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A NEW ALKALOID, MONTANINE, FROM *RUTA MONTANA*

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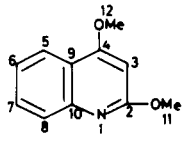
ABSTRACT.—A new alkaloid, montanine [**1**], has been isolated from the aerial parts of *Ruta montana*, in addition to a group of known alkaloids and coumarins. The structure of the new alkaloid was established by spectral data as well as by partial synthesis.

Previous studies with *Ruta montana* L. (Rutaceae) showed the presence of alkaloids (1) and coumarins (2,3). In the present study with *R. montana* a group of known coumarins [bergapten, rutamarin, xanthatoxin, chalepensin, and (±)-oxypeucedanin] (4) were obtained in a high yield together with the lignan, sesamin. In addition to the above compounds, minor amounts of additional coumarins (daphnerotin, daphnerotin methyl ether, bergaptol) (5) and alkaloids [1,2-dimethyl-4(1*H*)-quinolinone (6) and dictamnine] were isolated together with the new alkaloid, montanine [**1**]. Although bergaptol and 1,2-dimethyl-4(1*H*)-quinolinone are known compounds, they are reported here from *Ruta* species for the first time. The identification of the known compounds was established by spectral data and by tlc comparison with authentic samples; however, the standards were not available for tlc comparison for the last two compounds.

The mass spectrum of **1** exhibited a molecular ion peak at *m/z* 189 (100%) indicating the molecular formula $C_{11}H_{11}O_2N$ which correlated with the elemental analysis. The uv spectrum of **1** indicated a conjugated aromatic system [337 (sh), 321, 290 (sh), 276, 266, 241]; ir peaks supported the aromatic structure (1600, 1545, 1505 cm^{-1}). The ^{1}H-nmr spectrum of **1** showed four adjacent aromatic protons, at δ 7.97 (1H, dd, J = 2 Hz and 8 Hz, H-5), 7.59 (1H, dt, J = 2 Hz and 8 Hz, H-6*), 7.35 (1H, br d, J = 8 Hz, H-8), 7.24 (1H, dt, J = 2 Hz and 8 Hz, H-7*) (peaks marked with an asterisk are interchangeable); other peaks were at δ 6.05(1H, s, H-3), 3.95 (3H, s, OMe), 3.70 (3H, s, OMe). The chemical shifts in the ^{13}C nmr indicated C-2 (165.3 ppm) and C-4 (157.3 ppm) positions for the two methoxyl groups. The alternative positions could be at C-2 and C-3 or C-3 and C-4; in the former case the proton singlet (105.0 ppm) should be around 115–120 ppm, while in the later case it should be around 140 ppm. Other ^{13}C-nmr signals are in agreement with the suggested structure.



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Montanine was also prepared by the methylation of 2,4-dihydroxyquinoline with CH_2N_2 in Et_2O, and the product was cleaned on tlc plates: mp 81–82° [lit. (7) 82°]. The spectral data (uv, ir) as well as R_f values of the synthetic compound were comparable to those of the natural compound.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Uv spectra were recorded on a Varian Techtron model 635 spectrophotometer, ir on a Perkin-Elmer 577, ^{1}H nmr on a Bruker 200 MHz, ^{13}C nmr on FT at 50.323 MHz, and ms on a MAT 711.

PLANT MATERIAL.—Aerial parts of *R. montana* were collected from the Marmara region of Turkey in June 1988 and identified by Dr. Ertan Tuzlaci (University of Marmara). A voucher specimen has been deposited in the Herbarium of the Faculty of Pharmacy, University of Marmara (MARE 1451).

EXTRACTION AND FRACTIONATION.—Fresh

aerial parts of the plant (400 g) were extracted with Et_2O at room temperature; the Et_2O extract was evaporated under reduced pressure to yield 10 g of a residue. The residue was fractionated on a Si gel column (5 × 60 cm) eluting with light petroleum ether. A gradient of Et_2O was added up to 100%, followed by EtOH to 100%. The compounds were obtained in the following order: rutamarin (500 g), sesamin (130 mg), xanthatoxin (240 mg), chalepensin (300 mg), (±)-oxypeucedanin (260 mg), chalepin (200 mg), bergapten (240 mg), daphnoretin (10 mg), daphnoretin methyl ether (12 mg), dictamnine (10 mg), montanine (8 mg), 1,2-dimethyl-4(1*H*)-quinoline (8 mg), and bergaptol (10 mg).

MONTANINE (2,4-DIMETHOXYQUINOLINE) [**1**].—Uv λ max (Et_2O) 337 (sh), 321 (log ε 3.8), 290 (sh), 276 (log ε 3.5), 266 (log ε 3.4), 241 (log ε 4.1) nm; ir ν max ($CHCl_3$) cm^{-1} 3050, 2950, 2840, 1600, 1545, 1505, 1480, 1360, 1260, 1100, 850, 770; ^1H nmr is given in the text; ^{13}C nmr ($CDCl_3$) 165.3 (C-2), 105.0 (C-3), 157.3 (C-4), 126.9 (C-5), 125.6 (C-6), 129.6 (C-7), 129.6 (C-8), 127.2 (C-9), 143.8 (C-10), 55.3 (C-11), 55.0 (C-12); eims *m/z* $[M]^+$ 189 (100), $[M-Me]^+$ 174 (40), $[M-MeO]^+$ 158 (6), 130 (8), 97 (6), 83 (10), 77 (14); found C 69.90, H 5.86, N 7.42, calcd for $C_{11}H_{11}O_2N$, C 69.84, H 5.82, N 7.40%.

METHYLATION OF 2,4-DIHYDROXYQUINOLINE.—2,4-Dihydroxyquinoline (50 mg) was dissolved in 10 ml of MeOH and methylated with an excess of CH_2N_2 in Et_2O at 5°; the product was purified on preparative tlc plates using $CHCl_3$-EtOH (95:5). Two bands were separated. The one with an R_f 0.75 was crystallized from MeOH, mp 81–82°; uv (in Et_2O) 338 (sh), 321, 292 (sh), 275, 266, 240 nm; ir ($CHCl_3$) 3050, 2950, 2835, 1600, 1550, 1505, 1480, 1355, 1260, 1100, 840, 780 cm^{-1}.

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