Phytochemistry, 1976, Vol. 15, pp. 1065–1067. Pergamon Press. Printed in England.

COMMERSONINE, A NEW GLYCOALKALOID FROM TWO *SOLANUM* SPECIES

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(*Revised received* 20 *November* 1975)

Key Word Index—*Solanum chacoense*; *S. commersonii*; Solanaceae; demissine; commersonine; glycoalkaloids.

Abstract—Selected plant introduction lines of *S. chacoense* and *S. commersonii* contain two major glycoalkaloids, demissine and a new compound called commersonine. In contrast, other plant introduction lines of *S. chacoense* contain only solanine and chaconine as the major glycoalkaloids. The isolation and characterization of the new glycoalkaloid is described.

INTRODUCTION

Wild species of *Solanum* have been valuable sources of pest resistance in developing new cultivars of the Irish potato, *Solanum tuberosum*. Tubers of *S. tuberosum* usually contain small quantities of steroid glycoalkaloids (solanine and chaconine are the two major glycoalkaloids present in *S. tuberosum*); however, some of the tuber-bearing, wild *Solanum* species used in potato breeding contain high concentrations of these compounds. The incorporation of these wild species in a breeding program may therefore produce tubers high in glycoalkaloid concentration, or introduce compounds other than solanine and chaconine thus creating a potential human health hazard [1–3].

Several surveys of the glycoalkaloid composition of tuber-bearing wild *Solanum* species have been undertaken [4–7] because of the possible relationship of these compounds to pest resistance [8] and because of the bitterness they impart to tubers and their potential toxicity [1,9]. We have examined plant introduction (P.I.) lines of the species *S. chacoense* and *S. commersonii* Dun. ex Poir. In previous studies, Schreiber [4,8] and Prokoshev [5] found only solanine and partial hydrolysis products in these species. In addition, Kuhn and Löw [10] found three ammonia-soluble glycoalkaloids, Leptine I, II, and III in the leaves of *S. chacoense*. In our investigations we have found a significant number of P.I. lines that did not contain solanine and chaconine but which contained two other major glycoalkaloids. In this communication we describe the identification of demissine and characterization of a new glycoalkaloid which we call commersonine from these particular P.I. lines of *S. chacoense* and *S. commersonii*.

RESULTS

Demissine and commersonine were isolated from leaves of *S. chacoense* by column chromatography and preparative TLC. Commersonine was obtained as a white crystalline solid, mp 230–232° (uncorrected), $[\alpha]_D^{25}$-17° (pyridine). The MW of permethyl commersonine was determined by MS to be 1229. Hydrolysis of commersonine with H_2SO_4, followed by neutralization with NH_4OH, yielded a precipitate which was identical to demissidine by GLC; TLC and MS, M^+ $m/e = 399$; mp (216°) and mmp (no depression) confirmed that demissidine is the aglycone of commersonine. The aqueous NH_4OH filtrate from the hydrolysis of commersonine was analyzed for sugars by GLC of the aldononitrile derivatives [11], glucose and galactose (3:1) were the only detectable sugars (this was confirmed by TLC of the underivatized sugars). The sugar sequence was determined by analysis of the mono-, di- and trisaccharides obtained from partial hydrolysis of commersonine.

Three hydrolysates besides demissidine were isolated by preparative TLC. The band with R_f 0.58, on hydrolysis, yielded demissidine (determined by R_f and MS) and galactose (determined by GLC of the aldononitrile derivative); the next lowest band, on hydrolysis, yielded galactose and glucose in a ratio of 1 : 1 and demissidine. The slowest moving band was shown to be composed of demissidine and glucose and galactose in a 2 : 1 ratio. These three compounds were shown to be mono-, di-, and trisaccharide derivatives of demissidine by the MW's obtained from the MS of the methylated derivatives. The results for the sugar sequence are summarized in Table 1.

The position of the glycosidic linkages were determined from the GC–MS of the partially methylated alditol acetates [12]. These derivatives were not used for determining the sugar ratios because they exhibit partial instability during GLC analysis leading to poor quantitative results. In Table 2 we have summarized these results. Partial breakdown of the alditol acetate during MS analysis was responsible, we believe, for producing extraneous fragment ions; however, characteristic ions for deducing the correct structure were present. In any event GLC R_t's are definitive when this information is combined with a knowledge of the sequence, i.e. at least one glucose is unsubstituted (terminal), and one glucose and one galactose must be at least monosubstituted. The identification of the partially methylated alditol acetates was confirmed by co-chromatography with known derivatives prepared from the hydrolysis of permethylated

Table 1. Sugar sequence in commersonine

R_f	Sugars	Ratio	*M$^+$	Identity
0.58	Gal		617	demissine-gal
0.42	Gal, Glu	1:1	821	demissine-gal-glu
0.28	Gal, Glu	1:2	1025	demissine-gal-(glu)$_2$

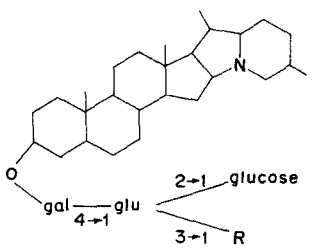
* Permethylated derivatives.

Table 2. Identification of glycosidic linkages

GLC R_t Reference	Observed	MS fragments (*m/e*)	Identification
1.0		117, 161, 205	2,3,4,6 tetramethyl-1,5 diacetyl glucose
2.42	2.40	117, 233	2,3,6 trimethyl-1,4,5 triacetyl galactose
4.02	4.00	161, 261	4,6 dimethyl 1,2,3,5 tetracetyl glucose

* Relative to tetramethyl diacetyl glucose.

demissine (2,3,6 trimethyl 1,4,5 triacetyl galactose, 3,6 dimethyl 1,2,4,5 tetracetyl glucose and 2,3,4,5 tetramethyl 1,5 diacetyl glucose). Commersonine therefore, is closely related to demissine, differing only in one sugar unit; a terminal glucose unit in commersonine (**1a**) replaces the terminal xylose in demissine (**1b**).



(**1a**) R = glucose
(**1b**) R = xylose

DISCUSSION

Solanine and chaconine are the only ammonia-precipitable glycoalkaloids that have been reported to be present in the species *S. chacoense* and *S. commersonii*. However, demissine alone [6] and in combination with solanine [5], has been reported in *S. horovitzii* Buk. which some taxonomists now include in *S. chacoense* in the broad sense [13]. Both species exhibit phenotypic variability in relation to glycoalkaloid composition because some collections of *S. chacoense* and *S. commersonii* have only solanine and chaconine, while we found collections of both species that contained demissine and commersonine but no solanine or chaconine.* We have found commersonine in combination with demissine in two different *solanum* species; therefore commersonine may be present in other tuber-bearing *Solanum* species particularly those that are known to have demissine as a major glycoalkaloid.

The particular tetrasaccharide combination found in commersonine has not been reported in any of the other glycoalkaloids of the *Solanum* group [8,10] but recent evidence we have obtained on the structure of another glycoalkaloid, as yet not fully characterized, indicates that the same carbohydrate unit is present. We have not established the configuration of the anomeric bonds; however, one might expect all β since D sugars have always been found to be β-linked in glycoalkaloids [15].

Although MS has been used in this study, mainly to determine MW's of the unhydrolyzed and partially hydrolyzed glycoalkaloid and to characterize partially methylated alditol acetates, examination of the spectra of permethylated commersonine and other permethylated glycoalkaloids indicates that this technique may be useful in determining the sugar sequence. We have observed a fragmentation pattern with commersonine and solanine analogous to that of a fragmentation reported by Schmid and Harborne for a permethylated kaempferol tetraglycoside [16]. They observed a fragment that results from glycosidic cleavage with concomitant methyl migration. This type of fragmentation is not generally observed with polysaccharides; however, it may be useful in structural characterization of glycoalkaloids.

*Schreiber describes the isolation of a tetraside from *S. horovitzii*, that he was unable to characterize, which may have been commersonine [14].

EXPERIMENTAL

MS were obtained on a double focusing instrument. GLC conditions for sugar derivatives and permethylated glycoalkaloids have ben described [11,12,17].

Glycoalkaloid isolation. Fresh leaves (200 g) of *S. chacoense* P.I.-217451, were extracted 2× with 3 l. $CHCl_3$–HOAc–MeOH (10:1:9). The combined extracts were filtered and evaporated almost to dryness *in vacuo*. To the syrupy residue 400 ml of 0.2 M aq. HOAc were added and this soln was extracted with 400 ml of $CHCl_3$ (3×). The aq. phase was concentrated to *ca* 100 ml, filtered, and the pH adjusted to 10.5 with conc. NH_4OH. After warming (70° for 20 min) and cooling (4° for 16 hr), the ppt was collected by centrifugation (30 min, 37000 *g*). Pellets were washed with 1% NH_4OH, dissolved in 0.2 M HOAc and reprecipitated (3×). After drying the glycoalkaloids were extracted from the pellets with 2 l. of boiling MeOH–H_2O (4:1), filtered, and the filtrate concentrated to about 100 ml. The precipitated glycoalkaloids were collected by filtration and dried to constant wt (yield, 470 mg). Essentially the same method was used for tubers of *S. commersonii*, P.I.-243405 except that only 10 g of tubers were available and all vols were scaled down accordingly. Individual glycoalkaloids were isolated from these mixtures by preparative TLC on precoated Si gel G (0.5 mm) plates: the developing solvent was MeOH–$CHCl_3$ (1/1) satd with 1%

NH_4OH; commersonine R_f 0.25 and demissine R_f 0.33 respectively. The compounds were eluted from the layers using the developing solvent.

Glycoalkaloid characterization. Complete and partial hydrolysis of the glycoalkaloids were carried out in 1 N H_2SO_4 with the partial hydrolysis being run at 80° and complete hydrolysis at 100°. Methylated glycoalkaloids were initially subjected to hydrolysis in 5% methanolic HCl for 2 hr at 95 (sealed tube), then concentrated and hydrolyzed to completion in 1 N H_2SO_4 at 100° for 2 hr. Dimsyl sodium was used in a modified methylation procedure [17] to prepare permethylated glycoalkaloids.

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