IRIDOID GLUCOSIDES IN *LITTORELLA UNIFLORA* (L.) ASCHERSON

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ABSTRACT

In *Littorella uniflora* two iridoid glucosides already known from the Plantaginaceae family are present: aucuboside and catalpol. The present and an earlier study of sugars and sucrose alcohols indicate a biochemical relationships of *Littorella* to *Plantago*.

KEY WORDS: *Littorella uniflora*, aucuboside, catalpol.

INTRODUCTION

The family Plantaginaceae is usually divided into 3 genera: *Plantago* L., *Bougueria* Decne and *Littorella* Berg. The genus *Plantago* is usually divided into two subgenera: *Plantago* with many sections and *Psyllium* with one section. Rahn (1996) proposed including the taxon *Littorella* – as subgenus *Littorella* (P.J. Bergius) Rahn – into the genus *Plantago*. According to the author, the main difference between the taxa of the genus *Plantago* sensu Pilger and *Littorella* Berg. is the kind of fruit: in *Plantago* – a pyxis, in *Littorella* – a nut – probably a result of adaptation for endozoic dispersal.

Among the three closely related species of the genus *Littorella* described so far only *Littorella uniflora* (L.) Ascherson is a European species. *L. uniflora* grows in the shallow littoral zone of oligotrophic and mesotrophic lakes (submerged and emerged specimens). It is mentioned in The Polish Red Book of Plants as vulnerable because of antropogenous activities (Szmeja 1993).

In the semen of *Littorella uniflora* the same sugars (planteose and sacharose) are present as in the semen of representatives of the genus *Plantago* and the same sucrose alcohol (sorbitol) in its leaves, just as in the leaves of the taxa of the genus *Plantago* (Bourdu et al. 1963; Wallaart 1981).

An iridoid glucoside – aucubin (aucuboside) is commonly occurring in representatives of the subgenus *Plantago*. The presence of an epoxide of aucuboside – catalpol is limited to a few sections of the subgenus *Plantago*: *Arnoglossum* Decne, *Oreades* Decne, *Bauphula* Decne and *Leucopsyllium* Decne (Andrzejewska-Golec 1997; Saadi et al. 1989). Whereas the iridoids: bartsioside and plantarenalosite are characteristic of subgenus *Psyllium* (Andrzejewska-Golec 1992; Andrzejewska-Golec et al. 1993). There have been no publications about iridoids of *Littorella* (only pers. comm.: Hegnauer 1969, Jensen – acc. Rahn 1996).

MATERIAL AND METHODS

The emerged specimens of *Littorella uniflora* were obtained from the shore of lobelia lake – Jeleń near Bytów (Pomera-

nia, Poland) in August 1994. The identity of this species was confirmed by checking with Chater and Cartier (1976) and Tacik (1967). 42 g of aerial parts of flowering and fruiting plants were stabilized and purified as in an earlier paper (Andrzejewska-Golec et al. 1993). Partially purified aq. solution was chromatographed over polyamide CC eluted with water. The fractions were checked for iridoids according to Trim & Hill and by TLC with Godin reagent. Next the iridoid fraction was subjected to silica gel CC using methylene chloride-methanol 8:2 (v/v) as solvent. The fractions were monitored by PC and TLC. Three fractions: α (compound 1), β (compound 1 and 2) and γ (compound 3 and 4) were obtained. From fraction α compound 1 (0.5 g) in crystalline state was obtained, tt. 175-180° (El-Naggar and Beal 1980: 180-182°). Compound 1 and compound 2 were separated from fraction β by preparative PC. Compounds 3 and 4 are present in species *Littorella uniflora* probably in small quantities. They were not isolated.

RESULTS AND DISCUSSION

On the basis of PC, TLC and HPLC study compound 1 was identified as aucuboside (Figs 1, 3-1), compound 2 – as catalpol (Figs 2, 3-2). These two iridoid glucosides are known in taxa of the genus *Plantago*. Catalpol and aucubin (the biosynthetic precursor to catalpol) coexist for example in the medicinal taxon – *Plantago lanceolata* L. These iridoids are biologically active compounds of the well-known drug – *Plantagininis lanceolatae folium*. After Bowers and Stamp (1992) the iridoid glycosides are the major components of plantain defensive chemistry. Catalpol and aucubin are toxic or deterrent to the majority of nonadapted insects (Bowers and Stamp 1992).

In *L. uniflora* iridoids characteristic of subgenus *Psyllium*: bartsioside and plantarenalosite are absent.

The present study of iridoids and an earlier study of sugars and sucrose alcohols indicated a biochemical relation of taxa *Littorella* to genus *Plantago*. Also my earlier anatomical investigations of hairs indicate the relationship of these taxa (Andrzejewska-Golec 1998).

Figs 1, 2. HPLC analysis. Column: RP 18/ODS; solution: methanol: water – 1:1; Det. UV 254 nm, flow rate: 0.5 cm³/min., room temp. Standards of aucubin (Roth) and catalpol (Roth) were used to qualitative identification.

Fig. 3. Chemical structures of aucuboside (1) and catalpol (2).

It seems to be correct to include the taxon *Littorella* to genus *Plantago* (*Plantago uniflora* L.).

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GLUKOZYDY IRIDOIDOWE *LITTORELLA UNIFLORA* (L.) ASCHERSON

STRESZCZENIE

U *Littorella uniflora* występują dwa glikozydy irydoidowe znane z obecności w podrodzaju *Plantago* rodzaju *Plantago*: aukubina i katalpol. Obecne, jak i wcześniejsze badania cukrów i alkoholi cukrowych, wskazują na biochemiczne pokrewieństwo *Plantago* i *Littorella*.

SŁOWA KLUCZOWE: *Littorella uniflora*, aukubina, katalpol.