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Alkylresorcinols in Cereals and Cereal Products

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The alkylresorcinol (AR) content of 8 commonly consumed cereals, 125 *Triticum* cultivars, milling fractions of wheat and rye, bread, and other cereal products was analyzed. ARs were found in wheat (489−1429 μg/g), rye (720−761 μg/g), triticale (439−647 μg/g), and barley (42−51 μg/g), but not in rice, oats, maize, sorghum, or millet. One durum wheat variety was found to have an exceptionally low level of ARs (54 μg/g) compared to other durum wheat varieties (589−751 μg/g) and *Triticum* species analyzed. The AR content of milling fractions closely followed the ash content and could be used as a marker of the presence of bran in flour. Using hot 1-propanol extraction, all ARs could be extracted from bread, contrary to previous studies which suggested that ARs were destroyed during baking. Cereal products varied greatly in AR content, with those containing wheat bran or whole rye having the highest content.

KEYWORDS: Alkylresorcinols; cereals; cereal products; rye; wheat; bran; biomarker; baking

INTRODUCTION

Alkylresorcinols (ARs) are amphiphillic 1,3-dihydroxybenzene derivatives, with an odd-numbered alkyl chain at position 5 of the benzene ring (**Figure 1**). They are found in a number of bacteria, fungi, and some higher plants. Most significantly for food and feed, ARs are found in some members of the Gramineae family (*1*). Of the major cereals, ARs have been reported to be present in high levels (>500 μg/g) in wheat, rye, and triticale and in low amounts in barley, millet, and maize. Although ARs are also found in rice seedlings, mango latex and peel, and cashew nut shell liquid, they are not present in the edible parts of these plants (*1*−*4*), or they are present in minute amounts as in the case of cashew nuts (*5*). **Table 1** shows the current literature data on the levels of ARs in cereals.

Cereal ARs have been reported to have anticancer and antimicrobial effects, as well as an ability to inhibit some metabolic enzymes in vitro. ARs have also been reported to have antioxidant activity, although they have been shown to be poor antioxidants compared to α-tocopherol in vitro (*22*). It has been suggested that they may be metabolized to antioxidant compounds in vivo (*1*). The biological effects of ARs have been comprehensively reviewed by Kozubek and Tyman (*1*).

ARs are found mainly in the outer layers (bran fraction) of cereal grains (*9*, *12*), which means that they are largely missing in refined cereal flour and conventional cereal products such as white bread and most breakfast cereals. There are limited data on the AR content of cereal grains other than wheat, rye, and triticale. Information on the AR content of cereal products is also limited, but Winata and Lorenz (*23*) have shown a reduction in AR content in wheat and rye sourdough bread and suggested that fermentation and/or the baking process destroys ARs. Lorenz and Al-Ruqaie (*24*) showed that extrusion processing, similar to that used for producing breakfast cereals and pasta, also destroys ARs.

Recommendations by the U.S. Food and Drug Administration (FDA) for an increased intake of whole grain cereals (*25*) would lead to an increased consumption of foods with ARs. It is important to have a better understanding of the amount and availability of ARs in our diet and the effects of processing on their content in foodstuffs. In this paper, we report the levels of ARs in the major food cereals and related species with an emphasis on wheat, milling fractions of wheat and rye, the effect of baking on AR content in rye bread, and the AR content of selected cereal products.

Table 1. Presence of Alkylresorcinols in Cereal Grains According to the Literature

cereal	range (μg/g of DM)	main homologues	references
rye (*Secale cereale*)	360–3200	C17, C19, C21	*6–12*
triticale (× *Triticosecale*)	580–1630	C19, C21, C23	*6*, *7*, *10*, *13*, *14*
durum wheat (*Triticum durum*)	460–1080	not determined	*15*
wheat (*Triticum aestivum*)	317–1010	C19, C21	*6–10*, *14*, *16*
spelt wheat (*Triticum spelta*)	337–494	not determined	*17*
barley (*Hordeum vulgare*)	44–500	C19, C21, C25	*6*, *18*, *19*
millet (*Pennisetum americanum*)	100	C17, C19, C21	*6*, *20*
maize (*Zea mays*)	unknown[b]	C1	*21*

[a] For structures of ARs, see **Figure 1**. [b] Value given as 0.1–2.6 μg/μL.

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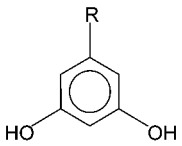

R	Names	[CAS No.]
$C_{15}H_{31}$	**5-n-pentadecylresorcinol**, 5-pentadecyl-1,3-benzendiol, cardol (trivial) (C15:0)	[3158-56-3]
$C_{17}H_{35}$	**5-n-heptadecylresorcinol** 5-heptadecyl-1,3-benzendiol (C17:0)	[41442-57-3]
$C_{19}H_{39}$	**5-n-nonadecylresorcinol** 5-nonadecyl-1,3-benzendiol (C19:0)	[35176-46-6]
$C_{21}H_{43}$	**5-n-heneicosylresorcinol** 5-heneicosyl-1,3-benzendiol (C21:0)	[70110-69-7]
$C_{23}H_{47}$	**5-n-tricosylresorcinol** 5-tricosyl-1,3-benzendiol (C23:0)	[70110-60-0]
$C_{25}H_{51}$	**5-n-pentacosylresorcinol** 5-pentacosyl-1,3-benzendiol (C25:0)	[70110-61-1]

Figure 1. Structure, names, and Chemical Abstracts Service Registry numbers [CAS No.] of the common 5-*n*-alkylresorcinols in cereal grains. Alkylresorcinols are synonymous with alkylresorcins.

MATERIALS AND METHODS

Cereal Samples. Swedish cereal samples [wheat (*Triticum aestivum*), rye (*Secale cereale*), triticale (× *Triticosecale*), barley (*Hordeum vulgare*), and oats (*Avena sativa*)] were donated by the Unit of Applied Field Research (Swedish University of Agricultural Sciences, Uppsala, Sweden). Rice (*Oryza sativa*) samples were provided by the International Rice Research Institute (Manila, The Philippines); millet (*Pennisetum americanum*) and maize (*Zea mays*) were obtained from the Institut für Pflanzgenetik und Kulturpflanzenforschung (Gatersleben, Germany). Sorghum (*Sorghum bicolor*) came from Department seed stores (SLU). *Triticum* species and 125 samples of common wheat (*Triticum aestivum*) grown in France, Germany, and the United Kingdom were a gift from the Morley Research Station (Norfolk, U.K.) and Plant Breeding International (Cambridge, U.K.).

Experimental Breads. Three experimental rye bran enriched breads were baked to represent three different methods of baking. The breads were a loaf baked in a baking tin (height = 5.5 cm, length = 21 cm, width = 9.5 cm), a northern European style loaf, baked without a baking tin (h = 4.5 cm, l = 23 cm, w =12.5 cm), and a flatbread, similar to small round "pancakes" (råg kaka) (h = 2 cm, diameter = 12 cm). The dough contained 500 g of high-protein white wheat flour, 400 g of rye bran, 20 g of sugar, 20 g of salt, 20 g of lactic acid powder, 50 g of yeast, 20 g of baking margarine, and 850 mL of water for the loaf baked in a baking tin and 750 mL of water (28 °C) for the loaf baked without a baking tin and flatbreads. Breads were baked using a sponge and dough process, with all ingredients except rye bran fermented at 37 °C for 30 min before rye bran was added and the breads were baked. The loaf baked in a baking tin, the loaf baked without a baking tin, and flatbreads were baked at 200 °C for 35, 25, and 15 min, respectively.

Milling Fractions. Milling fractions were made from one rye cultivar (Amando) and one wheat cultivar (Ritmo). Samples were milled using a Bühler MLU 202 laboratory roller mill (Laboratoriums-Mahlautomat model MLU 202, Gebruder Bühler Maschinenfabrik, Uzwill, Switzerland). Six different flour fractions were obtained (F1−6), as well as a shorts fraction (S1) and a bran fraction (B1). The ash content of the milling fractions was determined according to standard methods (AOAC method 942.05, 1990). Ash content is used as a marker of bran content in flour. In general, the lower the ash content of a flour, the better its baking properties are.

Cereal Products. Commercial bread, flour, and cereal products were purchased from a local supermarket in Uppsala, Sweden.

Chemicals and Reagents. Standard 5-*n*-heneicosylresorcinol (C21:0) was synthesized as per Ross et al. (*26*). 5-Pentadecylresorcinol (C15:0) was purified from an Aldrich C15:0 preparation (Aldrich, St. Louis, MO) according to Kamal-Eldin et al. (*22*). Olivetol (C5:0; Sigma Chemicals, St. Louis, MO), C15:0, and C21:0 were used for determining the analytical relative response factors against methyl behenate used as an internal standard (methyl docosanoate; Larodan Fine Chemicals AB, Malmö, Sweden). All other solvents and reagents were of analytical grade (E. Merck, Darmstadt, Germany, or BDH, Poole, U.K.) and were used without further purification.

Identification of ARs. ARs were identified using gas chromatography−mass spectrometry (GC-MS) as per Ross et al. (*12*), except that ARs were converted to their trimethylsilyl ether (TMS) derivatives. AR peaks were identified by total ion count (TIC) scans between *m*/*z* 100 and 700. Silylated ARs have a characteristic fingerprint, with the base peak at *m*/*z* 268, and the molecular ion. Fragmentation patterns of ARs were compared with known AR standards when available. See **Figure 2** for TIC and single ion recording (SIR) (*m*/*z* 268) of barley, rye, triticale, and wheat samples.

Extraction and Analysis. ARs extracted from intact cereal grains or flour were analyzed using the GC method of Ross et al. (*12*). Briefly, internal standard (0.5 mg/mL methyl behenate) was added to whole grains (1 g) or flour (0.5 g) and extracted with 40 mL of ethyl acetate (20 mL for flour) for 24 h with continuous shaking at 20 °C. Portions of the extract (4 mL) were then evaporated to dryness at room temperature in vacuo using a centrifuge evaporator (Speedvac concentrator, Savant Instruments Inc., Farmingdale, NY) in 5 mL glass test tubes. Ethyl acetate (200 μL) was added, and samples were analyzed by GC as described previously (*12*). Wheat grain samples obtained from the United Kingdom were analyzed using a slightly modified method, in which grains were coarsely ground in a coffee mill, and an external standard was used for quantification.

Bread and cereal products were extracted using hot 1-propanol as per Morrison et al. (*27*). Freeze-dried samples were milled (Cyclotech 1093 sample mill, Tecator AB, Sweden) to pass through a 0.5 mm sieve and then extracted with 10 mL of 1-propanol/water (3:1 v/v) with three extractions in a boiling water bath (2 × 2 h, 1 × 1 h) using fresh solvent each time. Extracts were pooled, and aliquots were evaporated to dryness in a rotoevaporator at 45 °C with the help of absolute ethanol to remove the remaining water, resuspended in ethyl acetate, and analyzed by GC as per Ross et al. (*12*). Initially, bread samples were extracted with ethyl acetate as for cereal grains and flour and also extracted with acetone and methanol using the same conditions for comparison.

All values are reported on a dry matter (DM) basis. DM was determined by drying samples in an oven at 105 °C overnight, cooling in a desiccator, and then weighing. All DM analysis was carried out in triplicate.

RESULTS AND DISCUSSION

Levels of ARs in Different Cereal Grains. Of the cereals analyzed, ARs were found in rye, triticale, wheat, and barley, but not in oats, rice, maize, millet, or sorghum (**Table 2**), although ARs have been previously reported in millet, maize, and oat bran. We scanned three different cultivars of each cereal using GC-MS and could not find any evidence for ARs in these cereals. In the case of oats, the fluorescence methods of Evans et al. (*6*) and Verdeal and Lorenz (*7*) were used for analysis previously. Mullin and Emery (*28*) observed that although fluorescence methods showed some ARs present in oat and polished barley samples, this could not be confirmed with either high-performance liquid chromatography (HPLC)

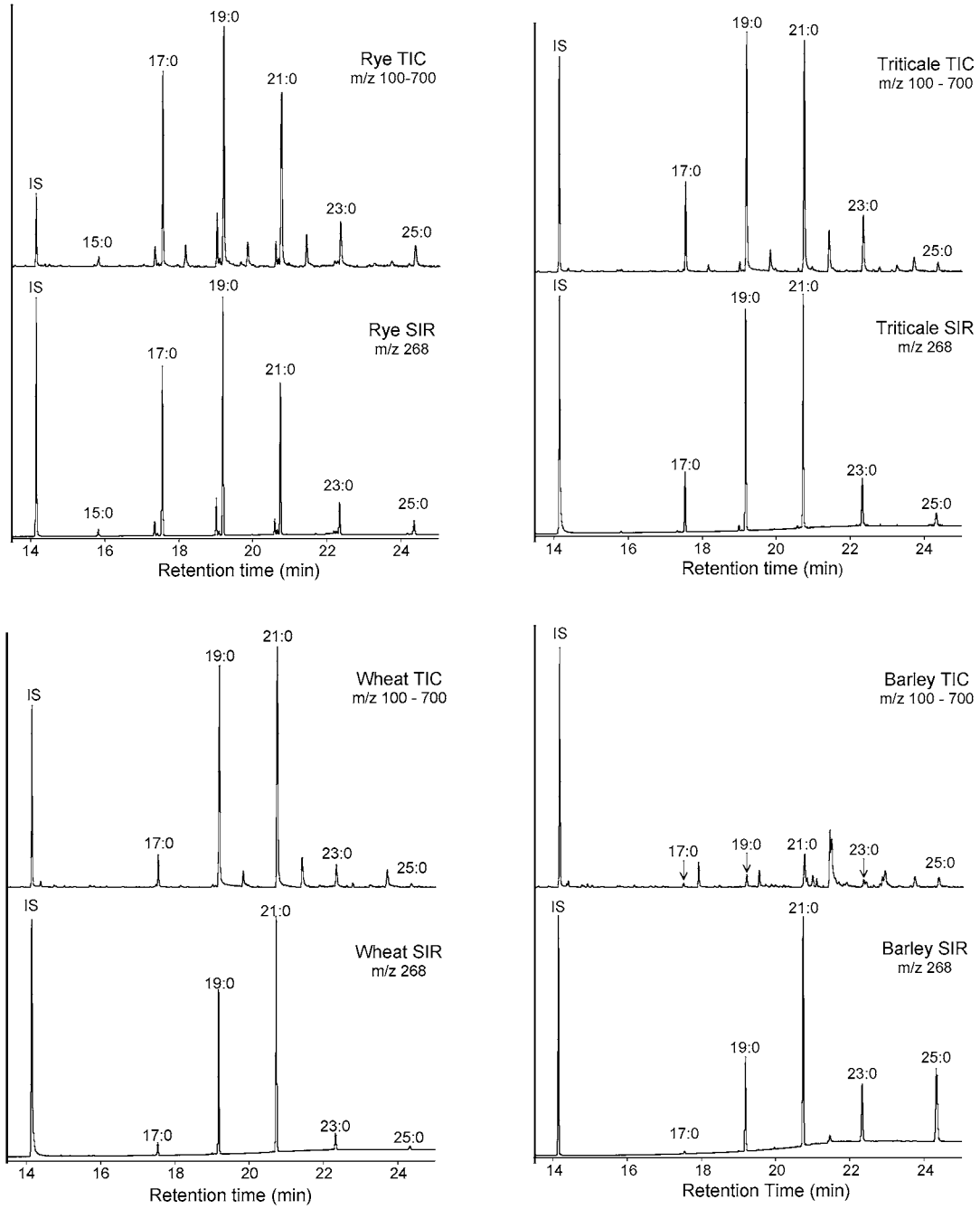

Figure 2. GC-MS analysis of TMS-derivatized cereal ARs as shown by TIC and SIR (*m/z* 268) chromatograms of rye, triticale, wheat, and barley grains. Internal standard (IS, methyl behenate) and main AR homologues are marked (see **Figure 1** for chemical structure).

or GC. The response from the fluorescence method was thought to be due to coextracted phenolic compounds. Chromatographic methods are considered to be more accurate and have the advantage that they can easily identify the different AR homologues. Hengtrakul et al. (*20*) reported the presence of ARs in millet, using HPLC and comparing peak retention times with a reference sample of rye. No attempt to quantify the amount of ARs in millet was made. 5-Methylresorcinol has been reported as an antifungal compound in maize (*21*), but we were unable to detect this compound in our samples. As this compound is present in only small amounts in the wax layer of maize, it may be below the detection limit of our method (5 μg/g).

Bouillant et al. (*4*) studied root exudate from rice and found ARs ranging in chain length from 13 to 17 carbons long. They were present in residual caryopses after germination but were not present in rice grains. Suzuki et al (*29*, *30*) found ARs in rice seedlings but did not mention whether they were present in rice grains or not. A compound similar to 1,3-alkylresorcinols, 4,6-dimethoxy-2-pentadecatrieneresorcinol, has been found in the exudate of *Sorghum bicolor* roots (*31*), but not in the grains.

Cereal cultivars analyzed were those commonly used in Swedish food production/feed for animals (**Table 2**). There is not much variation between the three different barley and rye cultivars, and values are within the range of those previously reported (**Table 1**). Previously, Briggs (*32*) found evidence for trace amounts of ARs with even-numbered alkyl chains in barley, and Hengtrakul et al. (20) reported that low amounts of C20:2 were found in rye. No work has since found even-numbered alkyl chains in barley, rye, or any other plant (*1*). The AR contents of wheat and triticale were also within the range of previously reported values but had more variation between different cultivars. Triticale, a cross between wheat and

Table 2. Content of Alkylresorcinols in Selected Cereals[a]

cereal	cultivar	% of each homologue 15:0	17:0	19:0	21:0	23:0	25:0	total ARs
barley	Alexis	nd[b]	10	12	27	17	35	42
	Baronesse	nd	7	13	27	16	37	51
	Olivia	nd	3	11	24	18	44	42
rye	Amilio	1	25	32	22	10	10	720
	Esprit	2	24	32	25	10	8	722
	Nikita	2	23	31	24	11	10	761
triticale	Algalo	nd	13	36	34	12	5	439
	Fidelio	nd	11	31	35	16	9	555
	Prego	nd	11	33	34	15	7	647
wheat	Kosack	nd	5	35	46	10	4	489
	Ritmo	nd	4	29	51	12	4	642
	Tarso	nd	5	35	48	9	3	618

[a] Micrograms per gram of DM, means of triplicates (CV < 5%). No ARs were detected in maize, millet, oat, rice, or sorghum samples. [b] Not detected (detection limit = 5 μg/g).

rye, has been reported as being intermediate between wheat and rye for AR content (*10*), but in this case, triticale cultivars were more similar to wheat in terms of both homologue composition and total content.

ARs with modified alkyl chains are also present in cereals. These are believed to differ from ARs only in side-chain unsaturation or oxidation (*1*, *33*, *34*). The amounts vary between ~0.5% for barley (*19*) and ~15% for rye (*33*). These compounds can be isolated by thin-layer chromatography and show up as one or two peaks eluting just prior to the major homologue peaks in a GC chromatogram (**Figure 2**). These AR analogues may be more bioactive than normal saturated ARs (*1*). The fragmentation patterns of these peaks were not good enough to resolve the exact structures of these compounds. It was evident, however, that these compounds have the 1,3-dihydroxybenzene group, characteristic of ARs, and a molecular ion fragment *m*/*z* −2 compared to the molecular ion of the next eluting AR peak, indicating that it has the same chain length but is monounsaturated. As we do not know the exact identities of these peaks, and no standards are available to confirm their identities, we have not included them in our quantification of total ARs. For wheat, triticale, and barley cultivars analyzed, there is only a small amount of the minor AR derivatives (ca. 7%, 6%, and trace amounts respectively), but the rye cultivars analyzed contained significant amounts (~20%).

Variation in AR Content of *Triticum* Grains. Thirteen *Triticum* species were analyzed for AR content to get an idea about the variation across the species. Results showed a large variation in the AR content in the different *Triticum* species (range = 200−1489 μg/g) (**Table 3**). This is broader than for *T. aestivum* cultivars analyzed previously (**Table 1**) and in this study. The homologue composition also varies greatly; *T. timophevi* had the highest content of ARs but the lowest amount of C21:0 (the main AR homologue in wheat), whereas *T. turanicum* had the lowest total content of ARs but the highest proportion of C21:0. No relationship between evolution and genome composition of the *Triticum* species and AR content could be determined. The only previous report of ARs in *Triticum* species other than for *T. aestivum* is for spelt (*Triticum spelta*) (337−494 μg/g) (*17*) and durum wheat (*Triticum durum)* (460−1080 μg/g) (*15*). Four of the five durum wheat samples analyzed in this study had an average content of 673 μg/g (range = 589−751 μg/g), lower than for other wheat varieties analyzed in this study. One durum wheat cultivar (Ardente) was exceptional in having only 54 μg of AR/g.

Table 3. Alkylresorcinol Content[a] of *Triticum* Species

species	homologue % 17:0	19:0	21:0	23:0	25:0	total AR
T. timophevi	6	28	36	19	11	1480
T. compactum	7	35	42	12	5	1090
T. ispahanicum	nd[b]	13	52	23	12	982
T. polonicum	nd	9	55	26	10	951
T. paleocolchicum	nd	19	53	21	7	916
T. aestivum	6	30	41	19	5	909
T. carthlicum	nd	10	55	25	10	876
T. sphaerococcum	6	28	50	11	5	862
T. spelta	6	28	43	15	8	819
T. dicoccum	nd	20	54	19	8	819
T. dicoccoides	nd	13	58	23	6	787
T. orientale	nd	9	59	24	8	691
T. durum	nd	9	51	27	13	687
T. araraticum	nd	11	55	27	8	599
T. turanicum	nd	nd	74	25	1	200

[a] Micrograms per gram of DM. [b] Not detected (detection limit = 5 μg/g).

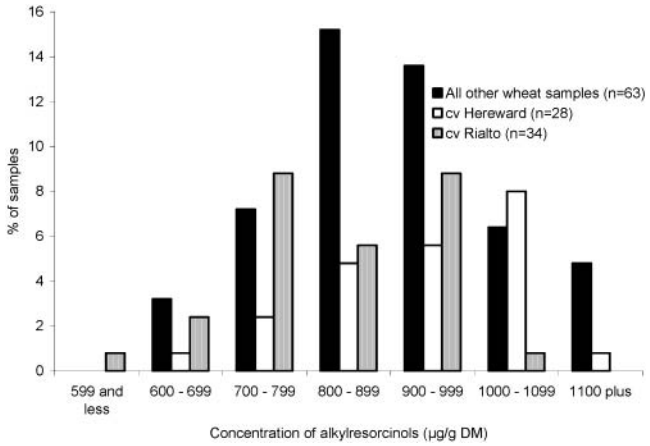

Figure 3. Distribution of total alkylresorcinol content in two cultivars [Hereward (*n* = 28) and Rialto (*n* = 34)] and 29 other wheat cultivars (*n* = 63) grown at different locations in France, Germany, and the United Kingdom.

Results for the analysis of common wheat grains showed that AR levels varied from 595 to 1429 μg/g for 125 samples (31 cultivars) grown in the United Kingdom, France, and Germany, with a mean of ~900 μg/g (**Figure 3**). These values are higher than those previously reported for Eastern European and North American wheats, with a range of 200−800 μg/g (*16*, *35*). However, levels up to 3000 μg/g have been reported in some wheat samples (*35*). This variation is probably due in part to differences in analytical methods with the more modern chromatographic methods (GC and/or HPLC) being more reliable. However, the AR content of cereals also appears to be highly variable, depending on cultivar and environmental conditions. Two cultivars of wheat, Hereward and Rialto (*Figure 3*), grown in the United Kingdom, France, and Germany at 28 and 34 different locations, respectively, showed marked variation in AR content. The levels of ARs in the two cultivars varied between 690 and 1100 μg/g (945 ± 115 μg/g) and between 595 and 1060 μg/g (825 ± 112 μg/g), respectively, although 82% of the Hereward samples were between 800 and 1099 μg of ARs/g and 85% of the Rialto samples were between 700 and 1000 μg of ARs/g (**Figure 3**). A single cultivar of wheat (cv. Hereward) was grown in a single field (20 m^2), and samples were taken from 20 different locations within the field. The AR content varied from 690 to 1200 μg/g (990 ± 110 μg/g), showing that factors other than cultivar are important for

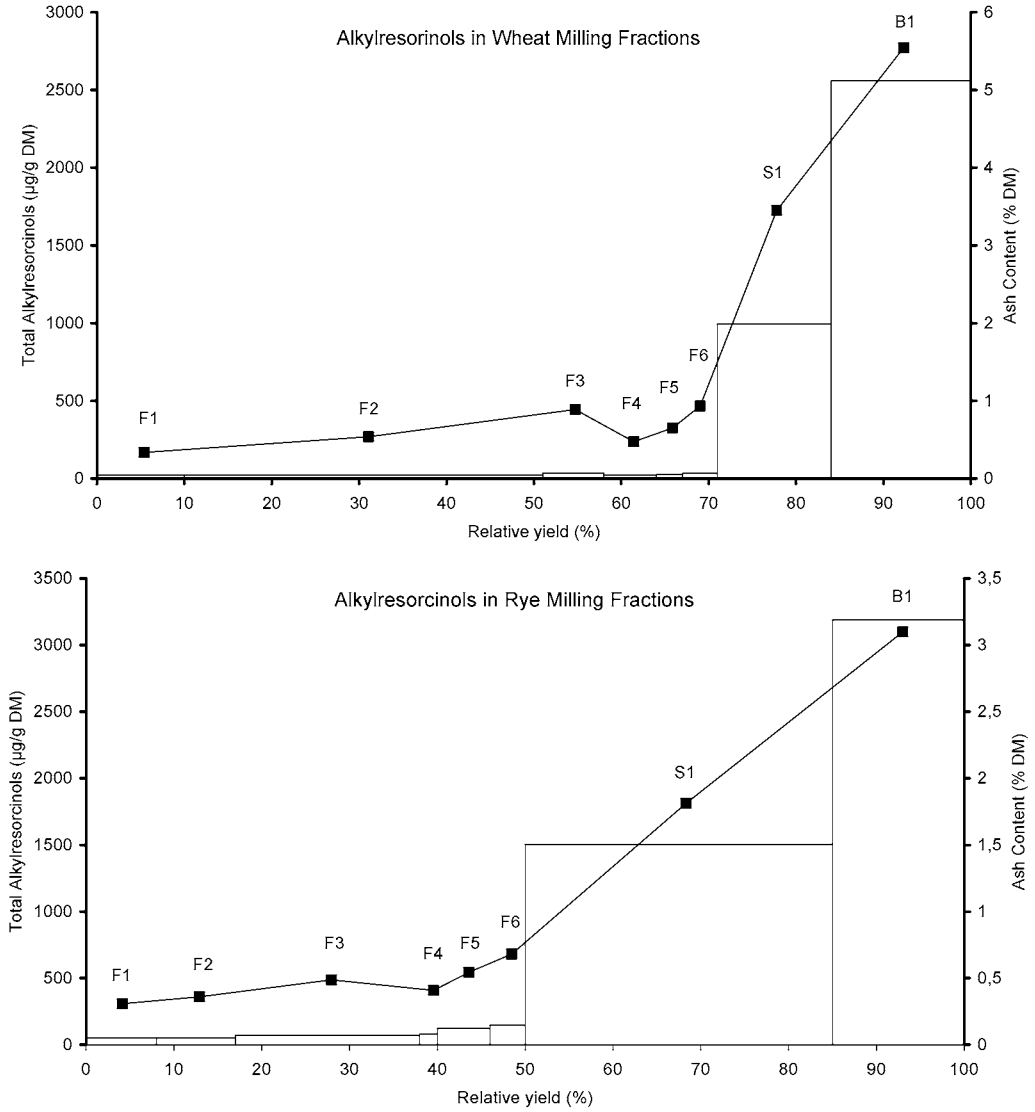

Figure 4. Yields (percent) and AR content of wheat and rye flour milling fractions (F1–6) and shorts (S1) and bran (B1) fractions. The line represents the ash content of the different milling fractions. The area of the bars represents the proportion of ARs in that milling fraction. For explanation of the milling fractions, see text.

determining AR content. Comparison of the AR content of nine wheat cultivars grown at five different locations in France did not reveal any obvious link between AR content and cultivar and/or location. Means for cultivar and location were similar (899 and 897 μg/g, respectively), but the range for all values was wide (650−1240 μg/g). Levels of ARs in Swedish wheat samples analyzed (**Table 2**) were at the lower end of the range of the samples from the United Kingdom. It is impossible to say at this stage whether this variation is due to climate or cultivar factors. Furthermore, no correlation was found between 1000-grain weight and AR content, expected from the fact that ARs are located in the outer layers of cereal grains (*12*) so a large surface area/weight ratio could mean a higher AR content.

ARs in the Milling Fractions of Wheat and Rye. Figure 4 shows that almost all ARs are present in the shorts and bran fractions of wheat and rye. A number of papers have reported that ARs occur exclusively or predominantly in the outer layers of wheat and rye, specifically, the aleurone layer and pericarp/testa (*7*, *9*, *12*). Wheat flour has a higher flour yield than rye, but both flours have low AR and ash contents. White wheat flour has essentially no ARs present, whereas rye flour has a low amount. Wheat bran separates easily from the endosperm, allowing easy production of flour with high extraction rates. The bran fraction of rye, often including the aleurone layer, the cereal tissue richest in ARs (*12*), adheres tightly to the endosperm, making clean separation of the aleurone layer and pericarp and testa impossible (*36*). Whereas white wheat flour products do not contribute to the overall amount of ARs eaten, rye flour may.

Weipert and El Bayâ (*8*) found that with increasing extraction rate and ash percent, AR content also increased. Extraction rates for flour depend on the grains, mill, milling company, and country, but in general a higher extraction rate could lead to a higher AR content in flour, especially rye flour.

AR Levels in Experimental Rye Breads. Three different rye bran enriched breads were baked in this study using the same flour mix but different baking conditions. The breads were a loaf baked in a baking tin, a traditional northern European style bread baked without a baking tin, and a small flatbread (rågkaka). During initial trials, it was found that methanol extracted more ARs from bread (~90%) than either ethyl acetate or acetone (~70%). Our results clearly show that methods used for extracting ARs from unprocessed cereals are not suitable for extracting ARs from bread. Essentially all ARs were

Table 4. Alkylresorcinol Content[a] of Flour and Three Experimental Rye Bran Enriched Breads Extracted with Ethyl Acetate or Hot Propanol

	ethyl acetate	hot propanol
flour	1824	1814
loaf baked in baking tin		
whole	1242	1871
crust	1273	1819
crumb	1239	1913
loaf baked without a baking tin		
whole	1238	1928
crust	1190	1924
crumb	1233	1917
flatbread		
whole	1207	1862
crust	1226	1805
crumb	1223	1866

[a] Micrograms per gram of DM, means of triplicates (CV < 5%).

recovered from the experimental breads when using the hot 1-propanol extraction method of Morrison et al. (*27*), designed to completely extract lipids from starch−lipid complexes (**Table 4**). From this, it appears that the baking process causes complexation rather than destruction of ARs. It is known that amylose forms inclusion complexes with other amphiphilic compounds such as monoacylglycerols and free fatty acids, but not with triacylglycerols (*37*, *38*). Irrespective of baking conditions, "apparent AR complexation" (difference between ARs extracted with ethyl acetate and ARs extracted with hot 1-propanol) was about the same.

Al-Ruqaie and Lorenz (*14*) and Winata and Lorenz (*23*) report that fermentation and baking decrease the AR content of bread, whereas other reports suggest that heating and autoclaving conditions do not significantly alter AR content in rye grains (*39*). We did not study if AR complexation started during fermentation or baking, although ARs have not been reported to be produced or metabolized by baker's yeast (*1*). It may be possible that other types of yeast may break down some ARs, as they are metabolized by some fungi (*1*).

ARs in Other Cereal Products. A range of cereal products was selected for analysis of ARs present in "everyday" foods (**Table 5**). Like most food components, content of ARs in cereal products is likely to vary as it does in cereal grains. Here we have selected a number of foods that were likely to contain ARs—that is, products high in cereal dietary fiber and flour commonly used in bread baking as well as some white wheat flour products for comparison.

Products made from white wheat and/or white rye flour had no or very low levels of ARs, consistent with the fact that ARs are located only in the outer layers of these grains. The products that contained most ARs were those containing wheat or rye bran (All Bran) or whole rye (rye crispbread). Oat bran contained no ARs, contrary to previous reports (*24*). As ARs appear to be closely linked to the bran fraction when milling, it could be a good indicator of how much bran is present in bread and other foods made from wheat, rye, or barley, although this could be complicated by the variation of AR content in these grains.

The FDA states that for a food to be labeled whole grain, a cereal product need have only 51% or more of the total dry ingredients as whole grain (*40*), so it is evident that some products are more "whole grain" than others. Slavin et al. (*25*) state that one of the difficulties linking whole grain cereals to health effects is the problem of determining whether a product is "whole grain" or not. There was marked variation in the two

Table 5. Alkylresorcinol Content[a] in Selected Swedish Cereal Products

	% of each homologue					total
cereal product	17:0	19:0	21:0	23:0	25:0	ARs
rye products						
rye crispbread (whole grain) a	22	34	24	11	10	1007
rye crispbread (whole grain) b	23	32	24	12	10	912
rye crispbread (whole grain) c	22	30	26	12	10	886
whole grain rye flour	22	31	26	12	10	865
whole grain rye bread a	23	33	25	11	8	707
rolled rye grains	26	34	24	10	8	698
whole grain rye bread b	21	32	25	12	11	380
pasta with rye bran	22	29	29	11	9	262
rye flatbread	16	44	24	10	6	81
sifted rye flour (40% rye flour, 60% wheat flour)	16	30	30	16	8	44
wheat products						
wheat bran	4	34	49	10	3	2672
wheat bran based cereal (All Bran)	4	30	52	11	4	1784
wheat breakfast biscuits (Wheetabix)	4	29	52	12	4	558
whole grain wheat flour	6	32	44	9	4	550
crusty whole grain wheat bread	3	38	47	9	3	222
wholemeal wheat crackers	4	33	50	9	3	179
wholemeal wheat bread	17	32	30	10	9	142
wheat crispbread	nd[b]	39	50	11	nd	58
digestive biscuits	nd	33	56	12	nd	57
white wheat flour	nd	nd	nd	nd	nd	nd
white wheat bread	nd	nd	nd	nd	nd	nd
other cereal products						
coarsely ground barley grains	nd	13	28	16	44	59
brown rice	nd	nd	nd	nd	nd	nd
oat bran	nd	nd	nd	nd	nd	nd

[a] Micrograms per gram of DM, means of triplicates (CV < 5%). [b] Not detected (detection limit = 5 μg/g).

whole grain rye breads analyzed—one had 380 μg/g and the other, 707 μg/g. Many "brown" breads contain little or no whole grain flour, the brown color being added using colorants. Some wheat products analyzed stated that they were "wholemeal" and, in fact, had a low AR content (<200 μg/g), indicating that some products may not contain as much whole grain flour as their labels imply. Measuring ARs may be a more selective way of determining whether a product contains whole grain wheat or rye than ash percent or ferulic acid content (*41*).

Sági et al. (*42*) analyzed the amount of ARs in macaroni and concluded that there were losses of up to 40% of ARs during processing and that pasta could be essentially considered to be AR-free. It is inconsistent that semolina used to make pasta (from the starchy endosperm) should contain ARs when studies on rye and wheat indicate that ARs are almost exclusively found in the outer layers of the grain. There are some pasta products that contain added cereal products, such as bran, which could also contain ARs, but the reports by Sági et al. (*42*) and Lorenz and Al-Ruquaie (*24*) that there are losses of ARs during the production of pasta require re-examination in the light of the possibility of starch−AR complexes.

Conclusions. Interest in knowing more about ARs in the diet is twofold. ARs may be useful as biomarkers for the presence of whole grain wheat and rye in food products and for estimating human intake of whole grain wheat and rye, and they may be bioactive in vivo. Accurately estimating daily intake for ARs is difficult due to the large variation in AR content in these cereals. However, the chance that a whole grain cereal product will have a very low AR content (<200 μg/g) is very low. From Swedish food intake tables (*43*), it can be estimated that a person eating a normal diet, but choosing whole grain wheat and rye

products for their cereal intake, would consume ~85−100 mg of ARs/day. This intake could easily be higher; for example, one serving of All Bran (a wheat bran based breakfast cereal) provides ~70 mg of ARs. As ARs are not destroyed during the baking process as previously thought, they may be present in food in high enough concentrations to have a bioactive effect. ARs have been shown to be bioactive in vitro, with antimicrobial and anticancer activities (*1*), among others. They have been shown to be absorbed in pig and rat models (*26*) and have been found in human blood (*44*). The presence of ARs in high amounts in whole grain wheat and rye products warrants the study of their significance as biomarkers of whole grain intake and as bioactive components in the diet.

ABBREVIATIONS USED

AR, alkylresorcinol; DM, dry matter; GC, gas chromatography; HPLC, high-performance liquid chromatography; GC-MS, gas chromatography−mass spectrometry; TIC, total ion count; SIR, single ion recording; FDA, U.S. Food and Drug Administration.

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