Thus dalbin can be represented as (−)-12*a*-hydroxyamorphigenin-8′-*O*-*β*-D-glycopyranoside (3). The assigned structure is supported by MS which showed a peak at *m/e* 208 as the base peak, a diagnostic feature of 12*a*-hydroxy rotenoids having a 2,3-dimethoxychroman system [3].

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METABOLISM OF HYGRINE IN *ATROPA*, *HYOSCYAMUS* AND *PHYSALIS*

BRIAN A. MCGAW and JACK G. WOOLLEY

School of Pharmacy, Leicester Polytechnic, Leicester LE1 9BH, U.K.

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Key Word Index—*Physalis alkekengi*; *Atropa belladonna*; *Hyoscyamus niger*; Solanaceae; biosynthesis; tropane alkaloids; cuscohygrine; D(+) and L(−)-hygrine precursors.

Abstract—Three-month-old plants of *Physalis alkekengi, Atropa belladonna* and *Hyoscyamus niger* were fed via the roots with either D(+) or L(−)-hygrine-$[2'\text{-}^{14}C]$. The feeding experiments were terminated after 7 days when the following alkaloids were isolated from the paired groups of plants: tigloidine, 3α-tigloyloxytropane and cuscohygrine from *Physalis*; hyoscyamine from *Hyoscyamus* and from *Atropa*. In contrast to *Datura* these genera appear to use both hygrine enantiomers in the biosynthesis of the tropane ring.

We have recently reported [1] that D(+) (5) but not L(−)-hygrine (6) is a precursor in the biosynthesis of the tropane ring of the tropoyl esters hyoscine and hyoscyamine, and the tigloyl esters 3α,6*β*-ditigloyloxytropane and 3α,6*β*-ditigloyloxytropan-7*β*-ol in *Datura innoxia*. In view of the stereoselectivity demonstrated, it seemed appropriate to examine other members of the Solanaceae to discover whether this is a general consideration or one peculiar to *Datura*. According to Wettstein [2], the Solanaceae may be divided into 5 tribes, and plants containing tropane alkaloids occur in all except the Cestreae. The largest tropane alkaloid bearing tribe is the Solaneae and for this investigation representatives from 3 of its 4 subtribes were chosen: *Atropa* from the subtribe Lyciinae, *Hyoscyamus* from the Hyoscyaminae and *Physalis* from the Solaninae.

Table 1. Specific activities of alkaloids isolated from *Physalis alkekengi*, *Atropa belladonna* and *Hyoscyamus niger*

	Hygrine-$[2'^{14}C]$ isomer fed	Alkaloid isolated	Sp. act. dpm/mmol × 10^{-5}*
Physalis alkekengi	(+)	(1)	0.50
	(−)	(1)	0.68
	(+)	(2)	3.82
	(−)	(2)	2.65
	(+)	(3)	2.13
	(−)	(3)	2.04
Atropa belladonna	(+)	(4)	0.63
	(−)	(4)	0.61
Hyoscyamus niger	(+)	(4)	2.52
	(−)	(4)	2.69

(1)—3α-Tigloyloxytropane; (2)—3*β*-tigloyloxytropane; (3)—cuscohygrine; (4)—hyoscyamine.

*Since the activity of the precursor was 1.0 × 10^7 then this figure also coincides with the % specific incorporation calculated as [Sp. act. base (dpm/mmol)]/[Sp. act. precursor (dpm/mmol)] × 100.

Hygrine is widely distributed in nature [3, 4] and it frequently co-occurs with tropane alkaloids. When isolated the base displays no optical activity but this could be due to the facile racemization of the alkaloid during extraction. However, the enantiomers are easily resolved [5] and (+)-hygrine (5) is known to have the *R* configuration [6]. Hygrine-$[2'\text{-}^{14}C]$ was synthesized and resolved by means of the D(+)-tartrate salt in which form it was administered in order to avoid possible racemization during the course of the experiment. The alkaloids listed in Table 1 were separated on pH 5.6 and 6.8 partition columns and isolated as the picrates [7, 8].

In contrast to our previous results in which (+)-hygrine proved to be a specific precursor of the tropane alkaloids in *Datura* [1], *Atropa, Hyoscyamus* and *Physalis* appear to be able to use either isomer equally well (see Scheme 1). Alternatively, it is possible that they are able to convert (−)-hygrine to the *dextro* isomer. This is a most unexpected finding as we had anticipated that all tropane alkaloid bearing genera would function in the same way. The apparent difference in *Datura* [1] cannot be attributed to poor transport of the *laevo* isomer since (−)-hygrine labels cuscohygrine to an extent which is well above the calculated incorporation of the (+) isomer impurity in the precursor and we conclude that both isomers reached the site of synthesis. Further experiments are in progress to confirm and to examine the extent to which this difference exists in the tropane alkaloid bearing plants of the Solanaceae.

EXPERIMENTAL

Plant material. Plants were grown under glass from seed obtained from the Zentralinstitut für Genetik und Kulturpflanzenforschung, Gatersleben, D.D.R.

Counting procedures. Duplicate samples were counted in commercially available dioxane based POP/POPOP scintillator in a liquid scintillation spectrometer.

Synthesis and resolution of hygrine-[2′-^{14}C] sp. act. 1.0 × 10^7 dpm/mmol was carried out as described previously [1].

Feeding experiments. All plants, which were 3 months old at the time of feeding, were washed free of soil and suspended in blackened beakers containing Phostrogen soln. *Physalis alkekengi* (26) received 20 mg of D(+)-hygrine D(+)-tartrate in H_2O, *Atropa belladonna* (2) 40 mg salt and *Hyoscyamus niger* (4) 9 mg salt. The *laevo* isomer was administered in an identical manner to separate groups of plants. After 7 days the plants were dried at 60° for 18 hr and the alkaloids were isolated as described previously [7, 8].

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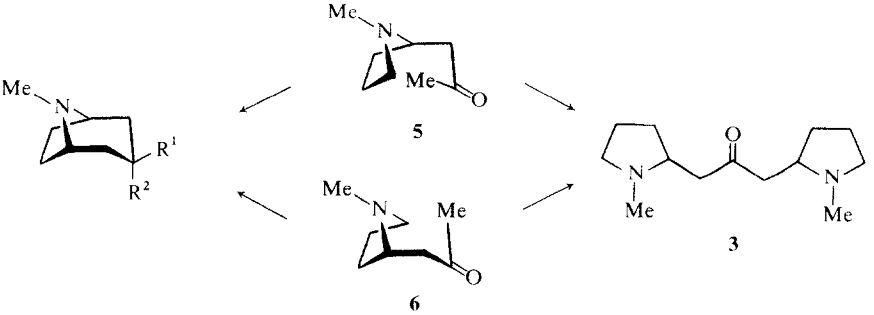
Scheme 1. Metabolism of D(+) and L(−)-hygrine.



(1) 3α-Tigloyloxytropane R^1 = H; R^2 = Tig
(2) 3β-Tigloyloxytropane R^1 = Tig; R^2 = H
(4) Hyoscyamine R^1 = H; R^2 = Trop