Extraction, characterization and application of antioxidants from the Nordic brown alga Fucus vesiculosus

Marine algae are a huge underutilized resource in the Nordic countries with a potential to be used in the development of new natural ingredients for the food, cosmetics and pharmaceutical industry. Such ingredients can act as natural preservatives and prevent spoilage and oxidation during storage, in particular in the form of rancidity due to oxidation of unsaturated fatty acids in the products.

A characteristic feature of Fucus vesiculosus, also known as bladder wrack, is a high content of phlorotannins – a particular type of polyphenol group. Previous studies have shown positive correlations between the phlorotannin content and radical scavenging capacity of extracts derived from Nordic F. vesiculosus. Radical scavenging capacity is an important antioxidant property in terms of preventing the oxidation of unsaturated fatty acids. The high content of antioxidative phlorotannins in F. vesiculosus therefore makes this alga particularly attractive for the development of new natural antioxidants. While the in vitro antioxidant properties of F. vesiculosus extracts are widely studied, studies evaluating the antioxidant efficacy of such extracts in food and skin care products are scarce.

This PhD study investigated the possibilities of using extracts from Nordic F. vesiculosus as natural antioxidants in food and skin care products. All tested food products were fortified with fish oil rich in polyunsaturated omega-3 fatty acids. The fish oil was added specifically in order to examine the effectiveness of the antioxidants in systems which are more likely to oxidize compared with conventional products. The products tested were all oil-in-water emulsions except for granola bars, which were instead added 70% fish oil-in-water emulsions. Tests were made on a selections of extracts made from water, acetone, and ethanol, as well as a fraction of purified phlorotannins. Investigations also highlighted the influence of the extraction medium on the antioxidant properties, the phlorotannin content as well as other co-extracted substances. Moreover, it was examined which phlorotannins were present in each of the extracts, and how each specific phlorotannin contributed to the overall antioxidant activity.

All extracts examined and also the phlorotannin-rich fraction were somewhat able to improve the oxidative stability of the food and skin care products. The effectiveness of these extracts was to a large degree dependant on their antioxidant properties and composition, which in turn depended on the extraction medium used. In general, water was efficient in extracting iron chelating compounds. However, it was also found that water was not effective in extracting phlorotannins, and that the iron chelating ability, according to our results, to a greater extent was due to the presence of the pigment 19-hex-fucosterin. It has also been discussed whether algal sugars with iron chelating ability may be extracted with water and hence affect the antioxidant properties of the water extract. However, this aspect was not investigated. The high iron chelating ability of the water extract proved particularly effective in FO-enriched mayonnaise. Previous studies have also shown that iron chelating ability is an important property of antioxidants to work efficiently in this particular food. Acetone and ethanol were highly effective in extracting phlorotannins, which were found to have good radical scavenging capacity as well as reducing power. In addition, these phlorotannins exhibited a high affinity to the interface between the hydrophilic and the hydrophobic phase, compared to phlorotannins extracted with water. The more amphiphilic phlorotannins were also found to be effective antioxidants in FO-enriched granola bars. It was examined from microscopy how the emulsified fish oil added seaweed extracts localized when added to the granola bars. Emulsions added extracts with more amphiphilic phlorotannins clearly improved incorporation of the fish oil emulsions into the granola bars, which in turn had a major impact on the oxidative stability of these products. It was concluded that the surface active phlorotannins were important radical scavengers in granola bars. These phlorotannins are chain-breaking antioxidants that deactivate lipid radicals formed in the first part of lipid oxidation. In addition, it was discussed whether some of these phlorotannins also regenerated antioxidative tocopherols from the oil phase.

A structural characterization and on-line detection of phlorotannins in the purified fraction was carried out in support of a further characterisation of phlorotannins and how they each contribute to the overall antioxidant activity. By mass spectrometry 13 phlorotannin isomers were identified with molecular weights between 374 and 870 Da (3 to 7 phloroglucinol units). It was found that the antioxidant activity is decreasing with increased molecular weight and hence with increased polymerization of the phlorotannins. This PhD work has contributed basic knowledge of relevance to future large scale development of natural antioxidants from seaweeds to the benefit of the food, cosmetic and pharmaceutical industrial sectors. It is clearly demonstrated that it is possible to produce antioxidants from seaweed thallus, and also that it is possible to use alternative environment-friendly extraction methods. In addition, the studies highlight examples of application possibilities of seaweed extracts as natural antioxidants, e.g. in the formulation of functional foods enriched with fish oil.