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LATIFOLINE AND LATIFOLINE-*N*-OXIDE FROM *HACKELIA FLORIBUNDA*, THE WESTERN FALSE FORGET-ME-NOT

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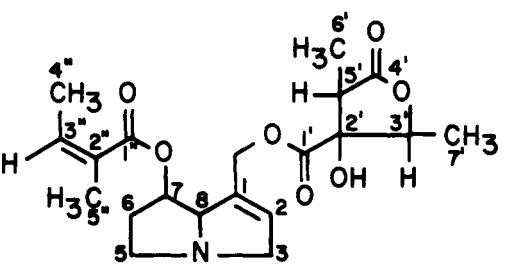
The Western false forget-me-not, *Hackelia floribunda* (Lehm) Johnston of the Boraginacae, was considered poisonous by the Ramah Navajo (1), and like many poisonous plants was thought to bring good luck in gambling and trading. As a medicine, the tips of the leaves were chewed with other plants and also rubbed on the body. The plant is known as stickseed, from the small nutlets that have hooked prickles and catch on animal fur or clothing.

We isolated and identified the major and minor alkaloids of *H. floribunda* as latifoline-*N*-oxide and latifoline (**1**) (10:1 ratio). Trace alkaloids of lower concentration than latifoline were also present but were not identified. The structures were assured by reduction of the *N*-oxide to latifoline and comparison (360 MHz ^{1}H nmr and tlc) of the latter with a standard sample (2), isolated from *Cynoglossum latifolium*. Since the *N*-oxide is a new substance and since latifoline was only reported once previously (2), ^{1}H and ^{13}C spectral data are given below for the *N*-oxide and ^{1}H-nmr assignments at high field for latifoline. Separate plant part analyses were accomplished with the following percent dry weight total alkaloid content found: leaves and stems (0.04%), roots (0.3%), and flowers and buds (0.4%). All parts showed similar ratios of latifoline and the *N*-oxide.

EXPERIMENTAL

PLANT MATERIAL.—Plants of *H. floribunda* were collected, in flower, 20 miles northwest of Fort Collins, Colorado, and 1 mile west of Como (Lake County), Colorado. Professor D.M. Wilken, Department of Botany, Colorado State University, provided the identification, and voucher specimens were deposited in the CSU herbarium. Isolation, purification, and characterization methods were essentially the same as in previous work (3), and details may be obtained from the senior author.

LATIFOLINE-*N*-OXIDE.—Isolated as an oil, $[\alpha]^{25}D$ +29.1° (EtOH; *c* 1.10); tlc Rf 0.34 (Si gel; 1:1 $CHCl_3$-MeOH; visualization was with iodoplatinic acid; *o*-chloranil/Ehrlich's reagent was negative). Ms (NH_3) Ci *m/z* 410 (MH^+ not visible), 393(2), 222(9), 134(17), 120(21), 118(100), 117(18), 35(78). ^{1}H nmr (360 MHz, $CDCl_3$) 1.19 (3H, d, J=7; H6′), 1.29 (3H, d, J=7; H7′), 1.80 (3H, s; H5″), 1.96 (3H, d, J=6; H4″), 2.25 (1H, br d, J=16; H6u)*, 2.95 (1H, q, J=7; H5′), 2.98 (1H, m; H6d), 3.73 (1H, m; H5u), 3.96 (1H, m; H5d), 4.40 (1H, q, J=7; H3′), 4.51 (2H, d, J=10.9; H3), 4.67 (1H, d, J=14; H9), 4.79 (1H, d, J=14; H9, H3), 5.13 (1H, d, J=4.8; H8), 5.80 (1H, br s; H7), 5.88 (1H, s; H2), 6.18 ppm (1H, q, J=6; H3″). ^{13}C nmr ($CDCl_3$, superscripts a and b refer to interchangeable assignments) 175.1 (c-4′), 170.7 (C-1′), 165.7 (C-1″), 140.9 (C-3″), 130.8 (C-2″), 126.3 (C-1), 122.4 (C-2), 93.8 (C-8), 83.7^a (C-2′), 81.7^a (C-3′), 80.3^a (C-3), 72.3^b (C-



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7), 69.6[b] (C-5), 61.3 (C-9), 46.7 (C-5′), 32.7 (C-6), 20.4 (C-4″), 16.0 (C-5″), 14.1 (C-7′), 8.8 ppm (C-6′).

2.76 (1H, m; H5u), 2.95 (1H, q, J=7; H5′), 3.38-3.45 (2H, m; H3u, H5d), 4.00 (1H, d, J=12; H3d), 4.36 (1H, br s; H8), 4.39 (1H, q, J=7; H3′), 4.71 (1H, d, J=14; H9), 4.85 (1H, d, J=14; H9), 5.43 (1H, br s; H7), 5.82 (1H, br s; H2), 6.08 ppm (1H, q, J=7; H3″).

*"u" refers to the upfield portion of a coupled proton pair and "d" to the downfield portion.

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