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BAYTOPINE, A NEW HOMOAPORPHINE ALKALOID ≠

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Abstract — Baytopine (2), a new alkaloid, was isolated from leaves and flowers of Merendera kurdica Bornm. and its structure was determined by spectroscopic means.

All eight presently known natural homoaporphine alkaloids were found in plants of the Liliaceae family[1]. This communication describes the structure of baytopine, a new homoaporphine alkaloid isolated during our recent phytochemical study of several Merendera species[2].

Baytopine, an optically active compound ($[\alpha]_D$ +74° (c 0.28, $CHCl_3$)), amorphous solid, was isolated from leaves and flowers of M. kurdica Bornm.[3]. It gave a positive $FeCl_3$ test for phenols. Its uv spectrum, which is characteristic of a homoaporphine type alkaloid[4], is pH-dependent and similar to that of bechuanine (7S-(+)-floramultine) (1)[5] (Table 1). The ir spectrum of baytopine showed the presence of hydroxyl functionality (bands at 3400-3500 cm^{-1}). Mass measurements (M^+ m/z 371) established the molecular formula $C_{21}H_{25}NO_5$. The base peak (m/z 354) in the mass spectrum (70 eV) of baytopine corresponds to M^+-17 which indicates, by analogy with other homoaporphines, that position C-1 or C-13 carries

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≠Dedicated to Professor Derek Barton on the occasion of his 70th birthday.

a phenolic hydroxy group[6,7]. According to its ^1H-nmr spectrum, baytopine contains the same building blocks as bechuanine (1): 3 methoxyls, one N-methyl, 2 isolated aromatic protons, one $ArCH_2CH_2N$ system, and one $NCHCH_2CH_2$ system. The presence of two phenolic hydroxyls is inferred from the difference between the total number of hydrogen atoms in the molecule (ms) and the number of protons attached to carbons (^{13}C-nmr). However, the nonidentical ^1H and ^{13}C-nmr spectra (Table 2) indicate that the two compounds are positional isomers. Only one methoxyl (3.92 ppm) exhibits a NOE (12%), to the 6.68 ppm singlet. Since the latter signal is assigned to H-3 on the basis of its long-range coupling to the proton at 3.15 ppm which forms part of the AA´BB´system of the CH_2CH_2 group, one methoxyl is located at C-2. Because of the single NOE between the methoxyl and aromatic proton, the second methoxyl cannot be placed at C-11. With both bechuanine and baytopine, one methoxyl resonates in higher field - an effect typical for methoxyl at C-1 or C-13 (ref. 8). That requires a reversed substitution pattern (OH at C-13, OCH_3 at C-1) in baytopine, leading to the formula 2. Both alkaloids exhibit a negative Cotton effect at ^1L_a transition (Table 1). Thus the 7(S) absolute configuration for baytopine (2) is directly assignable from CD spectrum[9].

Table 1. Spectral data of bechuanine (1) and baytopine (2).

Alkaloid		Uv λ_{max} nm ($\log\varepsilon$)	CD λ_{max} nm ($\Delta\varepsilon$)
1	A	216 (4.61), 258 (4.05), 285sh (3.72),	200 (14.90), 257 (-19.20)
	B	210 (4.58), 288 (4.16)	229 (15.75), 290 (-10.30), 305 (-10.80)
2	A	215 (4.55), 257 (4.02), 287sh (3.67), 296sh (3.62)	209 (20.09), 258 (-11.20)
	B	217 (4.39), 287 (4.00), 296sh (3.97)	222 (8.00), 279 (-6.25), 298 (-5.54)

A - in EtOH, B - in 0.001 M EtONa

Table 2. ^{1}H (400 MHz) and ^{13}C (100 MHz) nmr data of bechuanine (1) and baytopine (2) (δ ppm, J= Hz).

Proton	(1)	(2)	Carbon	(1)	(2)
H-3	6.66 s	6.68 s	C-1a	119.8 s	135.6 s^a
H-4a	3.02 m	3.15 m	C-1	140.7 s^a	149.8 s^b
H-4b	3.14 m	3.35 m	C-2	149.5 s^b	149.7 s^b
H-5a	2.63 m	2.83 m	C-3	110.7 d	110.6 d
H-5b	2.79 m	3.11 m	C-3a	121.8 s^c	124.2 s^a
H-7	3.34 dd	3.63 dd	C-4	30.5 t	30.0 t
	J=11.1, 6.8	J=11.7, 6.3	C-5	45.0 t	44.8 t
H-8a	2.00 m	2.07 m	C-7	57.9 d	58.6 d
H-8b	2.24 m	2.39 m	C-7a	127.6 s^c	122.4 s^a
H-9a	2.11 m	2.26 m	C-8	25.9 t	24.6 t
H-9b	2.42 m	2.48 m	C-9	33.2 t	33.7 t
H-10	6.64 s	6.65 s	C-9a	124.5 s^c	121.8 s^a
1-OCH_3	-	3.64 s	C-10	110.8 d	111.0 d
2-OCH_3	3.90 s	3.92 s	C-11	138.2 s^a	141.3 s^c
12-OCH_3	3.95 s	3.95 s	C-12	149.1 s^b	147.6 s^b
13-OCH_3	3.59 s	-	C-13	146.8 s^b	138.6 s^c
N-CH_3	2.40 s	2.59 s	C-13a	136.8 s^c	118.9 s
			1-OCH_3	-	61.2 q^d
			2-OCH_3	55.9 q	55.1 q
			12-OCH_3	61.2 q^d	61.2 q^d
			13-OCH_3	61.1 q^d	-
			N-CH_3	41.8 q	40.8 q

[a-d] Assignments may be reversed

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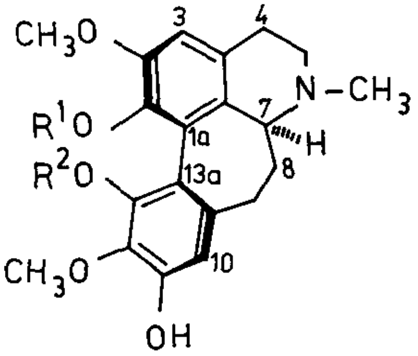

1 : $R^1 = H$, $R^2 = CH_3$
2 : $R^1 = CH_3$, $R^2 = H$

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6. Ms (m/z, rel. intensity, %) 371 (M^+, 53), 354 ($C_{21}H_{24}NO_4$, 100), 340 ($C_{20}H_{22}NO_4$, 97), 60 ($C_2H_4O_2$, 17), 58 (C_3H_8N, 8).
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