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Contents of Phenolic Acids, Alkyl- and Alkenylresorcinols, and Avenanthramides in Commercial Grain Products

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The contents of free and total phenolic acids and alk(en)ylresorcinols were analyzed in commercial products of eight grains: oat (*Avena sativa*), wheat (*Triticum* spp.), rye (*Secale cerale*), barley (*Hordeum vulgare*), buckwheat (*Fagopyrum esculentum*), millet (*Panicum miliaceum*), rice (*Oryza sativa*), and corn (*Zea mays*). Avenanthramides were determined in three oat products. Free phenolic acids, alk(en)ylresorcinols, and avenanthramides were extracted with methanolic acetic acid, 100% methanol, and 80% methanol, respectively, and quantified by HPLC. The contents of total phenolic acids were quantified by HPLC analysis after alkaline and acid hydrolyses. The highest contents of total phenolic acids were in brans of wheat (4527 mg/kg) and rye (4190 mg/kg) and in whole-grain flours of these grains (1342 and 1366 mg/kg, respectively). In other products, the contents varied from 111 mg/kg (white wheat bread) to 765 mg/kg (whole-grain rye bread). Common phenolic acids found in the grain products were ferulic acid (most abundant), ferulic acid dehydrodimers, sinapic acid, and *p*-coumaric acid. The grain products were found to contain either none or only low amounts of free phenolic acids. The content of avenanthramides in oat flakes (26−27 mg/kg) was about double that found in oat bran (13 mg/kg). The highest contents of alk(en)ylresorcinols were observed in brans of rye (4108 mg/kg) and wheat (3225 mg/kg). In addition, whole-grain rye products (rye bread, rye flour, and whole-wheat flour) contained considerable levels of alk(en)ylresorcinols (524, 927, and 759 mg/kg, respectively).

KEYWORDS: Phenolic acids; alk(en)ylresorcinols; avenanthramides; grain products

INTRODUCTION

The positive physiological effects of whole-grain products have been mainly ascribed to dietary fiber, but phenolics, which are also present in whole grains (e.g., wheat, rye, barley, and oats) may contribute to their beneficial effects as well (*1*, *2*). Phenolic acids, alk(en)ylresorcinols, and avenanthramides are phenolic compounds typically found in grain products, with avenanthramides only in oats *(Avena sativa*) (*3*). All of these compounds possess potential health-promoting properties, partly by virtue of their antioxidative action (phenolic acids and avenanthramides) (*1*, *4*) or membrane-modulating effects [alk(en)ylresorcinols] (*5*).

Phenolic acids are hydroxylated derivatives of benzoic and cinnamic acids (**Figure 1**). Hydroxycinnamic acids are more common than hydroxybenzoic acids and consist chiefly of *p*-coumaric, caffeic, ferulic, and sinapic acids (*1*, *6*). Several of these phenolic acids are also commonly found in grain products, with ferulic acid being the most abundant. (*1*, *6*). Phenolic acids are concentrated in the outer layers of the grain (*7*−*9*) and are particularly interesting because they are potentially protective against cancer and heart diseases (*1*, *6*, *10*). Alk(en)ylresorcinols are compounds that contain a long (typically 15−25 carbons) nonisoprenoid side chain attached to the hydroxybenzene ring (**Figure 2**). Alk(en)ylresorcinols are of interest because they occur in large quantities in certain cereals, especially in rye and wheat, and have a wide range of biological activities (*5*, *11*, *12*). Recent studies (*12*, *13*) have shown that they are relatively stable compounds during grain processing and are found in

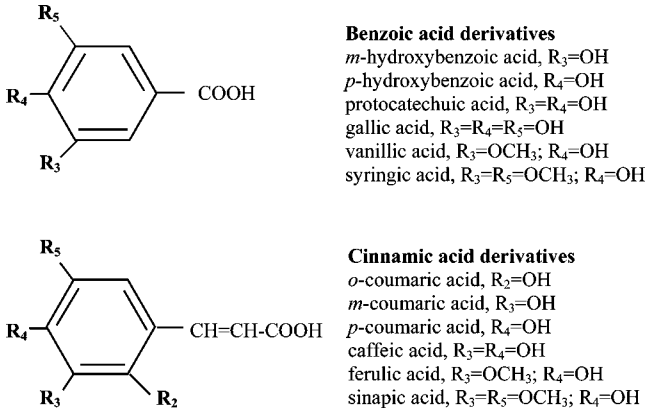

Figure 1. Chemical structures of monomeric phenolic acids (see structures for phenolic acid dehydrodimers, e.g., from refs *7* or *23*).

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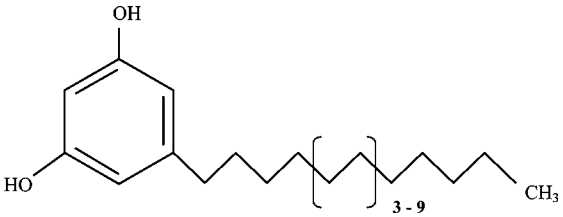
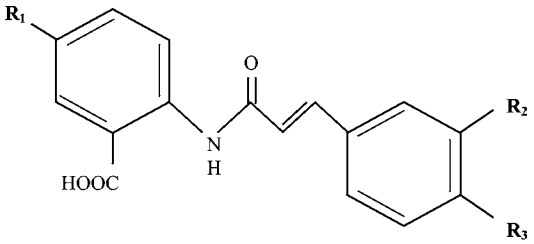


Figure 2. Chemical structures of al(ken)nylresorcinols.



Avenanthramide 2p, R_1=R_3=OH
Avenanthramide 2f, R_1=R_3=OH; R_2=OCH_3
Avenanthramide 2c, R_1=R_2=R_3=OH
Tranilast, R_2=R_3=OCH_3

Figure 3. Chemical structures of avenantramides and Tranilast.

considerable amounts in whole-grain products such as sourdough rye bread, which is a popular product in the Nordic countries. Similar to phenolic acids, alk(en)ylresorcinols are also concentrated in the outer layers of grains (*12*−*14*). Avenanthramides are a class of phenolic antioxidants typical of oats. These nitrogen-containing phenolic compounds were first characterized in oat groats and hulls by Collins (*3*). The most common avenanthramides are esters of 5-hydroxyanthranilic acid with *p*-coumaric (**2p**), caffeic (**2c**), or ferulic (**2f**) acid (*4*, *15*−*18*) (**Figure 3**). The potential of antioxidative compounds in oats has long been recognized, and some of their properties have been commercialized as well (*4*). A great deal of research has been devoted in recent years to investigate the characteristics of avenanthramides (*15*, *19*, *20*).

There are several reports on the contents of phenolics in different varieties of cereal grains or their different parts (e.g., *4*, *7*−*9*, *21*). More data are, however, needed regarding phenolics (especially phenolic acids) in commercial grain products. Despite the fact that phenolic compounds are purported to have health benefits, more epidemiological and clinical studies have to be performed to fully understand their actions. To assist these investigations, databases need to be established. The aim of the present study was to determine contents of phenolic acids, avenanthramides, and alk(en)ylresorcinols in mostly consumed grain products. To our knowledge, similar studies have not been published. The ultimate aim is to incorporate the analysis results into the Finnish Food Composition Database, Fineli, which is maintained by the National Public Health Institute of Finland.

MATERIALS AND METHODS

Standards. The standards of phenolic acids were obtained from various manufacturers. The following standards were from Sigma Chemical Co. (St. Louis, MO): chlorogenic acid, protocatechuic acid, *p*-hydroxybenzoic acid, vanillic acid, syringic acid, *p*-coumaric acid, *o*-coumaric acid, sinapic acid, caffeic acid, and ferulic acid. The standard of *m*-coumaric acid was from Fluka (Buchs, Switzerland), and the standard of *E*-cinnamic acid was from Aldrich (St. Louis, MO). All standards were prepared as stock solutions at 2 mg/mL in MeOH. The stock solutions were stored in darkness at −18 °C and remained stable for over 3 months.

Tranilast [*N*-(3′,4′-dimethoxycinnamoyl)anthranilic acid], which was used as the reference compound for avenanthramides, was purchased from Tocris (Bristol, U.K.). Authentic standards of the avenanthramides **2p**, **2c**, and **2f** were gifts from Dr. David Peterson (USDA-ARS, Cereal Crops Research, Madison, WI). Olivetol (5-pentylresorcinol), obtained from Aldrich (St. Louis, MO), was used for the quantification of alk(en)ylresorcinols. The standards were prepared in methanol at concentrations of 100 μg/mL, and these stock solutions were stored in a freezer at −18 °C.

Samples. Most consumed grain species: wheat (*Triticum* spp.), rye (*Secale cerale*), barley (*Hordeum vulgare*), rice (*Oryza sativa*), oat (*Avena sativa*), buckwheat (*Fagopyrum esculentum*), millet (*Panicum miliaceum*), and corn (*Zea mays*) were studied. Representative samples of their products (**Table 1**) were collected from three retail stores (four primary samples weighing 0.25−2 kg of each item from each store), representing the three major food chains in Finland during 2003−2005. For pooling, equal amounts (100 g) of each primary sample were combined to form one composite sample of a given grain product. The bread samples were cubed before pooling, and after pooling, the composite samples other than flours were homogenized by Braun 400 W homogenizor.

Moisture. To obtain their moisture contents, the samples of pooled grain products were weighed before and after drying at 97 °C overnight (16 h).

Analysis of Phenolic Acids. Free and total phenolic acids were analyzed according to a validated method (*22*) with modifications in HPLC elution conditions. Dependent upon a presumable phenolic acid content, a 0.1−0.5 g sample was homogenized in 7 mL of a mixture of methanol, containing 2 g/L of butylated hydroxyanisole (BHA) obtained from Acros Organics, NJ, and 10% acetic acid (85:15) with Heipolph Diax 900 homogenizor. The homogenized sample extract was ultrasonicated for 30 min and made to a volume of 10 mL with distilled water. After mixing, 1 mL was filtered for HPLC analysis of free phenolic acids. Next, 12 mL of distilled water and 5 mL of 10 M NaOH were added into the test tube, sealed, and stirred overnight (about 16 h) at 20 °C using a magnetic stirrer. The solution was then adjusted to pH 2, and the liberated phenolic acids were extracted 3 times with 15 mL of a mixture of cold diethyl ether and ethyl acetate (1:1). The organic layers were combined, evaporated to dryness, dissolved in 1.5 mL of methanol, filtered, and analyzed by HPLC. After alkaline hydrolysis, an acid hydrolysis was performed by adding 2.5 mL of concentrated HCl into the test tube and incubating in a water bath at 85 °C for 30 min. The sample was then cooled, and further sample handling was performed in the same manner as after alkaline hydrolysis. HPLC quantifications were performed, and the results of the alkaline and acid hydrolysates were calculated to represent the total phenolic acid content.

The analytical HPLC system consisted of an Agilent 1100 Series high-performance liquid chromatograph equipped with a diode array detector. The HPLC pumps, autosampler, column oven, and diode array system were monitored and controlled using the HP Chem Station computer program. The wavelengths used for the quantification of phenolic acids with the diode array detector were 254 nm for protocatechuic acid, *p*-hydroxybenzoic acid, and vanillic acid; 280 nm for syringic acid, *p*-coumaric acid, *m*-coumaric acid, *o*-coumaric acid, *E*-cinnamic acid, and ferulic acid dehydrodimers; and 329 nm for chlorogenic acid, caffeic acid, ferulic acid, and sinapic acid.

Phenolic acid separation was done with a 150 × 4.0 mm i.d., 3 μm, Inertsil ODS-3 column (GL Sciences, Inc., Japan) with

Table 1. Contents of Total Phenolic Acids in Grain Products

sample	DM[a] (%)	concentration[b] (mg/kg of FW)									
		I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**	total
rye flour, whole grain	90.0	10 ± 2.0	860 ± 71	120 ± 12	9.4 ± 1.6	22 ± 2.8	41 ± 2.8	6.8 ± 0.87	6.7 ± 0.33	290 ± 25	1366
rye flour, organic, whole grain	91.3	4.2 ± 0.49	860 ± 79	130 ± 13	nd[c]	30 ± 3.8	64 ± 4.4	9.7 ± 0.89	10 ± 1.2	254 ± 5.7	1362
rye bran	90.0	77 ± 12	2800 ± 150	480 ± 30	26 ± 0.08	46 ± 2.5	140 ± 16	24 ± 1.2	17 ± 0.42	580 ± 32	4190
rye bread, whole grain	60.1	1.9 ± 0.15	540 ± 25	74 ± 5.1	nd	16 ± 2.2	28 ± 0.83	4.6 ± 0.39	7.3 ± 0.90	93 ± 16	765
whole-wheat flour	89.7	37 ± 1.4	890 ± 40	63 ± 3.6	nd	15 ± 0.83	37 ± 1.2	7.4 ± 0.06	13 ± 0.007	280 ± 16	1342
white wheat flour	88.2	nd	120 ± 12	8.0 ± 0.01	nd	4.0 ± 0.57	3.8 ± 0.32	2.1 ± 0.22	2.7 ± 0.32	26 ± 1.4	167
white wheat flour, organic	91.3	nd	100 ± 7.1	8.0 ± 0.75	nd	3.7 ± 0.14	5.3 ± 0.39	2.3 ± 0.12	2.2 ± 0.14	28 ± 5.4	150
wheat bran	90.4	38 ± 4.0	3000 ± 180	200 ± 32	9.6 ± 0.62	35 ± 4.7	90 ± 9.8	22 ± 1.4	32 ± 3.7	1100 ± 78	4527
white wheat bread	68.8	nd	82 ± 2.3	6.9 ± 0.88	4.7 ± 0.51	2.6 ± 0.07	2.8 ± 0.18	1.6 ± 0.25	nd	10 ± 0.03	111
pasta	90.3	nd	120 ± 7.3	17 ± 0.94	nd	nd	3.6 ± 0.10	2.4 ± 0.10	nd	13 ± 2.9	156
barley flour, whole grain	90.3	1.7 ± 0.13	250 ± 32	11 ± 1.7	1.6 ± 0.15	7.1 ± 0.83	40 ± 4.9	3.1 ± 0.53	5.0 ± 0.33	130 ± 13	450
oat bran	90.3	5.4 ± 0.15	330 ± 30	90 ± 18	nd	24 ± 2.4	12 ± 0.22	22 ± 2.3	28 ± 3.6	140 ± 21	651
buckwheat grits, whole grain	90.9	85 ± 8.7	12 ± 0.69	21 ± 1.0	nd	5.3 ± 0.32	15 ± 0.89	110 ± 14	nd	nd	248
oat flakes, whole grain	91.2	3.1 ± 0.18	250 ± 18	55 ± 2.4	nd	18 ± 1.5	nd	16 ± 1.8	20 ± 1.5	110 ± 0.71	472
oat flakes, precooked, whole grain	90.5	3.6 ± 0.32	250 ± 28	52 ± 6.8	nd	17 ± 0.81	nd	16 ± 0.83	20 ± 1.4	110 ± 4.9	469
millet grits	89.4	1.1 ± 0.11	260 ± 7.9	nd	nd	11 ± 1.8	18 ± 1.3	3.0 ± 0.15	2.1 ± 0.95	78 ± 9.2	373
corn flour	88.9	26 ± 1.0	380 ± 14	57 ± 2.9	nd	4.6 ± 0.33	31 ± 1.5	5.7 ± 0.26	7.8 ± 0.14	89 ± 2.9	601
rice, long grain parboiled	89.6	nd	120 ± 5.9	17 ± 1.0	nd	nd	38 ± 2.3	13 ± 0.21	nd	8.8 ± 0.09	197
rice, brown, long grain parboiled	89.1	nd	240 ± 26	20 ± 1.6	nd	7.8 ± 1.2	76 ± 4.6	15 ± 0.68	nd	17 ± 2.3	376
rice, brown, long grain parboiled (cooked)	29.2	nd	92 ± 10	7.1 ± 0.01	nd	2.5 ± 0.30	29 ± 4.9	4.2 ± 0.45	nd	4.1 ± 0.40	139

[a] Dry matter. [b] **I** = caffeic acid, **II** = ferulic acid, **III** = sinapic acid, **IV** = protocatechuic acid, **V** = vanillic acid, **VI** = *p*-coumaric acid, **VII** = *p*-hydroxybenzoic acid, **VIII** = syringic acid, and **IX** = ferulic acid dehydrodimers (semiquantitative results). [c] nd = not detected, value below the limit of quantification (1 mg/kg).

a C-18 guard column. The temperature of the column oven was set at 35 °C. A gradient elution was employed with a mobile phase consisting of 50 mM H_3PO_4 at pH 2.5 (solution A) and acetonitrile (solution B) as follows: isocratic elution 95% A, 0−5 min; linear gradient from 95% A to 85% A, 5−17 min; linear gradient from 85% A to 80% A, 17−40 min, linear gradient from 80% A to 50% A, 40−60 min; isocratic elution 50% A, 60−65 min; linear gradient from 50% A to 95% A, 65−67 min; post-time, 6 min before the next injection.

The flow rate of the mobile phase was 0.7 mL/min, and the injection volume was 10 μL. All monomeric phenolic acids were quantified using an external standard method. Ferulic acid dehydrodimers were identified according to their spectra (*23*) and determined semiquantitatively by an internal standard method, with *E*-cinnamic acid as an internal standard. The response factor (0.16) used was the mean value of the response factors presented by Waldron et al. (*23*) and Andreasen et al. (*7*) for ferulic acid dehydrodimers. All quantifications were based on peak area, and the samples were analyzed in triplicate. Limit of determination was 1 mg/kg. The method used has been thoroughly validated earlier (*22*).

Analysis of Avenanthramides and Alk(en)ylresorcinols. Three typical avenanthramides, namely, **2c**, **2p**, and **2f** (**Figure 3**), were identified and quantified from the samples. According to a slightly modified method of Bryngelsson et al. (*18*), avenanthramides were extracted from 5 g oat samples twice with 50 mL of 80% methanol for 30 min on a magnetic stirrer. The samples were centrifuged, and the supernatants were evaporated to dryness in a rotary evaporator. For analysis, the samples were redissolved in methanol (2 mL). Alk(en)-ylresorcinols extraction was based on a modified method of Mullin et al. (*24*). Briefly, the samples (2.5 g) were extracted with 50 mL of methanol overnight on a magnetic stirrer, after which they were centrifuged. Remaining solids were washed with 50 mL of methanol. The combined supernatants were evaporated to dryness and redissolved in methanol (1 mL).

Avenanthramides and alk(en)ylresorcinols were identified and quantified using the same instrument as for phenolic acids. A 150 × 3.9 mm i.d., 4 μm, Nova Pak C18 column (Waters, Milford, MA) was used as the analytical column for both compound groups. The mobile phase for avenanthramides consisted of 0.05 M phosphate buffer (A) at pH 2.4 and methanol (B) (5−60% B in 50 min followed by 60−90% B in 6 min). For alk(en)ylresorcinols analysis, the mobile phase gradient was as follows: 5−60% B in 50 min, 60−90% B in 6 min, hold at 90% for 12 min, and finally to 100% within 32 min. Avenathramides were quantified at 350 nm, and alk(en)-ylresorcinols were quantified at 280 nm. For identification purposes, UV/vis spectra were recorded at 190−600 nm. A tentative identification of alk(en)ylresorcinols was made by referring to the chromatograms of HPLC elution profiles presented in the literature (*14*, *24*). Response factors for the different alk(en)ylresorcinols were calculated by taking into account their molecular weights versus olivetol and assuming that the responses did not depend upon the length of the side chain (**Table 3**).

RESULTS AND DISCUSSION

Phenolic Acids. *Analytical Method*. A number of the phenolic acids in grain products are linked to cell-wall material. Ferulic acid, for example, is probably linked to polysaccharides, lignins, and suberin (*1*). The challenging task in determining phenolic acids in grain material is liberating the bound forms from their compounds and from the matrix. In this study, we extracted the free phenolic acids by methanolic acetic acid. Total phenolic acids were determined using first alkaline and then acid hydrolyses. The strengths of the alkaline and acid solutions as well as the durations of the hydrolyses had been optimized earlier (*22*). In comparison with our previous study on phenolic acids (*22*), we developed the method further for the HPLC elution conditions to be able to separate ferulic and sinapic acids from each other. Ferulic acid dehydrodimers were semiquantified in addition.

Phenolic Acids in Rye Products. Low contents of free phenolic acids were detected in rye products. Rye bran contained free caffeic acid at 19 ± 1.1 mg/kg, and the contents of other free phenolic acids (ferulic and sinapic acids) were lower than 10 mg/kg. In other rye samples, only caffeic acid was detected and its content was lower than 10 mg/kg. However, all of the rye products contained high levels of total phenolic acids (**Table 1**). Our results for ferulic acid, ferulic acid dehydrodimers, sinapic acid, and *p*-coumaric acids in rye bran and rye flour are similar to those obtained by Andreasen et al. (*7*, *25*), who found these phenolic acids in rye bran in concentrations of 2020−3720, 686−980, 240−410, and 115−200 mg/kg of dry matter, respectively. The corresponding contents in the whole grain were 900−1170, 241−409, 70−140, and 40−70 mg/kg of dry matter. Rybka et al. (*8*) observed similar ferulic acid concentrations in whole grain of rye (1006−1138 mg/kg).

Phenolic Acids in Wheat Products. As in the case of rye, a minor content (less than 12 mg/kg) of free phenolic acids was detected in wheat products. On the other hand, high levels of total phenolic acids were also found in wheat bran and whole-wheat flour (4527 and 1342 mg/kg, respectively; **Table 1**). The other analyzed wheat products were prepared from the inner part of the wheat grain and thus showed much lower levels of total phenolic acids. Our ferulic acid results for whole-grain wheat were in accordance with Rybka et al. (*8*) (783−846 mg/kg). However, Sosulski et al. (*26*) and Peyron et al. (*9*) determined lower levels of ferulic acid in white wheat flour (63.6 and 4.6−8.3 mg/kg, respectively) than was obtained in the present study. The reason for these discrepancies probably lies in sampling and methodological differences.

Phenolic Acids in Oat Products. In oat products, free phenolic acids were not detected, although very low contents of free forms have been reported earlier (*4*). Further, oat bran contained nearly 10 times less total ferulic acid than wheat and rye brans. In addition to the species-derived variation, one reason for the lower levels might lie in the processing method: commercial wheat and rye brans are the outer layers of the grains, whereas oat bran contains a part of aleurone and endosperm as well. However, total phenolic acid levels in oat flakes were somewhat lower than in the more outer layer containing bran. The most important compounds were ferulic acid (250 ± 18 mg/kg), ferulic acid dehydrodimers (110 ± 0.71 mg/kg), and sinapic acid (55 ± 2.4 mg/kg). Sosulski et al. (*26*) reported a similar monomeric phenolic composition for debranned oat flour, but the levels were lower (e.g., *E*-ferulic acid at 63.7 mg/kg).

Phenolic Acids in Barley Products. No free phenolic acids were detected in commercial barley flour. Very low concentrations of chlorogenic acid (<16.3 mg/kg) and protocatechuic acid (<2.9 mg/kg) have, however, been reported previously in freshly milled barley grain (*27*). The three main phenolic acids in barley flour (**Table 1**) were ferulic acid (250 ± 32 mg/kg), ferulic acid dehydrodimers (130 ± 13 mg/kg), and *p*-coumaric acid (40 ± 4.9 mg/kg). In general, our results were of the same magnitude or somewhat lower than those obtained by Hernanz et al. (*28*), Yu et al. (*27*), and Zupfer et al. (*29*). Yu et al. (*27*) reported effective pretreatment for barley grains using acid, α-amylase, and cellulose hydrolyses before HPLC analysis. With their method, they were able to release high quantities of *p*-hydroxybenzoic acid, with contents ranging from 894 to 1343 mg/kg depending upon the variety. On the other hand, the recovered quantities of *p*-coumaric acid and ferulic acid in our study agree with their results. In addition to differences in methodological and milling practices, the variation between the phenolic acid amounts could be due to variations among different barley varieties (*27*−*29*).

Phenolic Acids in Rice, Buckwheat, Millet, and Corn Products. The samples of conventional and brown rice contained small amounts of free phenolic acids (*p*-coumaric acid, 16 ± 0.92 and 13 ± 1.2 mg/kg; ferulic acid, 3.7 ± 0.47 and 4.0 ± 0.30 mg/kg, respectively). In addition, a low content of free caffeic acid (6.6 ± 0.16 mg/kg) was analyzed from brown rice. The contents of total phenolic acids were, however, greater in rice samples (**Table 1**). Parboiled rice contained mainly ferulic acid (120 ± 5.9 mg/kg) and *p*-coumaric acid (38 ± 2.3 mg/kg). Double the amount of the contents of these phenolic acids were found in brown rice. Sosulski et al. (*26*) reported lower contents of free and total phenolic acids in debranned rice flour (e.g., free *p*-coumaric acid at 1.3 mg/kg and total ferulic acid at 75.1 mg/kg) than were obtained in the present study.

According to data compiled by Shahidi and Naczk (*1*), the chemistry of the common phenolics in buckwheat seed and buckwheat products differs markedly from other cereal products. This was also noted in the present study. The content of the total ferulic acid was low (12 ± 0.69 mg/kg), but the contents of *p*-hydroxybenzoic acid (110 ± 14 mg/kg) and caffeic acid (85 ± 8.7 mg/kg) were high as compared with other grain products (**Table 1**). Buckwheat along with millet grits were the only products containing soluble chlorogenic acid (97 ± 9.6 and 9.2 ± 0.28 mg/kg, respectively). In contrast to buckwheat, the composition of total phenolic acids in millet grits was typical of other grain products containing mainly ferulic and *p*-coumaric acids, as well as ferulic acid dehydrodimers. Ferulic acid and *p*-coumaric acids have also been found earlier in seeds of finger millet-ragi (*Eleusine coracana*), although the reported levels were higher (*30*). Corn flour contained moderate contents of phenolic acids, mostly ferulic acid. Sosulski et al. (*26*) reported somewhat lower levels of this phenolic acid (258.6 mg/kg) in corn flour.

Effect of the Processing and Cultivation Method on the Phenolic Acid Contents. We noted that the percent phenolic acid compositions among products made from the same grain species were similar (**Table 1**). In addition, baking, cooking, or other processing did not seem to destroy phenolic acids. For example, the total phenolic acid composition and content of traditional and precooked oat flakes were identical. On a dry matter basis, the contents of phenolic acids in rye and wheat flours and corresponding products made from these flours (bread and pasta) were found to be similar as well. Further, the composition and content of phenolic acids in uncooked and cooked brown rice were of the same magnitude on a dry matter basis. A comparison of the phenolic acid contents of organic and conventional rye and wheat flours showed only minor differences.

Table 2. Contents of **2c**, **2p**, and **2f** Avenanthramides in Oat Products[a]

sample	concentration (mg/kg of FW)[b]			
	2c	**2p**	**2f**	total
oat flakes, whole grain	9.0 ± 0.5	8.6 ± 0.3	9.0 ± 0.3	27
oat flakes, precooked, whole grain	9.1 ± 0.1	8.3 ± 0.1	8.8 ± 0.1	26
oat bran	4.4 ± 0.2	4.1 ± 0.2	4.3 ± 0.3	13
response factor to convert the amount obtained by Tranilast calibration to avenanthramides	1.15	1.42	1.37	

[a] Dry matter contents of the cereals are presented in **Table 1**. [b] Response ratios were obtained at 350 nm.

Avenanthramides and Alk(en)ylresorcinols. *Avenanthramides in Grain Products.* Avenanthramides **2c**, **2p**, and **2f** were the most dominant forms found in the three studied oat samples (**Table 2**). Only traces of other avenanthramides were detected. The content of avenanthramides was similar both in traditional and precooked rolled oats for porridge (27 versus 26 mg/kg of FW). According to our unpublished findings, these values are typical for the groats of Finnish oat cultivars. Although avenanthramides have been reported to be located mainly in the aleurone layer of the grain (*16*), we found that oat bran made by conventional milling techniques contained less avenanthramides than oat flakes. This could be due to the different raw materials used in the production of flakes and brans. However, these findings are in line with those reported by Bryngelsson et al. (*17*) that the commercial oat brans are not particularly enriched by avenanthramides compared to oat flakes. From simple processes such as steeping, germination, or malting, the contents of avenanthramides can be increased in oat products (*17*, *31*).

Tranilast could be used as a reference compound for the quantification of avenanthramides by applying the response factors presented in **Table 2**. Chemically, Tranilast resembles avenanthramides and exhibits a UV spectrum almost similar to the three avenanthramides typically found in oats. The publication of the response factors for the avenanthramides **2c**, **2p**, and **2f** against Tranilast would be of major interest, because these compounds are not commercially available.

Alk(en)ylresorcinols in Grain Products. Quantification of alk(en)ylresorcinols has been problematic because there are no commercially available reference compounds for those typically found in cereals. We have attempted to overcome this by using olivetol, i.e., 5-pentyl resorcinol, as a reference compound. Assuming that the hydrogen−carbon side chain does not affect molar responses, response factors could be calculated for different alk(en)ylresorcinols (**Table 3**).

Contrary to the case with avenanthramides, the location of most alk(en)ylresorcinols is clearly in the bran fraction. Rye and wheat brans are especially good sources (**Table 3**). Our results concerning the total amount of alk(en)ylresorcinols in conventional rye flour (927 mg/kg) and organic rye flour (1008 mg/kg) are somewhat higher than those reported (726 mg/kg) by Chen et al. (*32*). Our results for rye bran (4108 mg/kg), wheat bran (3225 mg/kg), and whole-wheat flour (759 mg/kg) are also higher than those (2758, 2211, and 339 mg/kg, respectively) obtained by Chen et al. (*32*). It further seems that the cultivation method, conventional versus organic, does not much affect the content of alk(en)ylresorcinols in rye or wheat flours. This is in line with our unpublished observations concerning rye cultivars. Baking seemed to destroy only minor amounts of alk(en)ylresorcinols (*13*), and relatively high amounts of these compounds (513 mg/kg) can be achieved in bread made with whole-grain rye flour (**Table 3**). Alk(en)ylresorcinols content was, however, below the quantification limit in bread baked with sifted wheat flour. Chen et al. (*32*) reported the ration of C17:0 alk(en)ylresorcinols to C21:0 in rye samples to be 1.0 and in wheat samples to be 0.1, which differ somewhat with our results (1.3−1.5 in rye samples and 0.2−0.6 in wheat samples). These differences are most likely due to unresolved alk(en)ylresorcinols in the HPLC analysis. Although the content in buckwheat is on the same level as in wheat flour, their presence adds extra value to this unique crop; none was found in oat products, rice millet, and corn flour.

Table 3. Contents of Alk(en)ylresorcinols in Grain Products (mg/kg of FW)[a]

sample	C17:0	C19:1	C19:0	C21:0	unknown	C23:0	C25:0	total
oat flakes, whole grain	nd[b]	nd	nd	nd	nd	nd	nd	nd
oat flakes, precooked, whole grain	nd	nd	nd	nd	nd	nd	nd	nd
oat bran	nd	nd	nd	nd	nd	nd	nd	nd
rye flour, whole grain	240 ± 1.9	33 ± 1.0	260 ± 1.7	180 ± 5.1	34 ± 5.0	110 ± 7.9	70 ± 7.6	927
rye flour, organic, whole grain	270 ± 10	38 ± 0	280 ± 9.7	190 ± 7.1	40 ± 1.6	120 ± 1.1	70 ± 2.0	1008
rye bran	1100 ± 110	130 ± 14	1300 ± 110	850 ± 96	48 ± 5.5	420 ± 45	260 ± 21	4108
rye bread, whole grain	150 ± 1.9	23 ± 0.2	150 ± 2.2	100 ± 2.0	20 ± 1.3	52 ± 1.9	29 ± 1.0	524
whole-wheat flour	71 ± 0.4	28 ± 0.5	242 ± 0.5	293 ± 4.5	30 ± 1.3	70 ± 0.5	23 ± 1.5	759
white wheat flour	nd	13 ± 0.2	11 ± 0.5	16 ± 0.3	6.5 ± 0.3	nd	nd	47
white wheat flour, organic	nd	13 ± 1.2	10 ± 0.7	16 ± 1.5	5.0 ± 0.3	nd	nd	44
wheat bran	260 ± 1.9	72 ± 5.3	950 ± 0.2	1500 ± 72.5	33 ± 7.3	310 ± 28	100 ± 12	3225
white wheat bread	nd	nd	nd	nd	nd	nd	nd	nd
buckwheat grits, whole grain	nd	nd	nd	41 ± 4.1	nd	nd	nd	41
pasta	11 ± 8.0	nd	9.3 ± 0.7	18 ± 7.4	nd	10 ± 7.6	nd	48
barley flour, whole grain	7.0 ± 2.6	nd	15 ± 0.5	nd	nd	10 ± 0.3	nd	32
rice, long grain parboiled	nd	nd	nd	nd	nd	nd	nd	nd
millet grits	nd	nd	nd	nd	nd	nd	nd	nd
corn flour	nd	nd	nd	nd	nd	nd	nd	nd
response factor to convert the amount obtained by olivetol calibration to AR	1.93	2.08	2.09	2.24	2.24	2.40	2.56	

[a] Dry matter contents of the cereals are presented in **Table 1**. [b] nd = not detected, value below the limit of quantification (3 mg/kg).

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