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Chemotaxonomic markers in Digitalideae (Plantaginaceae)

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Abstract

In a chemosystematic investigation of Digitalideae (Plantaginaceae), the water-soluble part of extracts of two species of *Digitalis*, two species of *Isoplexis*, as well as *Erinus alpinus* and *Lafuentea rotundifolia* were studied with regard to their content of main carbohydrates, iridoids and caffeoyl phenylethanoid glycosides (CPGs). *Digitalis* and *Isoplexis* contained sorbitol, cornoside and a number of other phenylethanoid glycosides including the new tyrosol β-D-mannopyranoside, sceptroside but were found to lack iridoid glucosides. *Erinus* contained mainly glucose, the new 8,9-double bond iridoid, erinoside, and a number of known iridoid glucosides including two esters of 6-rhamnopyranosylcatalpol, as well as the CPG poliumoside. Finally, *Lafuentea* was characterized by the presence of glucose, aucubin and cryptamygin B but apparently lacked CPGs. The chemosystematic significance of the isolated compounds is discussed.

Keywords: *Digitalis*; *Isoplexis*; *Erinus*; *Lafuentea*; Plantaginaceae; Chemosystematics; Sorbitol; Iridoid glucosides; Erinoside; Caffeoyl phenylethanoid glycosides; Sceptroside; Cornoside

1. Introduction

Recent extensive molecular systematic investigations of the heterogeneous family Scrophulariaceae have led to significant changes in its circumscription (Olmstead and Reeves, 1995; Oxelman et al., 1999; Olmstead et al., 2001). Many former members of the family have been assigned to a largely expanded Plantaginaceae (Veronicaceae *sensu* Olmstead, 2003), now comprising approximately 92 genera and 2000 species (APG, 2003; Albach et al., 2005). Within this family, we have recently reviewed the chemotaxonomy of *Plantago* (Rønsted et al., 2000, 2003b; Taskova et al., 2002b), *Aragoa* (Rønsted et al., 2003a), *Veronica* (Taskova et al., 2002a, 2004; Jensen et al., 2005), *Paederota* (Albach et al., 2004) and *Campylanthus* (Rønsted and Jensen, 2002).

Digitalis and its allies have been found to be closely related to Veroniceae and also belong to the extended Plantaginaceae (Oxelman et al., 1999; Olmstead et al., 2001; Bello et al., 2002). Tribes Veroniceae and Digitaleae were established by Bentham (1846) but subsequently lumped into one tribe (Bentham and Hooker, 1886; von Wettstein, 1898). Pennell (1935) reestablished Digitaleae as a small tribe comprising only *Digitalis* and perhaps *Rehmannia*. Recently, Albach et al. (2005) have found *Isoplexis* and *Erinus* to be the closest relatives of *Digitalis*. *Sibthorpia*, *Lafuentea* and *Campylanthus* have also been considered as members of the tribe by different authors (Bentham and Hooker, 1886; von Wettstein, 1898; Hallier, 1903; Melchior, 1964; Olmstead, 2003).

Digitalis and *Isoplexis* have been subjects of much chemical work mainly due to their content of heart-active cardenolides (Hegnauer, 1973; Ganapaty et al., 2003). A number of caffeoyl phenylethanoid glycosides (CPGs) have been detected or isolated from *Digitalis*

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(Lichius et al., 1995; Matsumoto et al., 1987; Baudouin et al., 1988; Brieger et al., 1995; Zhou et al., 1998; Calis et al., 1999a,b; Kirmizibekmez et al., 2002). Also, cornoside (**2**) has been reported from *Digitalis purpurea* (Jensen et al., 1975) and salidroside (**5**) from *Isoplexis chalcantha* (Gonzalez et al., 1985). In his survey for iridoid glucosides in Scrophulariaceae, Kooiman (1970) included *Digitalis*, *Isoplexis* and *Erinus*. However, only the latter was shown to contain aucubin (**15**) and some additional unidentified iridoids. Rønsted and Jensen (2002) have recently investigated *Campylanthus* and isolated mannitol and sorbitol as the major carbohydrates and a number of iridoid glucosides, similar to those found in some species of *Plantago*. Pinar (1977) has reported coumarins from *Lafuentea rotundifolia*. In the present work, we have investigated the water-soluble constituents of two species each of *Digitalis* and *Isoplexis* as well as of *Erinus alpinus* and *L. rotundifolia* and identified the isolated compounds by NMR.

2. Results and discussion

The plant material was extracted with cold or boiling ethanol and the water-soluble part of the extract was subjected to reversed phase column chromatography to give the compounds listed in Table 1. Both in the case of *D. purpurea* and *E. alpinus* fractions with additional, unidentified CPGs were collected. Unfortunately, the carbohydrate fraction was not investigated in for *D. purpurea*, but sorbitol (**1**) has previously been shown to be the main alditol present in mature leaves of this plant (Raymakers, 1973). One of us has previously isolated cornoside (**2**) from *D. purpurea* (Jensen et al., 1975), while **9** and **10** together with calceolarioside A (**8**) and forsythiaside (**13**) were reported by Matsumoto et al. (1987). With regard to the compound **9**, it was first isolated from cell-cultures of *Rehmannia glutinosa* (Shoyama et al., 1986) but not given a trivial name, then it was reported from *D. purpurea* as purpureaside A (Matsumoto et al., 1987), from *Plantago major* as plantamajoside (Ravn and Brimer, 1988), and finally from several species of *Plantago* as plantamoside (Andary et al., 1988). The name purpureaside A therefore have priority, but since plantamajoside is by far the most used name and since the compound is a characteristic for *Plantago* species (Rønsted et al., 2000, 2003b), we suggest that this name is retained for **9**.

From *D. thapsus* and *I. chalcantha* cornoside was accompagnied by **3** or **4**, repectively. We have recently

Table 1
Compounds isolated in the present work

Plant	Plant part	Extraction method	Main carbohydrate	Iridoids	Phenylethanoids
Digitalis purpurea	Fresh leaves and stems from flowering plant	Boiling EtOH	n.i.	–	Cornoside (**2**) Plantamajoside (**9**) Purpureaside B (**10**)
Digitalis thapsi	Frozen whole first year plant	Cold EtOH	Sorbitol (60%)	–	Cornoside (**2**) Cornoside agluc. (**3**) Calceolarioside A (**8**) Forsythiaside (**13**)
Isoplexis chalcantha	Fresh whole first year plant	Cold EtOH	Sorbitol (50%)	–	Cornoside (**2**) Rengyolone (**4**) Salidroside (**5**) Lugrandoside (**11**) Forsythiaside (**13**)
Isoplexis sceptrum	Fresh leaves from old plant	Cold EtOH	Sorbitol (90%)	–	Cornoside (**2**) Salidroside (**5**) Sceptroside (**6**) Dopaol glucoside (**7**) Calceolarioside A (**8**) Forsythiaside (**13**)
Erinus alpinus	Frozen whole plants	Boiling EtOH	Glucose	Aucubin (**15**) Geniposidic acid (**16**) 8-Epiloganic acid (**17**) Arborescosidic acid (**18**) Erinoside (**19**) Catalpol derivs. (**21**, **22**)	Poliumoside (**12**)
Lafuentea rotundifolia	Dry whole flowering plants	Boiling EtOH	Glucose Sucrose	Aucubin (**15**) Gardoside (**20**)	–