Summary

»An apple a day keeps the doctor away«. This saying has been the impetus for numerous studies. The focus of many of these studies lays on flavonoids and tannins (condensed or hydrolyzable tannins), so-called secondary phytochemicals. Flavonoids (occurring mostly as glycosides) and tannins are widespread in flora, e.g. in medicinal plants. Throughout centuries medicinal plants have been utilized for self-treatments of human diseases, e.g. diarrhea and inflammations, and were the basis of a daily nutrition, which acted to prevent infections and strengthen the immune system.

For utilization of those secondary phytochemicals, in particular tannins, a screening study of 47 European medicinal herbs and spice plants was conducted to identify plants with high tannin contents. 16 plants were identified with measurable tannin content. Out of those 16 plants, four plants were identified with tannin contents above 7 w% in the dried plant and tannin contents of up to 38.4 w% in the dried extracts. Furthermore, the flavonoid (quercetin) content of those plants was analyzed by hydrolyzing the extracts.

In the conventional production process of quercetin, the extracts are hydrolyzed with mineral acids (HCl, H₂SO₄, HNO₃). This requires a neutralization step with alkaline or salts after hydrolyzing the extract. The neutralization forms salts in high concentrations that have to be later removed during the wastewater treatment. To avoid this neutralization step, an alternative methodology – CO₂-intensified hydrolysis – was investigated. CO₂-intensified hydrolysis requires only water and CO₂-pressure to form H+ ions for lowering the pH-value. To study that reaction in detail rutin, a flavonoid glycoside and the most common flavonoid in plants was selected as model substance and was dissolved in purified water prior to hydrolysis. The temperature- and the CO₂ pressure-dependence of the CO₂-intensified hydrolysis were investigated by varying
the temperature between 373.15 K and 433.15 K and the CO₂ pressure between ambient pressure and 150 bar. Thereby, a temperature and pressure dependence model were obtained. In this model, a new H⁺-factor was introduced describing the influence of H⁺ ions and concentrations of the model substance in the CO₂-intensified hydrolysis process. The optimum process parameters were found to be 413.15 K and 150 bar (100 % conversion of rutin to quercetin).

For assessing the potential of the CO₂-intensified hydrolysis, a mass balance for the conventional quercetin production process was made up considering a conventional source (Fagopyrum, rutin content 5%). For a production volume of one ton of quercetin (assumed that rutin is 100% hydrolyzed to quercetin), 20 tons of Fagopyrum weed is needed. The extraction in a ratio of 1:10 with water as extraction solvent would result in a consumption of 200 tons of water. Depending on the used acid, different salts could be formed due to neutralization. H₂SO₄ would form 2.84 tons of Na₂SO₄, HNO₃ would form 1.7 tons of NaNO₃ and HCl would form 1.2 tons of NaCl after neutralization, which have to be separated prior to introducing it to wastewater treatment plants.

For testing the CO₂-intensified hydrolysis on plant extracts, Arctostaphylos uva-ursi and Fragaria were investigated regarding the potential of a combined production process of hydrolyzed extracts rich in flavonoids and tannins. In addition, hydrolysis was performed with a strong acid (HCl) at 363.15 K and ambient pressure to compare the results with conventional acid hydrolysis. Furthermore, hydrolysis with a weak acid (CH₃COOH) was conducted at 363.15 K and ambient pressure inspired by the CO₂-intensified hydrolysis at pH 3. It was observed that hydrolyzable tannins degraded to 20% during hydrolyzing the extract at 413.15 K and 150 bar CO₂-pressure. In contrast, condensed tannins did not degrade to such a high extent (a loss of 20 % was observed after eight hours of CO₂-intensified hydrolysis). For Fragaria, a quercetin content of
0.23w% and a tannin content of 19.6w% in the dried extract was generated. For *Arctostaphylos uva-ursi*, a quercetin content of 0.35w% and a tannin content of 5.8w% in the dried extract was produced.