Biotransformation of codeinone to codeine. Codeinone **3** (20.5 mg) was incubated for 3 days in 250 ml of a 3-week-old cell suspension culture grown in 0-B5 medium and worked up as above. Purification of the extract (136 mg) with PLC on Polygram® Si gel/UV_{254} plates (0.25 mm), using EtOAc–MeOH–NH_4OH (17:2:1) for development and $CHCl_3$–MeOH (8:2) as eluent afforded a yellow material (4.2 mg). The mass spectrum (GC/MS) was that of codeine.

The other precursors, codeine (20.5 mg) neopine HBr (20.7 mg), papaverine (20.0 mg) and D,L-laudanosoline HBr (20.8 mg) were incubated with the cell suspension cultures under the above conditions, but were not metabolized.

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N(1)-ACETYL-*N*(1)-DEOXYMAYFOLINE FROM *MAYTENUS BUXIFOLIA*

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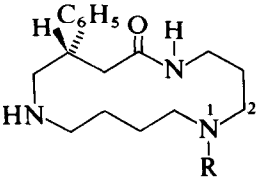
Key Word Index—*Maytenus buxifolia*; Celastraceae; spermidine alkaloid; *N*(1)-acetyl-*N*(1)-deoxymayfoline.

Abstract—A new alkaloid, *N*(1)-acetyl-*N*(1)-deoxymayfoline was isolated from *Maytenus buxifolia* growing in the vicinity of Santiago de Cuba. Plants of the same species obtained from other regions of Cuba, however, contain only mayfoline.

From *Maytenus buxifolia* collected in the Province of Matanzas (Cuba), in the vicinity of Lomas de Galindo, only the spermidine alkaloid mayfoline (**1**) could be detected [1]. The occurrence of the alkaloid in this species was confirmed in the present investigation using plants from Canasí in the same province. However, plants of the same species obtained from Santiago de Cuba, Oriente, contain another alkaloid, for which the structure **2** was proved.

The IR, UV and ^1H NMR spectra indicated an aromatic partial structure; absorption at 705 cm^{-1} corresponds to a mono-substituted C_6H_6 ring. Absorption maxima at 1660 and 1629 cm^{-1} are in accordance with the presence of amide groups and the band at 1560 cm^{-1} indicates a secondary amide. The elemental composition was shown to be $C_{18}H_{27}N_3O_2$ by high resolution MS. The fragmentation pattern is similar to that of mayfoline [1], thus proving the same skeleton. The *N*-acetyl group replacing the hydroxyl group of mayfoline gives rise to two singlets in the ^1H NMR spectrum at 2.10 and 2.12 ppm (two conformers). The ^1H NMR spectrum also shows the presence of a partial structure NH–CH(Ph)–CH_2 [2] thus proving the *N*(1)-position of the acetyl group. The similarity of the ORD curves of mayfoline [1] and of the new alkaloid proves the S-configuration for the latter compound.

As the plants of both populations were harvested at different seasons, the question of the existence of chemical races [3] in this species remains open, but it should be mentioned that both populations also differ in their morphology.



1 R = OH
2 R = Ac

EXPERIMENTAL

Plant material. Plants containing *N*(1)-acetyl-*N*(1)-deoxymayfoline were collected in March 1980 in Cuba, Oriente, in the vicinity of Santiago de Cuba, Morro Castle; plants containing mayfoline were collected in Sept. 1980 in Cuba, Province of Matanzas, Canasí. The plants were identified by Lic. Pedro Herrera, Havana. Voucher specimens are retained in the

Herbarium of the Institute of Botany, Academy of Sciences of Cuba, Havana.

N(1)-*Acetyl*-*N*(1)-*deoxymayfoline* (**2**). Dried and ground leaves of *M. buxifolia* (A. Rich.) Griseb. were extrd with EtOH at room temp. Evapn of the solvent *in vacuo* gave a residue which was partitioned between 0.5 M HCl and C_6H_6–Et_2O (1:1). After addition of $KHCO_3$ to the aq. layer, the latter was extrd with $CHCl_3$–EtOH (2:1). Evapn of the organic solvents gave crude alkaloid, which was chromatographed over Si gel with C_6H_6–MeOH (19:1). Crystallization from EtOAc afforded **2**; yield 0.02%; mp 177–178°, $[\alpha]_D^{22}$ −17.8° ($CHCl_3$; *c* 1.01). ν_{max}^{KBr} cm^{-1}: 1660, 1629 (NAc), 1560 (NHAc), 1493, 705 (Ph). λ_{max}^{MeOH} nm (log ε): 268 (2.23), 264 (2.37), 259 (2.49), 252 (2.48). ORD (MeOH): $[\phi]_{269}$ −300° (peak), $[\phi]_{264}$ −780° (*sh*), $[\phi]_{234}$ −3700° (*tr*). ^{1}H NMR (100 MHz, $CDCl_3$, TMS): δ 7.29 (*m*, 5 H, C_6H_5), 3.99 (*dd* after treatment with D_2O, J = 6 and 8 Hz, 1 H, CHPhNH), 2.12, 2.10 (2 *s*, together 3 H, NAc). MS 70 eV *m/z* (rel. int.): 317.2098 (calc. for $C_{18}H_{27}N_3O_2$: 317.2103, M^+; 43), 274.1974 (calc. for $C_{16}H_{24}N_3O$: 274.1919; 35), 160.1129 (calc. for $C_{11}H_{14}N$: 160.1126; 78), 146.0593 (calc. for C_9H_8NO: 146.0606; 100), 131.0499 (calc. for C_9H_7O: 131.0497; 26).

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