Avenanthramides—A Group of Phenolic Antioxidants in Oats

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ABSTRACT

Two avenanthramides belonging to a group of about 40 cinnamoylanthranilic acid derivatives in oat grains were isolated: *N*-(4′-hydroxy-3′-methoxy-(E)-cinnamoyl)-5-hydroxyantranilic acid (A1) and, not previously reported, *N*-(4′-hydroxy-3′-methoxy-(E)-cinnamoyl)-5-hydroxy-4-methoxyanthranilic acid (A2). The antioxidative capacities of the two avenanthramides, A1 and A2, were determined by measuring the oxygen consumption in a linoleic acid system. A1 had ~20% of the activity exerted by α-tocopherol and A2 had ~60%. Caffeic and ferulic acid, known to be antioxidative, had much lower activities: 6 and 4%, respectively. A1 was preferentially located in the outer part of the grain. It seems to be quite heat stable, at least when located within the oat tissue during steam treatment. A comparison of 10 different cultivars of oats revealed that the amount of A1 varied between 40 and 132 μg per gram of grain. The amount of A2 is at least 10 times lower.

Low molecular weight phenolic compounds in cereal grain have many important biological functions, including growth regulation and defense against parasites (Collins 1986). In cereal food products, various phenolic compounds are of particular interest in connection with different quality factors, such as color, aroma, stability, and nutritional value. Native phenols, as well as those formed during food processing and preparation, can also act as important protective factors against oxidative degradation of unsaturated fatty acids.

Oat grains are rich in lipids with a high content of unsaturated fatty acids (Youngs 1986). They also contain various compounds with antioxidative activities that protect the lipids from oxidation and are important for the storage stability of various oat products. Lipid oxidation in food impairs the food quality. Rancid flavor is the main consequence, but discoloration and loss of polysaturated fatty acids, vitamins, and other essential substances are other consequences (Eriksson 1982). The use of oat grain as an antioxidant source was first proposed in the 1930s (Lowen et al 1937, Peters and Musher 1937). However, despite this antioxidant content, certain oat products, such as oat meal and extruded products, have a high tendency to become rancid. This may be due to increased oxygen exposure of the fatty acids or thermal destruction of certain antioxidants.

Oat substances with known antioxidant activities include the tocopherols (Bauernfeind 1980, Burton and Ingold 1981) and various hydroxycinnamate esters of long-chain alcohols, ω-hydroxy fatty acids, or glycerol (Daniels and Martin 1967, Duve and White 1991). Also the oat sterol fractions containing Δ^5-avenasterol were reported to be antioxidative in soybean oil at 180°C but not at room temperature (White and Armstrong 1986, Gordon 1990). The cinnamic acid derivatives and tocopherols are reportedly sensitive to heat and light, especially with oxygen exposure (Daniels and Martin 1967, Bauernfeind 1980). Tocopherols also undergo degradation during storage and processing (Ames 1972, Bauernfeind 1980). Therefore, it is of interest to examine whether additional antioxidative substances, which are more stable than those mentioned, are present in oat grains.

This article focuses on antioxidative low molecular weight phenolic compounds that are less lipophilic than the ones mentioned. Some previous results are briefly discussed (Theander and Häll Dimberg 1991).

MATERIALS AND METHODS

Chemicals

Adenosine, caffeic acid, *p*-coumaric acid, ferulic acid, nicotinamide, syringic acid, DL-α-tocopherol, tryptophan, vanillic acid, and vanillin, all with a purity grade of at least 97%, were used as reference substances. Two avenanthramides were isolated from oat bran (cv. Sang): *N*-(4′-hydroxy-3′-methoxy-(E)-cinnamoyl)-5-hydroxyantranilic acid (A1) and *N*-(4′-hydroxy-3′-methoxy-(E)-cinnamoyl)-5-hydroxy-4-methoxyanthranilic acid (A2). A1 and A2 were structurally elucidated by nuclear magnetic resonance (^{1}H-NMR) spectroscopy (Fig. 1).

Sephadex LH-20 (Pharmacia LKB, Biotechnology AB, Sweden) and silica gel (60, 0.040–0.063 mm [Riedel deHaen]) were used for column chromatography. Thin-layer chromatography (TLC) was performed on silica gel HF-254 plates (Riedel deHaen).

Oat Samples

Ten different cultivars of oat (*Avena sativa*) were supplied by B. Mattson, Svalöv AB, Sweden. Dehulled oat grains (cv. Vital) were treated for 12 min at 80°C in a rotating drum and dried to 9% mc. One batch was sacked directly, and another batch was steamed for 18 min to reach 80–95°C and then dried to 12% mc. The kernels in the respective batches were divided into three morphological parts (bran, outer endosperm, and inner endosperm) that were milled separately. This procedure was performed by Västsvenska Lantmän, Sweden. In the preparative work, the oat bran (cv. Sang) used was delivered by the mill Kungsörnen, Sweden.

Extraction and Fractionation Procedures

For isolation of extractives in a preparative scale, 2.0 kg of oat bran was extracted in portions (~200 g) with a total of 18 L of 80% aqueous ethanol in an ultrasonic bath at room temperature for 10 min. The combined extract was filtered (Whatman no. 3), and the solvent was evaporated at 40°C. The residue was suspended in ~300 ml of distilled water; the aqueous suspension was extracted three times with 300 ml of petroleum ether (bp 40–60°C). Both liquid phases were evaporated (40°C). The aqueous fraction (20 g) was then suspended in 115 ml of distilled water and fractionated by column chromatography on Sephadex LH-20 (9 × 23 cm) with water, increasing concentrations of aqueous ethanol (stepwise 20, 40, 60, and 95%), and acetone (about

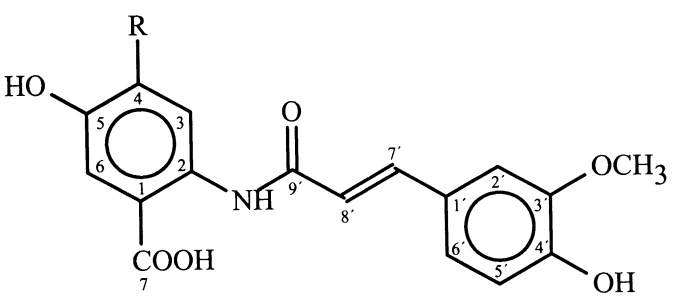

Fig. 1. Two avenanthramides structurally elucidated by nuclear magnetic resonance spectroscopy. Avenanthramide 1: R=H. Avenanthramide 2: R=OCH_3.

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2L of each) as eluents. Six fractions were collected: 6.74, 8.75, 0.50, 0.50, 0.31, and 0.60 g (I–VI, respectively). Fractions with high antioxidative activities were repeatedly subfractionated on silica gel columns using a mixture of EtOAc, MeOH, CH_3COOH, and H_2O (20:5:1:1) or a mixture of $CHCl_3$, MeOH, and H_2O (80:15:1 or 60:15:1) as eluents. In some cases, preparative TLC was performed with $CHCl_3$, MeOH, and H_2O (80:15:1 or 10:5:1) as mobile phases.

Subfractionation of VI (550 mg) on a silica gel column (1.5 × 20 cm) using $CHCl_3$, MeOH, and H_2O (250 ml at 60:15:1 and 400 ml at 10:15:1) as eluents yielded fractions with the two avenanthramides: A1 and A2 (Fig. 1). A portion of these fractions was refractionated on preparative TLC ($CHCl_3$, MeOH, and H_2O at 10:5:1) to isolate chromatographically pure A1 (5 mg) and A2 (0.5 mg).

For qualitative and quantitative analysis of the phenolic compounds in 10 dehulled cultivars, oat grains (10 g) were extracted twice with 100 ml of 80% aqueous ethanol for 2 min in an Ultra-Turrax homogenizer at room temperature. The oat bran and the oat meal samples were extracted with the same amount of 80% ethanol, but in an ultrasonic bath for 15 min. The two extracts from the respective samples were combined and filtered. The solvent was evaporated and the residue was suspended in 2 ml of methanol using ultrasonification for 1 min. The suspension was centrifuged, and the supernatant analyzed by high performance liquid chromatography (HPLC).

Analytical Determination

HPLC was performed on a Merck-Hitachi instrument equipped with a diode-array detector. A reversed-phase C-18 column (LiChrospher, 5 μm, 125-4, Merck) was used. A combination of 0.01*M* phosphate buffer, pH 2.8, and acetonitrile was used as mobile phase (0–30% acetonitrile in 60 min with a flow rate of 1.5 ml/min). The UV-absorbing substances were detected at 250 nm with a bandwith of 100 nm (200–300 nm). To identify the compounds in the chromatograms, the retention time and UV spectra of the peaks were compared to those of purified substances and authentic compounds. The concentration of certain compounds in an oat extract was determined by measuring the peak area and comparing the area with a standard curve of the corresponding reference sample.

^{1}H-NMR spectra were recorded in CD_3OD at 400 MHz. The spectra of the phenolic acids and vanillin were in agreement with reported data. The spectrum of A1 corresponded closely to that reported for *N*-(4′-hydroxy-3′-methoxy-(E)-cinnamoyl)-5-hydroxyanthranilic acid by Collins (1989). The spectrum of A2 was: δ 3.91 (3 H, s, OMe), 3.92 (3 H, s, OMe), 6.56 (1 H, d, J = 15.6 Hz, H-8′), 6.81 (1 H, d, J = 8.2 Hz, H-5′), 7.09 (1 H, dd, J = 2.1 Hz and 8.1 Hz, H-6′), 7.23 (1 H, d, J = 2.2 Hz, H-2′), 7.53 (1 H, d, J = 15.7 Hz, H-7′), 7.54 (1 H, s, H-6), 8.38 (1 H, s, H-3). Long-range ^{1}H–^{1}H COSY revealed a correlation between the OCH_3 signal at δ 3.91 and the aromatic proton singlet at δ 8.38.

Antioxidant Activity Determination

The antioxidant activities of the Sephadex LH-20 and silica gel fractions and of some purified oat compounds, including A1 and A2, were determined as described by Lingnert et al (1979), where the oxygen consumption was measured polarographically in a linoleic acid system. An oxygen analyzer (Medelco AB) equipped with a YSI 4004 electrode (Yellow Springs) was used. The volume of the measuring cell was 1 ml, and 100 μl of hemin solution was injected into the cell to initiate the oxidation.

RESULTS AND DISCUSSION

The extractives were removed from the oat samples with 80% aqueous ethanol at room temperature in an Ultra-Turrax homogenizer or an ultrasonic bath. These are effective and convenient procedures for removing hydrophilic and lipophilic low molecular weight extractives in various plant materials (Theander 1991).

The oat bran ethanol extractives were divided between water and petroleum ether (bp 40–60° C); compounds in the water phase were fractionated on a column of Sephadex LH-20. The water phase subfractions (I–VI) and the more lipophilic extractives in the petroleum ether phase were analyzed for antioxidative activities. Table I shows that the subfractions IV–VI and the petroleum

TABLE I
Antioxidant Activity of Extractive Fractions from Oat Bran[a]

Samples	Antioxidant Activities[b] (% of the activity of α-tocopherol)[c]
Water fraction	9
LH-20, fractions	
I	6
II	2
III	8
IV	32
V	32
VI	35
Petroleum-ether fraction	38

[a] Mean values from two replicates.
[b] 1.25 mg (dry weight) of extract per milliliter of linoleic acid emulsion.
[c] 1.25 mg of α-tocopherol per milliliter of linoleic acid emulsion.

TABLE II
Antioxidant Activities of Some Oat Grain Compounds[a]

Samples	Antioxidant Activities[b] (% of α-tocopherol on molar basis)[c]
Caffeic acid	6
Ferulic acid	4
Vanillin	2
Avenanthramide 1	18
Avenanthramide 2	57

[a] Mean values from two replicates.
[b] 25 μg of sample per milliliter of linoleic aid emulsion.
[c] 25 μg of α-tocopherol per milliliter of linoleic acid emulsion.

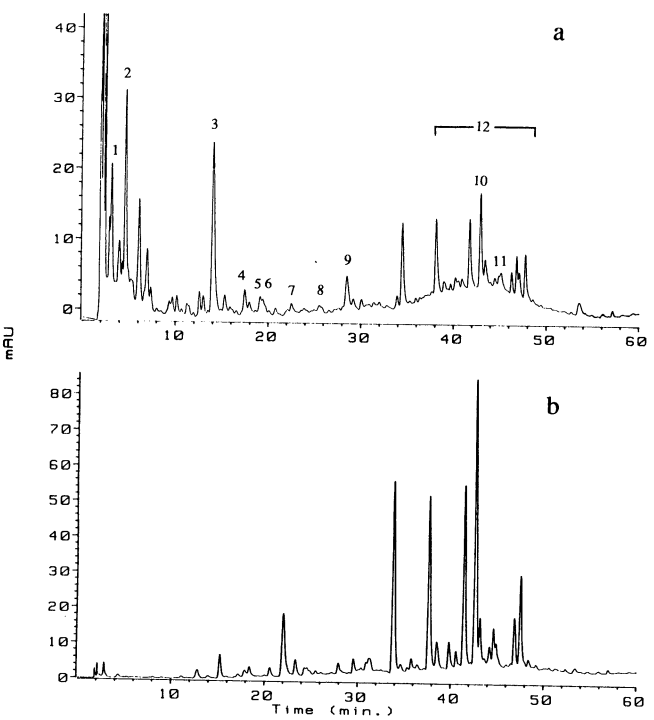

Fig. 2. UV-absorbing (200–300 nm) hydrophilic extractives in oat bran revealed by high-performance liquid chromatography. **a,** whole mixture. **b,** LH-20 subfraction VI. Nicotinamide (1), adenosine (2), tryptophan (3), vanillic acid (4), caffeic acid (5), syringic acid (6), vanillin (7), *p*-coumaric acid (8), ferulic acid (9), avenanthramide 1 (10), avenanthramide 2 (11), several peaks with avenanthramide-like UV spectra (12).

ether phase had quite significant antioxidative activity, around one-third of that of authentic α-tocopherol. The tocopherols constitute a considerable part of the antioxidative capacity of the oat oil, but none of the activities in the fractions tested was due to the tocopherols. Analysis (not shown) revealed that they were not present in the fractions.

In this study, no further purification was made of the active compounds in the petroleum ether phase, but the subfractions IV, V, and VI were further chromatographically fractionated. Figure 2 shows the HPLC chromatogram of the total water phase and the LH-20 subfraction VI of the oat bran extractives, which are UV-absorbing in the range of 200–300 nm. Compounds purified and identified were vanillic, syringic, *p*-coumaric, caffeic, and ferulic acids, as well as vanillin and the two avenanthramides (Fig. 1). The antioxidative activities of ferulic acid, caffeic acid, and vanillin (authentic samples), which all exert antioxidative activities (Daniels and Martin 1961, Burri et al 1989b), were tested in the linoleic acid emulsion system. The activities were rather low, ~5% of the α-tocopherol activity for the phenolic acids and ~2% for vanillin (Table II). In free form, ferulic and caffeic acids together rarely exceed 0.001% of the dry weight of the oat grain (Sosulski et al 1982), so their contribution to the antioxidative capacity of the oat grain must be rather low. However, the levels of soluble esters and glucosides of phenolic acids are about 2–5 times greater than the free phenolic acid levels. The total bound phenolic acids represent about 66% of the total phenolic compounds in oat flour (Sosulski et al 1982). Some of these compounds, especially cinnamic acids ester-bound to long-chain alcohols, ω-hydroxy fatty acids, or glycerol, exert antioxidant activities (Daniels and Martin 1967, Duve and White 1991). It seems that the capacities are correlated, primarily, to the caffeic acid content (Daniels and Martin 1967). Vanillin, which also contributes to the aroma, has been patented as an antioxidative food additive (Burri et al 1989a). It is also notable that vanillin is produced when simulating dry roasting of cereal grains by heating ferulic acid in air (Fiddler et al 1967, Tressl et al 1976).

Also, some nonphenolic compounds with absorbance in the UV-range of 200–300 nm were identified: nicotinamide, adenosine, and tryptophan. The compounds are indicated in Fig. 2. Nicotinamide and adenosine did not exert any antioxidative activity (not shown). Tryptophan was not tested in this study, but it has no antioxidative activity (Cadenas et al 1989). However, tryptophan is of special interest in that it acts synergetically with α-tocopherol in inhibiting fat oxidation (Minoru et al 1989).

The avenanthramides consist of various cinnamoylanthranilic acid derivatives. Around 40 hydroxy- and/or methoxy-substituted avenanthramides were found in oats (Collins 1989). Collins reported that the avenanthramides together constitute about 0.2–0.8 mg per gram of bran-rich mill fractions of oats (Collins 1986). So far, they have not been reported from other cereals. Two examples of avenanthramides, A1 and A2 (Fig. 1), were isolated in this study. The structures were elucidated with ^{1}H-NMR and UV spectroscopy. The data for A1 corresponded to that given by Collins (1989) for *N*-(4′-hydroxy-3′-methoxy-(E)-cinnamoyl)-5-hydroxyanthranilic acid. The ^{1}H-NMR spectrum of A2 differed from A1 only with respect to the signals from the anthranilic acid moiety of the compounds. Two possible isomers, 5-hydroxy-4-methoxy- or 5-methoxy-4-hydroxyanthranilic acid were proposed. However, long-range ^{1}H–^{1}H COSY elucidated A2 to be *N*-(4′-hydroxy-3′-methoxy-(E)-cinnamoyl)-5-hydroxy-4-methoxyanthranilic acid. This compound was not previously described in the literature. A1 was the major compound (~100 μg per gram of grain) (Sang, Table III). Unfortunately, A2 was co-detected with other substances and was far too low to be estimated. However, according to the peak height in the chromatogram, the amount of A2 must be at least ten times lower than the amount of A1 (Fig. 2). Figure 3 gives the UV spectra of A1 and A2. Similar spectra were also obtained from several other peaks in the HPLC diagram, indicating that other avenanthramides might be present among the water-soluble extractives of oat bran. Table II shows that both avenanthramides, especially A2, had significantly higher antioxidative activity than that of caffeic acid, ferulic acid, and vanillin. On molar basis, α-tocopherol had higher activity than that of A1 and A2. According to Collins (1989), the avenanthramide family consists of about 40 compounds. They could eventually all contribute to the antioxidative activity of an oat extract. Furthermore, several synthetic *N*-cinnamoylanthranilic acid compounds possess antiallergic, antihistamic, and antiasthmatic pharmacological characteristics (Devlin and Hargrave 1985). They also inhibit lipoxygenase, which is an important enzyme in the oxidation of fatty acids (Wakabayashi et al 1986). Therefore, the avenanthramides are certainly of interest for further studies.

In this article, the thermal stability of the predominant avenanthramide (A1) was examined by comparing its quantities in nontreated and steam-treated oat samples. Also, the distribution of this compound within the grain and the variation in 10 different cultivars were estimated.

In the preparative work, the yields of the two avenanthramides in pure state were low. This was probably due to a rather low solubility in the solvents used (H_2O and petroleum ether), as well as a partial degradation during the silica gel chromatography (Collins 1989). To avoid the solubility problem in the analytical studies, after evaporation, the 80% ethanol soluble extractives were suspended in methanol, which is a good solvent for the avenanthramides (Collins 1989) and for caffeic acid and tryptophan, which were also determined for a comparison.

Table III shows that the amount of A1 varied 40–132 μg per gram of grain (fresh weight) among the 10 different cultivars tested. The largest amount was found in Vital. On the other hand, the proportion of A1 in the methanol extract was almost the same (0.57–0.60%) for Sv 899081 and Sv 899082 as it was for Vital. This information could be valuable for breeders needing a cultivar with a high proportion of A1 antioxidant. Although A1 and related compounds are the most abundant of the UV-absorbing substances (Fig. 2), it is obvious that they represent only a minor part of the total 80% ethanol extractives, which constitute ~3% of the dry weight of the oat grain. No nonaromatic

TABLE III
Quantitative Analysis of Three Aromatic Compounds in Some Oat Grain Cultivars[a]

Oat Cultivar	Methanol Solubles (mg/g)[b]	Tryptophan (μg/g)	Caffeic acid (μg/g)	Avenanthramide 1 (μg/g)
Sang	23	17	5	109
Vital	22	21	5	132
Svea	21	21	5	58
Sv899081	19	22	4	112
Sv843675	18	20	4	40
Sv86635	17	17	4	57
Sv86712	17	20	4	76
Sv899085	16	8	3	64
Sv841170	14	7	3	43
Sv899082	14	13	3	80

[a] Values from single high-performance liquid chromatography analysis only.
[b] Grams of dehulled grain (fresh weight).

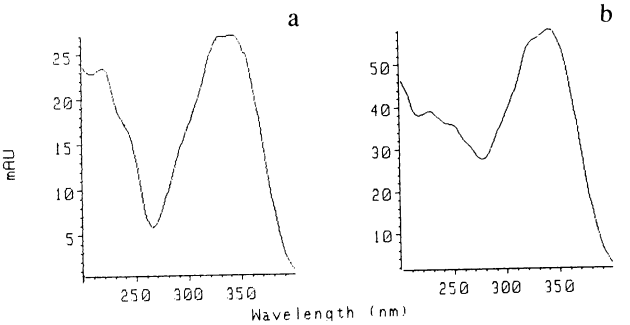

Fig. 3. UV-absorption curves of avenanthramides 1 and 2 (**a** and **b**, respectively) isolated from oats.

TABLE IV
Quantitative Analysis of Three Aromatic Compounds in Different Parts of Oat Grains Before and After Steam Treatment[a]

Oat Cultivar	Methanol Solubles (mg/g)[b]	Tryptophan (μg/g)	Caffeic acid (μg/g)	Avenanthramide 1 (μg/g)
Bran (unsteamed)	57	48	8	125
Bran (steamed)	50	52	4	150
Outer endosperm (unsteamed)	41	10	1	85
Outer endosperm (steamed)	36	15	< 1	70
Inner endosperm (unsteamed)	40	14	< 1	86
Inner endosperm (steamed)	25	21	< 1	84

[a] Values from single high-performance liquid chromatography analysis only.
[b] Grams of meal (fresh weight).

extractives have been analyzed in the present study, but previous studies at this university (Salomonsson et al 1984, Åman 1987) have shown that, together, the free sugars sucrose, glucose, and fructose constitute about half of the hydrophilic extractives.

Table IV shows that A1, like the total methanol solubles, is most abundant within the bran fraction. It is also of special interest that the amount of A1 in nontreated and steam-treated samples was almost the same (Table IV), indicating that this substance is rather heat stable, at least when located within the grain tissue during the steam treatment.

CONCLUSIONS

The oat grain has a significant antioxidative capacity that is exerted by several different kinds of phenolic compounds, both hydrophilic and lipophilic. Especially the avenanthramides, that have an intermediate lipophilicity and seem to be rather heat stable, are an interesting group. They can probably function as antioxidants, inhibiting both the lipoxygenase-activated fatty acid oxidation (Wakabayashi et al 1986) and the nonenzymatic oxidation. In daylight and UV-light, the avenanthramides may easily undergo Z-E rearrangement (Collins and Mullin 1988). In this study, only the E form was isolated, but, even though Collins (1989) also isolated the Z form, it could well be that the Z forms do not exist in situ (Collins and Mullin 1988). Future studies could test the antioxidative effect of an avenanthramide that, in light, has been isomerized to the Z form, because different isomers of cinnamic acid compounds can have different biological activities. For instance, the Z isomer of *N*-(3′,4′-dimethoxycinnamoyl)anthranilic acid has more than 10 times the antiallergic activity of the E isomer (Kakegawa et al 1985). Further detailed studies of the avenanthramides and their antioxidant capacity are in progress at our laboratories.

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