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γ-TOCOPHEROL IN BARLEY GERM

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Key Word Index—*Triticum aestivum*; *Triticum durum*; *Secale cereale*; *Hordeum vulgare*; *Avena sativa*; Gramineae; germ; tocopherol composition; vitamin E.

Cereal germ comprises the embryonic axis and scutellum of the seed and is noted for having very high concentrations of tocopherols. Wheat (*Triticum aestivum*) germ contains α- and β-tocopherols but maize (*Zea mays*) germ contains principally γ-tocopherol [1]. Of the eight naturally occurring tocopherols and tocotrienols, it is α-tocopherol that has the greatest vitamin E activity [2]. The tocotrienols are located predominantly in the non-germ fraction [3]. A number of investigations have reported the composition of tocopherols and tocotrienols in a range of whole cereal seeds but information concerning the germ is limited to wheat [3] and maize [4]. Knowledge of the composition of tocopherols in other types of cereal germ is essential to estimate their nutritional value in terms of vitamin E and to predict the antioxidant status of foodstuffs prepared from such materials. The differences between wheat and maize tocopherols suggest that the composition of these compounds might correlate with cereal taxonomy; the closely related cereals barley (*Hordeum* spp.), rye (*Secale cereale*) and wheat (*Triticum* spp.) in the tribe Triticeae might be expected to show a similar composition but differ from maize (*Zea mays*) of the tribe Andropogoneae. The germ tocopherol composition was determined for 12 cultivars representing seven different temperate cereals (Table 1).

Germ from all the cereal cultivars examined contained α- and β-tocopherols but only barley germ contained γ-tocopherol (Table 1). The presence of γ-tocopherol as a minor component in extracts of barley seeds has been reported [5–7] and the identification confirmed by GC/MS [8] but it was not detected in wheat, rye and oats [3, 5, 7, 8]. The germ of the temperate cereals discussed here represents only a small proportion (1–2% w/w) of the whole seed and the present results suggest that γ-tocopherol of barley seed is concentrated in the germ. The tentative identification of γ-tocopherol in barley germ is based upon the retention time and fluorescence behaviour in a HPLC system capable of separating the eight tocopherols and tocotrienols. However, there is a remote possibility that other closely related compounds may be present that would co-elute with γ-tocopherol [9]. As in

Table 1. Tocopherol composition of cereal germ (mg/kg dry wt)*

Cereal†	Cultivar	α-Tocopherol	β-Tocopherol	γ-Tocopherol‡
Triticum aestivum	Flinor	619	117	—
(bread wheat)	Timmo	385	139	—
T. durum	Valdur	204	118	—
(durum wheat)				
Secale cereale	King II	339	55	—
(rye)	Greenfold	321	66	—
Triticale	198	426	123	—
	39	412	104	—
Hordeum vulgare	Sonja	123	5	38
(*H. distichon*)	Mazurka	210	5	49
(2-row barley)				
H. vulgare	Athene	127	5	24
(6-row barley)				
Avena sativa	Peniarth	220	20	—
(oat)	Maris Oberon	272	14	—

*δ-Tocopherol and tocotrienols were not detected.

†Flinor, Sonja, Peniarth, Athene, Greenfold and King II are winter cultivars; Timmo, Mazurka, Maris Oberon spring cultivars. Triticale 39 is a winter triticale from Russia and incorporates the Rht_3 dwarfing gene from *T. aestivum* Tom Thumb. Triticale 198 is an F_4 spring selection from Beagle "sib" × [(6TA204 × T909) × Beaver "sib"] and incorporates the Rht_1 dwarfing gene from *T. aestivum* Norin 10.

‡Limit of detection of γ-tocopherol in these analyses was 4 mg/kg.

wheat germ, the major tocopherol of the germ of the other cereals studied was α-tocopherol. Although present in extracts of whole seeds, tocotrienols were not detected in the germ extracts in this study, thus confirming the previous observations that tocotrienols in these cereals are restricted to the non-germ fraction of the seed. Extracts of wheat germ from flour mills usually contain α- and β-tocotrienols in proportion to the contamination with bran and flour [10]. Hall and Laidman [3] in a study of dissected wheat seeds found α-tocotrienol to be absent from the germ but detected a small proportion of β-tocotrienol which may have been derived from residual bran or endosperm.

Wheat, barley, rye and triticale are placed in the tribe Triticeae and oat in the Aveneae, both tribes being included in the the temperate subfamily Pooideae. In contrast, maize is placed in the tribe Andropogoneae of the tropical subfamily Panicoideae. The results presented here show that the temperate cereals studied differ from maize in having α- rather than γ-tocopherol as the major germ tocopherol. However, barley also has a significant proportion of γ-tocopherol. β-Tocopherol (5,8-dimethyl tocopherol) and γ-tocopherol (7,8-dimethyl tocopherol) may be derived from alternative biosynthetic routes from the δ-(8-monomethyl) derivative and the α-(5,7,8-trimethyl) derivative but insufficient information is available to explain why γ-tocopherol should accumulate in the germ of barley but not in that of closely-related cereals.

EXPERIMENTAL

Wheat, barley and oat seeds were supplied by the Crop Science Department, Lord Rank Research Centre, High Wycombe, and rye and triticale by the Plant Breeding Institute, Cambridge, U.K. Cultivars were chosen to represent a range of types (Table 1). Germ was dislodged from seeds using an Entoleter impact mill (pilot scale) running at 3000 rpm and separated by sieving (fraction $>600\,\mu m$, $<1000\,\mu m$). Bran was removed from the germ in a stream of air and fragments of endosperm were manually removed. Freeze-dried germ (50 mg) was added to boiling *iso*-PrOH (2 ml) and refluxed for 10 min to inactivate enzymes. After grinding with pulverized glass, the mixture was allowed to reflux for a further 5 min then centrifuged at 3000 rpm for 10 min and the clear soln collected. The pellet was extracted with refluxing *iso*-PrOH–$CHCl_3$ (1:1, 2 ml) and refluxing $CHCl_3$ (2 ml) as above, the extracts were combined and the solvents evapd under N_2. The procedure is modified from that used by Hall and Laidman to extract tocopherols from dissected wheat [3]. At all stages of extraction, the sample was kept under an atmosphere of N_2. The extract was dissolved in hexane (5 ml) for determination of tocopherols and tocotrienols by HPLC with fluorescence detection as previously described [10].

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