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FOUR EUDESMANOLIDES FROM *MONTANOA FRUTESCENS**

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Key Word Index—*Montanoa frutescens*; Asteraceae; Heliantheae; eudesmanolides; sesquiterpene lactones.

Abstract—Chemical analysis of *Montanoa frutescens* afforded the known sesquiterpene lactones montafrusins A and B, as well as four new eudesmanolides which we have named montafrusins C, D, E and F. The structures of the new compounds were established by spectroscopic methods.

INTRODUCTION

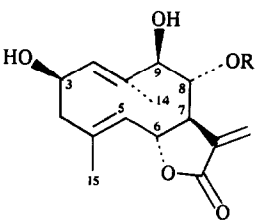
As part of our continuing study on the chemistry of plants of the genus *Montanoa*, we have examined the sesquiterpene lactones of the Mexican species *M. frutescens* [1], *M. tomentosa* [2, 3] and *M. grandiflora* [4].

Recently we re-investigated *M. frutescens* and isolated, besides the already described montafrusins A (**1a**) and B (**1b**), four new eudesmanolides which we have named montafrusins C, D, E and F.

RESULTS AND DISCUSSION

Montafrusin C (**2a**), $C_{20}H_{26}O_6$, mp 140–144°, gave rise to two one-proton doublets at δ6.14 (J = 3.0 Hz) and 5.48 (J = 3.0 Hz) and IR absorption at 1750 cm^{-1} typical of an α,β-unsaturated γ-lactone. Further IR absorptions at 1715 and 3400 cm^{-1} indicated the presence of an α,β-unsaturated ester and hydroxyl groups. The unsaturated ester was shown to be an angelate on the basis of the diagnostic ^{1}H NMR absorptions at δ6.24, 2.05 and 1.95 due to the vinyl proton and methyl groups together with mass spectral peaks at m/z 83 and 55.

Detailed ^{1}H NMR spin-decoupling experiments allowed the major structural assignments of montafrusin C (**2a**). Irradiation of the triplet of triplets at δ2.91 (H-7)



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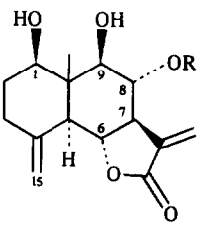
1b R = Sen



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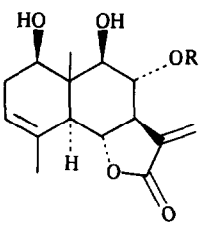

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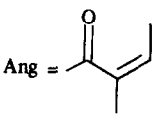

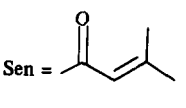

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collapsed the H-13 doublets at 6.14 and 5.48 to singlets and changed the doublet of doublets at 5.42 ($J = 11$, $J = 9.0$ Hz) to a doublet and the triplet at 4.16 ($J = 11.0$ Hz) to a doublet. The last two absorptions were assigned to the proton on the carbon carrying the ester group (H-8) and the proton at the lactonic carbon (H-6), respectively. In turn, irradiation at δ4.16 (H-6) changed the doublet at 2.26 ($J = 11.0$ Hz, H-5) to a broad singlet and the H-7 signal to a doublet of triplets. Saturation of the H-8 signal at δ5.42 collapsed the doublet at 3.89 ($J = 11.0$ Hz, H-9) to a broad singlet and the H-7 multiplet to a broad doublet. Irradiation at the frequency of H-9 and H-1 (δ3.88) collapsed the H-8 doublet of doublets at δ5.42 to a doublet and affected the one-proton multiplets centred at 1.84 (H-2a) and 1.55 (H-2b). Conversely, irradiation at the frequency of the H-2 multiplets affected the H-1 signal at δ3.87. The above spectral data established the structure **2a** for montafrusin C.

The stereochemistry of C-1, C-5, C-6, C-8 and C-9 followed from the couplings observed.

Montafrusins D (**2b**), E (**3a**) and F (**3b**) exhibited ^{1}H NMR (Table 1) and mass spectral signals which were nearly identical with those of montafrusin C (**2a**), except for absorptions that indicated differences in the ester group attached at C-8 and the double bond at C-4.

Table 1. ^{1}H NMR data of montafrusins C (**2a**), D (**2b**), E (**3a**) and F (**3b**) (80 MHz, $CDCl_3$, TMS as internal standard)

H	2a	2b	3a	3b
1	3.87 *dd*	3.85 *dd*	4.05 *dd*	4.02 *dd*
3	Obs.	Obs.	5.40 *s* (*br*)	5.40 *s* (*br*)
5	2.26 *d* (*br*)	2.24 *d* (*br*)	Obs.	Obs.
6	4.16 *t*	4.14 *t*	4.08 *t*	4.07 *t*
7	2.91 *tt*	2.85 *tt*	2.85 *tt*	2.83 *tt*
8	5.42 *dd*	5.33 *dd*	5.40 *dd*	5.40 *dd*
9	3.89 *d*	3.84 *d*	3.84 *d*	3.82 *d*
13a	6.14 *d*	6.13 *d*	6.12 *d*	6.12 *d*
13b	5.48 *d*	5.49 *d*	5.48 *d*	5.48 *d*
14	1.02 *s*	1.00 *s*	1.08 *s*	1.08 *s*
15a	5.09 *s* (*br*)	5.08 *s* (*br*)	1.86 *s* (*br*)	1.86 *s* (*br*)
15b	4.94 *s* (*br*)	4.92 *s* (*br*)		
OCOR	6.24 *qq*	5.78 *s* (*br*)	6.23 *qq*	5.78 *s*(*br*)
	2.05 *dq*	2.23 *d*	2.05 *dq*	2.23 *d*
	1.95 *quint.*	1.97 *d*	1.95 *quint.*	1.96 *d*

J (Hz): 1, 2 = 11; 1, 2′ = 5; 5, 6 = 6, 7 = 7, 8 = 11; 8, 9 = 9; 7, 13a = 7, 13b = 3; compounds **3a**, **3b**: 1, 2 = 10; 1, 2′ = 7.

EXPERIMENTAL

M. frutescens (Mairet) Hemsl. (2 kg) collected in Morelos, México, *ca* 60 km S. of México City in September 1981, was extracted as described before [1]. The $CHCl_3$ extract (85 g) was further fractionated on silica gel (800 g) using $CHCl_3$ and EtOAc. The EtOAc fraction (37 g) was chromatographed on silica gel (500 g) using petrol and petrol–EtOAc mixtures. Fractions eluted with petrol–EtOAc (17:3 and 7:3) were combined and rechromatographed on silica gel. Repeated TLC on fractions eluted with petrol–EtOAc (3:1 and 7:3) afforded the new eudesmanolides.

Montafrusin C (**2a**). $C_{20}H_{26}O_6$, mp 140–144° (Et_2O); UV λ_{max}^{MeOH} nm (ε): 209 (20 590); IR ν_{max}^{KBr} cm^{-1}: 3400, 1750, 1715, 1640; EIMS (probe) *m/z* (rel. int.): 362 $[M]^+$ ($C_{20}H_{26}O_6$) (1.98), 344 $[M-H_2O]^+$ (0.5), 262 $[M-AngOH]^+$ (1.0), 244 $[M-H_2O-AngOH]^+$ (3.0), 226 $[M-2H_2O-AngOH]^+$ (7.9), 83 $[C_5H_7O]^+$ (100.0), 55 $[C_5H_7]^+$ (40.0).

Montafrusin D (**2b**). $C_{20}H_{26}O_6$, mp 219–221°; $[\alpha]_D$ (MeOH) +109.9°; UV λ_{max}^{MeOH} nm (ε): 213 (31 800); IR ν_{max}^{KBr} cm^{-1}: 3410, 1765, 1715, 1640; EIMS (probe) *m/z* (rel. int.): 362 $[M]^+$ (0.02), 344 $[M-H_2O]^+$ (0.06), 262 $[M-C_5H_8O_2]^+$ (0.5), 244 $[M-H_2O-C_5H_8O_2]^+$ (4.0), 226 $[M-2H_2O-C_5H_8O_2]^+$ (7.3), 83 $[C_5H_7O]^+$ (100.0), 55 $[C_5H_7]^+$ (14.5).

Montafrusin E (**3a**). $C_{20}H_{26}O_6$, mp 209–211° (Et_2O); UV λ_{max}^{MeOH} nm (ε): 206 (16 800); IR ν_{max}^{KBr} cm^{-1}: 3410, 1745, 1712, 1635; EIMS (probe) *m/z* (rel. int.): 362 $[M]^+$ (0.5), 344 $[M-H_2O]^+$ (0.1), 262 $[M-C_5H_8O_2]^+$ (1.6), 244 $[M-H_2O-C_5H_8O_2]^+$ (2.3), 226 $[M-2H_2O-C_5H_8O_2]^+$ (1.5), 83 $[C_5H_7O]^+$ (100.0), 55 $[C_5H_7]^+$ (33.5).

Montafrusin F (**3b**). $C_{20}H_{26}O_6$, mp 200–202° (Et_2O); UV λ_{max}^{MeOH} nm (ε): 210 (25 600); IR ν_{max}^{KBr} cm^{-1}: 3420, 1765, 1710, 1635; EIMS (probe) *m/z* (rel. int.): 362 $[M]^+$ (0.5), 344 $[M-H_2O]^+$ (0.2), 262 $[M-C_5H_8O_2]^+$ (2.0), 244 $[M-H_2O-C_5H_8O_2]^+$ (3.2), 226 $[M-2H_2O-C_5H_8O_2]^+$ (3.5), 83 $[C_5H_7O]^+$ (100.0), 55 $[C_5H_7]^+$ (14.0).

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