l-CYCLOPROTOBUXINE C FROM Buxus sempervirens

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Continuing the separation of the combined alkaloids of Buxus sempervirens, the mother liquors from cyclobuxine D and cyclovirobuxine D [1, 2] were chromatographed on a column of silica gel (KSK).

From a chloroform–methanol–ammonia (7 : 4 : 0.2) eluate we isolated a base with mp 195-197°C, $[\alpha]_D$ −62° (c 0.25), $C_{27}H_{48}N_2$ (I). The IR spectrum of compound (I) had ν_{max} 3050, 1460 cm^{-1} (methylene of a cyclopropane ring) [3]. The NMR spectrum had (δ scale, ppm) singlets at 0.91 (6 H, C_4-CH_3), 0.88 and 0.72 (6 H, C_{14}-CH_3; C_{18}-CH_3), 2.39 (3 H, N-CH_3), 2.15 [6H, N-$(CH_3)_2$], and a doublet at 0.78 ppm (3 H, C_{20}-CH_3). The mass spectrum of compound (I) had as its main peaks those of ions with m/e 70, 71, 72 (100%), 329, 356, 385, and 400 (M^+). The maximum peak of the ion with m/e 72 shows that the $-N(CH_3)_2$ group is located at C_{20}.

The Hess methylation of (I) led to a N-monomethyl derivative (II) with mp 201-203°C, $[\alpha]_D$ −112.4° (c 0.31), 414 M^+. Acetylation formed a N-acetyl derivative (III) with mp 225-227°C, $[\alpha]_D$ −11.76° (c 1.02), 442 M^+. The IR spectrum of compound (III) showed an absorption band at 1650 cm^{-1} $\left(>N-CO-CH_3\right)$. Benzoylation gave an N-benzoyl derivative (IV) with mp 244-246°C, $[\alpha]_D$ −19.7° (c 0.71), 504 M^+. The IR spectrum of (IV) had ν_{max} 1630 cm^{-1} (N−CO−C_6H_5).

The IR, NMR, and mass spectra and the composition of the base (I) and its derivatives agree well with the corresponding characteristics of the alkaloid cycloprotobuxine C (V) [5-7], but a difference is observed in the sign of the specific rotation (Table 1).

Consequently, the base (I) that we isolated is the levorotary form of cycloprotobuxine C.

TABLE 1

Alkaloid	Composition	mp, °C	$[\alpha]_D$, deg (in chloroform)
(I)	$C_{27}H_{48}N_2$	195–197	−62
(V)	$C_{27}H_{48}N_2$	200–202	+80
(II)	$C_{28}H_{50}N_2$	201–203	−112,4
N-Methyl-(V)	$C_{28}H_{50}N_2$	207	+75
(III)	$C_{29}H_{50}N_2O$	225–227	−11,76
N-Acetyl-(V)	$C_{39}H_{50}N_2O$	227–230	+15
(IV)	$C_{34}H_{52}N_2O$	244–246	−19,7
N-Benzoyl-(V)	$C_{34}H_{52}N_2O$	218–220	+32

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