6 (s). FD-MS m/z: 478 $(\mathrm{M}-\mathrm{HCl})^+$. EI-MS m/z (%): 479 (27), 478 (69), 463 (17), 267 (100), 256 (14), 255 (17), 252 (18), 251 (17), 242 (26), 239 (27), 237 (27), 212 (30), 199 (10). *Anal.* Calcd for $C_{29}H_{26}N_4O_3 \cdot HCl \cdot CH_3OH/2$: C, 66.72; H, 5.50; N, 10.55. Found: C, 66.45; H, 5.40; N, 10.69.

Crystal Data for 1——$C_{29}H_{26}N_4O_3 \cdot HCl \cdot CH_3OH/2$. $M_r = 531.03$, $P\bar{1}$, triclinic, $a = 15.628$ (7), $b = 15.104$ (7), $c = 14.473$ (8) Å, $\alpha = 122.68$ (4), $\beta = 107.66$ (5), $\gamma = 95.55$ (5)°, $V = 2593.11$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.360\,\mathrm{g \cdot cm^{-3}}$, Absorption coefficient for MoK_α radiation ($\lambda = 0.71070$ Å), $\mu = 0.7\,\mathrm{cm^{-1}}$. Number of reflections = 4225. Final R value = 0.0797.

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