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HYDROXYTROPANE TIGLATES IN THE ROOTS OF *MANDRAGORA* SPECIES

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Key Word Index—*Mandragora autumnalis*; *M. vernalis*; Solanaceae; tropane alkaloids; tiglic acid esters.

Abstract—Roots of *Mandragora autumnalis* and *M. vernalis* contain hyoscyamine, hyoscine, cuscohygrine, apoatropine 3α-tigloyloxytropane and 3,6-ditigloyloxytropane. Belladonnine is present in the dried roots but could not be detected in fresh roots. No major differences were found in the alkaloids present in the two species. This is the first time the presence of tiglic acid esters has been reported in *Mandragora* species and the significance of this in the chemotaxonomy of the genus is indicated.

INTRODUCTION

ALTHOUGH *Mandragora* roots have, for many centuries, enjoyed a reputation as medicinally-active agents, very little detailed information is available about their constituents. Staub[1] showed the presence of atropine, hyoscyamine, hyoscine and cuscohygrine and indicated that other alkaloids are present which he was not able to identify. The botanical source of the roots is usually referred to as *Mandragora officinalis* (Solanaceae) but this comprises two distinct species, *M. autumnalis* Bertol. and *M. vernalis Bertol.* The roots from the two species are structurally similar, and this investigation was carried out initially in order to determine whether or not the two species could be differentiated on the basis of their alkaloid content.

RESULTS AND DISCUSSION

The total alkaloids were extracted from the roots of fresh and dried samples of both species and analysed, using TLC and GLC, by direct comparison with authentic substances. The presence of hyoscyamine, hyoscine and cuscohygrine was confirmed and apoatropine, the occurrence of which had been suggested by Staub on the basis of PC, was also shown to be present. Belladonnine was detected by TLC in extracts of the dried roots but could not be demonstrated in the extracts of fresh roots; this could be because it was masked by cuscohygrine which is present in large amounts in the fresh roots and has a very similar R_f value. It was not possible to confirm the presence of belladonnine by GLC due to on-column breakdown to its monomer, apoatropine. Fresh and dried roots of both species were found to contain two tigloyl esters of hydroxytropane; these were identified as 3α-tigloyloxytropane and 3,6-ditigloyloxytropane. Small amounts of an additional, unidentified alkaloid were also present.

The same alkaloids were found to occur in both species and the differences in the concentrations of the various alkaloids between the 2 species were no more than would be expected as a result of normal biological variation.

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This is the first time the presence of tigloyl esters has been reported in *Mandragora*. This genus is placed in the tribe Solaneae of Wettstein's classification,[2] which includes a number of genera containing tropane alkaloids; however, the presence of both tropic and tiglic acid esters has been reported in only one other genus, namely *Scopolia*.[3] It is possible that *Mandragora* and *Scopolia* can be considered as forming a chemotaxonomic subgroup linking the Solaneae with members of the tribes Daturae and Salpiglossideae (species of *Datura*, *Solandra* and *Duboisia*) in which the occurrence of both types of esters has been established.[4–6]

EXPERIMENTAL

Plant material. Roots of *M. autumnalis* were collected from plants growing near Seville and Los Barrios, S. Spain, and those of *M. vernalis* from plants cultivated in Sunderland. The plants complied with the descriptions given by Bertolini[7] for *Mandragora autumnalis* and *M. vernalis* respectively, and they were further authenticated by comparison with herbarium specimens at The Royal Botanic Gardens, Kew. Part of each sample was dried in a current of air at 45° for 48 hr and reduced to a coarse powder in a disintegrator. Fresh roots were cut into small pieces and minced in a domestic-type mincing machine.

Extraction of the alkaloids. The method used was essentially that of Staub,[1] modified to allow for differences in the amount of moisture present in the raw materials. EtOH–10% NH_4OH (10:1) was used for the fresh material and MeOH–$CHCl_3$–33% NH_4OH (12:7:1) for the extraction of the dried material. 0·47 g fresh material and 3 kg dried material (*M. autumnalis*) yielded *ca.* 0·1 and 3 g, respectively, of total alkaloids. 5% Solutions in $CHCl_3$ were prepared for TLC and 10% solutions in acetone for GLC analyses.

TLC. Silica gel G plates, 250 μm were developed in MeCOEt—MeOH—10% NH_4OH (3:1:0·5) and the spots located with Dragendorff's reagent.[8]

GLC. Pye series 104, Model 68 with dual FID glass columns, 0·9 m × 4 mm, with 1% EG-SS-Y on Celite 80–100, HMDS treated. Carrier gas N_2, flow rate 60 ml/min. temp. programme: 80° for 3 min—20°/min to 100°, then 80°/min to 230°—held at 230°.

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