

**B057 Analysis of flavonoids and caffeoylquinic acids in the *Achillea millefolium* group**

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Flavonoids, due to their antioxidative, antiphlogistic and spasmolytic activities (1), probably contribute to the pharmacological activity of the drug *Herba millefolii*, which is widely used in folk medicine (2). Furthermore these compounds may be of chemotaxonomical relevance. Thus, the composition of the flavonoid complexes of eleven different taxa of the *Achillea millefolium*-group were investigated by capillary electrophoresis. Aerial parts of the flowering plants of *A. setacea* W. et K., *A. asplenifolia* Vent., *A. roseo-alba* Ehrend., *A. ceretanica* Sennen (2n), *A. collina* Becker, *A. pratensis* Saukel & Länger, *A. ceretanica* Sennen (4n), *A. millefolium* L.S.I., *A. millefolium* subsp. *sudetica* Opiz, *A. styriaca* Saukel ined. (6n) and *A. pannonica* Scheele (8n), which occur in Austria and the surrounding regions were analysed. 17 flavonoids (luteolin-7,4'-O-diglucosid, apigenin-7-O-glucoside, luteolin-7-O-glucoside, isorhamnetin-3-O-rutinoside, vicenin-2, schaftoside, isoschaftoside, 6-hydroxy-luteolin-7-O-glucoside, rutin, luteolin-4'-O-glucoside, luteolin-7-O-glucuronide, isoorientin, vitexin, apigenin and 3 yet not identified flavonoids), being the main compounds in the different species, were selected for the comparison of the flavonoid patterns. The similarities in one species and remarkable differences between the taxa proved the chemotaxonomic relevance of the flavonoids. The determined amounts of 0.3 to 2.1 % in the drug pointed to their contribution to the pharmacological effects.

Investigations of the phenolcarboxylic acids in these *Achillea* taxa showed chlorogenic acid in all samples, besides four dicaffeoylquinic acids and related substances. The quantitative variability between the samples was observed, but the patterns of the caffeoylquinic acid-derivatives showed no remarkable differences. Because of the minor differences between the taxa these phenolics are of low chemotaxonomic value, but with amounts up to 3.1 % they may also contribute to the pharmacological effects of *Herba millefolii*.

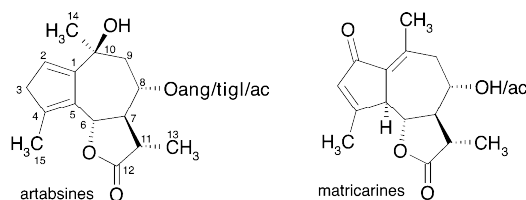
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**B058 APCI-MS – a helpful tool to identify sesquiterpenes in species of the *Achillea millefolium* group**

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Several species of the polyploid *Achillea millefolium* group are characterized by labile proazulenes ( $8\alpha$ -tigloxy- /  $8\alpha$ -angeloxy- /  $8\alpha$ -acetoxy-artabsin) and stable matricarine-derivatives (1). Their analysis is performed by HPLC on RP 8 material using a methanol-water gradient and diode array detection (220 nm and 255 nm) (2). Coupling of mass spectrometry as additional method for detection and identification is presented. Due to the low polarity of the compounds APCI was employed for ionization in the positive mode whereas ESI did not yield useful mass spectra. The matricarines show high intensity of their quasimolecular ions in contrast to the labile proazulenes which only yield fragments at the respective conditions. Addition of ammonium acetate to the water in a concentration of 10 mM and adaption of the respective lens voltages cause higher stability of the quasimolecular ions of the proazulenes. They are detectable with low intensity beside a prominent mass peak corresponding to the adduct  $[M+NH_4]^+$ . In contrast, the matricarines do not show any adduct with ammonium acetate. The influence of the temperature and respective lens voltages is discussed. This method represents a useful technique to identify and characterize labile sesquiterpenoids during analyses of different extracts and during isolation procedures.



References: 1. Kubelka, W. et al. (1999) *Biochem. Syst. Ecol.* 27: 437-444. 2. Glasl, S. et al. (1999) *J. Chromatogr. B.* 729: 361-368.