methylisoflavone 7-*O*-α-L-rhamnopyranoside which has not been reported previously from any plant source.

EXPERIMENTAL

Isolation. The heartwood of *P. marsupium* was extracted with boiling EtOH and the concd extract (150 ml) fractionated into petrol, C_6H_6 and EtOAc soluble portions. The isoflavone glycoside was precipitated by petrol from the EtOAc fraction using fractional precipitation to remove impurities and its purity checked by PC and TLC.

Isoflavone glycoside. $C_{24}H_{26}O_9$ (Found: C, 62.15; H,5.92%; requires: C, 62.43%; H, 5.67%). UV λ_{max}^{MeOH} nm: 258, 318 (sh); +NaOAc 258, 317 (sh). ^{1}H NMR (90 MHz, $CDCl_3$): δ 2.4 (3H, *s* 8-Me), 3.7 (6H, *d*, J = 2.5, 8.5 Hz, 4'-OMe, 5-OMe), 7.5 (2H, *d*, J = 2.5, 8.5 Hz, 2'-H, 6'-H), 6.7 (2H, *d*,J = 2.5, 8.5 Hz, 3'-H, 5'-H), 6.5 (1H, *s*, 6-H), 7.8 (1H, *s*, 2-H), 0.93 (3H, *br s*, Me-Rha), 5.15 (*s*, H-1, Rha) and 3.10–5.10 *m* (5 sugar protons).

Aglycone. $C_{18}H_{16}O_5$ (Found: C, 69.15; H, 5.51% requires: C, 69.23: H, 5.12%). UV λ_{max}^{MeOH} nm: 260, 316(sh); +NaOAc 272 and 317 (sh); +NaOMe 268, 326 (sh). Acetate (pyridine-Ac_2O; 24 hr at room temp.) mp 192° (Found: C, 67.59; H, 5.45: acetyl 12.10%; requires: C, 67.79: H, 5.08; acetyl, 12.14%. ^{1}H NMR (90 MHz, $CDCl_3$): δ2.3 (3H, *s*, 8-Me), 3.8 (*d*, J = 2.5, 8.5 Hz 4'-OMe, 5-OMe), 7.4 (2H, *d*, J = 2.5, 8.5 Hz 2'-H, 6'-H), 6.6 (2H, *d*, J = 2.5, 8.5 Hz 3'-H, 5'-H), 6.4 (1H, *s*, 6-H), 7.8 (1H, *s*, 2-H).

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REFERENCES

1. Seshadri, T. R. (1972) *Phytochemistry* **11**, 881.
2. Heilbron, Bunbury H. M. and Jones, W. B. (1964) in *Dictionary of Organic Compounds* p. 842.
3. Mabry T. J., Markham, K. R. and Thomas, M. B. (1970) in *Systematic Identification of Flavonoids*, p. 267. Springer. Heidelberg.

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A REVISED STRUCTURE FOR ACETYLHELIOSUPINE

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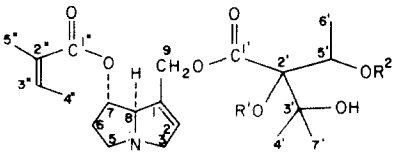
Key Word Index—*Cynoglossum officinale*; *Myosotis sylvatica*; Boraginaceae; hound's tongue; forget-me-not; pyrrolizidine alkaloids; acetylheliosupine.

Abstract—Acetylheliosupine, which has previously been isolated from *Cynoglossum officinale* and *Myosotis sylvatica*, is shown to be acetylated at the secondary hydroxyl group of heliosupine.

In 1970 Pedersen [1] described acetylheliosupine, a minor alkaloid of the hound's tongue, *Cynoglossum officinale* L. Structure **1** was proposed for this alkaloid, based largely on mass spectral evidence. Recently, Smith and Culvenor [2] reported that acetylheliosupine also occurs in the forget-me-not, *Myosotis sylvatica* Hoffm. We have also isolated acetyheliosupine from both of these species, but propose the revised structure **2** for this alkaloid.

Three lines of evidence support this conclusion. The ^{1}H NMR spectrum of acetylheliosupine shows a one-proton quartet at δ5.42, coupled only to a three-proton doublet at δ1.36. This suggests that the secondary alcohol at C-5′ is in fact the one acetylated, since the quartet for the corresponding methine occurs at δ4.19 heliosupine (**3**), the parent alcohol.

1 R′ = Ac, R^2 = H
2 R′ = H, R^2 = Ac
3 R′ = R^2 = H



The off-resonance decoupled ^{13}C NMR spectra for these two compounds support this structural assignment. The chemical shifts of the singlets for C-2′ and C-3′ differ little between acetylheliosupine and heliosupine, but the doublet for C-5′ exhibits a downfield shift of δ2.7 in acetylheliosupine relative to the parent alcohol. The magnitude of this shift demonstrates that the hydroxyl group on this carbon is the

one esterified. Finally, acetylheliosupine may be obtained in quantitative yield by acetylation of heliosupine using acetic anhydride and pyridine at room temperature, conditions under which secondary, but not tertiary, alcohols would be expected to react. Therefore, acetylheliosupine is represented by structure **2**. The stereochemical configuration at C-2′ and C-5′ remains unknown.

EXPERIMENTAL

Aerial parts of *Cynoglossum officinale* were collected in Cortland, New York, in August 1981, and *Myosotis sylvatica* was obtained in Ithaca, New York in May 1981. Voucher specimens are deposited in the herbarium of this university. Acetylheliosupine was isolated from *C. officinale* exactly as described by Pedersen [1], and showed EIMS and IR data identical in all essential respects to the published spectra. The same procedure applied to *M. sylvatica* (aerial parts, 113 g fr. wt.) afforded 16.6 mg crude alkaloids, which were submitted to prep. TLC (Si gel, 20 × 20 cm, 0.25 mm layer thickness). After developing with $CHCl_3$–MeOH–conc. NH_4OH (60:10:1), bands were located by UV-fluorescence quenching and eluted with MeOH. The least polar fraction gave acetylheliosupine, 3.1 mg, as a colorless oil, identical by NMR, IR and TLC to the alkaloid from *C. officinale*.

Acetylheliosupine was thus characterized as (1*S*,7a*R*)-7({[2-(1-acetoxyethyl)-2,3-dihydroxy-3-methylbutryl]-oxyl}-methyl)-2,3,5,7a-tetrahydro-1H-pyrrolizin-1-yl-(Z)-2-methyl-isocrotonate:* $[\alpha]_D^{24.5} - 1.8°$ (EtOH; *c* 0.567; UV λ_{max}^{MeOH} nm (log ε): 217 (3.95); ^{13}C NMR (75 MHz, $CDCl_3$): δ15.24 (*q*, $\underline{C}OCH_3$), 15.81 (*q*, C-4″), 20.46 and 20.97 (2*q*, C-6′ and C-5″), 24.51 and 26.57 (2*q*, C-4′ and C-7′), 30.32 (*t*, C-6), 54.26 (*t*, C-5), 62.17 and 62.66 (2*t*, C-3 and C-9), 72.59 (*d*, C-5′), 73.05 (*s*, C-3′), 76.73 and 78.84 (2*d*, C-7 and C-8), 82.76 (*s*, C-2′), 127.63 (*s*, C-2″), 128.81 (*d*, C-2), 134.52 (*s*, C-1), 138.51 (*d*, C-3″), 167.89 (*s*, C-1″), 169.47 (*s*, $\underline{C}OMe$), 173.24 (*s*, C-1′); ^1H NMR (300 MHz, $CDCl_3$): δ1.15 and 1.37 (2 × 3H, 2*s*, H-4′ and H-7′), 1.36 (3H, *d*, *J* = 6.3 Hz, H-6′), 1.58 (2H, *br s*, O$\underline{H}$), 1.85 (3H, *dq*, *J* = 1.5, 1.5 Hz, H-5″), 1.90 (2H, *m*, H-6), 1.95 (3H, *s*, $COC\underline{H}_3$), 1.95 (3H, d*q*, *J* = 7.2, 1.5 Hz, H-4″), 2.82 (1H, *m*, H-5), 3.17 (1H, *m*, H-5), 3.32 (1H, *br d*, *J* = 16 Hz, H-3), 3.93 (1H, *br d*, *J* = 16 Hz, H-3), 4.06 (1H, *m*, H-8), 4.83 and 4.94 (2H, AB*q*, *J* = 12.5 Hz, H-9), 5.04 (1H, *m*, H-7), 5.42 (1H, *q*, *J* = 6.3 Hz, H-5′), 5.77 (1H, *m*, H-2), 6.08 (1H, *qq*, *J* = 7.2, 1.5 Hz, H-3″); HRMS (probe) 70 eV, *m/z* (rel. int.): 439.2213 $[M]^+$ (4.0) ($C_{22}H_{33}O_8N$ requires 439.2206), 220.1344 $[M-219]^+$ (100) ($C_{13}H_{18}O_2N$ requires 220.1337).

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REFERENCES

1. Pedersen, E. (1970) *Dan. Tidsskr. Farm.* **44**, 287.
2. Smith, L. W. and Culvenor, C. C. J. (1981) *J. Nat. Prod.* **44**, 129.

*The systematic IUPAC numbering scheme (shown below) for the pyrrolizidine ring differs from the traditional scheme employed throughout this paper (cf. **1**–**3**).