ABSTRACT

Carotenoids in mature (green) and senescing leaves of invasive alien plant species Japanese (*Fallopia japonica* Houtt) and Bohemian (*Fallopia* x *bohemica*) knotweed were identified and quantified. Both plants showed similar pigment profiles.The amount of free xanthophylls and carotenes was significantly lower in senescing leaves in comparison to green leaves. On the other hand new xanthophyll compounds appeared in senescing leaves – xanthophyll fatty acid esters. Particularly green leaves of both studied knotweeds represent a rich and sustainable natural source of bioactive carotenoids, mainly β-carotene (69–97 mg/100g D.W.) and xanthophyll lutein (97–144 mg/100g D.W.), thus exploitation of these invaders can be used for the production of high added-value products. However, due to carotenoids chemical structure, they are very unstable outside of the plant matrix and they degrade fast in the presence of elevated temperature, light, oxidants, acids and metals. We found an inspiration to solve this problem in nature itself, where in autumn xanthophylls are converted into more chemically stable xanthophyll esters. To this end, we developed the first environmentally friendly and economically viable synthetic platform, where overall green, renewable, GRAS and recyclable materials were used. The synthesis was carried out in β-pinene as the reaction solvent and at ambient conditions (room temperaure, Atmospheric pressure), where 55 different xanthophyll esters (combining 5 model xanthophylls with 11 structurally and electronically distinct acid anhydrides) were prepared. We have shown that esterification can be performed also without use of a solvent and by exploitation of a waste plant material, e.g. extract of green leaves of Japanese knotweed or avocado peels, which represent rich renewable source of lutein and anteraxanthin, respectively. The synthesized compounds were purified and characterized by means of HPLC-PDA-MS and offline HRMS. Out of 55 compounds, 22 were successfully synthesized for the first time. The efficiency of our approach to achieve higher chemical stability of xanthophylls *via* esterification was tested on 13 different lutein diesters, which were synthesized either from pure lutein or from green leaves extract of Japanese knotweed. Each individual lutein diester was separately examined at each individual stress conditions: elevated temperature (60 °C), light (UV-A), oxidant (H_2O_2) and acidic environment. Based on systematic stability studies, we were first to identify a relationship between the chemical stability, chemical structure and the environment by which lutein esters were surrounded. Of all the prepared lutein esters, lutein di(2,2-dimethylpropanoate), lutein di(2-methylpropanoate) and lutein di(3-methylbutanoate) proved to be the most stable. They showed to be 1,4–20 times more stable than free lutein, regardless of the chosen stress condition. Depending on the stress condition the plant matrix can strongly (positively or negatively) affect the stability of an individual xanthophyll. The green leaves of Japanese knotweed, therefore, represent a suitable plant waste material that enables the preparation of potential high value-added products – xanthophyll esters with increased chemical stability.

Key words: Japanese knotweed (*Fallopia japonica* Houtt), carotenoids, xanthophylls esterification, xanthophyll esters, stability, chromatography (HPLC, HPTLC, GC), mass spectrometry