absorptions at λ_{max}^{EtOH} 231 and 272 nm. Its ^{1}H NMR ($CDCl_3$, δ) spectrum revealed the presence of 3 aromatic protons at 6.82 (1H, *d*, $J = 6$ Hz), 8.53 (1H, *d*, $J = 6$ Hz) and 8.56 (1H, *s*), and a methoxyl group at 3.94. The MS exhibited a M^+ at *m/e* 134 as the base peak. Finally, the structure of this alkaloid was established by direct comparison (mmp, IR and ^{1}H NMR) with synthetic 3-cyano-4-methoxypyridine (**11**) prepared by the method of Wieland *et al.* [8].

3-Cyano-4-methoxypyridine (**11**) has not been previously obtained from natural sources and we are investigating the biological role of this simple pyridine alkaloid.

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Phytochemistry, 1980, Vol. 19, pp. 162–163. 0031-9422/80/0101-0162 $02.00/0

MAYFOLINE, A NOVEL ALKALOID FROM *MAYTENUS BUXIFOLIA*

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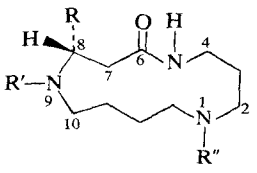
(*Received* 8 *May* 1979)

Key Word Index—*Maytenus buxifolia*; Celastraceae; spermidine alkaloid; mayfoline.

Compounds reacting with the Dragendorff reagent were detected in *Maytenus buxifolia* (A. Rich.) Griseb. (Celastraceae) [1]. Mayfoline has now been isolated from the aerial parts of the plant. Structure **1** with a characteristic hydroxylamine moiety is consistent with the spectroscopic and chemical properties of this alkaloid. Similar macrocyclic spermidine alkaloids occur in other *Maytenus* species and further Celastraceae [2, 3].



1 R = Ph, R′ = H, R″ = OH
2 R = Ph, R′ = Ac, R″ = OAc
3 R = C_6H_{11}, R′ = R″ = H

The IR, UV and ^{1}H NMR spectra indicated an aromatic partial structure; absorption at 707 cm^{-1} corresponds to a monosubstituted benzene ring. Absorption maxima at 1663 and 1547 cm^{-1} are in accordance with a secondary amide linkage. The empirical formula was shown to be $C_{16}H_{25}N_3O_2$ by high resolution MS. The base peak at *m/e* 274 is formed by loss of OH. The peaks at *m/e* 146 and 131 arise by elimination to yield a cinnamoyl derivative and subsequent cleavage of the C(4)–N(5) and N(5)–C(6) bond, respectively (see Fig. 1) [2]. The fragment at *m/e* 160 reveals four unsubstituted CH_2 groups between N-1 and N-9 [2]. By acetylation with Ac_2O–Py, mayfoline was converted into the *N,O*-diacetate (**2**) with absorption at 1747, 1663, 1645 and 1204 cm^{-1} as well as ^{1}H NMR singlets at δ 2.06 and 2.29 ppm. Like *N*-acetylcelacinnine [2], *N*-acetylcyclocelabenzene, and *N*-acetylisocyclocelabenzene [3], **2** shows a double doublet at δ 5.67 in the ^{1}H NMR spectrum for 8-H, thus indicating the partial structure N(Ac)–CH(Ph)–CH_2. The ^{1}H NMR spectrum of **2** lacks CHOAc

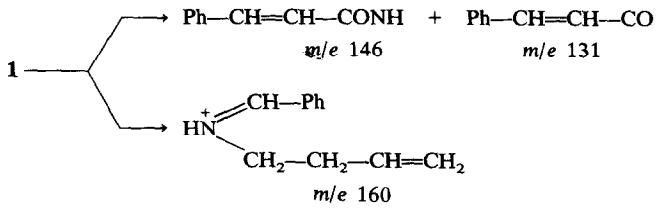


Fig. 1. MS fragmentation of mayfoline.

signals (between 4 and 6 ppm) suggesting that the hydroxy group of mayfoline is bound to N-1. By catalytic hydrogenation over Pt in HOAc, deoxyhexahydromayfoline (**3**) was obtained, the MS of which is in accordance with the given constitution, the base peak arising by cleavage of the cyclohexyl group. The observed elimination of the OH group is consistent with a hydroxylamine structure. $NaBH_4$ did not react with mayfoline, thus excluding a carbinolamine moiety. After treatment with $NaBH_4$ it proved difficult to isolate pure mayfoline, probably due to coordination with boron compounds. Therefore the diacetyl derivative **2** was prepared and identified. The antipodal nature of the ORD curve of mayfoline on the one hand and those of *R*-α-phenylethylamine and *R*-α-phenylpropylamine [4] on the other hand shows that mayfoline has the *S*-configuration.

EXPERIMENTAL

Plant material. The plants were collected in Cuba, district Matanzas, in the vicinity of Lomas de Galindo. A voucher specimen is retained in the Herbarium of the Central Institute for Genetics and Research of Cultivated Plants of the Academy of Sciences of the GDR, Gatersleben.

Mayfoline (**1**). Dried and ground aerial parts of *Maytenus buxifolia* (A. Rich.) Griseb. were extracted with MeOH at room temp. Evapn of the solvent *in vacuo* gave a residue which was partitioned between 0.5 N HCl and C_6H_6–Et_2O (1:1). After addition of NH_3 to the aq. layer, the latter was extracted with $CHCl_3$–EtOH (2:1). Evapn of the organic solvents gave raw alkaloid, which was chromatographed over Si gel with $CHCl_3$–MeOH (19:1). Crystallization from EtOAc afforded **1**, yield 0.073%; mp 200–204°, $[\alpha]_D^{22}$ +10.6° ($CHCl_3$, *c* 0.61), R_f 0.47 (Si gel G; $CHCl_3$–MeOH (4:1), detection by Munier reagent). ν_{max}^{KBr} cm^{-1}: 1663, 1547 (amide), 1499, 707 (C_6H_5). λ_{max}^{EtOH} nm (log ε): 267.5 (2.21), 264 (2.32, shoulder), 261.5 (2.33), 257 (2.39), 251 (2.33). ORD (EtOH): $[\phi]_{269}$ −320° (peak), $[\phi]_{265}$ −580° (trough), $[\phi]_{262}$ −510° (peak), $[\phi]_{258}$ −900° (trough), $[\phi]_{257}$ −870° (peak), $[\phi]_{252}$ −1150° (shoulder), $[\phi]_{231.5}$ −3400° (trough). ^1H NMR (100 MHz, $CDCl_3$, TMS): δ 10.17 (*m*, exchangeable with D_2O), 9.24 (*m*, exchangeable with D_2O), 8.21 (*m*, exchangeable with D_2O), 7.51 (*m*, C_6H_5). MS 70 eV *m/e* (rel. int.): 291.1945 (calc. for $C_{16}H_{25}N_3O_2$: 291.1947, M^+; 33), 274.1902 (calc. for $C_{16}H_{24}N_3O$: 274.1919; 100), 258.1704 (calc. for $C_{16}H_{22}N_2O$: 258.1732; 64), 160.1112 (calc. for $C_{11}H_{14}N$: 160.1126; 69), 146.0614 (calc. for C_9H_8NO: 146.0606; 43), 131.0500 (calc. for C_9H_7O: 131.0497; 41).

N,O-*Diacetylmayfoline* (**2**). Mayfoline was acetylated by Ac_2O–Py (3 days at room temp.). Chromatography over Si gel with $CHCl_3$–MeOH (99:1) gave **2**, yield 49%; viscous oil, $[\alpha]_D^{22}$ −3.0° ($CHCl_3$, *c* 1.0), R_f 0.55 (Si gel G, $CHCl_3$–MeOH (9:1), detection by chlorination, followed by spraying with benzidine and KJ in dilute HOAc). $\nu_{max}^{CCl_4}$ cm^{-1}: 3355 (amide), 3089, 3065, 3029 (C_6H_5), 1747 (OAc), 1663, 1645, 1532 (amide), 1497 (Ph), 1204 (OAc), 699 (Ph). λ_{max}^{EtOH} nm (log ε): 265 (2.29), 258 (2.40), 253 (2.34), 248 (2.27). ORD (EtOH): $[\phi]_{270}$ −190° (trough), $[\phi]_{267}$ −170° (peak), $[\phi]_{263}$ −200° (trough), $[\phi]_{259}$ −170° (peak), $[\phi]_{257}$ −195° (trough), $[\phi]_{241}$ −105° (peak), $[\phi]_{220}$ −7500° (trough). ^1H NMR (100 MHz, CCl_4, TMS): δ 7.90 (*m*, NH), 7.24 (*m*, C_6H_5), 5.67 (*dd*, *J* = 6 and 8 Hz, CHPhNAc), 2.29 (*s*, NAc), 2.06 (*s*, OAc). MS 6–16 eV *m/e* (rel. int.): 375 (M^+; 30), 333 ($M-CH_2CO$; 80), 316 (M−OAc; 67), 131 (43), 112 (100).

Deoxyhexahydromayfoline (**3**). Mayfoline was hydrogenated over PtO_2 in HOAc (7 hr at room temp.). Crystallization from C_6H_6–hexane afforded **3**, yield 81%; mp 158–163°, $[\alpha]_D^{22}$ −19.3° ($CHCl_3$, *c* 0.90), R_f 0.08 (conc. NH_3–$CHCl_3$–MeOH (5:4:1), lower phase, twice development, detection by Munier reagent). $\nu_{max}^{CCl_4}$ cm^{-1}: 3261, 1663, 1534 (amide). MS 6–16 eV *m/e* (rel. int.): 281 (M^+; 77), 264 (59), 238 (66), 198 ($M-C_6H_{11}$; 100).

Acknowledgements—The author thanks Dr. P. Franke, Berlin, for the high resolution MS and expresses his appreciation for the excellent technical assistance of Mrs. Eva-Maria Schneider. The plants were collected by Diplomchemiker O. Aurich and Dr. C. Horstmann, Gatersleben.

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