# ON THE OCCURRENCE OF TULIPOSIDES IN THE LILIIFLORAE

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Key Word Index—Alstroemeriaceae; Liliaceae; Relationships among Liliiflorae; allergenic plant constituents; post-inhibitins; tuliposides; chemotaxonomy.

Abstract—Approximately 200 samples of liliiflorous plants were investigated for the presence of tuliposides. Appreciable amounts of tuliposide A were detected in all species of *Erythronium*, *Tulipa*, *Gagea*, *Bomarea* and *Alstroemeria*. Large amounts of tuliposide B seem to be restricted to *Erythronium* and *Tulipa*. The occurrence of identical post-inhibitins in *Tulipa* and allied taxa and in *Alstroemeria* and allied taxa is interpreted as indicating a close relationship between Lilioideae and Alstroemeriaceae. At the same time the allergenic potentialities of all taxa of *Alstroemeria* are stressed.

#### INTRODUCTION

Tuliposide-A, the ester of glucose with  $\alpha$ -methylene- $\gamma$ -hydroxybutyric acid, occurs in large amounts in tulips. It is accompanied by tuliposide-B, the  $\beta$ -hydroxyderivative of the former [1]. The hydroxy-acids released by enzymic or spontaneous hydrolysis of tuliposides lactonize easily to the corresponding  $\alpha$ -methylenebutyrolactones under non-alkaline conditions [1, 2]. In recent times much attention has been paid to these tulip constituents by phytopathologists [3] and dermatologists [4] because they have strong fungitoxic and allergenic properties. For dermatologists, tuliposide-A and its reaction products seem much

more important than tuliposide-B, because the allergic skin disease caused by tulips seems to be caused by  $\alpha$ -methylene- $\gamma$ -butyrolactone derived from tuliposide-A; in this respect the  $\beta$ -hydroxyderivative seems to be inert [5]. Tuliposide-A is present in considerable amounts in bulbs, stems, leaves and flowers of cultivated tulips.

In a recent publication, we reported results of a preliminary screening of liliaceous and related plants for tuliposides [5]. We stressed the need for more precise information about the distribution of tuliposide-A, the precursor of the allergenic lactone, because many liliiflorous taxa are cultivated on a commercial scale as ornamental plants. We also draw attention to the possibility that accumulation of tuliposides may represent a character of interest to plant systematics. The preliminary nature of the results and conclusions was stressed because the number of taxa investigated was small.

Meanwhile we have extended our coverage of taxa and considerably improved our analytical procedures. The present paper summarizes the results of a more elaborate study of the distribu-

Arie Slob was the victim of a tragic accident in May 1974. This posthumous publication pays honor to an enthusiastic scientist and honest man, who is no longer with us. The final version of this article was drafted by Prof. R. Hegnauer (Laboratory for Experimental Plant Systematics, 5e Binnenvestgracht 8, Leiden, The Netherlands), to whom request for reprints should be addressed, Mrs. B. M. E. von Blombergv.d.Flier (Netherlands Institute for Preventive Medicine, TNO, Leiden) and Prof. Dr. H. L. Booy (Laboratory for Medical Chemistry, Leiden).

<sup>†</sup> Technical assistance.

<sup>‡</sup> Cultivation and documentation of plants.

tion of tuliposides and includes some revisions of our previous findings.

#### RESULTS

Almost all plants available to us were investigated during the flowering stage. Each sample

was divided in flowers, stems, leaves and underground parts (i.e. roots, rhizomes, bulbs). In each instance presence or absence of tuliposides was investigated by three analytical procedures, PC. TLC and GLC. In plant parts apparently containing tuliposides, the amounts present were deter-

Table 1. Taxa investigated for the presence of tuliposides, arranged according to the classification of Huber [6]

Main groups of		
Liliiflorae	Family	Taxa investigated*
Dioscoreoid	Dioscoreaceae	Dioscorea cf. hispida 22638, D. cf. quaternata 22706,
Liliiflorae: Dioscoreales†	Trilliaceae†	D. cf. villosa 22640, D, sp. 22639; Tamus communis 23068 Medeola virginiana 23314; Paris quadrifolia 23016;
Roxburghiales  Asparagoid	Timaceae	Scoliopus bigelovii 22665; Trillium erectum 23414,
		T. arandiflorum 23413, T. luteum 23414, T. sessile,
		T. stylosum 23411, T. undulatum
	Ruscaceae†	Ruscus aculeatus 22701
	Convallariaceae†	Convallaria majalis 22633; Majanthemum bifolium 22693,
		23061; Polygonatum sp. 20728, P. multiflorum 23063
		P. odoratum 20368, P. verticillatum 23019; Smilacina
	Asparagaceae†	racemosa; Streptopus amplexifolius 23047 Asparagus sp. 8370, A. sp. 8373
	Tecophilaeaceae†	Asparagus sp. 8370, A. sp. 8373 Tecophilaea cyanocrocus cv. violacea 23419,
	recopinacaccact	T. cyanocrocus cv. leichtlinii 20491
	Anthericaceae†	Anthericum liliago 20702, 23024, A. ramosum 23119;
		Paradisia liliastrum
Liliiflorae: Asparagales	Asphodelaceae†	Asphodeline liburnica 21434, A. lutea, 22627;
		Asphodelus microcarpus 20731; Bulbine annua 21796;
		Haworthia batesiana 22651, H. planifolia cv. variegata
		22652; Kniphofia × pfitzeri
	Agavaceae	Hosta cf. elata 22705, H. cf. fortunei 22697, H. cf. glauca 20713
	Hemerocallidaceae	Hemerocallis dumortieri, H. lilio-asphodelus 22702,
	Allingana	H. cv. 22696, 22698
	Alliaceae	Allium coeruleum (= A. azureum) 22704, A. cepa 23421 A. karataviense 22614, A. sativum 23576, A. ursinum
		22615; Brodiaea cf. hyacynthina 22628, B. cf.
		peduncularis 22629, 22630, B. terrestris 23574,
		B. sp. 23573; Ipheion uniflorum 22653; Nothoscordum
		inodorum (= N. fragrans) 22662
	Hyacinthaceae†	Lachenalia aloides 23392; Muscari armeniacum 23420.
		M. sp. 22658; Ornithogalum balansae 22663. O. cf.
		longibracteatum 22721, O. sp. 22664; Veltheimia
		viridiflora (= $V$ . capensis) 23429
	Amaryllidaceae	Galanthus elwesii 22645, G. ikariae 22646,
		G. nivalis 22647; Leucojum aestivum 22657,
		L. autumnale 22313, L. vernum 23386; Narcissus bulbocodium 22659, N. Jonquilla 22660, N. nanus
		(=N. lobularis), N. asturiensis (=N. minimus)
		22661; Pancratium maritimum; Sternbergia colchiciflora
		(= S. clusiana) 22666, S. lutea 22667
	Colchicaceae†	Bulbocodium vernum 23416, Colchicum autumnale 22631
		C. hyzantinum 22869, C. speciosum 22632; Gloriosa
Colchicoid		superba 22650, G. virescens cv. Rothschildiana 22648,
		cv. 22649; Uvularia grandiflora 22679, U. perfoliata
Liliiflorae:	Iridaceae	Crocus ancyrensis 22634, C. medius 22870, C. speciosus
		23384, C. susianus 22635, C. tomasianus 22636;
		Gladiolus byzantinus 22703, G. segetum 23575;
		Iris bucharica, I. florentina 22654, I. graminea
		22655, I. pseudacorus 22700, I. reticulata 23415, I. sibirica 22656, I. versicolor 23430; Tigridia

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