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Investigation of the flavan-3-ol patterns in willow species during one growing-season

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Flavonoids, proanthocyanidins (PAs) and salicylic alcohol derivatives are the main groups of ingredients in *Salix* needed as defensive tools and signal molecules, but have also pharmaceutical importance. The present study investigated total PA content, complete PA pattern, the oligomeric/total PAs quotient and the contents of catechin and epicatechin during one growing-season for the leaves and this year's sprouts in ten willows (*Salix pentandra* L. ♂, S. *alba* L. ♂, *S. fragilis* L. ♀, *S. caprea* L. ♂ & ♀, *S. cinerea* L. ♂, *S. caprea* x *cinerea* ♂, S. *daphnoides* Vill. ♂ & ♀ and *S. purpurea* L. ♀; all Salicaceae). Comparison of the different species revealed distinct seasonal fluctuations of the oligomeric and polymeric PA fractions, but the contents of both groups always developed in the same direction. All willows prefer the synthesis of PAs with DP-2 - DP-4 within the oligomeric fraction (DP-2 – DP-10) and species with rather low PA contents like *S. purpurea* (0.1–2.6 mg/g) as well as species with rather high PA contents like *S. alba* (3.8–14.7 mg/g) were found. Only slight gender specific differences could be observed for both sexes of *S. daphnoides* and *S. caprea.* The PA pattern of the hybrid *S. caprea* x *cinerea* seems to be influenced by both parents. Thus, the accumulation of the oligomeric PAs accorded to *S. caprea* and the polymeric PAs matched *S. cinerea* resulting in an overall depression of PAs in the sprouts and a varying seasonal trend in the leaves. In contrast, the content of catechin remained high and seemed to be not influenced in the hybrid. Although only one individual of each *Salix* species could be considered in this screening study, the present results demonstrate the variability of the flavan-3-ol pattern within the genus *Salix* but also some preliminary correlations could be observed. Future studies with more *Salix* species will provide more insights into chemotaxonomic correlations.

1. Introduction

Salix L. (willows, Salicaceae) is a genus of dioecious plants comprising ~500 species (Lauron-Moreau et al., 2015; Wu et al., 2015) and a nearly global distribution. Nevertheless, primarily distribution is on moist soils in cold and temperate regions of the northern hemisphere. Various growth habits from trees (e.g. *Salix fragilis* L.) to dwarf shrubs (*Salix herbacea* L.) can be found and all species are deciduous (Skvortsov and Zinovjev, 1999). The leaves are typically elongated, in some species round to oval, often characterized by serrated margins. Male and female flowers typically appear as catkins and are mainly insect-pollinated, whereby male catkins offer pollen and nectar as a reward, whereas female inflorescences offer nectar only. Due to a very early flowering period in March/April, various willow species have a great ecological impact as an important pollen and nectar resource for many insect species, including social and solitary bees, flies, butterflies, moths and beetles, resulting also to an enhancement of insect-pollinated agricultural crops such as fruits (Dötterl et al., 2014; Füssel et al., 2007; Holdenrieder et al., 1999; Kopelke et al., 2017; Totland and Sottocornola, 2001).

Willow species produce and accumulate a manifold pattern of specialised metabolites. Most abundant compounds are different groups of polyphenols mainly belonging to the flavonoids (Freischmidt et al., 2012), the proanthocyanidins (PAs) (Meier and Meier-Liebi, 2007), the simple phenylpropanoids (Poblocka-Olech et al., 2010) and the salicylic alcohol derivatives (Meier and Meier-Liebi, 2007). Accumulation of polyphenols is often realized as part of defensive strategies against herbivores, fungi and many other organisms. In willows, especially the salicylic alcohol derivatives have been investigated since decades in various ecological and analytical studies. The ecological function, distribution in

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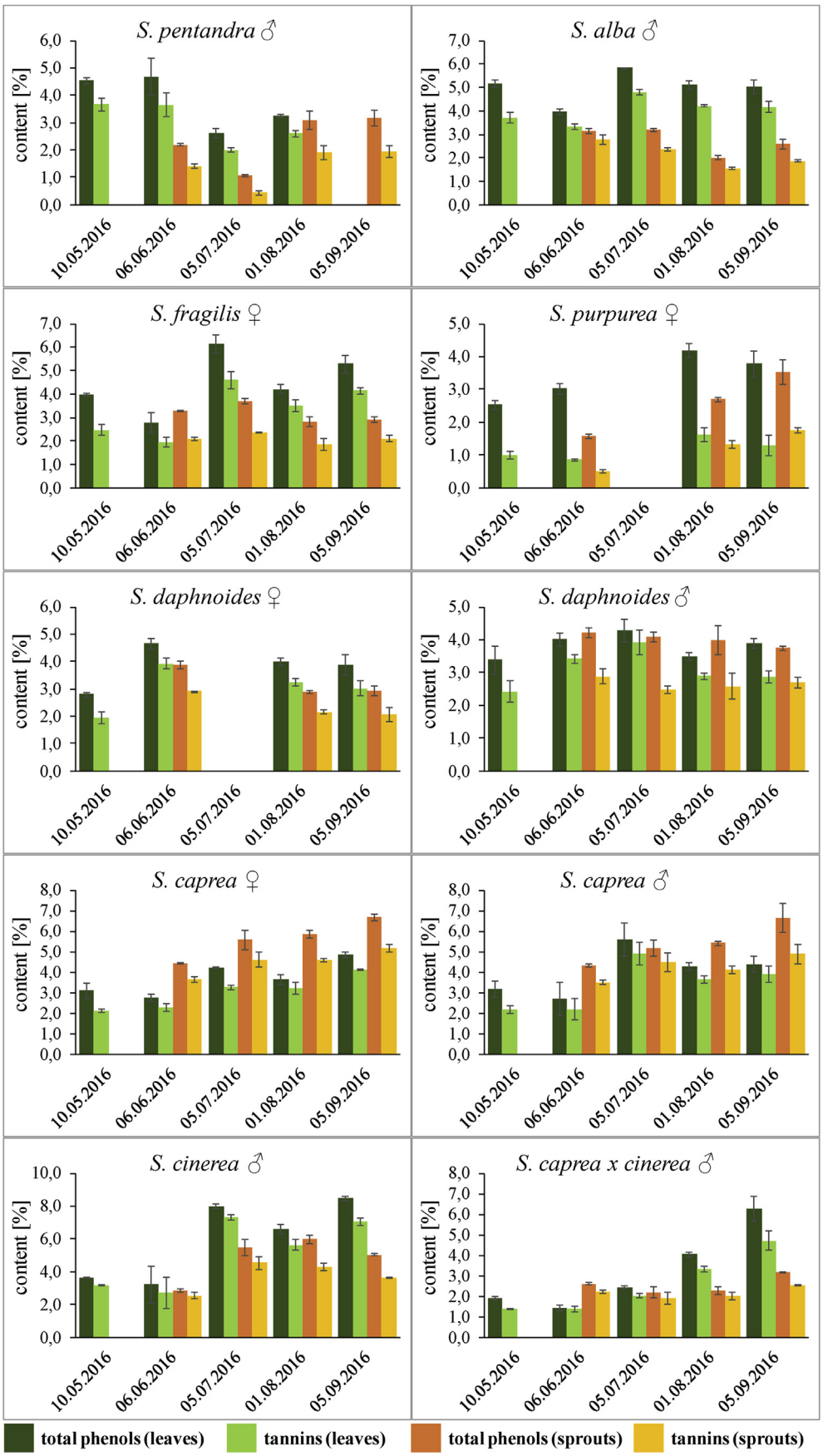

Fig. 1. Total phenols and tannins contents in the leaves and sprouts gained by a modified Folin-Ciocalteus Hide-powder method (Wiesneth and Jürgenliemk, 2017); all values were calculated as catechin and results are depicted in % [m/m] ± standard deviation (n = 3).