

Fig. 1. HPLC-ESI-MS chromatogram (negative ionization mode) of the crude ethyl acetate extract of *Hippophaë* juice concentrate: **1** = [M-H]⁻: *m/z* 623 = isorhamnetin 3-O- β -rutinoside, **2** = [M-H]⁻: *m/z* 507 = syringetin 3-O- β -D-glucoside, **3** = [M-H]⁻: *m/z* 463 = quercetin 3-O- β -D-glucoside, **4** = [M-H]⁻: *m/z* 477 = isorhamnetin 3-O- β -D-glucoside, **5** = [M-H]⁻: *m/z* 153 = protocatechuic acid, **6** = [M-H]⁻: *m/z* 447 = quercetin rhamnoside, **7** = [M-H]⁻: *m/z* 519 = isorhamnetin acetyl-glucoside, **8** = [M-H]⁻: *m/z* 461 = isorhamnetin rhamnoside, **9** = [M-H]⁻: *m/z* 301 = quercetin, **10** = [M-H]⁻: *m/z* 315 = isorhamnetin.

ESI-MS-MS: scan range *m/z* 50- 2200 amu (further conditions cf. Experimental)

HPLC-conditions: Prontosil C₁₈ Aqua, 5 μ m, 250 x 2.0 mm (Bischoff, Leonberg, Germany); gradient elution, 3 % ACN in H₂O from 0 to 10 min, starting a linear gradient in 30 min to 60 % ACN, in 15 min to 100 % ACN, hold for 10 min and back to initial conditions; flow-rate, 0.25 mL min⁻¹

Fig. 2. HSCCC chromatogramm of the crude ethyl acetate extract from concentrated juice of sea buckthorn berries (*Hippophaë rhamnoides* L. ssp. *rhamnoides*).

1 = isorhamnetin 3-O- β -rutinoside, *R_t* = 116-138 min; **2** = syringetin 3-O- β -D-glucoside, *R_t* = 172-206; **3** = quercetin 3-O- β -D-glucoside, *R_t* = 218-258 min; **4** = isorhamnetin 3-O- β -D-glucoside *R_t* = 258-440 min; **5** = protocatechuic acid, *R_t* = 460-600 min.

HSCCC multilayer coil planet centrifuge with three preparative coils connected in series; polytetrafluorethylene tubing: 2.6 mm i.d. x 165 m; total volume: 850 mL; sample loop: 25 mL; revolution speed: 800 rpm, injection of sample: 4.1 grams.

Two-phase solvent system: *n*-hexane - *n*-butanol - water (1:1:2, v/v/v); stationary phase: upper organic phase; elution mode in the coil system: 'head to tail'; flow rate: 3.0 mL min⁻¹; detection wavelength: $\lambda = 280$ nm; retention of the stationary phase: 90 %.

Fig. 3. The chemical structures of the components isolated by preparative HSCCC from concentrated juice of sea buckthorn berries (*Hippophaë rhamnoides* L. ssp. *rhamnoides*).

Fig. 4. HPLC-ESI-MS chromatogram (negative ionization mode) of the components isolated from the *Hippophaë* juice concentrate by means of HSCCC: **1** = [M-H]⁻ : *m/z* 623: isorhamnetin 3-O- β -rutinoside, $R_t = 29.9$ min; **2** = [M-H]⁻ *m/z* 507 : syringetin 3-O- β -D-glucoside, $R_t = 30.9$ min; **3** = [M-H]⁻ *m/z* 463 : quercetin 3-O- β -D-glucoside, $R_t = 29.6$; **4** = [M-H]⁻ *m/z* 477 : isorhamnetin 3-O- β -D-glucoside, $R_t = 30.8$; HPLC-ESI-MS conditions cf. Fig. 1.

Fig. 5 Structure relevant long-range HC-correlations in the HMBC of isorhamnetin 3-O- β -rutinoside (**1**), and quercetin 3-O- β -D-glucoside (**3**).