TAXONOMIC ASPECTS OF THE IRIDOID GLUCOSIDES OCCURRING IN THE GENUS *PLANTAGO* L.

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ABSTRACT

The results of studies of the iridoid glucosides distribution within the genus *Plantago* indicated the significance of catalpol, plantarenalloside and bartsioside for the taxonomy of this taxon.

KEY WORDS: chemotaxonomy, catalpol, plantarenalloside, bartsioside, *Plantaginaceae*.

INTRODUCTION

Numerous authors pay considerable attention to the importance of iridoid glycosides in the plant taxonomy (see: Andrzejewska-Golec 1995). Over twenty iridoid glycosides have been detected so far in various species of the genus *Plantago* L., Figs 1-7 (Endo, Taguchi & Yosioka, 1981; Oshio & Inouye, 1982; Debrauwer et al. 1989; Saadi, Nikolov and Handjieva 1989; Saadi et al. 1990, 1991; Afifi, Salama & Matooq 1990; Handjieva, Saadi & Evstatieva, 1991; Handjieva et al. 1991; Andrzejewska-Golec et al. 1993; Handjieva, Taskova & Popov, 1993; Damtoft, Falkesgaard & Jensen, 1994). The investigation of iridoids in the genus *Plantago* L., concerning their significance in the taxonomy of this taxon, was carried out by Kuzmanov et al. (1984), Andrzejewska-Golec and Świątek (1984), Andrzejewska-Golec (1992), Andrzejewska-Golec et al. (1993). The conclusion from the studies by Kuzmanov et al. (1984) are interesting, but not fully convincing because of too small number of the investigated taxa. On this basis of results obtained from the investigation of two species (*Plantago arenaria* Waldst. et Kit. and *P. afra* L.) belonging to the subgenus *Psyllium* (Miller) Harms, these authors regarded plantarenalloside as a component characteristic of the taxa.

The screening methods in study of the iridoid glycosides in the plants are based on paper and thin-layer chromatography (PC, TLC) (Andrzejewska-Golec & Świątek 1984; Nicoletti 1989). In isolation of iridoids from the plants the methods of column chromatography (CC), counter-current distribution (CCD), droplet counter current chromatography (DCCD), high performance liquid chromatography (HPLC) are used (Nicoletti 1989; Andrzejewska-Golec et al. 1993; Long et al. 1995). Elucidation of structure of the isolated iridoid glyco-

sides is carried out spectroscopical methods (Nicoletti 1989; Boros & Stermitz 1990; Bianco 1994).

IRIDIDS SIGNIFICANT FOR THE TAXONOMY OF THE GENUS *PLANTAGO*

From chemotaxonomical point of view three compounds seem to be the most significant ones for the taxonomy of the genus *Plantago*: catalpol, plantarenalloside and bartsioside (Tabl. 1).

Catalpol

So far the incidence of catalpol (Fig. 2, Tab. 1) in the taxa of four sections of subgenus *Plantago* was been reported (Andrzejewska-Golec & Świątek, 1984; Handjieva, Saadi & Evstatieva 1991). It is a component of almost all the examined representatives of sectio *Arnoglossum* Decne and *Oreades* Decne as well as of the only representative of the monotypical sectio *Bauphula* Decne (Tab. 2). Damtoft et al. (1994) isolated it also from the species *P. hookeriana* Fisch. et Mey. of the sectio *Leucopsyllium* Decne. The remaining species of this sectio has not probably been investigated yet for the presence iridoid glycosides. Catalpol is also found in *Littorella uniflora*, family *Plantaginaceae* (Jensen-pers. comm. -acc. Rahn 1996; Andrzejewska-Golec unpublished).

The presence of catalpol has been reported in over 30 genera of the *Scrophulariaceae* family (Kooiman 1970; Świątek 1973; Degot et al. 1983; Roby & Stermitz 1986; Yahara et al. 1986) which is often regarded as closely allied to the *Plantaginaceae* (Hegnauer 1969; Takhtadzhjan 1987; Ehrendorfer 1991). It also occurs in the other families belonging to the order *Scrophulariales*, as well as orders *Gentianales* and *La-*

TABLE 1. Distribution of some iridoid glucosides in the sections of the genus *Plantago* L.

Subgenus*	Section*	Catalpol	Plantarenaloside	Bartsioside
<i>Euplantago</i> Pilger (= <i>Plantago</i>)	1. <i>Polyneuron</i> Decne	–	–	–
	2. <i>Micropsyllium</i> Decne			
	3. <i>Palaeopsyllium</i> Pilger	–	–	–
	4. <i>Holopsyllium</i> Pilger			
	5. <i>Oliganthos</i> Barn.			
	6. <i>Microcalyx</i> Pilger			
	7. <i>Coronopus</i> DC.	–	–	–
	8. <i>Oreophytum</i> Decne			
	9. <i>Novorbis</i> Decne	–	–	–
	10. <i>Mesembrynia</i> Decne	–	–	–
	11. <i>Lamprosanthia</i> Decne	–	–	–
	12. <i>Eremopsyllium</i> Pilger			
	13. <i>Oreades</i> Decne**	+	–	–
	14. <i>Gentianoides</i> Pilger			
	15. <i>Bauphula</i> Decne **	+	–	–
	16. <i>Arnoglossum</i> Decne **	+	–	–
	17. <i>Leucopsyllium</i> Decne **	+	–	–
	18. <i>Hymenopsyllium</i> Pilger			
<i>Psyllium</i> (Juss.) Harms	19. <i>Psyllium</i> (Juss.) Barn. ***	–	+	+

* according to Pilger (1937)
** see also Table 2.
*** see also Table 3

TABLE 2. Distribution of catalpol in the species of the genus *Plantago* L.

Section	Species *, subspecies, varietas	Catalpol
<i>Arnoglossum</i> Decne (= <i>Lanceifolia</i> Barn.)	<i>Plantago lanceolata</i> L.	+
	<i>P. lanceolata</i> L. var. <i>lanuginosa</i>	+
	<i>P. leiopetala</i> Lowe	+
	<i>P. altissima</i> L.	+
	<i>P. lacustris</i> Maire	
	<i>P. argentea</i> Chaix	+
	<i>P. lagopus</i> L.	+
	<i>P. lagopus</i> var. <i>lusitanica</i> (Willd.) Ball	+
<i>Oreades</i> Decne (= <i>Montana</i> Barn.)	<i>P. montana</i> Lam. (= <i>P. atrata</i> Hoppe)	+
	<i>P. monosperma</i> Pourr.	+
	<i>P. atrata</i> subsp. <i>fuscescens</i> (Jordan) Pilger (= <i>P. fuscescens</i> Jordan)	+
<i>Bauphula</i> Decne	<i>P. amplexicaulis</i> Cav.	+
<i>Leucopsyllium</i> Decne **	<i>P. hookeriana</i> Fisch. et Mey.	+

* according to Pilger (1937)
** Pilger described 65 species of this section

miales (Wieffering 1966; Kooiman 1972; Chaudhuri 1980; Bianco et al. 1984, 1986; Jensen et al. 1988). Takhtadzhjan (1987) considers these orders related.

Plantarenaloside

According to our studies (Andrzejewska-Golec & Świątek, 1984) plantarenaloside (Fig. 7, Tab. 1) is absent in the taxa of subg. *Plantago*. It cannot however be considered (as suggested by Kuzmanov et al. 1984) as the iridoid fully separa-

ting the subgenera *Plantago* and *Psyllium* as it does not occur in the Canarian species: *P. arborescens* Poirlet, *P. webbii* Barn. of the subgenus *Psyllium*, Tab. 3 (Andrzejewska-Golec 1992). Plantarenaloside has been detected so far in c. twenty species belonging to the families: *Scrophulariaceae*, *Bignoniaceae*, *Verbenaceae* (see: Andrzejewska-Golec 1995). The three above mentioned families, as well as the *Plantaginaceae* family have been classified as belonging to the superorder *Lamiiflorae* (Dahlgren 1980) or *Lamianae* (Ehrendorfer 1991).

Figs 1-7. Iridoids have been isolated from the taxa of the genus *Plantago* L. Glu = glucose, Gent = gentiobiose.

aucubin:

R = Glu, R¹ = H, R² = H, R³ = β-OH, R⁴ = H

6-epi-aucubin:

R = Glu, R¹ = H, R² = H, R³ = α-OH, R⁴ = H

6'-O-β-glucosylaucubin:

R = Gent, R¹ = H, R² = H, R³ = β-OH, R⁴ = H

bartsioside:

R = Glu, R¹ = H, R² = H, R³ = H, R⁴ = H

melampyroside:

R = Glu, R¹ = H, R² = H, R³ = β-OH, R⁴ = benzoyl

melittoside:

R = Glu, R¹ = H, R² = OGlu, R³ = β-OH, R⁴ = H

monomelittoside:

R = Glu, R¹ = H, R² = OH, R³ = β-OH, R⁴ = H

10-acetylmonomelittoside:

R = Glu, R¹ = COOH, R² = OH, R³ = β-OH, R⁴ = H

geniposidic acid:

R = Glu, R¹ = COOH, R² = H, R³ = H, R⁴ = H

methyl ester of the desacetylasperulosidic acid:

R = Glu, R¹ = COOCH₃, R² = H, R³ = α-OH, R⁴ = H

Fig. 1. Aucubin and its derivatives.

catalpol: R = H

10-benzoylcatalpol: R = benzoyl

globularin: R = cinnamoyl

Fig. 2. Catalpol and its derivatives.

Fig. 3. 3, 4-dihydroaucubin.

Fig. 4. Asperuloside.

Fig. 5. Ixoroside.

majoroside: R = CH₃, R¹ = β - OH, R² = H

10-hydroxymajoroside: R = CH₃, R¹ = β - OH, R² = OH

hookerioside: R = Glu, R¹ = H, R² = COOCH₃

Fig. 6. Majoroside and its derivatives.

plantarenalioside: R = CHO, R¹ = OH, R² = H
 8-epi-loganic acid: R = COOH, R¹ = H, R² = β-OH

Fig. 7. Plantarenalioside and 8-epi-loganic acid.

Bartsioside

The presence of bartsioside (Fig. 1, Tab. 1, 3) is characteristic of the taxa of the subgenus *Psyllium* (Andrzejewska-Golec et al. 1993). Bartsioside has been reported also in some species of the *Scrophulariaceae* family (see: Andrzejewska-Golec 1995).

DISCUSSION

A marked biochemical distinctiveness of the taxon *Psyllium* (plantarenalioside and bartsioside) should be emphasized and may be treated as a distinct genus (Soják 1972; Holub 1973; Dietrich 1980). It is not, however, a biochemically homogenous taxon: plantarenalioside is present only in some of its species (Andrzejewska-Golec 1992).

The presence of catalpol in the taxa of the sections: *Oreades*, *Bauphula* and *Arnoglossum* indicates that these are biochemically related. They are also regarded as morphologically related (Pilger 1937). The old concept of Rahn (1978) to

include these sections in the subgenus *Psyllium* has not been accepted. Recently this author (Rahn 1996) has created a new subgenus *Albicans* including the sections: *Arnoglossum*, *Oreades*, *Bauphula*, *Leucopsyllium* and *Hymenopsyllium*.

The presence of catalpol, plantarenalioside and bartsioside in the species of the *Plantaginaceae* family supports the view that this family is biochemically related to the *Scrophulariaceae* family.

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TABLE 3. Distribution of plantarenalioside and bartsioside in the species of the subgenus *Psyllium* (Juss.) Harms.

Series*	Species**, varietas	Plantarenalioside	Bartsioside
<i>Squarrosae</i>	<i>Plantago squarrosa</i> Murray	+	+
<i>Arenariae</i>	<i>P. phaeostoma</i> Boiss. et Heldr.	+	+
	<i>P. arenaria</i> Waldst. et Kit.	+	+
	<i>P. exigua</i> Murray	+	+
	<i>P. afra</i> L.	+	+
<i>Sempervirens</i>	<i>P. sempervirens</i> Crantz (= <i>P. cynops</i> L.)	+	+
<i>Arborescens</i>	<i>P. euphratica</i> Decne ex Barn.	—	+
	<i>P. webbii</i> Barn.	—	+
	<i>P. sinaica</i> Barn.	—	+
	<i>P. famarae</i> Svent.	—	+
	<i>P. mauritanica</i> Boiss. et Reut.	—	+
	<i>P. arborescens</i> Poiret	—	+
	<i>P. arborescens</i> Poiret var. <i>maderensis</i> (Decne) Pilger	—	+

* according to Andrzejewska-Golec (1992)

** according to Pilger (1937)

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ZANACZENIE GLUKOZYDÓW IRYDROIDOWYCH W TAKSONOMII RODZAJU *PLANTAGO* L.

STRESZCZENIE

Wyniki badań rozpowszechnienia glikozydów irydoidowych w przedstawicielach rodzaju babka – *Plantago* wskazują, że dla chemotaksonomii tego rodzaju znaczenie mają przede wszystkim: katalpol, plantarenalozyd i bartsiozyd.

SŁOWA KLUCZOWE: chemotaksonomia, katalpol, plantarenalozyd, bartsiozyd, Babkowate – *Plantaginaceae*.