Barley Tocols: Effects of Milling, Malting, and Mashing[1]

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ABSTRACT

Barley (*Hordeum vulgare* L.) tocols were analyzed in products resulting from milling, malting, and mashing. Tocols in hand-dissected kernel fractions were also measured to explain results obtained with the milled fractions. Tocols were extracted with methanol and measured by fluorescence detection after high-performance liquid chromatography. Removal of the hull, aleurone, and germ by abrasion (pearling) significantly lowered the tocol concentration of the pearled barley as compared to whole kernels, but the by-product (material removed) was rich in tocols. Barley hulls and endosperm had substantial tocol concentrations, especially tocotrienols, whereas the germ contained a high concentration of α-tocopherol. The germ also contained significant quantities of β-tocotrienol. Malting had essentially no effect on tocol concentration, but brewers' spent grains were enriched in tocols. It was concluded that high tocol concentrations of milling by-product and brewers' spent grains could make them valuable additions to food products.

Biological effects of tocols (tocopherols and tocotrienols) include antioxidant activity (Burton and Traber 1990) and reduction of serum LDL-cholesterol in chickens (Qureshi et al 1986), swine (Qureshi et al 1991a), and human subjects (Qureshi et al 1991b). Cereal grains and certain vegetable oils are good sources of tocols, but the tocol concentration and composition (among eight possible isomers) varies considerably among sources (Barnes 1983). Barley (*Hordeum vulgare* L.) is one of the best sources, containing both a high concentration of total tocols and a favorable distribution of the most biologically active isomers (Peterson and Qureshi 1993).

Concentrations of tocol isomers in grain milling fractions were reported (Piironen et al 1986), but for barley, only meal was included in the study. Although it is recognized that tocols are more concentrated in barley *bran*, a fiber ingredient produced from brewers' spent grain (Weber et al 1990), no analysis of its tocol composition was reported. The effects of malting on barley tocols have not been reported.

Commercial barley milling fractions, experimentally micromalted barley, and spent grain from pilot-scale brewing were sampled and analyzed to determine effects of processing on tocol composition. Results were compared with analyses of hand-dissected barley fractions.

MATERIALS AND METHODS

Barley milling fractions (from an unknown, six-rowed cultivar), obtained from the Minnesota Grain Pearling Co., Cannon Falls, MN, were collected from the same runstream. The barley milling process (pearling) involved successive passes through seven hullers that abraded the outer layers of the kernels. The samples were dried overnight in a vacuum oven at 70°C and then ground to pass a 0.5-mm screen in a Retsch ZM-1 ultracentrifugal mill (Brinkman Instruments Co., Westbury, NY).

Barley kernels (cv. Morex) were hand-dissected into hull, germ, and endosperm fractions. First, the hulls were scraped from the caryopses with a dull knife. The caryopses (which contained some adhering hull in the crease region) were tempered for 2 hr in a petri dish. Then the germs were removed with a small spatula. The germ and endosperm fractions were freeze-dried. Hull and endosperm fractions were ground as described above. The germ fraction was ground directly in methanol with a mortar and pestle.

A 170-g sample of barley (cv. Morex) was micromalted by steeping to 45% moisture at 16°C, germinated four days at 16°C, and kilned to a final temperature of 85°C (Jones and Poulle 1989). Brewing was performed in a pilot-scale 18.9-L brewery, using a 70:30 ratio of Morex malt (obtained from a commercial malt house) to corn grits mash and an original gravity of 12° Plato (Jones and Poulle 1989). The spent grains were recovered after lautering, freeze-dried, and ground as described above.

The ground samples were extracted in duplicate with methanol (7 ml per 0.5 g of sample) during 20 min of shaking. They were then centrifuged, and the supernatant decanted and vacuum-dried at 38°C. The tocol-containing residues were dissolved in hexane and analyzed by high-performance liquid chromatography (Peterson and Qureshi 1993).

RESULTS AND DISCUSSION

The whole, cleaned, barley sample had a composition of tocols (Table I) similar to that reported previously for other barleys (Peterson and Qureshi 1993), although the total concentration (37 mg kg^{-1}) was slightly lower than the range reported for 30 genotypes from the USDA Western Regional Spring Barley Nursery (Peterson and Qureshi 1993). α-Tocotrienol was the predominant isomer, with substantial quantities of α-tocopherol, β-tocotrienol, and γ-tocotrienol. After it passed through the no. 2 huller, the barley sample lost about half its α-tocopherol concentration, but the other isomers were not significantly changed. The hand-dissected hull had 50% higher α-tocopherol concentration than that of the whole grain (Table II). Thus, the reduction in α-tocopherol with pearling could be accounted for by loss of the hull and, in addition, the loss of 10–15% α-tocopherol-rich germ (K. Nelson, *personal communication*). With each successive pass through the hullers, the kernels were further abraded. The average weight loss was 1.8 mg per pass per kernel; the weight loss range was 0.8–3.8 mg. Concentrations of all tocols decreased. This indicated a higher concentration of tocols in the aleurone and subaleurone than in the central region of the starchy endosperm. α-Tocopherol decreased more than the tocotrienols did, indicating additional loss of the germ.

Barley hulls contain substantial quantities of tocols (Table II), as do rice hulls (A. Qureshi, *unpublished data*), whereas oat hulls contain only traces of α-tocopherol and α-tocotrienol (D. Peterson, *unpublished data*). The hull tocols may remain from earlier development, when the hull (lemma and palea) was green and photosynthetically active. Green (1958) reported the presence of α-tocopherol in green "unripe ears" of barley 89 days after planting, but it is unclear whether these ears contained any grain.

The barley by-product consists of the abraded material, containing hull, aleurone, and subaleurone tissues (bran). The high content of all tocols found in this fraction reflect their concentration in the outer layers of the kernel. Each tocol isomer (except β- and δ-tocotrienol) and total tocols were at least twice as concentrated in the by-product as they were in whole barley; α-tocopherol was almost threefold higher.

Barnes and Taylor (1981) reported high α-tocopherol concen-

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TABLE I
Tocol Concentrations (mg kg^{-1}) of Barley Milling Fractions[a]

Fraction	Isomer									T3 (%)
	α-T	α-T3	β-T	β-T3	γ-T	γ-T3	δ-T	δ-T3	Total	
Whole, cleaned barley	5.94	20.40	0.00	5.02	0.23	4.36	0.14	0.79	36.8	83
After huller pass										
1	4.64	19.88	0.00	5.27	0.11	4.73	0.92	0.77	36.3	84
2	2.83	18.77	0.00	4.63	0.05	4.39	0.09	0.77	31.5	91
3	2.18	16.77	0.00	4.76	0.00	3.96	0.39	0.69	28.8	91
4	1.55	14.54	0.00	4.22	0.12	3.53	0.03	0.64	24.6	93
5	1.37	13.13	0.00	4.38	0.06	3.13	0.30	0.59	23.0	92
6	0.92	12.46	0.00	3.99	0.00	2.64	0.00	0.44	20.5	96
7	0.56	8.65	0.42	3.83	0.00	1.98	0.15	0.44	16.0	93
By-product	16.9	39.91	0.23	6.20	0.88	8.64	0.76	1.18	74.8	75
$LSD_{0.05}$[b]	0.94	2.34	0.02	0.36	0.15	0.49	0.46	0.09	4.6	1.5

[a]T = tocopherol, T3 = tocotrienol.
[b]Least significant difference.

TABLE II
Tocol Concentrations (mg kg^{-1}) of Hand-Dissected Morex Barley Fractions[a]

	Isomer									T3 (%)
	α-T	α-T3	β-T	β-T3	γ-T	γ-T3	δ-T	δ-T3	Total	
Whole grain	5.96 c	24.92 a	0.20 b	4.86 b	0.32 b	3.61 a	0.20 b	0.48 a	40.3 b	83.4 b
Hull	9.62 b	13.65 b	0.64 a	2.35 c	0.33 b	2.10 b	0.08 b	0.09 b	28.9 c	63.0 c
Endosperm	1.05 d	23.40 a	0.06 b	4.49 b	0.00 b	3.72 a	0.08 b	0.46 a	33.3 c	96.4 a
Germ	174.65 a	0.00 c	0.00 b	19.95 a	9.81 a	0.00 c	2.04 a	0.00 b	206.5 a	9.7 d

[a]T = tocopherol, T3 = tocotrienol. Means within columns followed by the same letter are not significantly different at $P = 0.05$.

TABLE III
Tocol Concentrations (mg kg^{-1}) of Morex Barley, Malt, and Spent Grains and Corn Grits[a]

	Isomer									T3 (%)
	α-T	α-T3	β-T	β-T3	γ-T	γ-T3	δ-T	δ-T3	Total	
Barley	10.96	32.52	0.78	6.09	0.62	4.66	0.39	0.72	56.7	77.5
Malt	10.02	30.69	1.41	4.55	0.42	3.92	0.40	0.56	52.0	76.4
Spent grain	20.24	92.06	3.05	16.00	0.90	17.64	1.21	1.75	152.9	83.4
Corn grits	1.25	3.85	0.61	6.72	0.39	6.93	1.03	0.40	21.2	84.5
$LSD_{0.05}$[b]	1.38	4.47	0.31	1.16	NS[c]	0.75	0.11	0.10	7.3	0.7

[a]T = tocopherol, T3 = tocotrienol.
[b]Least significant difference.
[c]No significant difference.

tration in barley germ (about 125 mg kg^{-1} for six-rowed barley, 210 mg kg^{-1} for two-rowed). Those workers detected no tocotrienols in barley germ, whereas in this study, a substantial quantity of β-tocotrienol was found in Morex germ. Analysis of another cultivar (Klages) confirmed the results obtained with Morex (data not shown). This is probably not attributable to adhering endosperm because the β-tocotrienol concentration was fourfold higher in germ than it was in endosperm (Table II). β-Tocotrienol has been reported in wheat germ (Hall and Laidman 1968, Piironen et al 1986), but no tocotrienols were found in oat germ (D. Peterson, *unpublished data*).

During the malting (germination) process, the tocol concentrations were not significantly altered (Table III). The spent grains, in contrast, had much higher levels of all tocols than did the barley or malt. This was because most of the starch and the soluble protein had been extracted, while the tocols remained in the insoluble material. The corn grits, which were 30% of the starting material, may have diluted the concentrations of α-tocopherol and α-tocotrienol in the spent grain fraction, but they contributed to the relatively greater increase in β- and γ-tocotrienols.

This study shows that barley by-product and brewers' spent grains are rich sources of tocols. This attribute could make them valuable additions to food products, particularly for persons attempting to reduce serum cholesterol levels through diet modification. Currently, their primary use is as animal feed, but if acceptable products for human consumption could be formulated, the value of these fractions would be increased. Brewers' spent grains have been incorporated into bread (Prentice and D'Appolonia 1977) and cookies (Prentice et al 1978) at levels that produced acceptable quality products. Recently, it was reported that dietary intervention with ingredients from brewers' spent grain increased the concentration of blood tocotrienol and lowered cholesterol in hypercholesterolemic human subjects (Weber et al 1991).

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