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Chemotaxonomy of Veroniceae and its allies in the Plantaginaceae

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Abstract

In a chemosystematic investigation of tribe Veroniceae (Plantaginaceae), representatives of *Camptoloma*, *Sibthorpia*, *Veronica* subg. *Pentasepalae* and subg. *Hebe*, *Veronicastrum*, *Wulfenia*, and the related *Ellisiophyllum* and *Globularia* were examined for non-flavonoid glycosides. From the 14 species studied, 28 different iridoid glucosides and 10 caffeoyl phenylethanoid glucosides (CPGs), as well as salidroside and arbutin were isolated and characterized by NMR; of these, five compounds were previously unknown. It was found that the representatives of Veroniceae, as well as *Globularia*, were characterized by mannitol, aucubin, catalpol and catalpol esters. Each of the three studied species of *Veronica* subg. *Hebe* contained at least one of the 6-*O*-catalpol esters typical for *Veronica s. str.* (verminoside), supporting the inclusion of *Hebe* in *Veronica*. However, their main constituents were esters of 6-*O*-rhamnopyranosylcatalpol; a CPG, hebeoside (2′-β-xylopyranosyl-verbascoside) was isolated from *V.* (*Hebe*) *salicifolia*. The two species of *Veronicastrum* also contained 6-*O*-rhamnopyranosylcatalpol esters, including the previously unknown 2″,3″- and 3″,4″-dicinnamoyl derivatives and, in contrast to the earlier reports, they lacked 6-*O*-catalpol esters. The main iridoid constituents in the three investigated species of *Wulfenia* were 10-*O*-aucubin and 10-*O*-catalpol esters (isoscrophularioside or globularin) while baldaccioside (10-*O*-cinnamoyl asystasioside E) was isolated from *W. baldaccii*. *Globularia vulgaris* contained 10-*O*-catalpol esters (e.g., globularin) and, in addition, asperuloside together with its benzoyl analogue named besperuloside. The representatives of *Sibthorpia* and *Ellisiophyllum* were almost completely devoid of iridoids; this, however, together with the CPGs present implied a close relationship between the two genera. *Camptoloma lyperiiflorum* lacked hexitols but contained esters of 6-*O*-rhamnopyranosylcatalpol different from those found in Veroniceae but known from *Buddleja*, *Scrophularia* and *Verbascum* (Scrophulariaceae *s. str.*).

Keywords: Chemotaxonomy; Plantaginaceae; Veroniceae; Mannitol; Iridoid glucosides; 6-*O*-Rhamnopyranosylcatalpol esters; Besperuloside; Baldaccioside; CPGs; Hebeoside

1. Introduction

The Scrophulariaceae *s.l.* is a large angiosperm family for which a systematic treatment and subdivision based on morphological grounds have been difficult and led to differences of opinion and taxonomic instability (Bentham, 1846, 1876; von Wettstein, 1891; Pennell, 1935; Melchior, 1964; Thieret, 1967). Much research has contributed to the ongoing efforts to create a phylogenetic classification of Scrophulariaceae using morphological microcharacters (Minkin and Eshbaugh, 1989; Argue, 1993; Bigazzi, 1993), as well as chemical characters including iridoid (Kooiman, 1970; Nicoletti et al., 1988a), flavonoid (Tomás-Barberán et al., 1988) or betaine distribution (Blunden et al., 2003).

In several recent molecular investigations the representatives of Bentham's (1876) tribe Digitaleae formed a strongly supported clade with *Plantago* (Olmstead and Reeves, 1995; Olmstead et al., 2001; Bello et al., 2002; Albach et al., 2005). They were nested in a large clade together with part of Bentham's tribes Antirrhineae, Cheloneae, Gratioleae, Angelonieae, including the small families Globulariaceae, Callitrichaceae and Hippuridaceae. This clade has been recognized as the family Plantaginaceae in the APG classification of the flowering plants (APG, 2003).

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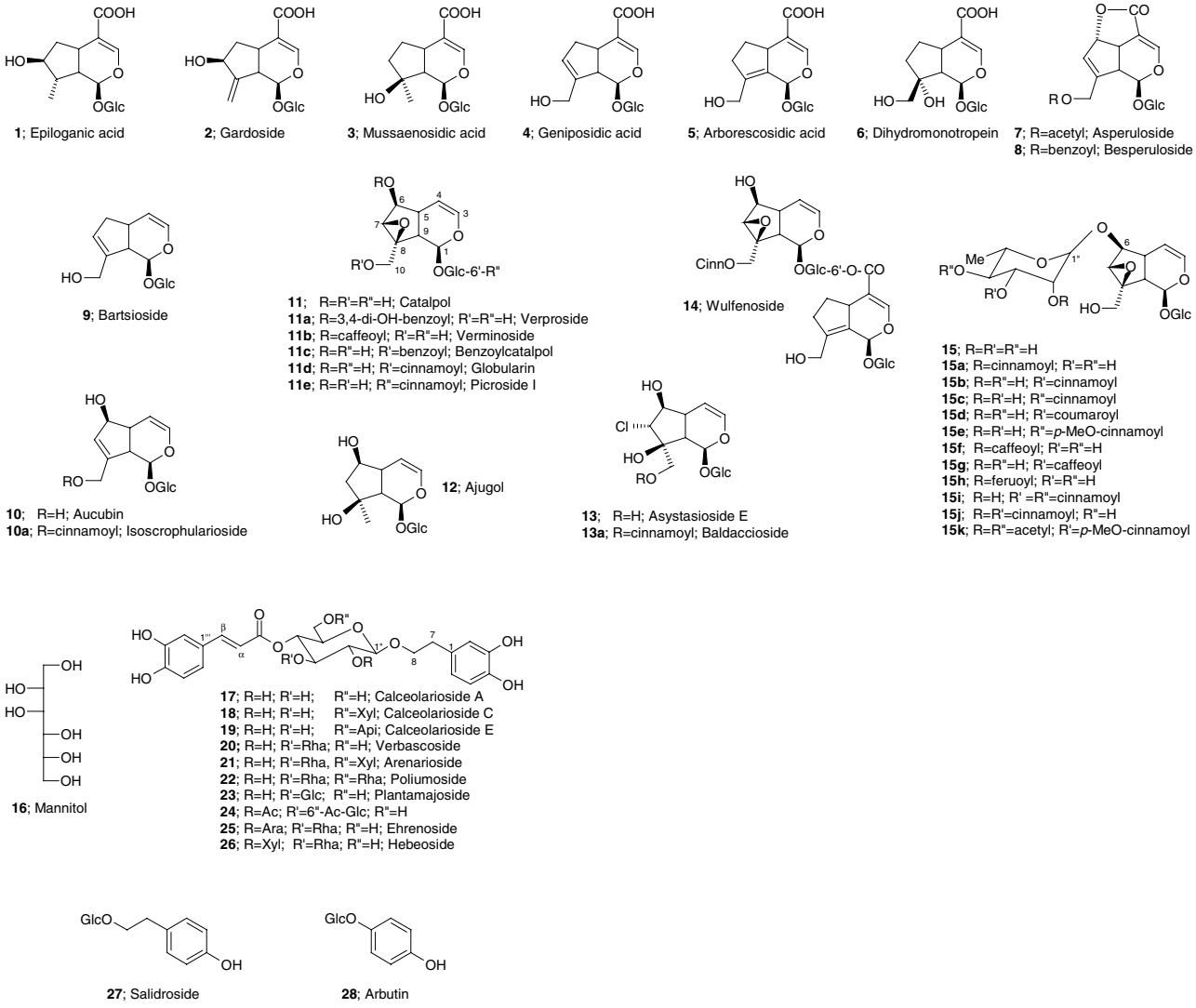

The present study is a chemosystematic investigation of non-flavonoid glycosides in certain tribes of the "new" Plantaginaceae (sensu Albach et al., 2005). The emphasis is on tribe Veroniceae for which the chemical characters are of special interest due to the reported incongruence of molecular data (Albach and Chase, 2004) and an uncertain position of some of its members. Comprehensive chemical information is provided for genera such as *Camptoloma*, *Sibthorpia*, *Hebe*, *Veronicastrum* and *Wulfenia*, which have not been studied properly for iridoid and other non-flavonoid glycosides before. The new phytochemical evidence is compared with previously published data and used to evaluate relationships proposed on the basis of morphological and molecular characters.

2. Results and discussion

The plant material was extracted with cold ethanol and the water-soluble part of the extract was subjected to reverse phase column chromatography to give the compounds listed in Table 1. The isolated compounds were identified mainly by NMR spectroscopy and this also included the sugar fraction for which the composition was deduced solely by ^{13}C NMR.

2.1. Camptoloma

No previous work has been reported on this genus which includes about three species. One of these (*C. lyperiiflorum*) was available and a number of compounds were isolated. The sugar fraction consisted of a mixture of glucose and sucrose. The only caffeoyl phenylethanoid glycoside (CPG) found was verbascoside (**20**). Several iridoids were present, namely the acids **1**, **2** and **3** as well as bartsioside (**9**), mainly precursors for aucubin (**10**) and catalpol (**11**). Additionally, we isolated two esters of 6-*O*-rhamnopyranosylcatalpol, namely verbascoside A (**15e**) and scrovalentinoside (**15k**).

2.2. Veronica subg. Pentasepalae

Extensive work has been done on *Veronica;* recently we have reviewed the content of iridoids and other glycosides