

express our appreciation. We are especially grateful for the help of Timothy Plowman and Bruce Nelson for obtaining the two plant collections from Brazil.

REFERENCES

1. Bohm, B. A. and Stuessy, T. F. (1981) *Phytochemistry* **20**, 1053.
2. Bohm, B. A. and Stuessy, T. F. (1981) *Phytochemistry* **20**, 1573.
3. Stuessy, T. F. (1977) in *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds.) pp. 621–671. Academic Press, New York.
4. Collins, F. W., Bohm, B. A. and Wilkins, C. K. (1975) *Phytochemistry* **14**, 1099.
5. Bohlmann, F., Zdero, C., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20**, 522.
6. Gorinsky, C., Templeton, W. and Zaidi, S. A. H. (1973) *Lloydia* **36**, 352.
7. Cascon, S. C., Mors, W. B., Tursch, B. M., Aplin, R. T. and Durham, L. J. (1965) *J. Am. Chem. Soc.* **87**, 5237.
8. Wilkins, C. K. and Bohm, B. A. (1976) *Can. J. Botany* **54**, 2133.
9. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids*. Springer, New York.

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THE GLYCOALKALOIDS OF *SOLANUM DEMISSUM*

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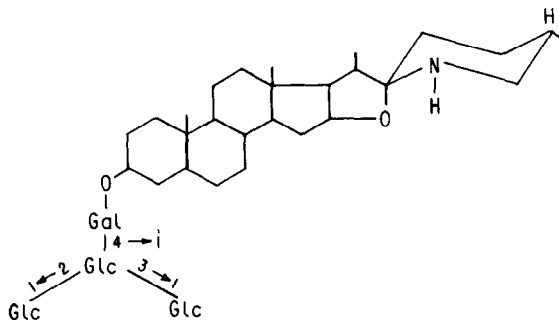
Key Word Index—*Solanum demissum*; Solanaceae; glycoalkaloids; commersonine; neotomatine.

Abstract—Two glycoalkaloids previously unreported in *Solanum demissum* have been isolated and identified as commersonine and neotomatine.

Solanum demissum has been reported to contain the glycoalkaloids demissine and tomatine. We now wish to report the isolation and characterization of two glycoalkaloids previously unreported from *S. demissum* in accession No. P.I. 205514.

The glycoalkaloid fraction of *S. demissum* foliage was isolated by basic precipitation using standard techniques. TLC of this fraction indicated the presence of four compounds, two of which were readily identified as demissine and tomatine on the basis of TLC and GC/MS characterization of the aglycones. The aglycones of the glycoalkaloids were identified by GC/MS following hydrolysis in hydrochloric acid in methanol; the structure of the carbohydrate moieties were determined by permethylation analysis. One of these unknown compounds was identified as commersonine, a glycoalkaloid we

recently isolated from *S. commersonii* [2]. The remaining glycoalkaloid which we have named neotomatine, was present in relatively small quantities. It was characterized as a tetraose derivative (1) of tomatidine, the tetraose moiety being identical to the



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tetraose (commertetraose) of commersonine. Therefore, *S. demissum* has a more complex glycoalkaloid composition than had previously been reported, resulting from the commertetraose moiety in combination with the aglycones that were previously identified in the lycotetraose glycoalkaloids of this species. This brings to three the number of *Solanum* species in which the commertetraose moiety has been found.

EXPERIMENTAL

MS were obtained on a Varian MAT-311A (direct probe) or a Hewlett Packard 5992B GC/MS, both in the EI mode at 70 eV. Si gel G (Analtech) was used in all TLC separations. GC analyses were carried out on a Varian 2100 equipped with 4 ft \times 1/8 in. glass columns packed either with 1% SE-30 or 3% ECNSS-M on Gas Chrom Q.

Glycoalkaloid isolation. *S. demissum* (P.I. 205514) leaves obtained from greenhouse plants produced from tubers supplied by the Plant Introduction Station, Sturgeon Bay, Wisconsin (10 g) were ground in a Waring Blendor with 100 ml CHCl_3 -MeOH (1:1). After filtration, the filtrate was diluted with 50 ml H_2O . The MeOH- H_2O layer was then evaporated to dryness under a stream of N_2 and the residue taken up in 1 N H_2SO_4 ; insoluble material was removed by filtration. The filtrate was made basic with NH_4OH , heated to 70° for 0.5 hr and then stored overnight at 4°. The resulting ppt was filtered and dissolved in 2 ml MeOH (a drop of 2 M HOAc was added to solubilize completely). The individual glycoalkaloids were purified by prep. TLC (500 μm plates) using Böll's solvent mixture[3] as the mobile phase. The compounds were eluted from the Si with MeOH.

Aglycone characterization. The glycoalkaloid (2 mg) was

hydrolysed in methanolic HCl (5%) at 75° for 1.5 hr. After evaporation of the MeOH the residue was taken up in 1% NH_4OH and extracted with CHCl_3 . The CHCl_3 extract was analysed by TLC using MeOH- CHCl_3 (1:19) as the mobile phase and by GC (temp. programming mode 200-275° at 4°/min). The aglycones also were analysed by mass spectrometry (direct probe).

Carbohydrate analysis. The glycoalkaloids were permethylated using dimsyl sodium and MeI as previously described [2]. The unpurified permethylated glycoalkaloid was hydrolysed in 2 N trifluoroacetic acid (TFA) at 121° for 1.5 hr. The TFA was removed by evaporation in N_2 at 50°. The residue was dissolved in 1% NH_4OH , and insoluble material was removed by filtration. To the filtrate, 5 mg NaBH_4 was added and allowed to stand at room temp. for 1.5 hr. The soln was then neutralized with HOAc and concd under N_2 , the residue was taken up in MeOH and recond. The residue was dissolved in 200 μl Ac_2O , heated to 121° for 1.5 hr, cooled, neutralized with Na_2CO_3 and extracted with CHCl_3 . GC analysis was carried out on an ECNSS-M column; identities of the methylated alditol acetates were confirmed by GC/MS [4].

REFERENCES

1. Schreiber, K. (1968) in *The Alkaloids* (Manske, R. H. F., ed.) Vol. 10, p. 1. Academic Press, New York.
 2. Osman, S. F., Herb, S. F., Fitzpatrick, T. J. and Sinden, S. L. (1976) *Phytochemistry* **15**, 1065.
 3. Böll, P. M. (1962) *Acta. Chem. Scand.* **16**, 1819.
 4. Bjørndal, H., Hellergvist, C. G., Lindberg, B. and Svensson, S. (1970) *Angew. Chem. Int. Ed. Engl.* **9**, 610.
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