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BASES FROM ROOTS OF *SOLANUM CAROLINENSE*

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Key Word Index—*Solanum carolinense*; Solanaceae; horse nettle; solaurethine; ethyl *N,N-bis*(4-dimethylaminobutyl) carbamate; solamine; cuscohygrine; anabasine.

Abstract—Ethyl *N, N-bis*(4-dimethylaminobutyl) carbamate (solaurethine), a new urethane derivative of solamine, has been isolated from the roots of *Solanum carolinense*. Other compounds reported for the first time in this species include solamine (principal base), cuscohygrine and anabasine. The chemotaxonomic significance of these compounds is noted.

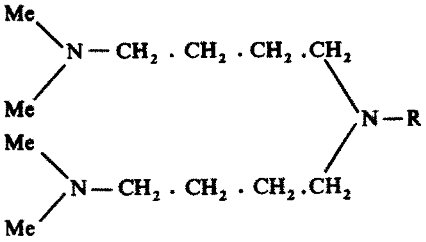
INTRODUCTION

The genus *Solanum* affords many species of horticultural, medicinal, toxicological and ornamental importance but relatively few species have been fully examined for groups of secondary metabolites which could be of chemotaxonomic value.

Solanum carolinense, the horse nettle, is a common weed of cultivated and waste land in the U.S. and Canada. The dried ripe fruits were formerly recognised in the NFV for the treatment of epilepsy, and previous investigations refer to the solanine [1] and solasodine [2] content of the plant, the presence of alkaloids in the roots and fruits [3], the antibacterial activity of an aqueous extract [4] and the general lack of cytotoxicity of the whole plant [5]. We report here the results of a study on the basic constituents of roots from plants raised in England.

RESULTS AND DISCUSSION

PLC of an EtOH–$CHCl_3$ extract of the alkalinized roots gave 4 bands of basic material (0.15% dry wt). Solamine (4,4′-*bis*dimethylaminobutylamine) (**1**) was the principal component and had the lowest R_f value. Anabasine and cuscohygrine were obtained from the two intermediate bands. The fourth base, designated solaurethine, gave a purple colour with iodoplatinate reagent [6] and was isolated as its picrate. IR analysis indicated the presence of a carbonyl group and MS gave the formula of the base as $C_{15}H_{33}N_3O_2$. A solamine moiety was suggested by ions at *m/e* 58, 71, 84, and 100 [7]. Loss of Me was indicated by *m/e* 272 (M^+-15); other significant ions occurred at *m/e* 243 (M^+-44), 216 (M^+-71) and 201 (M^+-86). Acid hydrolysis afforded solamine (TLC). From the above evidence a number of structural isomers involving the $C_3H_5O_2$ group of (**2**) are possible; most can be eliminated from IR evidence and the most plausible is a urethane structure (**3**), consistent with the low value of the carbonyl absorption (1690 cm^{-1}) and signals attributable to an Et group. Synthesis of this compound [ethyl *N,N-bis*(4-dimethylaminobutyl)carbamate] from synthetic solamine and ethyl chloroformate gave a product identical in chemical and spectroscopic properties with those of the natural product and differing from those of the methoxyacetyl isomer (**4**).



(**1**) R = H
(**2**) R = $C_3H_5O_2$
(**3**) R = CO.OEt
(**4**) R = $CO.CH_2OMe$

The occurrence of urethanes in plants is comparatively rare; physostigmine is probably the most well-known, novobiocin and mytomycin C are antibiotics produced by *Streptomyces sp.* and methylcarbamate [8] has been reported in *Salsola sp.* (Chenopodiaceae). The close structural relationship of solaurethine to some active synthetic insecticidal carbamates is of interest [9]. Solamine has previously been reported [10] as a moiety of the anti-tumour bases solapalmitine and solapalmitenine of *Solanum tripartitum*, and in the free form and as solacaproine [7] in the related *Cyphomandra betacea*. Anabasine does not appear to have been reported previously in the genus *Solanum* but it is characteristic of many *Nicotiana sp.*, the genus *Duboisia* and a number of isolated species from other unrelated families.

Thus the diversified range of *N*-containing secondary metabolites of *S. carolinense* might possibly afford a useful group for use in chemotaxonomic studies

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of the genus. Our findings in this respect will be reported separately.

EXPERIMENTAL

Plant material. Solanum carolinense plants were raised from seed by the Department of Botany, University of Birmingham, England. Seed (University of Birmingham, Accession No. S491), originated from Douglas City State Park, Kansas.

Isolation of bases. In a typical isolation, the powdered roots (50 g) mixed with $Ca(OH)_2$ (5 g), were treated with NH_4OH (15% soln, 10 ml) and set aside for 30 min. The bases were completely extracted with EtOH–$CHCl_3$ (1:9) by maceration followed by percolation. After removal of the solvent the basic mixtures was purified by the Stas–Otto procedure [11] and subjected to PLC (Si gel; Et_2NH–$CHCl_3$, 1:9). 4 Iodoplatinate-positive bands were worked up. All other quoted R_f values refer to the above system.

Solamine (**1**). Recovered (9 mg) from lowest band, R_f 0.1, tripicrate mp 151–152° (Found: C, 39.38; H, 4.38; N, 18.9. Calc. for $C_{12}H_{29}N_3.3C_6H_3N_3O_7.H_2O$: C, 39.13; H, 4.35; N, 18.26%). MS gave *m/e* 215 (M^+ for base) and an identical fragmentation pattern to that of the authentic material. *Cuscohygrine.* Isolated as the picrate, mp 203–204° from TLC band of R_f 0.45; IR spectrum (KBr disc) identical with that of authentic cuscohygrine picrate. *Anabasine.* Recovered in small yield as the picrate, clusters of plates mp 157–159°, from band 3, R_f 0.53. MS gave *m/e* 162.1147 (M^+ for base. Calc. for $C_{10}H_{14}N_2$: MW 162.1157) and fragmentation pattern identical with that of an authentic sample. IR (KBr disc) identical with that of anabasine picrate. Lack of material prevented purification of the sample (lit. value [12] for mp of dl-anabasine picrate 214°). *Solaurethine* (**3**). The principal component of the basic fraction R_f 0.64 afforded a *picrate*, rosettes from aq. EtOH, mp 122°. Found M^+ for base 287.2560. $C_{15}H_{33}N_3O_2$ requires MW 287.2573; IR: ν_{max} (KBr disc), 3050 (CH_2), 2750 (N-Me), 1690, 1385, 1190, 1000, 840 cm^{-1}; MS (picrate): *m/e* 287 (M^+ for base), 272, 243, 216, 100, 84, 71, 58 (100%). Hydrolysis (H_2SO_4 50%, 130°, 20 hr) gave solamine (TLC R_f 0.1).

Ethyl N,N-bis(*4-dimethylaminobutyl*) *carbamate* (**3**). To a cooled (0°) Et_2O soln of solamine (**1**) (22 mg) was added, with constant stirring, an Et_2O soln of ethyl chloroformate (11 mg); continued stirring (25°, 2 hr) left no detectable solamine (TLC). The base remaining after evapn of the solvent was converted to a *picrate*, rosettes mp 121°. Found C, 43.6; H, 5.80; N, 16.7. $C_{15}H_{33}N_3O_2.2C_6H_3N_3O_7$ requires C, 43.5; H, 5.2; N, 16.7%.

N-*Methoxyacetyl*-N;N-bis(*4-dimethylaminobutyl*)amine (**4**). Obtained by reaction of methoxychloroacetate (11 mg) and solamine (22 mg) under the same conditions as for (**3**). The base (R_f 0.49) yielded a *picrate*, clusters of needles from aq. EtOH, mp 120–124° with softening at 97°. Found M^+ (for base) 287.2572, $C_{15}H_{33}N_3O_2$ requires MW 287.2573.

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BUXOZINE-C, A NOVEL TYPE OF *BUXUS* ALKALOID*

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Key Word Index—*Buxus sempervirens*; Buxaceae; steroid alkaloids; buxozine-C; constitution; configuration.

Buxus sempervirens L. was collected in the Arboretum SAV, Mlyňany, Slovakia. Previous work on this and sister species is given in refs [2–5]. In the present work a cyclosteroid alkaloid of a novel type **1** has been isolated from the 'strong bases' fraction [6]. This base of molecular formula $C_{27}H_{46}N_2O$ (mp 137°, di Et ether; $[\alpha]_D^{21}$ + 65°, $CHCl_3$), is the first *Buxus* alkaloid possessing a tetrahydro-oxazine ring joined to positions 16α, 17β of the androstane skeleton.

Its IR spectrum had absorption bands attributable to a C—O—C bond, a cyclopropyl —CH_2—, a *gem*-Me grouping and a *sec*- and *tert*-amino groups. The PMR spectrum showed signals diagnostic of methylene protons of a cyclopropane ring and further protons indicative of 4 *tert*-Me groups, one *sec*-Me group, methyls of two Me-amino groupings and a —CH_2— between two heteroatoms. The MS of this alkaloid exhibited characteristic peaks [7] of a Me-amino group at C-3 and a fragmentation pattern substantially different from that of other dibasic *Buxus* alkaloids, with $M^+ - 15$ as base peak, thus

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*Part 16 in the series '*Buxus* alkaloids'; for part 15 see ref. [1].