Effect of Temperature and Oil Composition on the Ability of Phenolic Acids to Protect Naturally Present α-Tocopherol during the Heating of Plant Oils

Zuzana RÉBLOVÁ, Jakub FIŠNAR, Dana TICHOVSKÁ, Marek DOLEŽAL and Kristýna JOUDALOVÁ

Department of Food Chemistry and Analysis, Faculty of Food and Biochemical Technology, Institute of Chemical Technology Prague, Prague, Czech Republic

Abstract

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The ability of phenolic acids (ferulic, gallic, protocatechuic, and sinapic; 600 mg/kg) to protect naturally present α-tocopherol was tested during the heating of sunflower oil on a hot plate set at 120, 150, 180, 210, or 240°C, and during the heating of rapeseed, olive and soybean oils on a hot plate set at 180°C. In all the studied conditions, α-tocopherol was significantly protected only by gallic acid. This phenolic acid prolonged the half-life of α-tocopherol (calculated as the time needed for the α-tocopherol content to decrease to 50% of the original value) typically two- to four-fold. Hence the ability of phenolic acids to protect α-tocopherol in bulk oils does not markedly depend on the experimental conditions as is seen in antioxidant activity, i.e. in the ability of antioxidants to protect fatty acids.

Keywords: vitamin E; lipid oxidantion; antioxidants; frying

The best way to examine changes in plant oils during frying (and/or heating at temperatures higher than 100°C) is the determination of polymerised triacylglycerols and/or total polar compounds. Under these conditions, changes in fatty acids are monitored, with the maximum acceptable content of polymerised triacylglycerols at 12% and total polar compounds at 24% (Anonymous 2000). However, the tocopherols (vitamin E) are largely destroyed during frying as well. They are usually completely destroyed before the point at which the frying oil should be replaced based on the content of polymerised triacylglycerols or polar compounds (Normand *et al.* 2001; Barrera-Arellano *et al.* 2002; Réblová *et al.* 2009) and the losses of these compounds during food preparation by one-shot frying are tens of percent (Steinhart & Rathjen 2003).

Therefore, methods of tocopherol stabilisation during frying should be investigated. In a previous study, the ability of eight phenolic acids (gallic, gentisic, protocatechuic, syringic, vanillic, ferulic, caffeic, and sinapic; 600 mg/kg) to protect naturally present α-tocopherol was studied during the heating of sunflower oil on a hot plate set at 180°C (Réblová & Okrouhlá 2010). Under these conditions, the half-life of α-tocopherol (calculated as the time taken for the α-tocopherol content to decrease to 50% of the original value) was extended significantly by gentisic, caffeic, and gallic acids (from 1.16 to 1.77, 1.78, and 2.26 h, respectively).

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However, the ability of antioxidants to protect tocopherols can depend on the experimental conditions, as seen with antioxidant activity (i.e. the ability to protect fatty acids from oxidation) (Kamal-Eldin & Appelqvist 1996; Yanishlieva 2001). The ability to protect tocopherols in some cases and not in others has already been reported, for example for phospholipids (Koga & Terao 1995) or for epicatechin and epicatechin gallate (Zhu *et al.* 1999; Hashimoto *et al.* 2000; Hiramoto *et al.* 2002; Murakami *et al.* 2002; Raneva *et al.* 2004), whereas epigallocatechin and epigallocatechin gallate protected tocopherols under all the studied conditions (Zhu *et al.* 1999; Hashimoto *et al.* 2000; Hiramoto *et al.* 2002; Murakami *et al.* 2002; Raneva *et al.* 2004).

Factors that are known to affect antioxidant activity are the concentration of antioxidants, temperature, light, type of substrate, physical state of the system, as well as numerous microcomponents acting as pro-oxidants or synergists (Kamal-Eldin & Appelqvist 1996; Yanishlieva 2001). In bulk fats and oils, the dominant parameters affecting antioxidant activity are temperature, fatty acid composition of the stabilised substrate and initial content of tocopherols (Pokorný 1986; Ratuzs *et al.* 2002). These factors can increase (or decrease) antioxidant activity manifold (Marinova & Yanishlieva 1994, 1998; Yanishlieva & Marinova 1996). However, their effect on the ability of antioxidants to protect tocopherols has been studied only marginally (Wada & Fang 1994; Koga & Terao 1995). Therefore, the effect of these parameters on the ability of phenolic acids to protect α-tocopherol in bulk oils was studied in the present study. The effect of temperature on the ability of phenolic acids (ferulic, gallic, protocatechuic, and sinapic; 600 mg/kg) to protect naturally present α-tocopherol was studied during the heating of sunflower oil on a hot plate set at 120, 150, 180, 210, or 240°C and the ability of the studied phenolic acids to protect naturally present α-tocopherol in different plant oils (differing in fatty acid composition and tocopherol content) was compared during the heating of rapeseed, olive, soybean, and sunflower oils on a hot plate set at 180°C.

MATERIAL AND METHODS

Material. The plant oils investigated in this study (i.e. olive, rapeseed, soybean, and sunflower) were purchased in ordinary shops. Their chemical characterisation is summarised in Table 1.

The phenolic acids tested were purchased from Sigma-Aldrich (St. Louis, USA) with the following purities: gallic acid (higher than 98%), gentisic acid (98%), protocatechuic acid (higher than 97%), syringic acid (higher than 97%), vanillic acid (higher than 97%), ferulic acid (higher than 98%), sinapic acid (higher than 97%) (all Fluka, Buxchs, Switzerland), and caffeic acid (purity higher than 98%; Sigma, St. Louis, USA).

Experiments. The phenolic acids were added to the oils separately, at 600 mg/kg each, using the following procedure: 10 ml of the solution of the studied acid in acetone (150 mg/100 ml) were pipetted into 25 g ± 1% of the oil in a 100 ml beaker with an internal diameter of 43 mm. The oil and acetone solution were mixed and the beakers were placed in a fume cupboard in which the acetone evaporated at room temperature overnight.

On the next day, the beakers were heated on a hot plate (Präzitherm PZ 28-2; Harry Gestigkeit GmbH, Düsseldorf, Germany, using a steel adapter with outlets; internal diameter 60 mm and depth 28 mm) set at the selected temperature until the α-tocopherol content was lower than 50% of the original content. The sunflower oil was heated on a hot plate set at 120, 150, 180, 210, or 240°C and the other oils were heated on a hot plate set at 180°C only.

Table 1. Chemical characterisation of the investigated plant oils

	Olive	Rapeseed	Soybean	Sunflower
Total tocopherols (mg/kg)	200.0	550.5	992.9	672.2
α-Tocopherol (mg/kg)	190.2	243.6	113.3	627.5
Saturated fatty acids (%)	17.0	7.6	16.4	11.7
Monoenoic fatty acids (%)	70.0	62.8	24.2	27.8
Linoleic acid (%)	12.1	19.7	52.1	60.0
Linolenic acid (%)	0.6	8.0	6.4	0.1

Under these conditions, the real temperature of the hot plate was 120 ± 1, 150 ± 1, 180 ± 2, 210 ± 2, and 240 ± 2°C. The temperature of the oil increased for approximately 15 min and then fluctuated in the range of 98–101, 118–125, 143–150, 170–174, and 197–202°C, respectively.

For all conditions, three or six experiments were performed with each phenolic acid and three or six control experiments were performed with acetone only. For sampling, the whole beaker was always removed from the hot plate. Thus, the oil volume in the beakers was constant during the entire heating period.

Determination of tocopherols. The tocopherols were determined using reverse-phase HPLC with amperometric detection under the following conditions: mobile phase methanol/acetonitrile (1:1, v/v) mixture with $LiClO_4$ (0.02 mol/l) and NaCl (0.005 mol/l); flow rate 1 ml/min (LCP 4020.31 non-steel pump; Ecom, Prague, Czech Republic); injected volume 20 µl; sample preparation – solution in acetone; column Hypersil ODS, 200 × 4.6 mm, particle size 5 µm (Hewlett-Packard, Palo Alto, USA); column temperature 28°C (LCO 101 column heater; Ecom, Prague, Czech Republic); detection potential +1.05 V (HP 1049A amperometric detector equipped with a glassy-carbon working electrode; Hewlett-Packard, Palo Alto, USA).

Oxidation potential assessment. The reactivity of the investigated phenolic acids and α-tocopherol was studied in a flow system consisting of an LCP 4020.31 non-steel pump (Ecom) and an HP 1049A amperometric detector equipped with a glassy-carbon working electrode (Hewlett-Packard) under the following conditions: base electrolyte 0.2% (m/m) H_3PO_4/acetonitrile (1:4, v/v) mixture with NaCl (0.005 mol/l) for the measurements containing 0.1 ml of methanol (baseline) per 50 ml or 0.1 ml of a solution of the studied phenolic acid or α-tocopherol in methanol (2.5 mmol/l) per 50 ml; flow rate 0.2 ml/min; detection potential 0–1.2 V (rising speed 5 mV/s). Three parallel assessments were performed for each tested compound and the oxidation half-wave potentials were determined as the points of inflexion of the curves.

Ability of phenolic acids to scavenge free radicals. The ability of the selected phenolic acids (gallic, caffeic, and gentisic) to scavenge free radicals was determined using the modified DPPH method (Buřičová & Réblová 2008) in methanol. The results were expressed as the number of DPPH radicals reduced by one molecule of the studied phenolic acid, providing that one molecule of ascorbic acid reduces two molecules of DPPH (Staško *et al.* 2007).

Data processing. The half-life of α-tocopherol in the particular oils was calculated as the time taken to decrease to 50% of the original content. Differences between values were tested using Student's *t*-test at the 0.01 level of probability.

RESULTS AND DISCUSSION

Effect of temperature

Temperature is one of the most important factors affecting antioxidant activity (Pokorný 1986; Yanishlieva 2001). In the present study, the effect of temperature on the ability of phenolic acids to protect α-tocopherol was studied during the heating of sunflower oil on a hot plate set at 120, 150, 180, 210, or 240°C. Under these conditions, only gallic acid significantly protected α-tocopherol (Table 2). It prolonged the half-life of α-tocopherol (calculated as the time needed for the α-tocopherol content to decrease to 50% of the original value) approximately two- to four-fold.

Table 2. Ability of phenolic acids to protect α-tocopherol (based on the time taken for the content of α-tocopherol to decrease to 50% of the original content, $t_{\alpha T}$) during the heating of sunflower oil on a hot plate set at 120, 150, 180, 210, and 240°C (h; mean ± *s*)

Acid	120°C	150°C	180°C	210°C	240°C
–	8.38 ± 0.60	2.35 ± 0.10	1.24 ± 0.21	1.29 ± 0.04	1.80 ± 0.09
Ferulic	8.03 ± 0.05	2.22 ± 0.10	1.33 ± 0.07	1.27 ± 0.10	1.98 ± 0.06
Gallic	33.10 ± 3.43*	5.59 ± 0.64*	2.69 ± 0.29*	3.30 ± 0.08*	3.98 ± 0.21*
Protocatechuic	12.74 ± 3.72	2.74 ± 0.42	1.38 ± 0.10	1.45 ± 0.13	2.26 ± 0.17
Sinapic	8.20 ± 0.20	2.46 ± 0.19	1.31 ± 0.20	1.26 ± 0.02	2.15 ± 0.08

*significantly different from the control values ($P < 0.01$; $n = 3$)

Table 3. Ability of phenolic acids to protect α-tocopherol (based on the time taken for the content of α-tocopherol to decrease to 50% of the original content; $t_{\alpha T}$) during the heating of different plant oils on a hot plate set at 180°C (h; mean ± *s*)

Acid	Olive	Rapeseed	Soybean
–	0.38 ± 0.13	1.01 ± 0.08	1.13 ± 0.16
Ferulic	0.40 ± 0.08	1.08 ± 0.13	1.21 ± 0.15
Gallic	1.17 ± 0.28*	2.09 ± 0.33*	2.81 ± 0.49*
Protocatechuic	0.50 ± 0.08	1.61 ± 0.67	1.34 ± 0.13
Sinapic	0.49 ± 0.09	1.32 ± 0.23	1.25 ± 0.07

*significantly different from the control values ($P < 0.01$; $n = 6$)

Although the ability of gallic acid to protect α-tocopherol was slightly higher at a set temperature of 120°C (compared to the other set temperatures), no significant relationship was found between temperature and the protective effect. This is in conflict with the generally marked effect of temperature on the antioxidant activity (i.e. ability to protect fatty acids) of phenolic acids (Réblová 2012) and other antioxidants (Marinova & Yanishlieva 1998; Réblová 2006).

Comparison of activity in different plant oils

During the heating of different plant oils on a hot plate set at 180°C, only gallic acid was able to significantly protect α-tocopherol (Table 3), which was also seen during the heating of sunflower oil (see previous). This phenolic acid prolonged the half-life of α-tocopherol (calculated as the time needed for the α-tocopherol content to decrease to 50% of the original value) from two- to three-fold.

The activity of antioxidants (i.e. their ability to protect fatty acids from oxidation) in different fats and oils is affected by the fatty acid composition (their degree of unsaturation) and by the content of tocopherols (Ratuzs *et al.* 2002). Both these factors markedly affect antioxidant activity. For example, the activity of phenolic acids in triacylglycerols isolated from pork lard was many times higher than the activity of these same compounds in triacylglycerols isolated from sunflower oil (Marinova & Yanishlieva 1994). Likewise, the activity of caffeic and protocatechuic acids was markedly higher in triacylglycerols isolated from sunflower oil than in sunflower oil with a natural tocopherol content (Yanishlieva & Marinova 1996). On the contrary, no significant relationship between the ability of gallic acid to protect α-tocopherol and the composition of the stabilised oils (i.e. their fatty acid composition and content of tocopherols) was found in this study, although the protective effect of gallic acid was slightly higher in olive oil (compared to the other oils) which had the lowest iodide value and the lowest total tocopherol content.

Generalisation of the results

As is evident from the present results, the ability of phenolic acids to protect tocopherols in bulk oils does not markedly depend on the experimental conditions (as opposed to antioxidant activity, i.e. the ability to protect fatty acids from oxidation). It means that the ability to protect tocopherols (in these systems) is not affected by the speed of the initiation reactions [which above all affects antioxidant activity in fats and oils (Pokorný 1986)], but is probably driven only by the reactivity of tocopherols and the studied antioxidants (and also partly by the ratio of their concentrations) (Pazos *et al.* 2007). However, different results can be obtained in heterogeneous systems, where antioxidant activity (and also the ability to protect tocopherols) (Raneva *et al.* 2001, 2002) is affected by the distribution of antioxidants and other reactive compounds between phases (Decker *et al.* 2005).

In solution, the reactivity of the present compounds can be affected by the solvent and pH (Amorati *et al.* 2006). However, in fats and oils, the reactivity of compounds against free radicals (Becker *et al.* 2004; Karadag *et al.* 2009), and so also the ability of antioxidants to protect tocopherols (Pazos *et al.* 2007), is given by the

bond dissociation energy of the respective bonds. This parameter can be (and often is) replaced by the standard reduction potential (Becker *et al.* 2004; Choe & Min 2009; Karadag *et al.* 2009) or, even better, the formal reduction (oxidation) potential, which is easily measurable and characterises the reactivity (oxidisability) of compounds under concrete conditions (Becker *et al.* 2004). Therefore, the relationship between the oxidation potentials of phenolic acids and their ability to protect α-tocopherol was also investigated in this study. The oxidation half-wave potentials were measured not only for the four phenolic acids used in this study, but for all eight phenolic acids used in this investigation and in the previous study (Réblová & Okrouhlá 2010). The potentials were determined in an acidic medium to suppress the dissociation of phenols (affecting their reactivity) (Amorati *et al.* 2006), similar to that which occurs in bulk fats and oils.

Under the investigated conditions, the oxidation half-wave potential of α-tocopherol was 447 mV (s = 13 mV, n = 3). The oxidation potentials of all the studied phenolic acids were statistically significantly higher ($P < 0.01$; Table 4).

It is logical that the ability to protect α-tocopherol is observed in compounds with lower oxidation potential (compared to α-tocopherol), such as ascorbic acid and its derivatives (Pazos *et al.* 2007) or epigallocatechin gallate (Jia *et al.* 1998). However, as is evident from the present and previous (Réblová & Okrouhlá 2010) results, the ability to protect α-tocopherol can be found also in compounds with slightly higher oxidation potentials, i.e. gentisic, gallic, and caffeic acids in this case. Additionally, such compounds (gallic acid and epicatechin) were also able to regenerate α-tocopherol from the tocopheroxyl radical, which is an important mechanism in the protection of α-tocopherol (Pazos *et al.* 2007).

Table 4. Oxidation potentials ($E_{1/2}$) of the studied phenolic acids determined in an acidic medium (n = 3)

Acid	$E_{1/2}$ (mV; mean ± s)
Gentisic	499 ± 5
Gallic	512 ± 3
Caffeic	522 ±3
Sinapic	639 ± 5
Protocatechuic	651 ± 3
Ferulic	733 ± 5
Syringic	770 ± 3
Vanillic	886 ± 8

Hence the compounds with slightly higher oxidation potentials than α-tocopherol are able to compete with α-tocopherol in reactions with lipid radicals and/or to regenerate α-tocopherol from the tocopheroxyl radical. However, such compounds only slow down the initiation speed of α-tocopherol losses (Figure 2 in Réblová & Okrouhlá 2010), while compounds with lower oxidation potentials than α-tocopherol almost completely (or completely) inhibit α-tocopherol decay in the initial stages (Jia *et al.* 1998). Furthermore, the ability to regenerate α-tocopherol from the tocopheroxyl radical is lower in compounds with higher oxidation potentials than α-tocopherol compared to compounds with lower oxidation potentials than α-tocopherol (Pazos *et al.* 2007).

During the regeneration of α-tocopherol from the tocopheroxyl radical, the reaction Tocx + ArOH ↔ TocH + ArOx is assumed, where TocH (Tocx) is α-tocopherol (tocopheroxyl radical) and ArOH (ArOx) is any tested antioxidant (and its radical) (Pazos *et al.* 2007). For compounds with higher oxidation potentials than α-tocopherol, the equilibrium is shifted to the left. However, for a quantitative course of the reaction, the difference between oxidation (reduction) potentials of the reactive compounds has to be higher than 200 mV to 400 mV (depending on the ratio of reactant concentrations and stoichiometric coefficients) (Holzbecher & Churáček 1987). Therefore the compounds with slightly higher oxidation potentials than α-tocopherol can also protect it. Moreover, at high molar excess, even protocatechuic acid was able to regenerate α-tocopherol from the tocopheroxyl radical, although its effect was small (Pazos *et al.* 2007).

The greater ability of gallic acid to protect α-tocopherol compared to gentisic and caffeic acids (as was observed in the previous study – Réblová & Okrouhlá 2010) was probably caused by the greater free radical scavenging capacity of gallic acid, because the half-wave oxidation potentials of gentisic and caffeic acids are not significantly different from that of gallic acid ($P < 0.01$). Although the number of free radicals reduced by one molecule of antioxidant depends on the experimental conditions (such as pH or solvent) (Magalhães *et al.* 2007; Staško *et al.* 2007), gallic acid generally reduces a greater number of free radicals than other phenolic acids (Magalhães *et al.* 2007).

In this study, one molecule of gallic acid reduced six molecules of DPPH, while caffeic and gentisic acids reduced four molecules only.

CONCLUSIONS

In the present study, the ability of phenolic acids (ferulic, gallic, protocatechuic, and sinapic; 600 mg/kg) to protect naturally present α-tocopherol was tested during the heating of sunflower oil on a hot plate set at 120, 150, 180, 210, or 240°C, and during the heating of rapeseed, olive and soybean oils on a hot plate set at 180°C. In all the studied conditions, α-tocopherol was significantly protected only by gallic acid. This phenolic acid prolonged the half-life of α-tocopherol (calculated as the time needed for the α-tocopherol content to decrease to 50% of the original value) typically two- to four-fold, i.e. the ability of phenolic acids to protect α-tocopherol in bulk oils does not markedly depend on the experimental conditions (temperature and oil composition), which expressively influence antioxidant activity. Therefore, the ability of antioxidants to protect tocopherols in bulk fats and oils need not be tested under concrete conditions and can be predicted by the easily observable oxidation potential.

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Corresponding author:

Doc. Ing. Zuzana Réblová, Ph.D., Vysoká škola chemicko-technologická v Praze, Fakulta potravinářské a biochemické technologie, Ústav chemie a analýzy potravin, Technická 5, 166 28 Praha 6, Česká Republika
tel. + 420 220 443 181, e-mail: zuzana.reblova@vscht.cz