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ANGELOYL, TIGLOYL AND SENECIOYLOXYTROPANE ALKALOIDS FROM *SCHIZANTHUS HOOKERII*

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Key Word Index—*Schizanthus hookerii*; Solanaceae; tropane alkaloids.

Abstract—6β-Angeloyloxytropan-3α-ol, 3α-senecioyloxytropan-6β-ol and 6β-tigloyloxytropan-3α-ol, tropine and two diasteromeric hygrolines were isolated from *Schizanthus hookerii*.

Schizanthus (tribe Salpiglossideae), an endemic genus distributed along the south-western slopes of the Andes, has been questioned as a member of the Solanaceae on account of its serological relationships, endosperm and pollen, which distinguish it from other members of the family [1–3]. Recently, we reported the isolation of several alkaloids from the roots of *S. hookerii* [4]. They included two known diastereomeric hygrolines, tropine and two new hydroxytropane esters, 6β-angeloyloxytropan-3α-ol and 3α-senecioyloxytropan-6β-ol. Previously, two other new tropane-derived alkaloids had been reported from *S. pinnatus* [5]. We now report the results from an examination of the alkaloids present in the stems and leaves of *S. hookerii*.

In addition to the aforementioned compounds, (3*R*,6*R*)-tropan-3α,6β-diol and (−)-6β-tigloyloxytropan-3α-ol, were isolated. These findings are significant in a number of ways. The accumulation of tropane alkaloids indicates that *Schizanthus* is, from the chemical point of view, a typical member of the Solanaceae. Hygrolines, on the other hand, have not so far been detected in the family, but their trivial derivation from hygrine makes them common side-products of the well-established biosynthetic route leading to the tropane alkaloids [6]. Moreover, the peculiar botanical characteristics of *Schizanthus* are also reflected in the equally peculiar chemical nature of the alkaloids it accumulates: thus, there have been no reports so far of the occurrence of natural tropane alkaloids esterified with either senecioic or angelic acids, although tiglic acid, the geometric isomer of angelic acid, is of common occurrence in the Solanaceae [7]. The coexistence of both tiglic and angelic esters in *Schizanthus* is also of biochemical interest in view of previous attempts to demonstrate the interconvertibility of these esters in *Datura* species [8] and of other work related to the metabolism of diacyl esters of this type in the Solanaceae [9].

Additional work has shown that hygroline derivatives and angeloyl- and senecioyl-esters appear to be main alkaloids of *Schizanthus*, which would indicate that they could constitute taxonomic markers for the genus.

EXPERIMENTAL

For exptal details see ref. [4]. The known compounds isolated were identified by direct comparison with authentic samples. GC analyses were performed with a 25 m SE-30 capillary column.

Extraction and isolation of alkaloids. The plant material was collected at Baños Morales (Santiago) in January. Voucher specimens are kept at the Herbarium of the University of Concepción. Dried and ground stems and leaves (8 kg) were extracted with EtOH in a Soxhlet apparatus.

(3R, 6R)-*Tropan-3α,6β-diol.* After removal of most of the alkaloids, the remaining basic aq. soln was further extracted by liquid–liquid partition with $CHCl_3$. After cooling the organic phase, a solid (400 mg) separated. It was purified by sublimation (100°, 10^{-3} mm); mp 210°, $[\alpha]_D$ + 19.6° (EtOH; *c* 0.27) (lit. 212°, + 24°) [10]. ^{1}H NMR (D_2O): δ 2.40 (3H, *s*, N-Me), 3.0 (1H, *m*, H-1), 3.25 (1H, *m*, H-5), 3.94 (1H, *br t*, H-3), 4.68 (1H, *dd*, *J* = 9.7, 3.4 Hz). EIMS *m/z* (rel. int.): 157 $[M]^+$ (20), 113 (100), 112 (21), 96 (28), 94 (18), 84 (12), 80 (20), 57 (45).

The crude alkaloid mixture (27 g), obtained by standard procedures, was subjected to countercurrent distribution in 12 separatory funnels between $CHCl_3$ (moving phase) and McIlvane's buffer pH 8. Fractions 1–4 (4.8 g) contained mainly tropine. Fraction 5 (0.68 g) consisted of a mixture of (+)-pseudohygroline and (−)-hygroline, whereas fractions 6 and 7 (1.6 g) contained (+)-pseudohygroline only. The remaining fractions (16 g) were partitioned at pH 6.2. Fractions 2–5 (5.6 g) were combined and adsorbed on Al_2O_3. Elution with CH_2Cl_2 afforded (−)-6β-angeloyloxytropan-3α-ol. Further elution with ammoniacal–CH_2Cl_2 gave (−)-6β-tigloyloxytropan-3α-ol. Hydrobromide, mp 187–188° (EtOH–H_2O), $[\alpha]_D$ − 25.0° (EtOH; *c* 0.53) (lit. 185°, − 28.1° [11]. IR ν_{max}^{KBr} cm^{-1}: 3350, 2950, 1700, 1640, 1260. ^{1}H NMR ($CDCl_3$): δ 1.83 (6H, *m*), 2.50 (3H, *s*, N-Me), 3.10–3.30 (2H, *m*, H-1, H-5), 4.05 (1H, *br t*, H-3), 5.7 (1H, *dd*, *J* = 8.0, 3.4 Hz, H-6), 6.82 (1H, *br q*). EIMS *m/z* (rel. int.): 239 $[M]^+$, (11), 156 (10), 140 (5), 122 (11), 113 (100), 112 (20), 96 (40), 83 (22).

(−)-3α-*Senecioyloxytropan-6β-ol.* Isolated from fraction 1 (0.8 g) (pH 6.2) by countercurrent distribution (pH 6.8) and prep. TLC. From the remaining fractions of the pH 6.2 distribution it was not possible to isolate any pure compound.

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METABOLISM OF [METHYL-$^{14}C_2$]HORDENINE IN *HORDEUM VULGARE* PLANTS

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Key Word Index—*Hordeum vulgare*; Gramineae; barley; metabolism; [methyl-$^{14}C_2$]hordenine.

Abstract—Intact plants of *Hordeum vulgare* quantitatively degrade [methyl-$^{14}C_2$]hordenine to $^{14}CO_2$.

We have recently reported [1] that homogenates from root tissue of *Hordeum vulgare* seedlings degrade [methyl-$^{13}C_2$]hordenine to *N*-methyltyramine and probably tyramine. The uncertainty regarding the fate of the *N*-methyl groups came from the fact that in the sequence of ^{13}C NMR spectra there appeared no signal indicating the fate of the [^{13}C]methyl groups. This result suggested either a dispersion of the labelled methyl groups or their elimination as $^{13}CO_2$ whose resonance signal is very difficult to observe because of its long T_1 value.

In order to solve this problem, we fed 8-day-old *H. vulgare* plants with [methyl-$^{14}C_2$]hordenine under similar conditions to those previously described [2] and the carbon dioxide expelled by the plants was collected. The results (Table 1) indicated that, considering the amount of alkaloid not metabolized, the methyl groups were almost completely eliminated as $^{14}CO_2$.

This degradation pathway is in agreement with that reported by Frank and Marion [3] and also with our earlier results [1, 2, 4] and explains the lack of a third signal in the experiment with [^{13}C]hordenine [2].

EXPERIMENTAL

Plant material. Similar to that previously described [2, 4].

Synthesis of [*methyl-*$^{14}C_2$]*hordenine.* To a soln of tyramine hydrochloride (108 mg) in MeOH (15 ml), [^{14}C]formaldehyde (2%, 38.4 μl, 500 μCi) (Amersham, U.K.) and formaldehyde (32.7%, 40 μl) were added and the mixture was hydrogenated over 10% Pd–C (20 mg) at room temp. and atmospheric pres. for 4 hr. Then, formaldehyde (32.7%, 90 μl) was added and the hydrogenation was continued for 12 hr. The catalyst was filtered off and the filtrate was evaporated to dryness. The residue was taken-up in MeOH (2 ml) and evaporated again; this procedure was repeated twice more. The residue was taken-up in NH_4OH (1 ml) and evaporated. Sublimation (0.001 torr, 110°) of the residue afforded pure (IR) hordenine (103 mg) with a sp. act. of 0.68 mCi/mmol.

Feeding experiment and collection of the expelled CO_2. The development of the seedlings, the administration of the tracer, the collection of CO_2 as $BaCO_3$ and the assays for radioactivity were performed as previously described [2, 4, 5]. The results are shown in Table 1.