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Kinetics of tocols degradation during the storage of einkorn (*Triticum monococcum* L. ssp. *monococcum*) and breadwheat (*Triticum aestivum* L. ssp. *aestivum*) flours

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ABSTRACT

The kinetics of tocols degradation in wholemeal and white flours from einkorn cv Monlis and bread wheat cv Serio were studied during storage at five different temperatures (−20, 5, 20, 30 and 38 °C) up to 242 days. Tocols decreased as a function of time and temperature, following first-order kinetics. Degradation rates and their dependence upon temperature were similar for the two *Triticum* species studied. Tocols decrease was quicker in white flour than in wholemeal flour (on average for total tocols at 38 °C, $k = 7.79 \times 10^{-3}$ days^{-1} vs 3.15×10^{-3} days^{-1}, respectively). The temperature-dependent degradation was similar for all homologues (Ea = 34.3–49.4 kJ/mol) except for α-T, less thermostable in white flours (Ea = 61.2 kJ/mol in einkorn and Ea = 54.7 kJ/mol in bread wheat).

The results clearly indicate that storing flours under refrigeration or at temperatures not exceeding 20 °C better preserved their tocols contents.

1. Introduction

Increasing evidence links the regular consumption of antioxidants to a reduction of ageing and chronic disease incidence (Anderson & Hanna, 1999; Greenberg & Sporn, 1996; Jacobs, Marquart, Slavin, & Kushi, 1998). Wheat is a major component of the human diet and, besides its importance as a carbohydrate source, plays a significant role as a source of antioxidant compounds, such as phenols, carotenoids and tocols (Andlauer & Fürst, 1998; Baublis, Chongrun, Clydesdale, & Decker, 2000; Miller, Rigelhof, Marquart, Prakash, & Kanter, 2000). Tocols (vitamin E) are present in both bread wheat (74.3 μg/g dm) and durum wheat (60.6 μg/g dm) (Panfili, Fratianni, & Irano, 2003). They are more abundant (84.5 μg/g dm) (Hidalgo, Brandolini, Pompei, & Piscozzi, 2006) in einkorn (*Triticum monococcum* L. ssp. *monococcum*), a diploid hulled wheat, highly valued for its high protein (Borghi, Castagna, Corbellini, Heun, & Salamini, 1996; D'Egidio, Nardi, & Vallega, 1993) carotenoid and tocol contents (Abdel-Aal et al., 2002; Hidalgo et al., 2006).

Wheat is harvested during the summer period, when the climate is dry and hot. The kernels have about 13% humidity and, properly stored, can thus be kept over long periods. Most of the wheat produced in the world is processed into white flour or semolina for preparation of bread, biscuits or pasta. In the production of white flour from whole-grain wheat, vitamin E content is reduced by about 50–65%, due to the removal of bran and germ (Hidalgo & Brandolini, 2008; Wennermark & Jägerstad, 1992). A further loss, resulting from the oxidative degradation of tocols, is experienced during storage: after 12 months, Piironen, Varo, and Koivistoinen (1988) reported a 60–80% decrease at room temperature and Wennermark and Jägerstad (1992) a 28–40% loss at 20 °C.

The relevance of tocols for disease prevention, as well as for freshness and shelf life of food products (Paradiso, Summo, Trani, & Caponio, 2008; Shahidi, 2000), makes their preservation during processing a priority. However, information on their degradation kinetics in cereals is extremely scarce. Thus, the aim of this study was to evaluate the influence of different storage temperatures on the stability of tocols in *Triticum* flour. To this end, tocols contents of wholemeal and white flours from one einkorn and one bread wheat cultivar were determined during storage at five different temperatures.

2. Materials and methods

2.1. Samples

Kernels of einkorn cv Monlis and bread wheat cv Serio were harvested in 2006 at S. Angelo L. (Po plain, Italy) from 10 m^2 plots with three replications, cropped following standard cultural practices (Castagna, Borghi, Di Fonzo, Heun, & Salamini, 1995).

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2.2. Sample preparation and analytical methods

Kernels of the three replications were blended and ca 3 kg of recently harvested seeds of Monlis were de-hulled with an Otake FC4S apparatus (Satake, Japan); this step was not required for the free-threshing Serio. Einkorn and bread wheat wholemeal flours were produced using a Cyclotec 1093 lab mill (FOSS Tecator, Denmark); white flours were obtained using a Bona-GBR lab mill (Bona, Monza, Italy), that separates flour from bran and shorts. All types of flour were put in 500 ml glass bottles with screw caps and placed in refrigerated cells (Igloo, Italy) for storage at −20 ± 1.5 and 5 ± 1.5 °C, and in termostatted ovens (Heraeus, Germany) for storage at 20 ± 1, 30 ± 1 and 38 ± 2 °C. The storage was maintained up to 242 days.

Kernel weight was determined by weighing four independent replications of 50 seeds each; the value was then corrected to 15% humidity. Dry matter, protein (N × 5.7) and ash contents were determined following methods 44-15, 46-10 and 08-03 (AACC, 1995), respectively. Lipids extraction was performed following the Soxhlet method, with ethylic ether as solvent after acid hydrolysis of the samples (Method 136; ICC & Technology, 1995). Tocopherol and tocotrienol quantifications were performed by normal phase HPLC, following Panfili et al. (2003). A detailed description of the whole system, including a reference chromatogram, is reported by Hidalgo et al. (2006). The repeatability of the α-tocopherol (α-T), β-tocopherol (β-T), α-tocotrienol (α-T3), and β-tocotrienol (β-T3) analytical method was assessed by performing, in each case, six replicate measurements on the same einkorn wholemeal sample. The coefficients of variation (CV%) were 2.38%, 2.28%, 2.61%, and 2.08%, respectively.

All measurements were performed twice; the results are presented as means on a dry matter base (DM).

2.3. Degradation kinetics modelling

To determine the degradation reaction order of each tocol, zero- and first-order kinetics were hypothesised by applying the general reaction rate expression $-dC/dt = kC^n$, where C is the concentration of the compound (mg/kg DM), k is the reaction rate constant (days^{-1}), t is the reaction time (days) and n is the order of the reaction (Atkins & De Paula, 2006). The order which gave the best regression (r) and the best correspondence among the experimental values and the theoretical half-life ($t_{1/2}$) of the compound was selected as representative of the current degradation reaction; in the formula, $t_{1/2} = C_0/2k$ for zero order (C_0 is the initial concentration), while $t_{1/2} = \ln 2/k$ for first-order (Atkins & De Paula, 2006).

The reaction rate to temperature link was quantified by the Arrhenius equation $k = k_0^{-(Ea/RT)}$, where Ea is the activation energy of the reaction (kJ/mol), and k_0 is the pre-exponential constant; R is the gas constant (8.314 J mol^{-1} K^{-1}); T is the mean absolute temperature of the considered storage temperature range (K). The activation energy of each compound analysed was computed following this relationship. Finally, the z value ($z = 2.303RT^2/Ea$) was also calculated; z represents the increase in temperature that causes a 10-fold increase in the reaction rate.

Kinetics data were analysed by regression analysis, using Microsoft® Excel 2000 and TableCurve™ 2D version 4 (Jandel Scientific Software, CA, USA).

3. Results and discussion

3.1. Flour characteristics

Table 1 shows the weight of 1000 kernels and some characteristics of freshly prepared flours for both *Triticum* species. The 1000 kernels weight was significantly lower for Monlis than for Serio. Einkorn showed higher lipid and protein contents; this result is partially due to the smaller size of the seeds, leading to a higher proportion of bran and germ fractions in wholemeal flour (Hidalgo & Brandolini, 2008a; Pomeranz, 1988), as evidenced especially by the ash content. The difference is still detectable in the white flours, because laboratory milling might lead to slight flour contamination by bran and germ.

Monlis showed higher total tocol contents (84.4 and 41.4 mg/kg DM in wholemeal flour and flour, respectively) than Serio (46.2 and 28.5 mg/kg DM); a similar trend was observed for the different homologues, with the exception of β-tocopherol. Total tocol concentration in wholemeal flour of both samples falls within the range observed by Hidalgo et al. (2006) among 54 einkorn and seven bread wheat accessions, by Leenhardt et al. (2006) for one einkorn and one bread wheat mixture sample, and by Wennermark and Jägerstad (1992) for a commercial bread wheat flour. The only discrepancy was observed in Serio for β-T3 content (22.3 ± 0.229 mg/kg DM), which was smaller than previously reported values by Hidalgo et al. (2006) (34.7 ± 3.84 mg/kg DM) and by Leenhardt et al. (2006) (45.0 mg/kg DM) for other *Triticum aestivum* accessions.

The most abundant tocol in all types of flours was β-T3, followed by α-T (with the exception of Monlis wholemeal flour, which was richer in α-T3 than in α-T). On the other hand, the scarcest tocol in Monlis was β-T while, in Serio, it was α-T3, closely followed by β-T. The wholemeal flour data were similar to those reported by Hidalgo and Brandolini (2008a) for the very same einkorn cultivar, and by Leenhardt et al. (2006) for mixture samples. For white flour, the total tocol content was higher than the levels reported by Hidalgo and Brandolini (2008a) for the endosperm fraction: since α-T and β-T are present only in the germ, while their homologues are concentrated in the bran, a possible reason of the difference is a slight contamination of the flour fraction during milling.

Table 1
Characteristics of *T. monococcum* cv Monlis and of *T. aestivum* cv Serio samples (mean values ± SD).

	Monlis		Serio	
	Wholemeal flour	Flour	Wholemeal flour	Flour
Kernel weight (mg)	23.6 ± 0.16		31.5 ± 0.057	
Dry matter (g/100 g)	90.6 ± 0.03	89.6 ± 0.05	90.8 ± 0.01	89.0 ± 0.00
Lipids (g/100 g DM)	4.5 ± 0.03	2.5 ± 0.04	3.2 ± 0.03	1.8 ± 0.00
Proteins (g/100 g DM)	16.4 ± 0.18	15.2 ± 0.32	13.6 ± 0.33	12.3 ± 0.10
Ash (g/100 g DM)	2.6 ± 0.04	0.7 ± 0.03	1.8 ± 0.07	0.5 ± 0.01
α-Tocopherol (mg/kg DM)	15.4 ± 0.638	8.98 ± 0.501	12.5 ± 0.291	7.11 ± 0.290
α-Tocotrienol (mg/kg DM)	19.3 ± 0.790	6.77 ± 0.027	5.50 ± 0.082	2.03 ± 0.062
β-Tocopherol (mg/kg DM)	5.72 ± 0.095	3.63 ± 0.093	5.82 ± 0.025	3.07 ± 0.190
β-Tocotrienol (mg/kg DM)	44.0 ± 0.687	22.0 ± 0.410	22.3 ± 0.229	16.3 ± 0.515
Total tocols (mg/kg DM)	84.4 ± 0.513	41.4 ± 0.278	46.2 ± 0.137	28.5 ± 0.284

3.2. Degradation kinetics of tocols

Lipid, protein and dry matter contents did not significantly change during storage. The degradation kinetics of each tocol homologue and of the total tocols, during storage at different temperatures, of Monlis wholemeal and white flour, are presented in Figs. 1 and 2, respectively; the kinetics of Serio (not shown) closely mirrored those of Monlis. Both the coefficients of regression (r) and the half-life times ($t_{1/2}$) suggested a first-order equation (whose parameters are shown in Tables 2 and 3) for the best modelling of tocols degradation. The sometimes reduced r values at 5 and −20 °C were a consequence of random experimental errors on trends with minimal fluctuations.

The first reaction order best explained the data from all substrates. Few studies are available on degradation kinetics of tocols. First-order kinetics were observed in a model system containing α-T kept between 20 and 37 °C (Widicus, Kirk, & Gregory, 1980), in a model system of α-T, γ-T, δ-T and glycerol during high temperature treatments (100, 150 and 250 °C) (Chung, 2007a, 2007b), in a composting system (İpek, Arslan, Öbek, Karataş, & Erulaş, 2005), in extra-virgin oil kept at 25 and 40 °C for eight months (Lavelli, Fregapane, & Salvador, 2006), in extra-virgin oil stored at 30 °C for six months (Gutiérrez & Fernández, 2002) and in rice bran extruded at temperatures between 110 and 140 °C (Shin, 1999).

During storage, tocols decreased as a function of temperature and time; the reaction rate constant k increased as the temperature

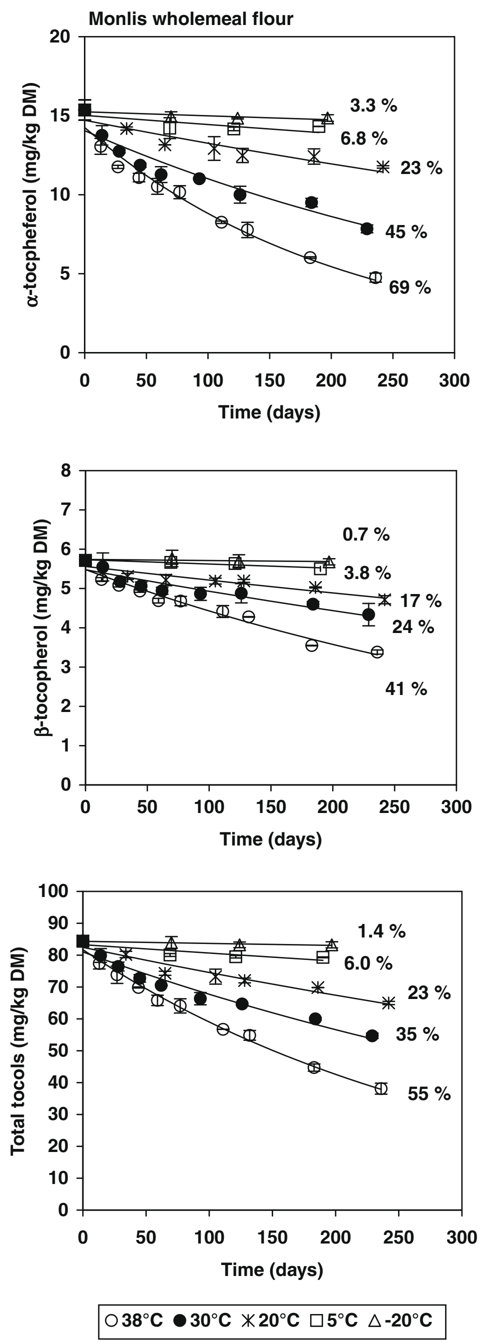

Fig. 1. Isothermal degradation kinetics of tocols during the storage of the einkorn Monlis wholemeal flour. The points represent experimental mean values and the error bars the standard deviations; the curves follow the first-order kinetics equation ($C = C_0 \exp^{-kt}$). The numbers indicate percentage loss of the compound at the last experimental point.

increased, indicating a quicker degradation of the compounds. The values reported in Tables 2 and 3 suggest that, for all tocols and at each specific temperature, k variation was smaller between species than between flour types. Hence, tocols degradation was generally quicker in white flour than in wholemeal flour (e.g., on average for total tocols at 38 °C, $k = 7.79 \times 10^{-3}$ days^{-1} vs 3.15×10^{-3} days^{-1}, respectively). The loss percentages in einkorn flours (Figs. 1 and 2) and in bread wheat flours (not shown, but similar to einkorn) describe a similar pattern. Several factors influence tocols stability: temperature, light, concentration and substrate. A possible explanation for their better stability in wholemeal flour could be their higher concentration. Yoshida, Kajimoto, and Emura (1993) showed that, in rapeseed, soybean and palm oils, the most abundant tocols were also the most stable. A similar observation was reported for carotenoids, another class of antioxidant compounds: in einkorn they were more plentiful and more stable than in bread wheat (Hidalgo & Brandolini, 2008b). Furthermore, wholemeal flours are complex substrates and other compounds (such as phenolic acids, lignans and flavonoids, mostly localised in the external layers of the kernel) might influence the degradation rate of tocols, through synergic or competitive effects on their antioxidant activity, as well as by protecting them against oxidation (Kamal-Eldin & Appelvist, 1996).

In both wholemeal flours rich in tocols, α-T and α-T3 were less stable (higher k and superior degradation percentages) than were β-T and β-T3, as already observed by Wennermark and Jägerstad (1992) during the storage of bread wheat wholemeal flour at 20 °C. Peterson (1994) in oat flour, as well as Yoshida et al.

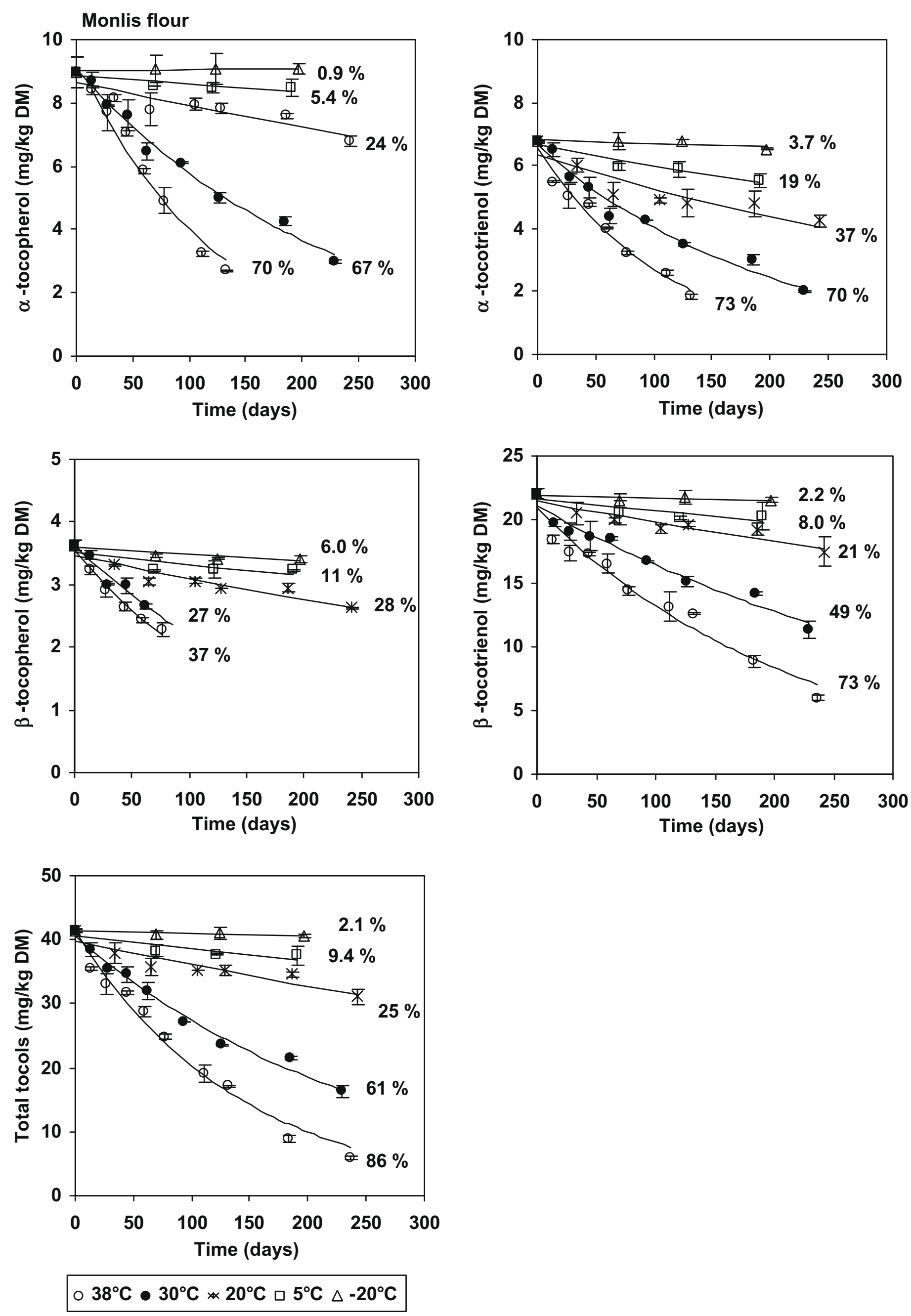

Fig. 2. Isothermal degradation kinetics of tocols during the storage of the einkorn Monlis flour. The points represent experimental mean values and the error bars the standard deviations; the curves follow the first-order kinetics equation ($C = C_0 \exp^{-kt}$). The numbers indicate percentage loss of the compound at the last experimental point.

Table 2
Rate parameters of the tocols degradation reaction in wholemeal flour and flour of the einkorn cv Monlis, fitted by first-order kinetic ($\ln C = \ln C_0 - kt$).

	Monlis wholemeal flour				Monlis flour			
	$k \times 10^{-3}$ ($days^{-1}$)	$\ln C_0$	r	$t_{1/2}$ (days)	$k \times 10^{-3}$ ($days^{-1}$)	$\ln C_0$	r	$t_{1/2}$ (days)
α-Tocopherol								
38 °C	4.64	2.65	0.99	149	9.50	2.28	0.99	73
30 °C	2.25	2.63	0.96	308	4.59	2.21	0.99	151
20 °C	0.99	2.68	0.93	702	0.90	2.16	0.92	766
5 °C	0.35	2.71	0.73	1986	0.28	2.18	0.83	2446
−20 °C	0.17	2.72	0.85	4181	0.04	2.20	0.66	17,460
α-Tocotrienol								
38 °C	4.89	2.97	1.00	142	9.17	1.89	0.99	76
30 °C	2.00	2.93	0.99	347	4.92	1.89	0.99	141
20 °C	0.77	2.95	0.88	903	1.68	1.83	0.91	413
5 °C	0.24	2.96	0.91	2940	1.03	1.89	0.96	675
−20 °C	0.10	2.97	0.86	6942	0.18	1.92	0.83	3901
β-Tocopherol								
38 °C	2.12	1.70	0.98	327	5.98	1.26	0.99	116
30 °C	1.02	1.70	0.94	678	5.00	1.29	0.97	139
20 °C	0.64	1.72	0.94	1088	1.11	1.24	0.93	625
5 °C	0.20	1.75	0.96	3549	0.57	1.26	0.79	1224
−20 °C	0.05	1.75	0.60	14,365	0.31	1.28	0.90	2219
β-Tocotrienol								
38 °C	2.44	3.76	0.99	285	4.93	3.06	0.98	141
30 °C	1.55	3.75	0.98	446	2.52	3.05	0.98	275
20 °C	1.13	3.76	0.98	614	0.77	3.06	0.93	896
5 °C	0.35	3.76	0.79	1975	0.43	3.07	0.85	1600
−20 °C	0.04	3.78	0.66	17,797	0.09	3.09	0.69	7621
Total tocols								
38 °C	3.23	4.41	1.00	215	8.15	3.78	0.99	85
30 °C	1.73	4.39	0.98	401	3.86	3.70	0.99	180
20 °C	0.98	4.41	0.97	705	0.97	3.68	0.94	718
5 °C	0.31	4.42	0.86	2213	0.50	3.70	0.88	1376
−20 °C	0.08	4.43	0.93	9078	0.10	3.72	0.88	7275

Table 3
Rate parameters of the tocols degradation reaction in wholemeal flour and flour of the bread wheat cv Serio, fitted by first-order kinetic ($\ln C = \ln C_0 - kt$).

	Serio wholemeal flour				Serio flour			
	$k \times 10^{-3}$ ($days^{-1}$)	$\ln C_0$	r	$t_{1/2}$ (days)	$k \times 10^{-3}$ ($days^{-1}$)	$\ln C_0$	r	$t_{1/2}$ (days)
α-Tocopherol								
38 °C	4.22	2.34	0.96	164	8.84	1.87	0.99	78
30 °C	2.96	2.40	0.95	234	4.30	1.84	0.97	161
20 °C	1.67	2.44	0.94	415	2.14	1.88	0.97	324
5 °C	0.57	2.49	0.71	1214	0.65	1.93	0.87	1070
−20 °C	0.11	2.52	0.86	6138	0.06	1.96	0.73	10,736
α-Tocotrienol								
38 °C	4.37	1.60	0.97	159	12.00	0.71	1.00	58
30 °C	3.17	1.66	0.99	219	9.90	0.70	1.00	70
20 °C	1.33	1.66	0.91	522	4.94	0.73	0.99	140
5 °C	0.37	1.67	0.66	1880	1.27	0.66	0.90	544
−20 °C	0.06	1.71	0.87	11,268	0.46	0.70	0.94	1516
β-Tocopherol								
38 °C	2.38	1.58	0.92	291	10.34	1.10	0.97	67
30 °C	1.24	1.63	0.84	559	8.44	1.13	0.99	82
20 °C	0.72	1.66	0.80	962	2.08	1.08	0.95	333
5 °C	0.45	1.73	0.72	1530	0.66	1.08	0.81	1046
−20 °C	0.09	1.75	0.68	7666	0.38	1.11	0.93	1823
β-Tocotrienol								
38 °C	2.46	2.98	0.96	281	4.89	2.68	0.99	142
30 °C	1.45	3.01	0.93	477	2.31	2.69	0.96	300
20 °C	0.65	3.07	0.86	1067	1.11	2.74	0.93	624
5 °C	0.32	3.09	0.65	2163	0.44	2.78	0.92	1569
−20 °C	0.05	3.11	0.95	13,172	0.06	2.79	0.87	12,716
Total tocols								
38 °C	3.07	3.68	0.96	226	7.44	3.22	0.99	93
30 °C	1.98	3.73	0.95	351	3.86	3.23	0.95	180
20 °C	0.99	3.78	0.92	701	2.36	3.33	0.99	294
5 °C	0.41	3.80	0.71	1693	0.57	3.33	0.89	1212
−20 °C	0.07	3.83	0.97	9276	0.12	3.35	0.91	5827

Table 4
Activation energy (*Ea*; kJ/mol) and *z* value (°C) of the tocols degradation reaction during the storage of wholemeal flour and flour of einkorn cv Monlis and bread wheat cv Serio.

	Monlis wholemeal				Monlis flour			
	Ea	*z*	$\ln k_0$	*r*	*Ea*	*z*	$\ln k_0$	*r*
α-Tocopherol	36.8	43.1	8.45	0.96	61.2	25.9	18.7	0.98
α-Tocotrienol	42.6	37.1	10.7	0.96	42.8	37.0	11.6	0.99
β-Tocopherol	41.9	37.8	9.85	0.99	34.3	46.2	7.87	0.92
β-Tocotrienol	47.0	33.7	12.3	1.00	43.4	36.5	11.1	0.98
Total tocols	41.9	37.8	10.3	0.99	48.4	32.8	13.5	0.97
	Serio wholemeal				Serio flour			
α-Tocopherol	41.5	38.1	10.6	1.00	54.7	28.9	16.3	1.00
α-Tocotrienol	49.4	32.0	13.7	1.00	39.1	40.6	10.7	0.98
β-Tocopherol	34.9	45.4	7.26	0.99	39.2	40.4	10.3	0.93
β-Tocotrienol	42.5	37.3	10.3	1.00	49.3	32.2	13.6	1.00
Total tocols	41.8	37.9	10.3	1.00	46.7	33.9	13.1	0.99

(1993) and Rossi, Alamprese, and Ratti (2007) in oils, noticed that α-T was less stable than was β-T. Yoshida et al. (1993) attributed this inferior stability to a higher antioxidant activity, and Kamal-Eldin and Appelvist (1996) related it to the presence, in the structure of α-T, of three methyl groups linked to the aromatic ring. On the other hand, no differences in degradation rate between tocopherols and tocotrienols are reported, even though Suarna, Hood, Dean, and Stocker (1993) described a higher antioxidant activity of α-T3 than of α-T.

The comparison of homologue stabilities in white flour is difficult because this substrate showed low initial levels of β-T (3.6 and 3.0 mg/kg DM in Monlis and Serio, respectively) and α-T3 (6.7 and 2.0 mg/kg DM), that quickly diminished below the detection limit (after 80 and 130 days in Monlis, and after 30 and 70 days in Serio) at 38 °C. To evaluate the relationship between reaction speed and temperature, the Arrhenius equation was computed; its parameters are reported in Table 4. The Arrhenius parameters showed only limited differences, especially considering such a complex reaction in a real-life food substrate. The *Ea* and *z* values indicated that the dependencies of degradation rate upon temperature were similar for all homologues (*Ea* = 34.3–49.4 kJ/mol; *z* = 46.2–32.0 °C), with the exception of α-T, which was less thermostable in white flour (*Ea* = 61.2 kJ/mol; *z* = 27.4 °C in einkorn, and *Ea* = 54.7 kJ/mol; *z* = 28.9 °C in bread wheat).

It is rare to find studies that present *Ea*, and that can be compared with the results of this research. Nevertheless, the values reported in the present study fall within the range (37.0–54.6 kJ/mol) described by Widicus et al. (1980) working with α-tocopherol in a model system at room temperature (20–37 °C), and by Labuza (1972) during drying of seaweed meal (41.1–43.9 kJ/mol). They are above those observed for different homologues, but at substantially higher temperatures, by Shin (1999) (13.2–30.8 kJ/mol) during rice extrusion at 110–140 °C, and by Chung (2007a, 2007b) (8.12–3.4 kJ/mol) for a model system at 100–250 °C.

4. Conclusions

Tocols decreased as a function of time and temperature during storage, following first-order kinetics. The degradation was slower in wholemeal flour, probably because of their higher initial concentration and of the co-presence of other antioxidant compounds. The temperature-dependent degradations were similar for all homologues, with the significant exception of α-T, less thermostable in white flours. The results clearly indicate that storing flours under refrigeration or at temperatures not exceeding 20 °C better preserved their tocol contents.

It has to be stressed that, even though the degradation rates of tocols and their dependence upon temperature were similar for the two *Triticum* species studied, the final concentration in einkorn cv Monlis remained above those of bread wheat cv Serio, because of the high initial levels of the former species: furthermore, in wholemeal flour α-T3 and β-T3 contents were always higher than the initial contents of Serio.

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