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Secondary metabolites variation in *Hypericum maculatum* and its relatives

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1. Subject and source

The secondary metabolites of the tetraploid *Hypericum perforatum* L. have been well studied, but less is known about the chemistry of related taxa. For example, *Hypericum maculatum* Crantz is a diploid species ($2n = 16$), from which further taxa are derived. Probable autopolyploidization (Robson, 2002) led to a facultatively apomictic tetraploid ($2n = 32$) species, *Hypericum dubium* Leers. Hybridization of these two taxa in shared localities with a participation of unreduced female gamete of *H. dubium* can lead to a pentaploid ($2n = 40$) nothospecies *Hypericum* $\times$ *carpathicum* Mártonfi (Mártonfi, 2001). The hybridization of *H. maculatum* $\times$ *H. perforatum* gave rise to a pentaploid ($2n = 40$) *Hypericum* $\times$ *carinthiacum* A. Fröhl. and *H. dubium* $\times$ *H. perforatum* to the hybrid *Hypericum* $\times$ *desetangsii* Lamotte. (Robson, 2002). Following samples were used for study (in brackets: number of plants for study, area of collections, collector(s), voucher identification): *H. maculatum* (120, Slovakia – Slovenské Rudohorie Mts. and High Tatras Mts., P. Mártonfi and

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partially P. Zanvit, Mártonfi 2233–2262, 2401–2490); *H. ×carpaticum* (34, Slovakia – Slovenské Rudohorie Mts., P. Mártonfi, Mártonfi 2209–2232, 2272–2281); *H. ×carinthiacum* (31 – cultivated plants coming from seeds of hybrid plant were studied because of scarcity of the hybrid, locality of the original plant: Slovakia – village of Prakovce, P. Mártonfi, Mártonfi 1452: deposited in British Museum Herbarium, BM); *H. dubium* (55, England – West Kent and East Sussex, P. Mártonfi and N. K. B. Robson, Mártonfi 2570–2624); *H. ×desetangsii* (60, England – Surrey, P. Mártonfi and N. K. B. Robson, Mártonfi 2625–2684). Except for the voucher in BM, the voucher specimens are deposited in KO herbarium (Botanical Garden, P. J. Šafárik University, Košice, Slovakia).

2. Previous work

Secondary metabolites of the taxa from the group *H. maculatum* have not been studied yet in detail, except for *H. maculatum*. Brockmann and Sanne (1957) detected hypericin. Flavonoids hyperoside, quercitrin and quercetin were identified by Michaluk (1961) and Leifertová (1966), isoquercitrin by Kment et al. (1990), I3,II8-biapigenin and amentoflavone by Umek et al. (1999). Flavonoid rutin (usually present in the flowers of *H. perforatum*) is absent from the flavonoid pattern of *H. maculatum*, or present only in trace amounts (Michaluk, 1961; Leifertová, 1966; Brantner et al., 1994; Mártonfi et al., 1996; Umek et al., 1999; Kitanov, 2001; Radušienė and Bagdonaitė, 2002). The data on other taxa are only sporadic (Mártonfi et al., 1996, 1999; Mártonfi, 2001). Quantitative data from different authors vary significantly. This can be caused by different methods of sampling and analyzing. Gaudin et al. (2002) have shown that for *H. perforatum* the chemical profile defining the quality of flowering tops is dependent upon the plant development stage upon harvest but it does not seem to be influenced by the soil type, the altitude or the age of the culture.

3. Present study

Two fully opened flowers were taken from each of the plant studied. Air-dried flowers were extracted in methanol and analysed by HPLC using the method described in Mártonfi et al. (2001). Results are presented in Table 1.

4. Chemotaxonomic significance

A comparison of main secondary metabolites in the flowers of *H. maculatum* and a well-known species *H. perforatum* (for review, see Hölzl and Petersen, 2003) shows that their chemical profile is very similar (presence of hyperoside, isoquercitrin, quercitrin, quercetin, biapigenin, pseudohypericin, hypericin). *H. maculatum* and its derivatives *H. dubium* and *H. ×carpaticum*, however, do not contain rutin and

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