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.

Acknowledgements—We thank Dr. R. N. Lester, University of Birmingham, for the supply and authentication of plant material and Dr. R. J. Grout, University of Nottingham for helpful discussion relevant to this work. One of us (A.S.) gratefully acknowledges the award of a Colombo Plan Scholarship by the British Government.

REFERENCES

1. Kingsburg, J. M. (1964) *Poisonous Plants of the U.S. and Canada.* Prentice Hall, New Jersey.
2. Willaman, J. J. and Li, H. L. (1970) *Lloydia* **33**, *suppl.* 3A, 212.
3. Aurich, O., Grehard, O., Romeike, A., Ronsch, H., Schreiber, K. and Sembdner, G. (1965) *Die Kulturpflanze* **13**, 621.
4. Pitts, O. M., Thompson, H. S. and Hoch, J. H. (1969) *J. Pharm. Sci.* **58**, 379.
5. Muni, I. A., Bhatti, W. H. Schermeister, L. J. and Vincent, M. C. (1967) *J. Pharm. Sci.* **56**, 50.
6. Smith, I. (1960) *Chromatographic and Electrophoretic Techniques* Vol. 1, 2nd ed. 92. Heinemann, London.
7. Evans, W. C., Ghani, A. and Woolley, V. A. (1972) *J. Chem. Soc.* 2017.
8. Karawya, M. S., Wassel, G. M., Bagdadi, H. H. and Ahmed, Z. F. (1972) *Phytochemistry* **11**, 441.
9. Kuhr, R. J. and Dorough, H. W. (1976) *Carbamate Insecticides.* CRC Press, Cleveland.
10. Kupchan, S. M., Davis, A. P., Barboutis, S. J., Schnoes, H. K. and Burlingame, A. L. (1969) *J. Org. Chem.* **34**, 3888.
11. Evans, W. C. (1966) Pharmaceutical Chemistry (Chatten, L. G. ed.), Vol. 1, 279. Dekker, New York.
12. Späth, E. and Mamoli, L. (1936) *Chem. Ber.* **69**, 1082.

Phytochemistry, 1977, Vol. 16, pp. 1860–1861. Pergamon Press. Printed in England

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

ZDENO VOTICKÝ†, OLDŘIŠKA BAUEROVÁ†, VLADIMÍR PAULÍK† and LADISLAV DOLEJŠ‡

†Institute of Chemistry, Slovak Academy of Sciences, 809 33 Bratislava, Czechoslovakia; ‡Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Prague, Czechoslovakia

(*Received* 15 *April* 1977)

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.

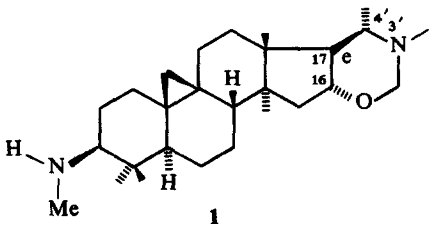
Its IR spectrum had absorption bands attributable to a C—O—C bond, a cyclopropyl —CH_2—, a *gem*-Me grouping and a *sec*- and *tert*-amino groups. The PMR spectrum showed signals diagnostic of methylene protons of a cyclopropane ring and further protons indicative of 4 *tert*-Me groups, one *sec*-Me 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

---

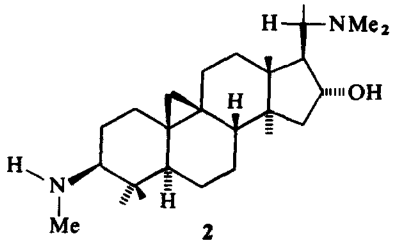
*Part 16 in the series '*Buxus* alkaloids'; for part 15 see ref. [1].

suggesting some modification of the α-amino-C_{17}-side chain of the pregnane backbone. The arguments presented, biogenetic considerations and the requirement for 6 loci of unsaturation would allow postulation of the structural formula of the base under investigation as being **1**.

To verify this suggestion the **1** was hydrogenized to afford cyclovirobuxine-C [8] (**2**) identical in all respects with the authentic specimen. This experiment produced evidence not only the correctness of the proposed structure, but also proof of the stereochemical arrangement of the alkaloid designated buxozine-C. The semisystematic name of this alkaloid of a new type is (4′*S*)-3′,4,4,4′,14α-pentamethyl-3β-methylamino-9,19-cyclo-5α-androstano-[16β,17α-e] tetrahydro-13-oxazine.



1



2

REFERENCES

1. Votický, Z. and Paulík, V. (1977) *Coll. Czech. Chem. Commun.* **42**, 541.
2. Černý, V. and Šorm, F. (1967) *The Alkaloids* (Manske, R. H. F. ed.) Vol. IX, p. 378. Academic Press, New York.
3. Tomko, J. and Votický, Z. (1973) *The Alkaloids* (Manske, R. H. F. ed.) Vol. XIV, p. 1. Academic Press, New York.
4. Goutarel, R. (1971) *The Alkaloids* Vol. 1, p. 407. The Chemical Society, London.
5. Raffauf, R. F. (1970) *A Handbook of Alkaloids and Alkaloid Containing Plants*, Wiley-Interscience, New York.
6. Schlitter, E., Heusler, K. and Friedrich, W. (1949) *Helv. Chim. Acta* **32**, 2208.
7. Votický, Z., Tomko, J., Dolejš, L. and Hanuš, V. (1965) *Coll. Czech. Chem. Commun.* **30**, 3705.
8. Khuong-Huu, F. and Magdeleine, M.-J. (1970) *Ann. Pharm. Franc.* **28**, 211.

Phytochemistry, 1977, Vol. 16, pp. 1861–1862. Pergamon Press. Printed in England.

SOLAQUIDINE, A NEW STEROIDAL ALKALOID FROM *SOLANUM PSEUDOQUINA*

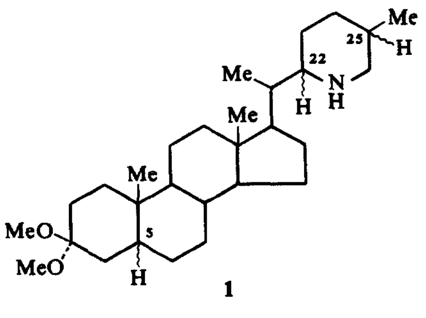
Alfredo Usubillaga*, Gisela de Castellano*, Judith Hidalgo†, Carmela Guevara†, Pablo Martinod†
and Alfredo Paredes†

*Instituto de Investigación Química, Facultad de Farmacia, ULA, Mérida, Venezuela; † Escuela Politécnia Nacional, Quito, Ecuador

(*Revised received* 22 *April* 1977)

Key Word Index—*Solanum pseudoquina*; Solanaceae; fruits; 3,3-*dimethoxy*-22,26-*epiminocholestane*; stereoidal alkaloids.

Solanum pseudoquina St. Hil was identified by Alfredo Paredes, and a voucher kept at Escuela Politécnica, Quito; trivial name, pululo. This was obtained from the Ecuadorian Andes, on the outskirts of Quito. In previous work, tests have been made for steroidal alkaloids [1]. In the present work green berries of this plant were crushed and extracted with MeOH. Chromatography of the alkaline $CHCl_3$ extract yielded solaquidine (**1**) as colourless needles, mp 278–281°. The PMR spectrum showed the presence of two OMe groups, (δ 3.10 and 3.15), a most unusual feature in steroidal *Solanum* alkaloids. The MS showed a parent peak at *m*/*e* 444. Since an elementary analysis indicated the presence of only one N the true MW was established as 445 ($C_{29}H_{51}NO_2$). The base peak at *m*/*e* 98 showed the presence of a Me piperidine side chain [2], and the two very abundant fragments at *m*/*e* 101 (60%) and *m*/*e* 127 (32%) indicated that both OMe groups were located at C-3. It has been demonstrated that an ethylene ketal function at C-3 produces mainly fragments at *m*/*e* 99 and 125, if rings A and B of a steroid are not substituted [3]. Since solaquidine has two OMe groups at C-3 instead of an ethylene ketal, the fragmentation proceeds in a similar manner, but it produces fragments two a.m.u. greater, *m*/*e* 101 instead of 99, and *m*/*e* 127 in place of 125. The fact that both OMe groups are attached to the same carbon produces some shielding and explains why these protons appear at higher field than normally expected. The IR of the acetate (**2**) showed a strong *N*-



1