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Kinetics of Carotenoids Degradation during the Storage of Einkorn (*Triticum monococcum* L. ssp. *monococcum*) and Bread Wheat (*Triticum aestivum* L. ssp. *aestivum*) Flours

ALYSSA HIDALGO[†] AND ANDREA BRANDOLINI*[,‡]

Dipartimento di Scienze e Tecnologie Alimentari e Microbiologiche (DISTAM), Università degli Studi di
Milano, via Celoria 2, 20133 Milano, Italy, and CRA-Unità di Ricerca per la Selezione dei Cereali e la
Valorizzazione delle varietà vegetali (SCV), Via Forlani 3, 26866 S. Angelo Lodigiano (LO), Italy

To evaluate the effect of storage temperature, the degradation kinetics of carotenoids in wholemeal and white flour of einkorn cv. Monlis and bread wheat cv. Serio, stored at −20, 5, 20, 30, and 38 °C, was assessed by normal-phase high-performance liquid chromatography. In Monlis, the carotenoids content (8.1 and 9.8 mg/kg for wholemeal and white flour, respectively) was 8-fold higher than in Serio (1.0 and 1.1 mg/kg). Only lutein and zeaxanthin were detected in bread wheat, while significant quantities of (α and β)-carotene and β-cryptoxanthin were observed in einkorn. Carotenoids degradation was influenced by temperature and time, following first-order kinetics. The degradation rate was similar in wholemeal and white flour; however, loss of lutein and total carotenoids was faster in Serio than in Monlis. The activation energy E_a ranged from 35.2 to 52.5 kJ/mol. Temperatures not exceeding 20 °C better preserve carotenoids content and are recommended for long-term storage.

KEYWORDS: Bread wheat; carotenoids; einkorn; kinetics; storage; *Triticum*

INTRODUCTION

Carotenoids, the most widespread pigments in nature, are liposoluble antioxidants produced by plants, where they contribute to the photosynthetic pathway as both light collectors and photoprotectors. In humans, they are involved in several functions, such as vitamin A biosynthesis, and, because of their antioxidant activity, protection of cells and tissues from free radicals and oxygen ions (*1*). Lutein and zeaxanthin, in particular, safeguard the macula region of the retina (*2*) and help in the prevention of cataracts (*3*). Additionally, in the food industry, carotenoids and other antioxidants contribute to improve freshness and shelf life of products (*4*).

Bread wheat (*Triticum aestivum* ssp. *aestivum*), a basic food staple for humankind, contains limited quantities of carotenoids; they are more plentiful in durum wheat (*Triticum turgidum* ssp. *durum*), because the yellow color of pasta is a major quality characteristic. Carotenoids are abundant in einkorn (*Triticum monococcum* ssp. *monococcum*), a diploid hulled wheat closely allied to durum and bread wheat. Its light-yellow flour is rich in lutein, with values 2−5 times higher than durum and bread wheat (*5*−*8*). The hue intensifies during processing, leading to einkorn-based foods with a deep yellow color (*9*), an appealing characteristic for many consumers.

Wheat is harvested during a limited time period but consumed all around the year. After harvesting, therefore, wheat grains are stored in bins or elevators, where they are dried, fumigated to control pests, and possibly cooled with aeration (*10*). After milling, the flour is stored, for varying periods of time, in sacks of different material, preferably stockpiled in cool, dark rooms.

The limited water content of ripe cereal seeds and their flours favors conservation over time. In spite of this, pronounced chemical changes are fostered by high temperature and humidity, as well as strong light (*11*). Antioxidant compounds like carotenoids are degraded by both direct and lipoxygenase-mediated oxidation (*12*). Limited information is, however, available in the literature on their behavior in cereals during storage.

The objective of this research was therefore to assess the influence of storage temperature on carotenoids stability in wheat flours. To reach this goal, the carotenoid contents of wholemeal and white flour from one einkorn cultivar, Monlis, and one bread wheat cultivar, Serio, were repeatedly measured during their storage at five different temperatures (−20, 5, 20, 30, and 38 °C).

MATERIALS AND METHODS

Materials. Kernels of the einkorn cv. Monlis and the bread wheat cv. Serio were harvested with a plot combine in 2006 at S. Angelo L. (Po plain, Italy) from 10 m^2 research plots with three replications, cropped following standard cultural practices (*13*).

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* To whom correspondence should be addressed. Tel: +39 0371 211261. Fax: +39 0371 210372. E-mail: andrea.brandolini@entecra.it.

[†] University of Milan.

[‡] Agricultural Research Council (CRA-SCV).

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Table 1. Carotenoids Composition (Mean Values ± SD) of Einkorn cv. Monlis and Bread Wheat cv. Serio Flours[a]

	Monlis		Serio	
	wholemeal flour	flour	wholemeal flour	flour
lutein (mg/kg DM)	6.75 ± 0.099	8.42 ± 0.014	0.90 ± 0.018	1.03 ± 0.044
(α and β)-carotene (mg/kg DM)	0.96 ± 0.038	0.98 ± 0.042	ND	ND
zeaxanthin (mg/kg DM)	0.29 ± 0.026	0.27 ± 0.015	0.11 ± 0.003	0.07 ± 0.015
β-cryptoxanthin (mg/kg DM)	0.10 ± 0.000	0.10 ± 0.001	ND	ND
total carotenoids (mg/kg DM)	8.09 ± 0.035	9.77 ± 0.014	1.01 ± 0.021	1.10 ± 0.029

[a] ND, nondetectable, that is, lower than the detection limit.

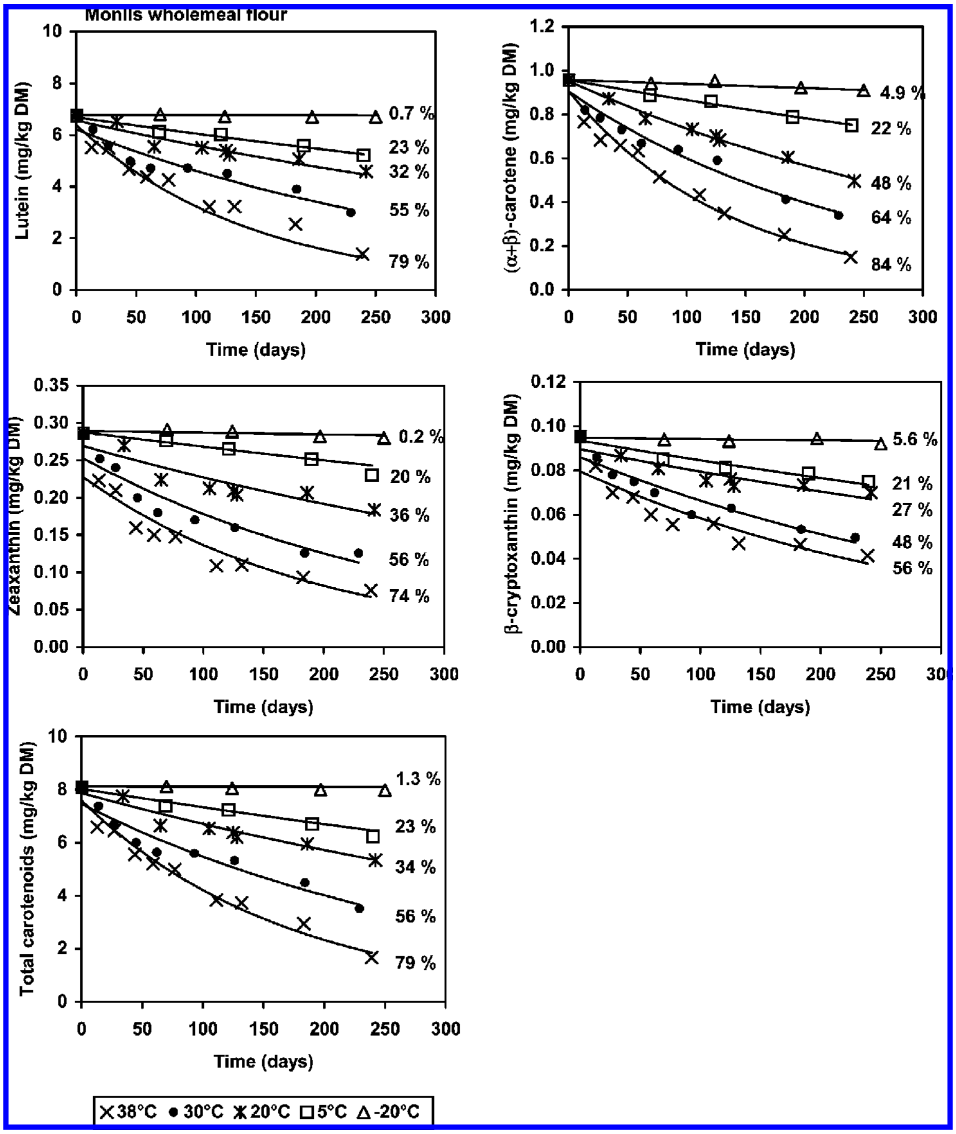

Figure 1. Isothermal degradation kinetics of lutein, (α and β)-carotene, zeaxanthin, β-cryptoxanthin, and total carotenoids during the storage of wholemeal flour from einkorn cv. Monlis. The points represent experimental mean values; the curves follow the first-order kinetics equation ($C = C_0 \exp^{-kt}$). Numbers indicate percentage loss of the compound at the end of storage.

Sample Preparation and Analytical Methods. Approximately 3 kg of recently harvested seeds of the einkorn cv. Monlis was dehulled with an Otake FC4S thresher (Satake, Japan); dehulling was not required for the free-threshing bread wheat cv. Serio. Wholemeal flours were produced using a Cyclotec 1093 laboratory mill (FOSS Tecator, Denmark); white flours were obtained using a Bona-GBR laboratory mill (Bona, Monza, Italy) that separates white flour from bran and shorts. The white flour recovery rate was 60.9 and 58.6% for Monlis and Serio, respectively. All flours were put in 500 mL glass bottles with a screw cap and placed under darkness in refrigerated cells (Igloo, Italy) for storage at −20 ± 1.5 and 5 ± 1.5 °C and in thermostat cabinets (Heraeus, Germany) for storage at 20 ± 1, 30 ± 1, and 38 ± 2 °C. The storage was maintained up to 239 days.

Dry matter was determined following AACC Official Method 44-15 (*14*). Carotenoids quantification was performed by normal phase high-performance liquid chromatography (HPLC), following Panfili et al. (*15*). For peak quantification, calibration curves were built using seven different concentrations (between 0.3 and 3.0 mg/L) of the lutein standard (Fluka, St. Louis, MO) stock solution, seven different concentrations (between 0.15 and 1.5 mg/L) of the β-carotene standard (Sigma, St. Louis, MO) stock solution, 10 different concentrations (between 0.05 and 1.03 mg/L) of the zeaxanthin standard (Extrasynthese, Genay, France) stock solution, and seven different concentrations (between 0.02 and 0.13 mg/L) of the β-cryptoxanthin standard (Extrasynthese) stock solution, diluted with isopropyl alcohol (10%) in hexane. The standard stock solutions of lutein and zeaxanthin were

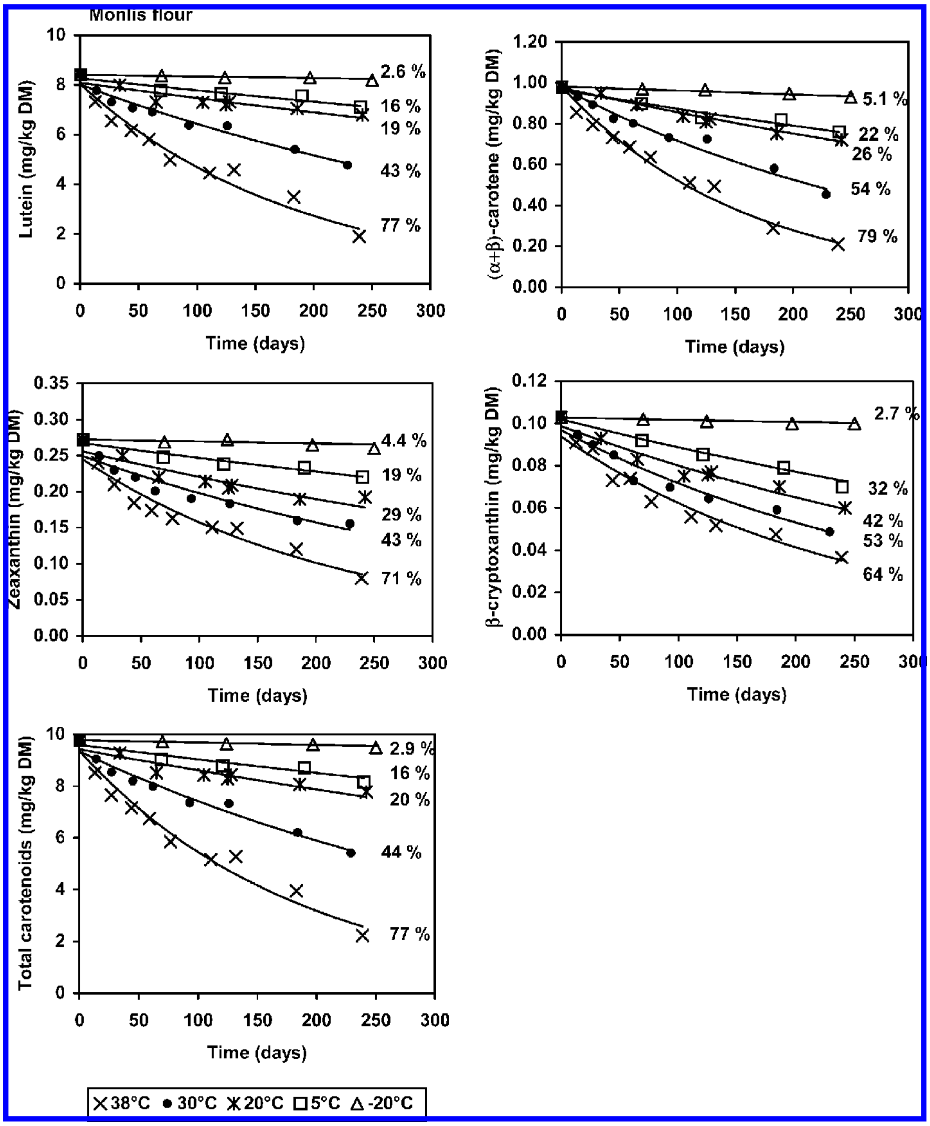

Figure 2. Isothermal degradation kinetics of lutein, (α and β)-carotene, zeaxanthin, β-cryptoxanthin, and total carotenoids during the storage of white flour from einkorn cv. Monlis. The points represent experimental mean values; the curves follow the first-order kinetics equation ($C = C_0 \exp^{-kt}$). Numbers indicate percentage loss of the compound at the end of storage.

prepared in ethanol, of β-carotene in petroleum ether, and of β-cryptoxanthin in hexane; their concentrations were confirmed spectrophotometrically using the known absorption coefficient of each compound (*16*). On the basis of the calibration curves, the detection limits were calculated as the intercept value of the regression line plus three times the standard error of the estimate (*17*). The results are expressed as mg/kg on a dry matter (DM) basis. Lutein, β-carotene, zeaxanthin, and β-cryptoxanthin calibration curves were linear ($r^2 = 1.00$; $p \leq 0.001$) in the concentration ranges considered and showed detection limits in the standard solution of 0.06, 0.05, 0.01, and 0.004 mg/L, respectively, corresponding to 0.15, 0.14, 0.03, and 0.01 mg/kg DM in flour, considering a mean dry matter content of 89.0 g/100. The repeatability of the lutein, (α and β)-carotene, zeaxanthin, and β-cryptoxanthin analytical method was assessed by performing, in each case, six replicate measurements on the same einkorn wholemeal sample. The coefficients of variation (CV%) were 2.51, 3.68, 2.36, and 4.87%, respectively. All measurements were performed twice; the results are presented as means of the measurements.

Degradation Kinetics Modeling. To determine the degradation reaction order of each carotenoid, zero- and first-order kinetics were hypothesized 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 (*18*). The order with the best correlation (r) and the best correspondence among the experimental values and the half-life of the compound ($t_{1/2}$) [time for the concentration of a reactant to fall to half its initial value, where $t_{1/2} = C_0/2k$ for zero order and C_0 is the initial concentration ($t_{1/2} = \ln 2/k$ for first order)] was selected.

The reaction rate to temperature relationship was quantified by the Arrhenius equation $\ln k = \ln k_0 - (E_a/RT)$, where E_a is the activation energy of the reaction (kJ/mol), $\ln k_0$ is the pre-exponential constant, R is the gas constant (8.314 J/mol/K), and T is the mean absolute temperature of the considered storage temperature range (K). From the slope of the Arrhenius line, the z value ($z = 2.303\ RT^2/E_a$) was computed: z represents the increase in temperature that causes a 10-fold raise in the reaction rate. Kinetics data were analyzed by regression analysis using Microsoft Excel 2000 and TableCurve 2D version 4 (Jandel Scientific Software, CA).

RESULTS AND DISCUSSION

Carotenoids Composition. Table 1 shows carotenoids content in freshly milled flours. Total carotenoids in einkorn cv. Monlis (8.1 and 9.8 mg/kg DM in wholemeal and white flour, respectively) were significantly superior to bread wheat cv. Serio (1.0 and 1.1 mg/kg DM). The carotenoids identified in Monlis wholemeal and white flour were, in order of abundance, lutein (83.4 and 86.2% of total carotenoids, respec-

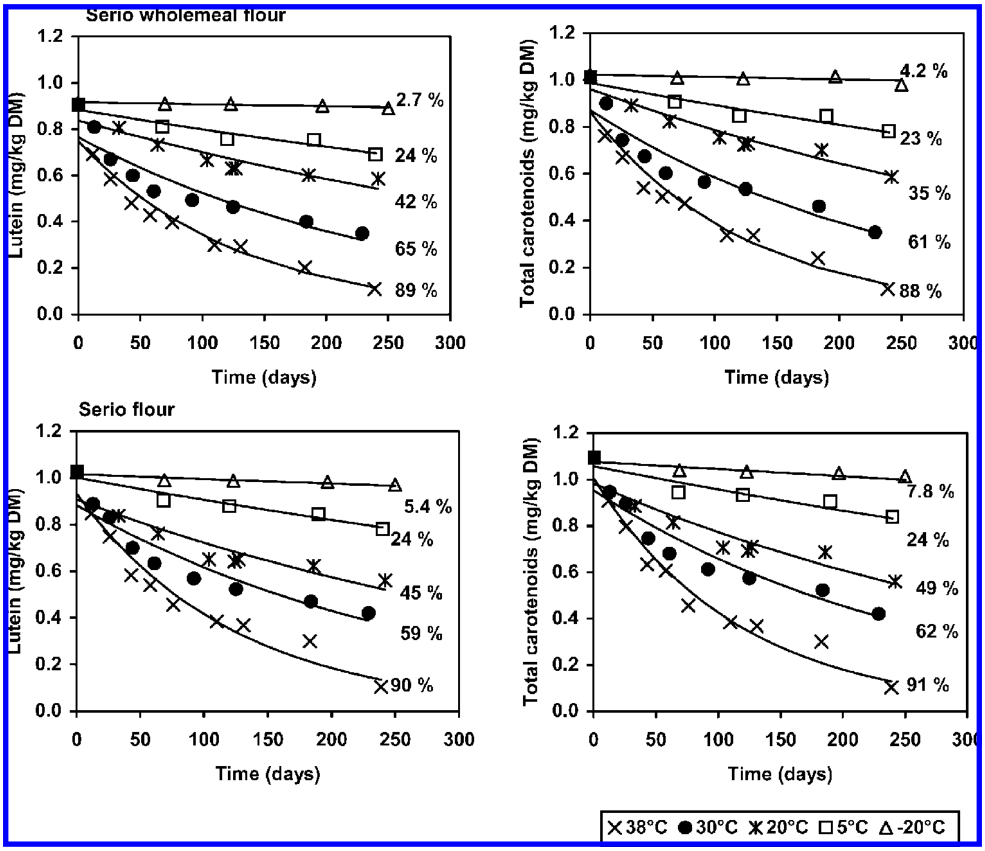

Figure 3. Isothermal degradation kinetics of lutein and total carotenoids during the storage of wholemeal flour and white flour from bread wheat cv. Serio. The points represent experimental mean values; the curves follow first-order kinetics equation ($C = C_0 \exp^{-kt}$). Numbers indicate percentage loss of the compound at the end of storage.

Table 2. Activation Energy (E_a; kJ/mol) and *z* Value (°C) for the Carotenoids Degradation Reaction during the Storage of Wholemeal Flour and White Flour of the Einkorn Monlis and the Bread Wheat Serio

	E_a	*z*	ln k_0	*r*	E_a	*z*	ln k_0	*r*
	Monlis wholemeal				Monlis flour			
lutein	52.5	30.2	15.19	0.98	41.9	37.8	10.58	0.97
(α and *β*)-carotene	40.4	39.2	10.61	1.00	36.0	44.0	8.54	0.98
zeaxanthin	42.1	37.6	11.04	1.00	35.2	45.0	8.04	1.00
β-cryptoxanthin	38.0	41.7	9.07	0.98	39.0	40.6	9.78	0.97
total carotenoids	48.7	32.5	13.65	0.99	40.7	38.9	10.16	0.98
	Serio wholemeal				Serio flour			
lutein	46.7	33.9	13.08	0.99	40.4	39.2	10.60	0.99
total carotenoids	45.3	34.9	12.56	1.00	37.7	42.1	9.51	0.99

tively), (α and *β*)-carotene (11.9 and 10.0%), zeaxanthin (3.6 and 2.8%), and *β*-cryptoxanthin (1.2 and 1.0%), while in Serio, only lutein (89.1 and 93.6%) and zeaxanthin (10.9 and 6.4%) were detected. In both *Triticum* species, carotenoids composition and concentration changed only slightly between flour type because carotenoids, although more abundant in the germ, are plentiful in the endosperm fraction, which contributes 72% of total kernel lutein (*19*).

The carotenoid contents observed in both species were similar to those reported previously (*5, 19*–*21*). Higher zeaxanthin and lower *β*-carotene levels (0.94 ± 0.05 and 0.13 ± 0.02 mg/kg DM, respectively) were found in einkorn wholemeal flour by Abdel-Aal et al. (*6*); these small discrepancies are probably a consequence of different accessions and cropping conditions.

Degradation Kinetics of Carotenoids. DM content did not change significantly during storage. **Figures 1** and **2** depict the degradation kinetics of each carotenoid as well as of total carotenoids in wholemeal and white flours from einkorn cv. Monlis during storage under five different temperatures. For bread wheat cv. Serio, the zeaxanthin content, although detectable, was too low to allow a meaningful degradation kinetics; therefore, **Figure 3** shows only lutein and total carotenoids storage behavior.

The coefficients of correlation (*r*) and the half-life ($t_{1/2}$) suggested a first-order equation for the best modeling of carotenoids degradation; the equation parameters are shown in the Supporting Information. The sometimes reduced *r* values at −20 °C are due to the strong influence of small experimental errors on trends with minimal variations. Zeaxanthin and *β*-cryptoxanthin were scarce even in einkorn (less than 0.3 mg/kg DM in fresh wholemeal flour); although their degradation was clearly assessed, nevertheless, a minor correspondence between observed values and first-order interpolation curves was observed (Supporting Information and **Figures 1** and **2**).

To our knowledge, similar studies in cereals are not available in literature. However, a first-order kinetics is often observed in different substrates during carotenoids degradation, as reported for *β*-carotene in dehydrated carrots stored between 27 and 57 °C (*22*), for *β*-carotene and capsanthin in a model system kept between 15 and 45 °C (*23*), for violaxanthin during fermentation in green olives processing (*24*), for total carotenoids in saffron stored between 25 and 60 °C (*25*) for *β*-carotene and *β*-cryptoxanthin in lemon juice treated at 75–100 °C (*26*), for lycopene, lutein, and *β*-carotene in safflower oil heated between 75 and 95 °C (*27*), and for *β*-carotene and capsanthin in papaya puree heated between 70 and 105 °C (*28*). Mínguez-Mosquera and Jarén-Galán (*29*), nevertheless, in an anhydrous model system, observed a zero-order kinetics for *β*-carotene and capsanthin degradation.

During storage, carotenoids decreased as a function of temperature and time; the reaction rate constant k increased as the temperature augmented (Supporting Information), indicating a quicker degradation of the compounds at higher temperatures. Rate constants were similar between flours but different between species. Pinzino et al. (*30*) attributed the analogous lutein degradation rate that they observed in wholemeal and white flour from durum wheat stored at 10 °C for 37 years, to the similar initial lutein content of both types of flour. The lutein degradation percentage at 38 °C reached by Serio flours was similar to the result observed by Calucci et al. (*31*) in bread wheat seeds (32%) after a 10 day storage period at 40 °C.

Carotenoids stability was higher in Monlis flours (on average, $k = 5.70 \times 10^{-3}$ for total carotenoids at 38 °C) than in Serio flours ($k = 8.35 \times 10^{-3}$). The difference might be related to the higher initial concentration of these compounds in Monlis wholemeal and white flours, as shown for durum wheat by Trono et al. (*32*), that reduce the antioxidant activity of carotenoids (*33*). Other possible explanations could be the lower lipoxygenase activity observed in einkorn (*20, 34*) and the superior content of other antioxidant compounds, such as tocols (*8*), that may have protective or synergistic effects (*35, 36*). The lutein content in Monlis, even after 239 days at 38 °C and notwithstanding its strong degradation (>75%), was still superior to the initial bread wheat values.

In einkorn, all of the carotenoids, except β-cryptoxanthin, were slightly more stable in white flour than in wholemeal flour, maybe for the higher concentration of lipoxygenase in the bran fraction (*37*); this trend was not observed in bread wheat Serio. The degradation ranking was as follows: (α and β)-carotene > lutein > zeaxanthin > β-cryptoxanthin. A higher stability of lutein, as compared to β-carotene, was also described by Henry et al. (*27*) and Mortensen and Skibsted (*38*).

The Arrhenius model was used to determine the influence of temperature on the reaction rates; activation energy (E_a), z value, and pre-exponential constant ($\ln k_0$), as well as correlation coefficient (r) are presented in **Table 2**. In Monlis, the activation energy of the different carotenoids ranged between 35.2 and 52.5 kJ/mol; in Serio, the only measurable carotenoid, lutein, varied from 40.4 to 46.7 kJ/mol. The overall variation, considering the complex substrate analyzed, was minimal. As compared to white flour, wholemeal flour presented a superior activation energy for all of the compounds, with the exception of β-cryptoxanthin. Although in einkorn lutein displayed slightly higher E_a and lower z (on average, 47.2 kJ/mol and 34.0 °C, respectively) than the other compounds, the thermal sensitivity of the four carotenoids was similar.

Comparing these results with those reported in literature is somewhat difficult because different substrates and temperatures are involved. When similar temperature ranges are considered, the (α and β)-carotene E_a values are similar to those for β-carotene observed by Jarén-Galán and Mínguez-Mosquera (*23*) in model systems kept between 15 and 45 °C (32.7−48.81 kJ/mol) and by Koca et al. (*22*) in dehydrated carrots stored between 27 and 57 °C (38.9−66.4 kJ/mol), but they are lower than the E_a values reported by Tsimidou and Biliaderis (*25*) for saffron carotenoids during storage between 25 and 60 °C (83.6 kJ/mol). However, under higher temperatures significantly superior activation energies are reported by Dhuique-Mayer et al. (*26*) for β-carotene and β-cryptoxanthin (110.0 and 156.0 kJ/mol, respectively) in lemon juice thermically treated between 75 and 100 °C and by Henry et al. (*27*) for lutein and β-carotene (104.23 and 109.67 kJ/mol) in safflower oil heated between 75 and 95 °C.

Einkorn wheat shows a slower carotenoids loss than bread wheat, possibly because its higher initial content of carotenoids and other antioxidants reduces oxidative degradation, as well as its lower lipoxygenase activity. Remarkably, carotenoids concentration in einkorn at the end of the storage period is significantly superior even to freshly prepared bread wheat flour.

In conclusion, the stability of carotenoids in flour is a function of storage conditions. Higher temperatures exert a strong influence on the kinetics of degradation, accelerating the rate of pigments decomposition. Therefore refrigeration, or at least storing temperatures not exceeding 20 °C, better preserve carotenoid stability, therefore safeguarding the nutritional value of wheat flours.

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Supporting Information Available: Table of rate parameters for the carotenoids degradation reaction in wholemeal flour and white flour of einkorn cv. Monlis and bread wheat cv. Serio. This material is available free of charge via the Internet at http://pubs.acs.org.

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