Journal of Natural Products
Vol. 51, No. 2, pp. 309-310, Mar-Apr 1988

BUXAMINONE—A NEW ALKALOID FROM THE LEAVES OF *BUXUS PAPILLOSA*

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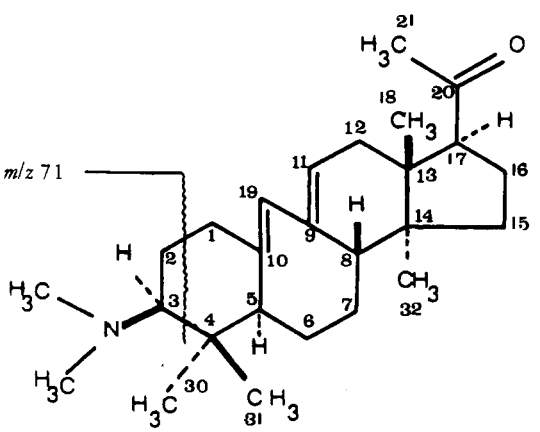
Previously, we reported the isolation of several new steroidal alkaloids from the alcoholic extract of *Buxus papillosa* C.K. Schneider (Buxaceae) leaves collected from the northern regions of Pakistan (1–8). In the course of our studies, we have isolated another new steroidal alkaloid, buxaminone [**1**]. Its structure was established through spectroscopic studies.

Buxaminone, $C_{26}H_{41}NO$, was obtained as a colorless amorphous solid, $[\alpha]^{20}D$ −22° ($CHCl_3$). The uv spectrum (MeOH) showed maxima at 238 and 248 nm with shoulders at 225 and 254 nm, characteristic of a 9(10↦19) *abeo* diene system (1–3). The ir spectrum ($CHCl_3$) of the compound displayed absorptions at 1690 (ketonic carbonyl) (3) and 1596 (C=C) cm^{-1}. The ^1H-nmr spectrum ($CDCl_3$, 400 MHz) of compound **1** bore a distinct similarity to that of (+)-papilicine (1). It included four singlets at δ 0.66, 0.76, 0.77, and 1.07 for the four tertiary methyl groups. Another singlet at δ 2.10 was due to the C-21 methyl group. A singlet at 2.35 was assigned to the $N(CH_3)_2$ group attached to C-3 of ring A. The vinylic protons at C-11 and C-19 appeared as a doublet of doublets at δ 5.55 (J_1=2.3 Hz, J_2=1.8 Hz) and a singlet at δ 5.93, respectively. In accord with all other related *Buxus* alkaloids, the C-3 aminated substituent in (−)-buxaminone [**1**] has been placed in a β configuration. Configurations at various other asymmetric centers were established on the basis of its close resemblance to the known *Buxus* alkaloid, (+)-papilicine (1).

The mass spectrum of the compound included a molecular ion at *m/z* 383.3186, corresponding to the molecular formula $C_{26}H_{41}NO$ (calcd 383.3187). A peak at *m/z* 340 was due to the loss of the C-17 carbonyl-containing side chain from the molecular ion. Another peak at *m/z* 338 resulted from the loss of the $N(CH_3)_2$ group. The compound showed the base peak at *m/z* 71.1072 (C_4H_9N, calcd 71.0734), which was due to the ion CH_2=CH-$N^+(CH_3)_2$, common in *Buxus* alkaloids containing a dimethylamino substituent at C-3 of ring A (9). A very



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large peak at *m/z* 57 also resulted from the cleavage of ring A along with the nitrogen-containing substituent.

On the basis of the above spectroscopic studies, structure **1** was assigned to (−)-buxaminone. Biogenetically, it may arise from (+)-papilicine (1) or buxamine-B (10) by oxidation of the *N*-bearing side chain to the corresponding ketimine, followed by its hydrolytic removal.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mass spectra were recorded on a Varian MAT 312 double focusing spectrometer connected to a PDP 11/34 computer system. The ^{1}H-nmr spectra were recorded on a Bruker AM-400 nmr spectrometer. The uv spectra were recorded on Shimadzu UV 240 instrument. The ir spectra were recorded on a Jasco IRA-1 infrared spectrophotometer. Optical rotation was taken on a polaratronic D polarimeter. The purity of the sample was checked on tlc (Si gel, SiF, precoated plate).

PLANT MATERIAL.—The leaves of *B. papillosa* were collected in northern Pakistan by the Forest Institute, Peshawar. The plant was identified at the Department of Botany, University of Karachi, and a specimen has been deposited in the Department of Botany, University of Karachi.

ISOLATION AND IDENTIFICATION.—The EtOH extract of the air-dried leaves (50 kg) of *B. papillosa* was evaporated under vacuum to afford a gum (200 g). This was taken up in 10% HOAc. The aqueous acidic extract was basified with NH_4OH to pH 9.0 and extracted with $CHCl_3$. The crude alkaloids (75 g) obtained upon evaporation of the organic solvent were loaded on a Si gel column (70–230 mesh, Merck, diameter 70 mm, 3.2 kg). Elution was with $CHCl_3$/MeOH. A fraction obtained by using $CHCl_3$-MeOH (90:10) (5.4 g) was again placed on another Si gel column (200 g) and eluted with $CHCl_3$. Further purification of a fraction by tlc on Si gel afforded buxaminone [**1**] as a colorless, amorphous solid (3.5 mg), $[\alpha]^{20}D$ −22° (*c*=1.58, $CHCl_3$); uv λ max (MeOH) 225 (log ε 3.89), 238 (log ε 4.03), 248 (log ε 4.81), 254 nm (log ε 3.91); ir ν max ($CHCl_3$) 1690 (C=O), 1596 (C=C) cm^{-1}; ^{1}H nmr ($CDCl_3$, 400 MHz) 0.66 (3H, s, t-C*H*$_3$), 0.76 (3H, s, t-C*H*$_3$), 0.77 (3H, s, t-C*H*$_3$), 1.07 (3H, s, t-C*H*$_3$), 2.10 (3H, s, 21-C*H*$_3$), 2.35 (6H, s, N(C*H*$_3$)$_2$), 2.90 (1H, dd, J_1=17.7 Hz, J_2=10.8 Hz, 17-*H*), 5.55 (1H, dd, J_1=2.3 Hz, J_2=1.8 Hz, 11-*H*), 5.93 (1H, s, 19-*H*); ms *m/z* (%) $[M]^+$ 383.3186 (8), 368 (6), 340 (15), 338 (13), 72 (55), 71 (100), 58 (36), 57 (45), 44 (33).

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Received 1 May 1987