Characterization of Free and Cell-Wall-Bound Phenolic Compounds in Chinese *Brassica* Vegetables

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About 40 flavonoids and hydroxycinnamic acid derivatives were identified in Chinese cabbages (pak choi and Chinese leaf mustard) by HPLC-ESI-MS^n. The detailed fragmentation of phenolic compounds and their fragmentation pattern identified the main flavonoids as kaempferol derivatives, glycosylated and esterified with different hydroxycinnamic acids. Hydroxyferulic acid as a moiety of flavonoids was characterized for the first time by NMR spectroscopy. The main hydroxycinnamic acids were shown to be malic acid derivatives, which were identified for the first time in cabbages. Hydroxybenzoic acids were not detected as moieties of free phenolic compounds. However, various cell-wall-bound hydroxybenzaldehydes, hydroxybenzoic, and hydroxycinnamic acids were identified. These compounds represent only minor amounts (stem 0.80-1.04%; blade 0.05-0.08%) of the total phenolic content in fresh plants cultivated in China. In pak choi and leaf mustard, the free phenolic content is affected by cultivation conditions and varies quantitatively according to plant part. The content differs among plants cultivated in China under field conditions and in Germany under greenhouse conditions. The differences were attributed to the different climatic conditions, e.g. light supply (plants exhibited approx. two- to threefold higher flavonoid content in China). No tendency was observable vis-à-vis differences in the content of free phenolic compounds among the outer and inner leaves cultivated in China. However, the content in the leaf blade was much higher than in the leaf stem, particularly for the flavonoid derivatives, and the overall content in the plant was shown to be dependent on the leaf blade/stem ratio of each cultivar. Flavonoids were not detected in the leaf stems of plants cultivated under greenhouse conditions, but were found in trace amounts in the stems of the plants grown in China under field conditions. Additionally, the cell-wall-bound phenolic content was also predominantly higher in the leaf blade than in the leaf stem, for pak choi cultivars in particular (approx. 140 µg/g cell wall of leaf blade and 70 µg/g cell wall of leaf stem).

Post-harvest treatments such as fermentation and storage resulted in qualitative and quantitative polyphenolic changes. The qualitative changes resulting from fermentation were analyzed in detail by HPLC-ESI-MS^n. The analysis showed a partial loss of glycoside or organic acid moieties of flavonoids and hydroxycinnamic acids as well as the formation of aglycones, which was attributed to microorganism activity. An increase of the antioxidative potential was observable for all fermented cultivars in the TEAC and total phenolic content (Folin Ciocalteu) assays; the increase might be explained by the qualitative changes in the polyphenolic structures (i.e. the formation of hydroxyl groups). Changes in the content of cell-wall-bound phenolic compounds were marginal; the content did not change significantly during the fermentation process and microorganism activity can be excluded.

Additionally, the storage of cabbages resulted in increased polyphenolic content within the first few days (approx. 6 days).