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Original Research Article

Phenolic compounds in wholegrain rye and its fractions

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ABSTRACT

Rye (*Secale cereale* L.) has traditionally had an important role in the daily diet especially in Northern and Eastern Europe, and in addition to dietary fibre, rye grain is a good source of various phytochemicals in our diet. The focus of the present work was to find out how various phenolic compounds are distributed in rye grain fractions prepared by air-classification, and compare rye brans produced by different separation techniques (sieving or air classification). Of the phenolic compounds, phenolic acids were analyzed as organic solvent soluble (OSS) free, esterified and glycosylated residues, organic solvent insoluble (OSI) esterified and etherified residues and OSI ferulic acid esterified to water extractable fibre. In addition alkylresorcinols, flavonoids, hydroxamic acid DIBOA (2,4-dihydroxy-1,4-benzoxazin-3-one), flavonoids and lignans were analyzed. Based on the determined concentrations, alkylresorcinols formed the most dominant group of OSS phenolic compounds in rye and its fractions, followed by smaller amounts of OSS esterified phenolic acids and hydroxamic acid DIBOA. In wholegrain rye and rye fractions, the major part (86–92%) of the total amount of phenolic acids was present as OSI-form bound to the fibre complex either via ester or β-aryl ether bonds. All of the analyzed phenolic compound groups were enriched in the bran fraction, which encourages usage of this part of rye grain in foods. The content and profile of phenolic compounds did not differ much between the two differently produced rye brans.

1. Introduction

Rye (*Secale cereale* L.) has traditionally had an important role in the daily diet, especially in Northern and Eastern Europe, and is most commonly used as wholemeal bread. In various studies the consumption of rye bread has been shown to result in positive physiological effects especially related to glucose metabolism and inflammation (Juntunen et al., 2003; Kallio et al., 2007). In addition to dietary fibre, various phytochemicals, vitamins and minerals have been suggested to contribute to the health effects of wholegrain foods (Fardet, 2010). Among the phytochemicals in rye, phenolic acids, alkylresorcinols and lignans, in particular, have gained a special focus (Bondia-Pons et al., 2009). Many of these phytochemicals are known to be concentrated in the bran fraction of the rye kernel (Glitsø and Bach Knudsen, 1999; Glitsø et al., 2000; Heiniö et al., 2008; Liukkonen et al., 2003; Landberg et al., 2008; Nyström et al., 2007; Michalska et al., 2007).

Phenolic acids are an important group of the phytochemicals of cereal grains. Soluble phenolic acids (free, soluble esterified and glycosylated forms) have been reported to contribute to the flavour (Heiniö et al., 2008) and antioxidant activity (Adom and Liu, 2002) of cereal foods. However, the majority of the phenolic acids of cereals are in an insoluble bound form (Adom and Liu, 2002; Heiniö et al., 2008; Sosulski et al., 1982), mainly linked to polysaccharides by ester bonds and to lignin by ether bonds (Renger and Steinhart, 2000). Although they exist in bound form, a part of these phenolic acids can also contribute to the antioxidative capacity in vitro (Gökmen et al., 2009; Liyanapathirana and Shahidi, 2004), and be bioavailable along the GI-tract (Aura, 2008; Hemery et al., 2010; Mateo Anson et al., 2009; Vitaglione et al., 2008). Alkylresorcinols (ARs) are 1,3-dihydroxybenzene derivates with an odd-numbered alkyl chain attached at position 5 of the benzene ring. In the human diet, whole grain wheat and rye are the main source of ARs. In rye, these compounds have received considerable interest during the past 10 years because of their possible contribution to the health effects (Bondia-Pons et al., 2009; Ross et al., 2004), but also as biomarkers of intake of wholegrain rye (Andersson et al., 2011; Ross et al., 2012; Ross, 2012; Söderholm et al., 2009). Lignans are

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phenolic compounds widely distributed in the plant kingdom and also found in cereals, especially in rye. Recently, Smeds et al. (2007) and Hanhineva et al. (2012) brought up new insight on the diversity of different lignans in rye and other cereals. The role of lignans in human health has been reviewed by Adlercreutz (2007).

Despite the substantial number of studies on the distribution and quantities of certain phytochemicals in the rye kernel, there are still compounds such as flavonoids (Michalska et al., 2007; Zieliński et al., 2007) and benzoxazinoids (Adhikari et al., 2012, 2013; Hanhineva et al., 2011; Katina et al., 2007; Pedersen et al., 2011; Tanwir et al., 2013), about which only limited data are available. The mono and dihexose conjugates of cyclic hydroxamic acid DIBOA (2,4-dihydroxy-1,4-benzoxazin-3-one) and the corresponding lactam HBOA (2-hydroxy-1,4-benzoxazin-3-one) are the major benzoxazinoids in rye (Pedersen et al., 2011; Hanhineva et al., 2011; Tanwir et al., 2013), while other benzoxazinoid forms are found in wheat and maize (Hashimoto and Shudo, 1996). Recently, Adhikari et al. (2013) reported that dietary benzoxazinoids are absorbed and metabolized in humans.

The objective of this study was to provide new insight on the distribution and location of various phenolic compounds, i.e. phenolic acids, alkyresorcinols (ARs), DIBOA, flavonoids and lignans, in wholegrain rye and its fractions prepared by sieving and air-classification.

2. Materials and methods

2.1. Standards

Phenolic acid standards were obtained from Sigma–Aldrich (St. Louis, MO, USA) or from Carl Roth GmbH (Karlsruhe, Germany). Quercetin was from Carl Roth GmbH (Karlsruhe, Germany). Alkylresorcinols (C17:0, C19:0, C21:0, C23:0, C25:0) were from ReseaChem GmbH (Burgdorf, Switzerland). Syringaresinol was purchased from Planttech (Reading, UK), pinoresinol, isolariciresinol, matairesinol, secoisolariciresinol, lariciresinol were from Arbo-Nova (Turku, Finland) and 7-hydroxymatairesinol was a gift from Hormos Medical (Turku, Finland). PCB 53 was from Dr. Ehrenstorfer (Augsburg, Germany) and 4,4′-dichloro benzhydrol was from Alfa Aesar (Karlsruhe, Germany). All commercial reference compounds were at least of p.a. quality.

DIBOA was isolated and purified from germinated rye at MTT Agrifood Research Finland (Kurri, 2007).

2.2. Samples

Preparation of the rye fractions is described in detail by Nordlund et al. (2013) and in Fig. 1. Briefly, for fractionation of rye by air-classification, rye kernels (cultivar Amilo, falling number 264) were first milled to obtain commercial medium-coarse wholegrain rye flour R1. This wholemeal rye flour was fractionated using a consecutive milling and air classification process to produce first a coarse fraction R2 and a fine, endosperm rich fraction R3. Then with further milling and air-classification of the coarse fraction R2, a second coarse rye fraction, i.e. bran R4, and a fine fraction R5 were produced. To compare the conventional rye bran to the air-classified bran fraction, rye kernels were also milled using progressive milling to prepare a coarse fraction, i.e. bran R7. The yields and chemical characteristics of the fractions are described by Nordlund et al. (2013).

All chemical analyses were performed in duplicates. Mean values of results were accepted if their difference was <20%. Each sample batch contained a certain mixture QA/QC-standards in order to verify the performance of the analytical instrument.

2.3. Extraction of phenolic compounds

An outline of the method used to isolate organic solvent soluble (OSS) and organic solvent insoluble (OSI) phenolic acid fractions, is presented in Fig. 2.

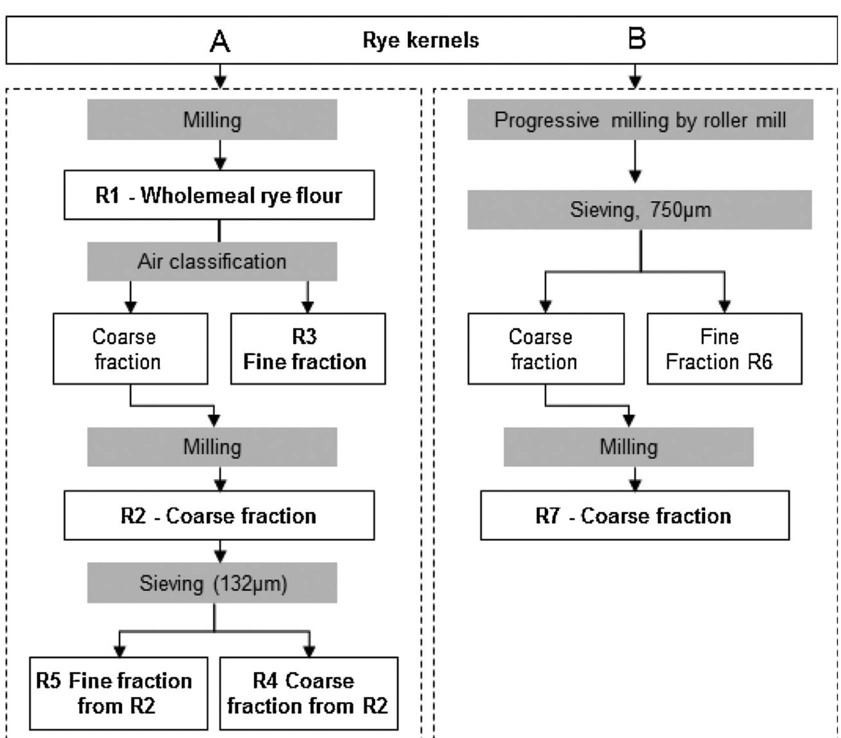

Fig. 1. Mechanical processing of rye kernels for fractionation of rye. Consecutive milling and air classification process rye flour R1 to produce rye fractions R2, R3, R4, R5 (A) and progressive milling and sieving of rye kernels to produce rye bran R7 (B).