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Glycoalkaloids of *Solanum* Series *Megistacrolobum* and Related Potato Cultigens

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Key Word Index—*Solanum* Series *Megistacrolobum*; *Solanum* × *ajanhuiri*; Solanaceae; potato; Bolivia; glycoalkoloids; domestication.

Abstract—Glycoalkaloids were used as evidence of the affinities of nine taxa of *Solanum* Series *Megistacrolobum* and related potato cultigens from western Bolivia. *S. boliviense, S. sanctae-rosae* and *S. toralapanum* contain the commertetraose sugar moiety and appear to represent a relatively wild group within the Series. *S. megistacrolobum, S. sogarandinum* and *S. raphanifolium* show anomolous glycoalkaloid profiles that probably reflect hybridization associated with human disturbance. Primitive forms of the *S.* × *ajanhuiri* cultigen are indistinguishable chemically from conspecific weeds that were previously classified as *S. megistacrolobum.* Variation in total glycoalkaloid content within Series *Megistacrolobum* likely reflects direct selection by humans for reduced glycoalkaloid levels during the domestication process.

Introduction

Solanum megistacrolobum Bitt. is among the most frost-resistant potato species and is reputedly well adapted to arid conditions [1, 2]. The natural introgression of genes of *S. megistacrolobum* into the cultivated gene pool via the cultigen *S.* × *ajanhuiri* Juz. et Buk. has been important for extending the range of potato cultivation by Aymara-speaking farmers into the frigid and arid areas of western Bolivia. On the other hand populations of *S. megistacrolobum* have received genes from cultivated species through introgression; the nature of wild potatoes reflects human disturbance associated with the domestication process [3, 4]. *S. megistacrolobum,* in particular, is a highly variable species [1, 5]. In general, discontinuities within the Series *Megistacrolobum* are difficult to delineate and make taxonomic decisions problematic. Surveys of steroidal glycoalkaloid constituents of wild species of tuber-bearing *Solanum* have neglected Series *Megistacrolobum* [6–8]. Chemotaxonomic information was expected to given new insight into interspecific affinities within the Series *Megistacrolobum,* as well as the origins of the cultigen, *S.* × *ajanhuiri.*

The ready hybridization of *S. megistacrolobum* and the diploid cultigen *S. stenotomum* Juz. et Buk. indicates that *S. megistacrolobum* may have excellent potential in potato breeding. Assessment of glycoalkaloid content, in itself, is important for determining the suitability of wild species in breeding programs [9].

Results and Discussion

Structural relationships of aglycones and glycoalkaloids identified in this study are recorded in Figure 1. Glycoalkaloid analyses of *S. megistacrolobum* (Table 1) are consistent with the morphological variability typical of this species. Accessions obtained from the Potato Introduction Station, Sturgeon Bay, were characterized by tomatine (**12**), with some accessions also containing demissine (**6**) as either the major or minor constituent.

Accession PI320303 contained commersonine (**7**), **6** and trace amounts of **12**. It closely resembled PI458397, identified as *S. toralapanum* Card. et Hawkes, in both glycoalkaloid constituents and leaf morphology. Both collections were made in the southern part of the range of these species. Ochoa [10] has recently reduced *S. toralapanum* (referred to

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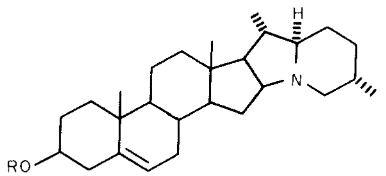
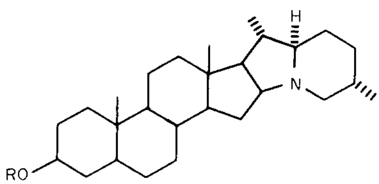
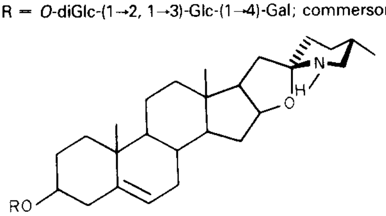


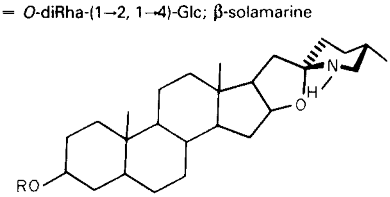
1 R = H; solanidine
2 R = *O*-Glc-(1→3)-[Rha-(1→2)]-Gal; α-solanine
3 R = *O*-diRha-(1→2, 1→4)-Glc; α-chaconine
4 R = *O*-diGlc-(1→2, 1→3)-Glc-(1→4)-Gal; dehydrocommersonine



5 R = H; demissidine
6 R = *O*-Xyl-(1→3)-[Glc(1→2)]-Glc-(1→4)-Gal; demissine
7 R = *O*-diGlc-(1→2, 1→3)-Glc-(1→4)-Gal; commersonine



8 R = H; tomatidenol
9 R = *O*-Glc-(1→3)-[Rha(1→2)]-Gal; α-solamarine
10 R = *O*-diRha-(1→2, 1→4)-Glc; β-solamarine



11 R = H; tomatidine
12 R = *O*-Xyl-(1→3)-[Glc(1→2)]-Glc-(1→4)-Gal; tomatine
13 R = *O*-diGlc-(1→2, 1→3)-Glc-(1→4)-Gal; sisunine

FIG. 1. STRUCTURAL RELATIONSHIPS OF GLYCOALKALOIDS AND AGLYCONES IDENTIFIED IN THIS STUDY.

here as taxon *toralapanum*) to a synonym of *S. megistacrolobum*. Two field collections of taxon *toralapanum* from the Department of La Paz, Bolivia, were, like the more southern accessions, characterized by the commertetraose [*O*-diglc-(1→2, 1→3)-glc-(1→4)-gal] sugar moiety (**14**). However, the major glycoalkaloids in these plants were dehydrocommersonine (**4**) and **6**.

Glycoalkaloid patterns in the Series *Megistacrolobum* (Table 2) are closer across species lines than within *S. megistacrolobum* (*sensu lato*) alone (Table 1) and show distinct geographical patterns. *S. boliviense* Dun. (PI310974 and PI310975) has a glycoalkaloid profile very similar to PI458397 (taxon *toralapanum*). *S. sanctae-rosae* Hawkes (PI205397 and PI218221) from Argentina is similar to PI320303 from Argentina, as well as having affinity to its Bolivian relatives, *S. boliviense* and taxon *toralapanum*.

Peruvian species assigned to Series *Megistacrolobum* stand out chemotaxonomically. *S. raphanifolium* (PI310951 and PI310999) from the Department of Cuzco contained α-solanine (**2**) and α-chaconine (**3**) exclusively. These glycoalkaloids are characteristic of other series in the genus including the cultigen containing Series *Tuberosum*; *S. raphanifolium* may be misplaced in Series *Megistacrolobum* or may show introgression from Series *Tuberosum* via the cultivated gene pool.

S. sogarandinum (PI230510) from north-central Peru was characterized by the α- (**9**) and β- (**10**) solamarines. This unique glycoalkaloid pattern of *S. sogarandinum* resembles the trace glycoalkaloids that typify populations of wild potato from north-west Bolivia (Table 2: weed *S.* × *ajanhuiri*). *S. sogarandinum* shows clear morphological affinities to these populations [5] and may be simply an isolate from them. Dispersal of *S. sogarandinum* to northern Peru may reflect the association of *S. sogarandinum* and related Bolivian populations of this taxon with domesticated potatoes and their human cultivators. The Bolivian populations, while previously classified as *S. megistacrolobum* are, in fact, conspecific weeds of the cultigen, *S.* × *ajanhuiri* [11]. These weeds are indistinguishable taxonomically [11] and chemically (Tables 1 and 2) from *yari* cultigens of *S.* × *ajanhuiri* that are reputedly F1 hybrids between *S. megistacrolobum* (2*n*) and the diploid cultigen *S. stenotonum* [2, 12]. *Ajawiri* clones have been demonstrated to be backcrosses with *S. stenotonum* [12]. Clones of *ajawiri* and *S. stenotonum* studied here are identical to those studied previously; both contain (**2**) and (**3**) [7] (Table 3).

Total glycoalkaloids (TGA) varied consider-

TABLE 1. GLYCOALKALOIDS OF *SOLANUM MEGISTACROLOBUM SENSU LATO,* INCLUDING TAXON *TORALAPANUM* AND WEEDS OF *S.* × *AJANHUIRI*

Taxon and accession	Collection location	TGA mg/100 g	Aglycones as % of total 1	5	8	11	Glycoalkaloids
S. megistacrolobum							
PI210034*	Pot-BOL						**12**
PI265578*	Tar-BOL						**12**
PI265873†	Pot-BOL						**12**
PI265874‡	Pot-BOL	2.4					
PI275149‡	ARG	1.2					
PI283133*	ARG						**12**
PI4583461‡	ARG	26.0					**12**
PI458347§	ARG						**12**
PI458350§	ARG						**12**
PIOKA4520*	ARG		0	0	0	100	**12**
PI275148†	ARG						**6, 12**
PIOKA6758*	ARG		0	22	0	78	**12, 6**
PI233124†‖	ARG						6 TLC spots
PI320303†‖	Vic-ARG						**7, 6, 12**
Taxon *toralapanum*							
P14583975	Tar-BOL	57	0	100	0	0	**7, 6**
Johns 83-92	Lpz-BOL Huaynacota, Prov. Inquisivi	125	75	22	0	0	**4, 6**
Johns 83-102	Lpz-BOL Palca, Prov. Murillo	88	29	71	0	0	**6, 4**
weed *S.* × *ajanhuiri*							
7 collections	Lpz-BOL Prov. Pacajes and Ingavi	<4.0					**9, 10**¶
Johns 83-38	Lpz-BOL Ulloma, Prov. Pacajes						**7, 12**
Johns 83-87	Lpz-BOL General Campero, Prov. Pacajes	12.0					

‡Tubers grown at Matthaei Botanical Gardens.
§Tubers from Potato Introduction Station.
*Vegetative material grown at Mattaei Botanical Gardens.
†Rhizomes grown at Mattaei Botanical Gardens.
‖Leaf morphology similar to taxon *toralapanum*.
¶Best guess on basis of co-chromatography with other standards.
Departmental codes: Pot, Potosi; Tar, Tarija; Vic, San Victoria; Lpz, La Paz. Country codes: BOL, Bolivia; ARG, Argentina.

ably within the material studied. Differences in TGA between field collected and greenhouse-grown material and between large and small tubers make comparisons using TGA content difficult. However, it is apparent that wild species have higher levels of TGA than cultigens and conspecific weeds.

We have recently described the glycoalkaloids of the cultivated clones, *sisu* [13]. *Sisu,* designated taxonomically as *S. acaule* × *ajanhuiri,* contains **7** and the novel hybrid glycoalkaloid, sisunine (**13**). The commertetraose moiety (**14**) in this cultigen supports its derivation from Series *megistacrolobum* ancestors. TGA content of *sisu* clones reported here reflect the intermediate nature of *sisu* between low TGA containing *S.* × *ajanhuiri* cultigens and high TGA containing *S. acaule* Bitt. (Series *Acaule*) [7].

The interactions of Series *Megistacrolobum* and cultivated potatoes is most apparent in the highly variable *S. megistacrolobum* and *S.* ×

TABLE 2. GLYCOALKALOID CHARACTERIZATION OF ACCESSIONS OF SERIES *MEGISTACROLOBUM* OBTAINED FROM POTATO INTRODUCTION STATION, STURGEON BAY, WISCONSIN

Species and accession	Collection location	TGA mg/100 g	Aglycones as % of total 1	5	8	11	Glycoalkaloids
S. boliviense							
PI310974	BOL	72	11	89	0	0	**7, 6***
PI310975	BOL	61	10	90	0	0	**7, 6***
S. raphanifolium							
PI310951	Cuz-PER	37	100	0	0	0	**3, 2***
PI310999	PER	28	100	0	0	0	**3, 2***
S. sanctae-rosae							
PI205397	ARG	20					**6, 7, 12***
PI218221	Tac-ARG	25	8	75	0	17	**6, 7, 12***
S. sogarandinum							
PI230510	Lib-PER	28	0	0	100	0	**9, 10**

*Traces of glycoalkaloids with aglycone **2**.
Country codes: BOL. Bolivia; PER, Peru; ARG, Argentina. Department Codes: Cuz, Cuzco; Tac, Tacuman; Lib, Libertad.

TABLE 3. GLYCOALKALOIDS OF CULTIGENS OF *SOLANUM* × *AJANHUIRI* AND *S. STENOTONUM*

Species and clone identity	TGA mg/100 g	Aglycones as % of total 1	5	8	11	Glycoalkaloids
S. × *ajanhuiri*						
ajawiri (two clones)	10.5–13.0	100	0	0	0	**2, 3**
yari (six collections of three clones: Y1, Y2, Y5 [2])	<4.3					**9, 10***
S. stenotomum (three clones)	11.3–20.8	100	0	0	0	**2, 3**
S. acaule X *ajanhuiri sisu* (three clones)	12.0–24.8	0	55	0	45	**7, 13**

*Best guess on the basis of co-chromatography with other standards.
All analyses were made on tubers collected in the Departments of La Paz and Oruro, Bolivia.

ajanhuiri. S. sogarandinum and *S. raphanifolium*, as well, are commonly found as weeds in crop potato fields [5]. All of these species are apparently involved in reticulate hybridization among wild species and between wild and cultivated species. Human influence takes the form of habitat disturbance and plant dispersal. As well, glycoalkaloid content in Series *Megistacrolobum* likely reflects direct selection by humans resulting in reduction in TGA levels during the domestication process. Taxon *toralapanum, S. boliviense* and *S. sanctae-rosae* appear, on the basis of 14, to represent a cohesive unit within the Series. The high TGA levels in taxon *toralapanum* and *S. boliviense* suggests that they are relatively wild. The characteristic of generally simple leaves shared by these two taxa [1] may represent a primitive condition of the Series *Megistacrolobum* before the onset of domestication.

Experimental

Material designated by PI accession numbers was obtained from the Potato Introduction Station, Sturgeon Bay, Wisconsin, as tubers or seeds. Seeds were grown at the Matthaei Botanical Gardens, University of Michigan, to obtain leaf and rhizome material. Material was freeze-dried and stored at −10°. Field collections of *S. megistacrolobum, S.* × *ajanhuiri, S. acaule* × *ajanhuiri* and *S. stenotomum* were made in Bolivia. Vouchers are deposited in the University of Michigan Herbarium. Tubers were preserved in 95% EtOH at room temperature.

All samples were extracted exhaustively in 5% methanolic HOAc. Ethanolic extracts were concd to dryness and tubers were re-extracted with acidic MeOH. Extracts were concd to dryness, taken up in 0.1 N H_2SO_4 and precipitated with concd NH_4OH.

Individual glycoalkaloids were characterized by TLC on silica gel using the lower phase of MeOH–$CHCl_3$ (1:1) saturated with 0.5 parts of 1% NH_4OH. Comparisons were made with standard compounds. Aglycones of total precipitates were obtained as described previously [14]. Aglycones were characterized by TLC on silica gel using $CHCl_3$–MeOH (97:3) and by GLC as described previously [15]. Ambiguities between pairs of saturated and unsaturated aglycones were resolved by the differential hydrolysis method of Osman and Sinden [14]. Where possible aglycones were quantified using a Hewlett–Packard 3390A Integrator.

Where identities of glycoalkaloids remained ambiguous compounds were purified by preparative TLC. Aglycones were identified using the methods described above or by GC/Ms using a 20m OV-101 capillary column. The column was temperature programmed from 150 to 250° at 4° per min. Total glycoalkaloids were determined using a titration method [16].

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