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# ABSTRACT OF PhD THESIS

## *Extraction, Identification and Antioxidant Activity of the Phenolic Secondary Metabolites Isolated from the Leaves, Stems and Fruits of Two Shrubs of the Ericaceae Family*

For century fruits and aerial parts of bilberry and lingonberry, two shrubs of the *Ericaceae* family, are known as natural sources of food, beverage and dietary supplements due to their richness in nutritional and bioactive compounds. Although bilberry and lingonberry constituents have multiple biological activities, most of the research has focused on the phenolic compounds. Generally, the quality and quantity of phenolic compounds in plants are influenced by the stage of growth, the parts of the plant to be used and the environmental growing conditions.

In this thesis the dynamic accumulation of phenolic compounds in leaf, stem, and fruit extracts of bilberry and lingonberry was studied by comparing the total phenolic content, the phenolic composition at three different periods of vegetation during two years. Contents in total polyphenols, evaluated by the Folin-Ciocalteu method or specifically by UPLC, and the antioxidant capacity in the DPPH test are also tentatively correlated. Additionally, an original analysis of the oligomeric procyanidins is proposed addressing degree of polymerization and flavanol unit constitution. Last, the evaluation of *in vitro* antioxidant activity of fruits, leaves and stems of bilberry and lingonberry extracts and their phenolic compounds in lipid oxidation under simulated digestion conditions was performed.

Qualitative analysis on bilberry phenolics revealed the presence of 8 new compounds among which several p-coumaroyl di- and triacetyl glycosides, caffeoyl- and *p*-coumaroylmalonyl glycosides, quercetin glycosides, and various A-type and B-type flavanol oligomers up to the tetramers. The more

important groups in bilberry extracts were in the following order: caffeoyl derivatives, *p*-coumaroyl derivatives, flavon glycosides, anthocyanins, and flavanol monomers and oligomers. Thioacidolysis revealed low degrees of polymerization (2-3) and (-)-epicatechin as the main flavan-3-ol unit. The antiradical activity (Total Polyphenol Content, DPPH test) was higher in leaves than in stems and fruits and this could result from the predominant presence of chlorogenic acid. The leaf extracts from July and September presented almost similar antiradical activity and showed higher phenolic contents than the extract from May. Similar antiradical activity and phenolic contents were found in bilberry stems whatever the period of vegetation, although it appears lower in the extract from May.

For lingonberry, qualitative and quantitative analyses by UPLC/MS showed the predominant presence of monomers and oligomers of catechin and epicatechin and quercetin glycosides in all the morphological parts. The structures of fifty phenolic compounds detected in all lingonberry extracts were characterized for the first time. Thioacidolysis showed that lingonberry extracts contain (+)-catechin as well as (-)-epicatechin unit. This study has also demonstrated a high antioxidant activity of leaf, stem and fruit extracts of lingonberry. Among the three periods of vegetation, leaves and stems can be collected in any one, May, July or September, as sustainable sources of natural phenolic compounds with a significant antioxidant activity.

Aqueous extracts from bilberry and lingonberry proved to be efficient inhibitors of metmyoglobin-initiated lipid oxidation in oil-in-water emulsions stabilized either by BSA or egg yolk phospholipids in the early phase of digestion (pH 5) than in the midcourse of digestion (pH 3). Powdered fruits of lingonberry and bilberry highly inhibited the accumulation of lipid-derived conjugated dienes in the PL emulsion at pH 5 with initiator metmyoglobin. These results indicated that they can be used directly, without extract preparation, for the lipid oxidation protection. Finally, the antioxidant activity of an extract of bilberry leaves toward lipid oxidation was evaluated in a static *in vitro* digestion model (oral, gastric and intestinal phase). Bilberry leaf extract inhibited the lipid oxidation in the gastric step (BSA and PL emulsion systems).

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