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Inhibition of corn oil oxidation by *N*-acetyl-cysteine and glutathione

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Abstract

The ability of *N*-acetyl-cysteine and glutathione to inhibit the oxidation of corn oil was evaluated.

The absorbances at 234 nm and 270 nm, and *p*-anisidine value were monitored during storage of corn oil at 50 °C, 120 °C and 180 °C for up to 30 days, 12 h and 180 min, respectively. Both thiols exhibited inhibitory action that was dose dependent in the range 0–40 mg/L, while *N*-acetyl-cysteine was more effective than glutathione. At 50 °C and 120 °C, each thiol at 10, 20 or 40 mg/L was less effective than BHA at 200 mg/L. At 180 °C, *N*-acetyl-cysteine at 20 and/or 40 mg/L was more effective than BHA at 200 mg/L, while glutathione slightly less.

Volatile aldehydes were also determined after storage of corn oil at 60 °C for 5 days. *N*-Acetyl-cysteine and glutathione, each at 20 mg/L, inhibited the formation of several volatile aldehydes such as hexanal to an extent equal to BHA at 200 mg/L.

Present results indicate that *N*-acetyl-cysteine and glutathione may be taken into account as antioxidants in corn oil during storage, cooking or frying.

Keywords: Corn oil; Oxidation; *N*-Acetyl-cysteine; Glutathione

1. Introduction

Edible oils are major components of human diet because of their high energy value, good solubility of vitamins and essential fatty acid content. Though vegetable oils are popular as cooking media, their oxidation is accepted to bring about deleterious effects, such as deterioration and toxicity. Off-flavorings, nutritional losses and other deterioration changes in oil are concerned with the changes that result from reaction with atmospheric oxygen during storage and heating (Jadhav, Nimbalkar, Kulkarni, & Madhavi, 1996; Naz, Sheikh, Siddiqi, & Sayeed, 2004).

The problem of ensuring a high quality of lipids and prolonging their storage time is directly associated with their optimum stabilization by addition of suitable antioxidants. The high oxidation stability of lipids is important for health protection and for economic reasons. Synthetic antioxidants such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) are commonly added to oils to retard oxidative changes during storage and heat because they are effective and cheaper than natural ones (Jadhav et al., 1996). However, the safety and toxicity of synthetic antioxidants, such as BHA and BHT, have raised important concerns (Madhavi & Salunkre, 1996). Hence, considerable interest has been given to the use of natural antioxidants because of their potential nutritional and therapeutic properties (Jadhav et al., 1996).

SH-containing amino acids and peptides are good inhibitors of browning in fruit juices and other foods (Molnar-Perl & Friedman, 1990). Moreover, their antioxidant activities against the peroxidation of lipids have been reported (Ahmad, Al-Hakim, & Shehata, 1983; Papadopoulou & Roussis, 2000; Yin & Cheng, 2003). Some thiols are natural components in our diet and play significant physiological roles in vivo as nucleophiles and scavengers of free radicals. Glutathione is a naturally occurring tripeptide present in many foods. *N*-Acetyl-cysteine is garlic-derived and is used as a drug to reduce lung congestion.

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It is an excellent nutritional source of cysteine for humans and acts as an antimutagen and anticarcinogen (Friedman, 1994, 1997).

The effort of present study was to evaluate the ability of *N*-acetyl-cysteine and glutathione to inhibit the oxidation of corn oil.

2. Materials and methods

N-Acetyl-cysteine, glutathione, and BHA were purchased from Sigma (St. Louis, MO, USA). Corn oil was commercial 'flora' corn oil (Elais, Athens, Greece).

The ability of *N*-acetyl-cysteine and glutathione, along with BHA, to inhibit the oxidation of corn oil was monitored at 50 °C, 120 °C and 180 °C. Each thiol and BHA was added in solid form and dissolved using ultrasonic bath for 10 min. A standard amount of corn oil was put into glass bottles of 5 mL capacity ($D = 2.3$ cm, $h = 2.4$ cm). Two milliliters were used for experiments at 50 °C while 1 mL for those at 120 or 180 °C. Bottles were put open in an oven at the appropriate temperature. Bottles were taken at periodic intervals and the oxidative stability of oil was evaluated.

The oxidative stability of corn oil was evaluated by measuring conjugated dienes, conjugated trienes and *p*-anisidine value, which are good indexes for the determination of oxidative stability of oils (IUPAC, 1987).

For the assessment of conjugated dienes and conjugated trienes, 10 μL of each oil sample were mixed with 10 mL of iso-octane and the absorbances at 234 nm and 270 nm were measured using quartz cells of 1 cm. Iso-octane was used as a blank. When it was necessary, the mixtures were diluted more with iso-octane in order to take a measurable absorbance, which was then corrected according to this extra dilution. In the experiments at each temperature, samples analysed at the same storage time were mixed with the same volume of iso-octane in order to have the same oil concentration. For *p*-anisidine value, 0.1–0.2 g of each sample to the nearest 0.001 g were put into a 5 mL volume flask and diluted up to 5 mL with iso-octane. The absorbance at 350 nm (Ab) was measured using cells of 1 cm and the solvent as a blank. Five milliliters of each oil solution or solvent were mixed with 1 mL *p*-anisidine reagent (2.5 g/L in acetic acid). After exactly 10 min the absorbance at 350 nm (As) of each oil sample mixture was measured using the solvent mixture as blank. The *p*-anisidine value (*p*-AV) was calculated by the formula $p\text{-AV} = 5x$ (1.2 As–Ab):*m*, where As is the absorbance of oil solution after reaction with *p*-anisidine reagent, Ab is the absorbance of the solution of the oil, *m* is the mass, in gr, of the test portion. In all cases, the absorbance was taken using a Jenway 6505 UV/vis spectrophotometer (Jenway, Dunmow, England).

The ability of *N*-acetyl-cysteine and glutathione to inhibit the oxidation of corn oil was also evaluated by determining volatile aldehydes formed during its storage at 60 °C for 5 days. Each thiol, and also BHA, was added in solid form and dissolved using ultrasonic bath for 10 min. Eight gram of corn oil was put into glass bottles of 30 mL capacity ($D = 2.6$ cm, $h = 7$ cm). Bottles were put open in an oven at 60 °C.

All corn oil samples were analysed by solid phase microextraction (SPME) along with gas chromatography–mass spectrometry (GC–MS).

A 65 μm Carbowax™-Divinylbenzene fiber (Supelco, Bellefonte, PA, USA) was used for the absorption of volatiles. Two milliliters of each corn oil sample and 50 μL of internal standard in 10% ethanol (4-methyl-1-pentanol, 1.5 μg/g) were transferred into a 4 mL screw-capped glass vial with a Teflon-rubber septum (12 mm; Sun-Sri, Rockwood, PA, USA). The contents were stirred for 10 min at 60 °C. Then, a constant length of the fiber was exposed to the headspace for another 60 min, under the same conditions. Desorption of volatiles took place at 250 °C using a 0.75 mm ID liner (Supelco, Bellefonte, PA, USA) for 5 min. Split/splitless mode was used, splitless for 2 min and split ratio was 1:20. GC–MS analysis was carried out on an HP 5973 quadrupole mass spectrometer directly coupled to an HP 6890 gas chromatograph (Hewllet Packard, Palo Alto, CA, USA). MS was operated in the electron impact mode with the electron energy set at 70 eV and a G1701BA Chemstation was employed. Source and quadrupole temperatures were set at 230 °C and 150 °C, respectively. The transfer line was kept at 250 °C. An HP-5MS column was used (30 m × 0.25 mm, 0.25 μm film thickness) (Aligent Technologies, Wilmington, DE, USA). The carrier gas was helium at a constant flow rate of 0.7 mL/min and average velocity 30 cm/sec. Oven temperature was programmed from 40 °C for 2 min and then raised to 160 °C and 220 °C at rates of 6.0 and 8 °C/min, respectively. It was held at 220 °C for 10 min. Mass range, 29–300 m/z, and 2.73 scan s^{-1} were applied.

All peaks were identified by comparing mass spectra to those obtained from Wiley 275 and NIST 98 libraries. Moreover, the identification of hexanal, octanal and nonanal (Merck, Darmstadt, Germany) was confirmed with mass spectra and retention times of standard compounds determined in the same analysis conditions.

Semiquantitative data were expressed in micrograms per gram [(area of compound/area of internal standard) × concentration of internal standard].

Each experiment was repeated three times, and results reported here are the means of the three runs. The one way analysis of variance (ANOVA), using the Duncan test at a level of significance $P < 0.05$ was used for the statistical analysis (SPSS 11.5).

3. Results and discussion

N-Acetyl-cysteine and glutathione were tested as inhibitors of corn oil oxidation at 50 °C, 120 °C and 180 °C, while BHA was also used for comparison. The heating at 50 °C simulates oil behaviour during storage, and at 120 °C and 180 °C the cooking and frying conditions,

respectively. The absorbances at 234 nm and 270 nm, and *p*-anisidine value were measured. The determination of conjugated dienes by the absorbance at 234 nm is related to the content of hydroperoxides, i.e. primary products of lipid oxidation. It is a sensitive method to follow the early stages of lipid oxidation under conditions in which hydroperoxides undergo little or no decomposition. The absorbance at 270 nm is an index mainly of secondary oxidation products. It is known that at advanced stages of oxidation, the hydroperoxides decompose into secondary and polymeric products that absorb at 234 nm, but with lower extinction than the hydroperoxides, and at 270 nm due to conjugated trienes. The *p*-anisidine value is extensively used to measure the secondary oxidation products, mainly non-volatile carbonyls, formed during lipid oxidative degradation. It is assessed after reaction of carbonyls in oil and the *p*-anisidine reagent and measuring the coloured product at 350 nm (Frankel, 1998; IUPAC, 1987).

The effect of *N*-acetyl-cysteine and glutathione on conjugated dienes, conjugated trienes and *p*-anisidine value of corn oil stored at 50 °C is presented in Tables 1 and 2, respectively. Both thiols inhibited the increase of the absorbances at 234 nm and 270 nm, and also *p*-anisidine value. Their action was dose dependent, while glutathione at 10 and 20 mg/L was equally effective. *N*-Acetyl-cysteine appeared to be statistically more effective than glutathione (statistical analysis not shown). At $t = 30$ days, samples containing 40 mg/L *N*-acetyl-cysteine exhibited % inhibition of the increase of A234 nm, A270 nm and *p*-anisidine value 50, 33 and 23 of those of the control, respectively. In samples containing 40 mg/L glutathione these values were 32%, 18% and 13% of those of the control, respectively. Both thiols at any concentration tested were less effective than BHA at 200 mg/L. At $t = 30$ days, sample containing BHA exhibited % inhibition of the increase of A234 nm, A270 nm and *p*-anisidine value 60, 40 and 32 of those of the control, respectively.

The effect of *N*-acetyl-cysteine and glutathione on conjugated dienes, conjugated trienes and *p*-anisidine value of corn oil stored at 120 °C is presented in Tables 3 and 4, respectively. Both thiols inhibited the increase of the absorbances at 234 nm and 270 nm, and also *p*-anisidine value. Their action was dose dependent. *N*-Acetyl-cysteine appeared to be statistically more effective than glutathione (statistical analysis not shown). At $t = 12$ h, samples containing 40 mg/L *N*-acetyl-cysteine exhibited % inhibition of the increase of A234 nm, A270 nm and *p*-anisidine value 40, 43 and 32 of those of the control, respectively. In samples containing 40 mg/L glutathione these % values were 25, 35 and 19 of those of the control, respectively. Both thiols at any concentration tested were less effective than BHA at 200 mg/L. At $t = 12$ h, sample containing BHA exhibited % inhibition of the increase of A234 nm, A270 nm and *p*-anisidine value 50, 43 and 34 of those of the control, respectively.

The effect of *N*-acetyl-cysteine and glutathione on conjugated dienes and conjugated trienes of corn oil stored at 180 °C is presented in Tables 5 and 6, respectively. Both thiols inhibited the increase of the absorbances at 234 nm and 270 nm. Their action was dose dependent. *N*-Acetyl-cysteine appeared to be statistically more effective than glutathione (statistical analysis not shown). At $t = 180$ min, samples containing 40 mg/L *N*-acetyl-cysteine exhibited % inhibition of the increase of A234 nm, and A270 nm 61 and 46 of those of the control, respectively. In samples containing 40 mg/L glutathione these % values were 34 and 34 of those of the control, respectively. Glutathione at any concentration tested was less effective than BHA. However, *N*-acetyl-cysteine at 20 or 40 mg/L was more effective than

Table 1
Effect of *N*-acetyl-cysteine on the absorbances at 234 nm and 270 nm, and *p*-anisidine value during storage of corn oil at 50 °C

Sample	0 day	5 days	10 days	15 days	20 days	25 days	30 days
Absorbance at 234 nm							
Control	0.201^{a}	0.296^{a}	0.334^{a}	0.486^{a}	0.574^{a}	0.627^{a}	0.726^{a}
BHA, 200 mg/L	0.201^{a}	0.221^{b}	0.229^{c}	0.336^{c}	0.366^{e}	0.398^{e}	0.411^{e}
N-Acetyl-cysteine,10 mg/L	0.201^{a}	0.239^{b}	0.261^{b}	0.366^{b}	0.427^{b}	0.497^{b}	0.543^{b}
N-Acetyl-cysteine, 20 mg/L	0.200^{a}	0.234^{b}	0.240^{c}	0.357^{b}	0.413^{c}	0.475^{c}	0.497^{c}
N-Acetyl-cysteine, 40 mg/L	0.200^{a}	0.219^{b}	0.227^{c}	$0.345^{b,c}$	0.401^{d}	0.421^{d}	0.462^{d}
Absorbance at 270 nm							
Control	0.099^{a}	0.102^{a}	0.180^{a}	0.198^{a}	0.219^{a}	0.225^{a}	0.243^{a}
BHA, 200 mg/L	0.098^{a}	0.100^{a}	0.118^{b}	0.144^{c}	0.171^{c}	0.179^{c}	0.184^{d}
N-Acetyl-cysteine, 10 mg/L	0.097^{a}	0.098^{a}	0.126^{b}	0.160^{b}	0.199^{b}	0.209^{b}	0.217^{b}
N-Acetyl-cysteine, 20 mg/L	0.098^{a}	0.099^{a}	0.122^{b}	0.150^{b}	0.191^{b}	0.199^{b}	0.206^{c}
N-Acetyl-cysteine, 40 mg/L	0.099^{a}	0.100^{a}	0.118^{b}	0.143^{c}	0.176^{c}	0.188^{b}	0.195^{d}
p-Anisidine value							
Control	4.6^{a}	6.3^{a}	6.9^{a}	8.1^{a}	8.4^{a}	8.8^{a}	9.4^{a}
BHA, 200 mg/L	4.6^{a}	5.7^{a}	6.3^{b}	6.9^{b}	7.1^{c}	7.6^{c}	7.9^{d}
N-Acetyl-cysteine, 10 mg/L	4.6^{a}	5.8^{a}	6.6^{b}	7.1^{b}	7.6^{b}	8.5^{b}	8.7^{b}
N-Acetyl-cysteine, 20 mg/L	4.6^{a}	5.7^{a}	6.6^{b}	7.0^{b}	7.5^{b}	8.4^{b}	8.6^{b}
N-Acetyl-cysteine, 40 mg/L	4.7^{a}	5.6^{a}	6.4^{b}	7.0^{b}	$7.3^{b,c}$	8.2^{b}	8.3^{c}

Means in every column and index without common superscript differ significantly at $P < 0.005$.

Table 2
Effect of glutathione on the absorbances at 234 nm and 270 nm, and *p*-anisidine value during storage of corn oil at 50 °C

Sample	0 day	5 days	10 days	15 days	20 days	25 days	30 days
Absorbance at 234 nm							
Control	0.201[a]	0.296[a]	0.334[a]	0.486[a]	0.574[a]	0.627[a]	0.726[a]
BHA, 200 mg/L	0.201[a]	0.221[c]	0.229[d]	0.336[d]	0.366[c]	0.398[c]	0.411[c]
Glutathione, 10 mg/L	0.202[a]	0.272[b]	0.290[b]	0.397[b]	0.583[a]	0.640[a]	0.708[a]
Glutathione, 20 mg/L	0.200[a]	0.256[b]	0.274[c]	0.376[c]	0.573[a]	0.634[a]	0.702[a]
Glutathione, 40 mg/L	0.201[a]	0.245[b]	0.261[c]	0.367[c]	0.418[b]	0.515[b]	0.560[b]
Absorbance at 270 nm							
Control	0.099[a]	0.102[a]	0.180[a]	0.198[a]	0.219[a]	0.225[a]	0.243[a]
BHA, 200 mg/L	0.098[a]	0.100[a]	0.118[c]	0.144[c]	0.171[c]	0.179[c]	0.184[c]
Glutathione, 10 mg/L	0.099[a]	0.100[a]	0.136[b]	0.173[b]	0.216[a]	0.239[a]	0.250[a]
Glutathione, 20 mg/L	0.099[a]	0.101[a]	0.133[b]	0.156[c]	0.211[a]	0.234[a]	0.245[a]
Glutathione, 40 mg/L	0.100[a]	0.101[a]	0.125[b]	0.151[c]	0.200[b]	0.210[b]	0.217[b]
p-Anisidine value							
Control	4.6[a]	6.3[a]	6.9[aB]	8.1[a]	8.4[a]	8.8[a]	9.4[a]
BHA, 200 mg/L	4.6[a]	5.7[a]	6.3[c]	6.9[c]	7.1[b]	7.6[c]	7.9[c]
Glutathione, 10 mg/L	4.6[a]	6.0[a]	6.7[b]	7.6[b]	8.4[a]	8.8[a]	9.4[a]
Glutathione, 20 mg/L	4.6[a]	5.9[a]	6.6[b]	7.3[c]	8.2[a]	8.8[a]	9.4[a]
Glutathione, 40 mg/L	4.7[a]	5.8[a]	6.6[b]	7.1[c]	8.0[b]	8.5[b]	8.8[b]

Means in every column and index without common superscript differ significantly at $P < 0.005$.

Table 3
Effect of *N*-acetyl-cysteine on the absorbances at 234 nm and 270 nm, and *p*-anisidine value during storage of corn oil at 120 °C

Sample	0 h	3 h	6 h	12 h
Absorbance at 234 nm				
Control	0.245[a]	0.797[a]	1.864[a]	3.138[a]
BHA, 200 mg/L	0.245[a]	0.324[d]	0.567[d]	1.708[d]
N-Acetyl-cysteine, 10 mg/L	0.245[a]	0.412[b]	0.969[b]	2.286[b]
N-Acetyl-cysteine, 20 mg/L	0.244[a]	0.392[b]	0.744[c]	2.038[c]
N-Acetyl-cysteine, 40 mg/L	0.245[a]	0.353[c]	0.732[c]	1.986[c]
Absorbance at 270 nm				
Control	0.101[a]	0.179[a]	0.309[a]	0.659[a]
BHA, 200 mg/L	0.102[a]	0.122[c]	0.147[d]	0.418[c]
N-Acetyl-cysteine, 10 mg/L	0.101[a]	0.141[b]	0.224[b]	0.444[b]
N-Acetyl-cysteine, 20 mg/L	0.102[a]	0.134[b]	0.183[c]	0.432[c]
N-Acetyl-cysteine, 40 mg/L	0.101[a]	0.131[b,c]	0.177[c]	0.420[c]
p-Anisidine value				
Control	4.6[a]	50.9[a]	149.5[a]	231.9[a]
BHA, 200 mg/L	4.6[a]	13.9[c]	41.5[c]	154.9[d]
N-Acetyl-cysteine, 10 mg/L	4.6[a]	15.1[b]	47.0[b]	188.2[b]
N-Acetyl-cysteine, 20 mg/L	4.6[a]	14.7[b]	46.2[b]	165.9[c]
N-Acetyl-cysteine, 40 mg/L	4.7[a]	14.0[b,c]	43.2[c]	159.6[c,d]

Means in every column and index without common superscript differ significantly at $P < 0.005$.

Table 4
Effect of glutathione on the absorbances at 234 nm and 270 nm, and *p*-anisidine value during storage of corn oil at 120 °C

Sample	0 h	3 h	6 h	12 h
Absorbance at 234 nm				
Control	0.245[a]	0.797[a]	1.864[a]	3.138[a]
BHA, 200 mg/L	0.245[a]	0.324[e]	0.567[e]	1.708[d]
Glutathione, 10 mg/L	0.246[a]	0.568[b]	1.490[b]	2.720[b]
Glutathione, 20 mg/L	0.246[a]	0.543[c]	1.048[c]	2.518[c]
Glutathione, 40 mg/L	0.245[a]	0.520[d]	0.975[d]	2.496[c]
Absorbance at 270 nm				
Control	0.101[a]	0.179[a]	0.309[a]	0.659[a]
BHA, 200 mg/L	0.102[a]	0.122[d]	0.147[d]	0.418[e]
Glutathione, 10 mg/L	0.101[a]	0.160[b]	0.271[b]	0.558[b]
Glutathione, 20 mg/L	0.102[a]	0.160[b]	0.234[c]	0.516[c]
Glutathione, 40 mg/L	0.101[a]	0.151[c]	0.230[c]	0.463[d]
p-Anisidine value				
Control	4.6[a]	50.9[a]	149.5[a]	231.9[a]
BHA, 200 mg/L	4.6[a]	13.9[e]	41.5[d]	154.9[e]
Glutathione, 10 mg/L	4.6[a]	21.8[b]	77.6[b]	209.2[b]
Glutathione, 20 mg/L	4.6[a]	17.5[c]	51.6[c]	199.9[c]
Glutathione, 40 mg/L	4.7[a]	15.2[d]	47.9[c]	189.2[d]

Means in every column and index without common superscript differ significantly at $P < 0.005$.

Table 5
Effect of *N*-acetyl-cysteine on the absorbances at 234 nm and 270 nm during storage of corn oil at 180 °C

Sample	0 min	30 min	60 min	120 min	180 min
Absorbance at 234 nm					
Control	0.245[a]	0.758[a]	1.561[a]	2.187[a]	2.582[a]
BHA, 200 mg/L	0.245[a]	0.466[b]	0.613[d]	1.002[c]	1.644[c]
N-Acetyl-cysteine, 10 mg/L	0.245[a]	0.454[b]	0.824[b]	1.065[b]	1.802[b]
N-Acetyl-cysteine, 20 mg/L	0.244[a]	0.442[b]	0.739[c]	0.991[c]	1.351[d]
N-Acetyl-cysteine, 40 mg/L	0.245[a]	0.419[c]	0.566[e]	0.924[d]	1.157[e]
Absorbance at 270 nm					
Control	0.101[a]	0.315[a]	0.444[a]	0.587[a]	0.679[a]
BHA, 200 mg/L	0.102[a]	0.187[b]	0.273[c]	0.375[c]	0.461[c]
N-Acetyl-cysteine, 10 mg/L	0.101[a]	0.197[b]	0.295[b]	0.448[b]	0.506[b]
N-Acetyl-cysteine, 20 mg/L	0.102[a]	0.191[b]	0.271[c]	0.346[d]	0.464[c]
N-Acetyl-cysteine, 40 mg/L	0.101[a]	0.174[c]	0.240[d]	0.326[e]	0.414[d]

Means in every column and index without common superscript differ significantly at $P < 0.005$.

BHA at 200 mg/L. At $t = 180$ min, sample containing BHA exhibited % inhibition of the increase of A234 nm and A270 nm 40 and 38 of those of the control, respectively.

The ability of *N*-acetyl-cysteine and glutathione to inhibit the formation of volatile aldehydes was also determined after storage of corn oil at 60 °C. At $t = 0$, corn oil did not exhibit any volatile aldehyde. At $t = 5$ days, corn oil exhibited some amounts of pentanal, hexanoal, octanal, nonanal and decanal, while both thiols inhibited their formation

Table 6
Effect of glutathione on the absorbances at 234 nm and 270 nm during storage of corn oil at 180 °C

Sample	0 min	30 min	60 min	120 min	180 min
Absorbance at 234 nm					
Control	0.245[a]	0.758[a]	1.561[a]	2.187[a]	2.582[a]
BHA, 200 mg/L	0.245[a]	0.466[d]	0.613[d]	1.002[e]	1.644[e]
Glutathione, 10 mg/L	0.246[a]	0.554[b]	1.002[b]	1.364[b]	2.219[b]
Glutathione, 20 mg/L	0.246[a]	0.516[c]	0.861[c]	1.216[c]	2.051[c]
Glutathione, 40 mg/L	0.245[a]	0.459[d]	0.626[d]	1.066[d]	1.798[d]
Absorbance at 270 nm					
Control	0.101[a]	0.315[a]	0.444[a]	0.587[a]	0.679[a]
BHA, 200 mg/L	0.102[a]	0.187[d]	0.273[d]	0.375[e]	0.461[e]
Glutathione, 10 mg/L	0.101[a]	0.233[b]	0.371[b]	0.521[b]	0.569[b]
Glutathione, 20 mg/L	0.102[a]	0.211[c]	0.352[c]	0.482[c]	0.516[c]
Glutathione, 40 mg/L	0.102[a]	0.196[d]	0.279[d]	0.466[d]	0.484[d]

Means in every column and index without common superscript differ significantly at $P < 0.005$.

Table 7
Effect of *N*-acetyl-cysteine, glutathione on volatile aldehydes formation after storage of corn oil at 60 °C for 5 days

Volatile aldehydes	Control	BHA, 200 mg/L	*N*-Acetyl-cysteine, 20 mg/L	Glutathione, 20 mg/L
Pentanal	1.05[b]	0.13[a]	0.10[a]	0.20[a]
Hexanal	0.27[b]	0.09[a]	0.00[a]	0.07[a]
Octanal	1.10[b]	0.48[a]	0.53[a]	0.37[a]
Nonanal	2.91[b]	0.12[a]	0.37[a]	0.75[a]
Decanal	3.57[b]	0.21[a]	0.56[a]	0.80[a]

Values, μg/g as 4-methyl-1-pentanol, are the means of the three trials.
Means in every row without common superscript differ significantly at $P < 0.005$.

(Table 7). Samples containing *N*-acetyl-cysteine or glutathione, each at 20 mg/L, and those containing BHA at 200 mg/L exhibited similar concentration of each volatile. Volatile aldehydes are products of the secondary oxidation of oils, while hexanal is commonly used as an index of oil oxidation. Several volatile aldehydes such as hexanal, octanal and nonanal have been determined by others after storage of different vegetable oils at 60 °C (Jelen, Obuchowska, Zawirska-Wojtasiak, & Wasowicz, 2000; Snyder, 1995).

Present results show that *N*-acetyl-cysteine and glutathione inhibit corn oil oxidation at 50 °C, 120 °C and 180 °C. Thiols are well known as free radical scavengers and thus as antioxidants (Friedman, 1994), while free radical reactions of peroxidizing lipids with sulphydryls have been observed (Schaich & Karel, 1976). There have been reports on the antioxidant activities of thiols in edible oils. It has been shown that cysteine or glutathione inhibits the oxidation of linoleate, and of Bint oil and sunflower oil (Ahmad et al., 1983). Moreover, we previously reported that *N*-acetyl-cysteine and glutathione inhibited corn oil oxidation during storage at 40 °C for up to 17 days, as indicated by peroxide values (Papadopoulou & Roussis, 2000). Present results indicate that both these thiols, each at max 40 mg/L, are less effective than BHA at 200 mg/L at 50 °C and 120 °C. However, they inhibited corn oil oxidation at these temperatures to a great extent, especially *N*-acetyl-cysteine. They also indicate that *N*-acetyl-cysteine at 20 or 40 mg/L is more effective than BHA at 200 mg/L in inhibiting corn oil oxidation at 180 °C. This is of high interest, since corn oil is often used in frying.

N-Acetyl-cysteine and glutathione are hydrophilic compounds. It has been reported that hydrophilic antioxidants are more effective than lipophilic ones in bulk oil, and this may be explained by their affinities toward the air–oil interface in bulk oil (Frankel, Huang, Kanner, & German, 1994). This concept may explain the good antioxidant activity of two thiols in corn oil.

N-Acetyl-cysteine and glutathione are protein-based water-soluble materials and therefore, these two compounds may be safe and acceptable additive toward food systems. Glutathione is present in many foods. *N*-Acetyl-cysteine has been proposed for use in foods for particular nutritional uses and in foods for special medical purposes (Anton et al., 2003). However, their safety should be clarified by appropriate studies before their possible general use in foods.

4. Conclusions

Present results indicate that *N*-acetyl-cysteine and glutathione may be taken into account as antioxidants in corn oil during storage, cooking or frying.

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References

Ahmad, M. M., Al-Hakim, S., & Shehata, A. A. Y. (1983). The antioxidant activity of amino acids in 2 vegetable-oils. *Journal of the American Oil Chemists Society, 60*, 837–840.

Anton, R., Barlow, S., Boskou, D., Castle, L., Crebelli, R., Dekant, W., et al. (2003). *N*-Acetyl-L-cysteine for use in foods for particular nutritional uses and in foods for special medicinal purposes. *The European Food Safety Authority Journal, 21*, 1–8.

Frankel, E. N. (1998). *Lipid oxidation*. Dundee: The Oily Press.

Frankel, E. N., Huang, S.-W., Kanner, J., & German, J. B. (1994). Interfacial phenomena in the evaluation of antioxidants: Bulk oils vs emulsions. *Journal of Agricultural and Food Chemistry, 42*, 1054–1059.

Friedman, M. (1994). Improvement in the safety of foods by SH-containing amino acids and peptides. A review. *Journal of Agricultural and Food Chemistry, 42*, 3–20.

Friedman, M. (1997). Chemistry, biochemistry, and dietary role of potato polyphenols. A review. *Journal of Agricultural and Food Chemistry, 45*, 1523–1540.

International Union of Pure and Applied Chemistry (IUPAC) (1987). In C. Paquot & A. Hautfenne (Eds.), *Standard methods for the analysis of oils, fats and derivatives* (7th ed.). Oxford, England: Blackwell Scientific Publications.

Jadhav, S. J., Nimbalkar, S. S., Kulkarni, A. D., & Madhavi, D. L. (1996). Lipid oxidation in biological and food systems. In D. L. Madhavi, S. S.

Deshpande, & D. K. Salunkhe (Eds.), *Food antioxidants*. New York: Marcel Dekker.

Jelen, H. H., Obuchowska, M., Zawirska-Wojtasiak, R., & Wasowicz, E. (2000). Headspace solid-phase microextraction use for the characterization of volatile compounds in vegetable oils of different sensory quality. *Journal of Agricultural and Food Chemistry, 48*, 2360–2367.

Madhavi, D. L., & Salunkre, D. K. (1996). Toxicological aspects of food antioxidants. In D. L. Madhavi, S. S. Deshpande, & D. K. Salunkhe (Eds.), *Food antioxidants*. New York: Marcel Dekker.

Molnar-Perl, I., & Friedman, M. (1990). Inhibition of browning by sulfur amino acids. Apples and potatoes. *Journal of Agricultural and Food Chemistry, 38*, 1652–1656.

Naz, S., Sheikh, H., Siddiqi, R., & Sayeed, S. A. (2004). Oxidative stability of olive, corn and soybean oil under different conditions. *Food Chemistry, 88*, 253–259.

Papadopoulou, D., & Roussis, I. G. (2000). Inhibition of corn oil oxidation by thiols. *Italian Journal of Food Science, 2*, 239–242.

Schaich, K. M., & Karel, M. (1976). Free-radical reactions of peroxidizing lipids with amino-acids and proteins: ESR study. *Lipids, 11*, 392–400.

Snyder, J. M. (1995). Volatile analysis of oxidized oils by a direct supercritical fluid extraction method. *Journal of Food Lipids, 2*, 25–33.

Yin, M.-C., & Cheng, W.-S. (2003). Antioxidant and antimicrobial effects of four garlic-derived organosulfur compounds in ground beef. *Meat Science, 63*, 23–28.