Antioxidant Properties of Myricetin and Quercetin in Oil and Emulsions

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ABSTRACT: The effect of quercetin and myricetin on the stability of sunflower oil and oil-in-water emulsions was studied by storage experiments monitored by measurement of peroxide values, conjugated dienes, and headspace volatile analysis. Myricetin showed strong antioxidant activity in oils stored at 60 or 30°C and in oil-in-water emulsions stored at 30°C, whether tocopherols or citric acid were present or not; however, quercetin showed similar antioxidant activity in stripped sunflower oil but no activity in oils that contained tocopherols and citric acid. This showed that myricetin is effective owing to strong radical scavenging and metal-chelating properties, whereas quercetin has weaker radical scavenging activity, although it is also active by metal-chelation. The effects of copper and iron salts on the antioxidant activity of myricetin and quercetin were studied in sunflower oil and oil-in-water emulsions. Quercetin and myricetin enhanced the prooxidant effect of cupric chloride in oil-in-water emulsions (pH 7.4), but this effect was not observed with cupric stearate. The addition of myricetin to emulsions that contained ferric chloride at pH 5.4 also produced a strong prooxidant effect, and small prooxidant effects of flavonols were also detected in the presence of cupric chloride under these conditions. However, myricetin and quercetin reduced the prooxidant effect of ferric palmitate in oils. Myricetin also showed a strong antioxidant effect in oil that contained cupric stearate, although quercetin had no significant effect on the oxidative stability of this system. It therefore appears that flavonols may exert a prooxidant effect in the presence of metal salts, but the nature of the metal salt is important in determining whether a prooxidant effect occurs.
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KEY WORDS: Antioxidant, emulsion, myricetin, oil, quercetin.

Flavonoids occur in a variety of fruits, vegetables, leaves, and flowers and consequently are common dietary constituents (1). Average intake of flavonols and flavones in The Netherlands is about 23 mg/d, mainly from black tea, onions, and apples (2). Flavonoids have been widely investigated in recent years because of their potential antioxidant activity, which improves the stability of lipid-containing foods and their possible beneficial effects on human health. Effects of flavonoids on the incidence of cardiovascular disease (CVD), cancer, allergic and inflammatory responses, and antiviral and bacteriostatic activity have been suggested (3–5), although effects on CVD are not fully proven, and most epidemiological evidence indicates no effect on cancer (6). Quercetin is a major dietary flavonol, and occurs mainly in tea, apples, and onions among common foods (7). Quercetin inhibits oxidation and cytotoxicity of low-density lipoproteins *in vitro* (8,9). Above-average consumption of quercetin, myricetin, kaempferol, apigenin, and luteolin by elderly men has been associated with reduced mortality from coronary heart disease (7) and reduced incidence of strokes (10). Quercetin was the major flavonoid in both studies, and analysis of the association between quercetin intake and disease yielded essentially the same results as total flavonols and flavones (11).

Flavonoids may act as antioxidants by scavenging radicals that include superoxide anions (12,13), lipid peroxide radicals (14,15), and hydroxyl radicals (14,16,17). Other mechanisms of action of selected flavonoids include singlet oxygen quenching (18,19), metal chelation (20,21), and ultraviolet filtration (1). The antioxidant activity of flavonoids may vary with the test medium. Rutin and apigenin have high antioxidant activity in an aqueous medium, but their activity is low in a lipid medium (22). Quercetin and myricetin may have prooxidant activity under alkaline conditions by generation of superoxide anions, which react further to produce hydroxyl radicals in the presence of hydrogen peroxide and iron (23,24).

The antioxidant activity of quercetin and myricetin in the presence and absence of iron and copper has been investigated in this study. Although myricetin occurs in less common foods than quercetin, namely, black currants, black grapes, cranberries, bilberries and broad beans (25), and consequently is consumed at lower levels than quercetin, previous research indicated that it can have greater antioxidant activity than quercetin (26,27) under some conditions, although it may be less active than quercetin in inhibiting oxidation of low-density lipoproteins (28,29).

Quercetin and myricetin can chelate copper, but an equilibrium involving weak complexation occurs because >100 times molar excess of quercetin is required to inhibit the prooxidant effect of copper (20). Chelation of metal ions is pH-dependent, with reduced chelation at low pH (30). Under

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aerobic conditions, flavonoid–metal complexes are not stable; the flavonol becomes oxidized (31), most rapidly at high pH (32).

The aim of this study was to investigate the effects of oxidation medium, namely, oil or oil-in-water emulsion, on the antioxidant activity of quercetin and myricetin in the presence and absence of copper and iron salts. Previous work has been limited to homogeneous media, whereas foods are commonly multiphase systems.

MATERIALS AND METHODS

Chemicals. Quercetin, butylated hydroxytoluene (BHT), ferric chloride, cupric chloride, and Tween 20 were purchased from Sigma Chemical Company (Poole, United Kingdom), and myricetin was supplied by Extrasynthese (Lyons-Nord, France). Refined sunflower oil of a brand known to lack added antioxidants was purchased from a local retail outlet.

Removal of tocopherols from sunflower oil. Tocopherols were removed from sunflower oil by the procedure of Yoshida (33). Complete removal of tocopherols was confirmed by high-performance liquid chromatography.

Addition of antioxidants. Antioxidants were prepared as stock methanol solutions for quantitative addition to oil for preparation of emulsions or storage. The samples were warmed at 50°C, with a current of nitrogen to remove the solvent. Quercetin was added at concentrations in the range of 10^{-4} to 5×10^{-4} M, which is close to the solubility limit in oil at room temperature. Myricetin was added at concentrations in the range of 10^{-4} to 10^{-3} M. BHT was added at a concentration of 0.02% (9×10^{-4} M), which is a commonly used concentration and the upper limit allowed in food in many countries.

Preparation of emulsions. Sunflower oil-in-water emulsions (25 g) were prepared by dissolving Tween 20 (1%) in a phosphate buffer (0.1 M, pH 7.4) or an acetate buffer (0.1 M, pH 5.4) and adding the oil, containing antioxidants, dropwise to the sample cooled in an ice-bath while sonicating with a Vibracell High Intensity Ultrasonic Processor (Sonics & Materials Inc., Danbury, CT). Sonication was continued for 4 min after the oil had been added.

Storage and sampling of emulsions or oils. All samples were stored in duplicate in glass beakers in the dark. Oil experiments were performed with 20-g samples, stored in 50-mL beakers at either 30 or 60°C; and emulsion experiments involved storage of 50-g samples in 100-mL beakers at 30°C. The beakers were covered with plastic film or aluminum foil, and aliquots (approximately 2 g for oil and 2–6 g for emulsion experiments, depending on analyses required) were removed periodically from each sample for analysis. Aliquots from emulsions were successively frozen at −70°C, thawed, and centrifuged to separate oil for analysis.

Synthesis of metal salts. Ferric palmitate and cupric stearate were prepared as described previously (34,35). The salts were added to oil as solutions in 1-butanol (0.5 mL), and the solvent was removed under vacuum.

Analytical methods. Peroxide value (PV) was determined by AOCS Official Method Cd 8-53. Conjugated diene content was determined by AOCS Official Method Ti 1a-64 (36).

Static headspace analysis of pentane and hexanal was performed by a method based on that of Warner *et al*. (37), with the modification that a temperature of 150°C was used to heat the sample. A BPX-5 capillary column (25 m × 0.32 mm i.d.), programmed at 0°C (10 min) followed by a ramp to 165°C at 5°C min^{-1}, was used for the analysis of volatiles.

High-performance liquid chromatography on a silica column (250 × 4.6 mm i.d.), with hexane/2-propanol (99.5:0.5) as eluant at a flow rate of 1 mL min^{-1} with fluorescence detection at 290 nm excitation and 330 nm emission was used to analyze the tocopherol content of oil samples. The tocopherol content of the refined sunflower oil was 657 μg/g α-tocopherol, 27 μg/g β-tocopherol, and 13 μg/g γ-tocopherol. Tocopherols were not detected in stripped sunflower oil (detection limit about 10 μg/g).

Statistical analysis. Data from the PV measurements were plotted against time. The times to certain PV were determined for each stored sample, and subjected to one-way analysis of variance to determine the pooled standard deviation. The mean times for the duplicate stored samples were compared by a two-sample *t*-test by using the pooled standard deviation to determine significant differences.

RESULTS AND DISCUSSION

Quercetin (10^{-4} M) and myricetin (10^{-4} M) demonstrated significant ($P < 0.05$) antioxidant effects in sunflower oil stripped of tocopherols and stored at 60°C. The PV (Fig. 1) and the headspace pentane levels (Fig. 2) both showed significant antioxidant activity, and this was confirmed by monitoring the conjugated diene levels (not shown). In the presence of the natural level of tocopherols (697 μg/g, including 657μg/g α-tocopherol; 1.5 mM), quercetin (10^{-4} M) and myricetin (10^{-4} M) also showed a significant antioxidant effect at 60°C, as shown by both the PV (Fig. 3) and the headspace pentane levels (Fig. 4). However, the effect in the presence of tocopherols was less than in the absence of tocopherols, especially for quercetin, as shown in Table 1. Because α-tocopherol is a better radical scavenger than quercetin (38), it appeared likely that quercetin was acting mainly as a metal-chelating agent in the presence of α-tocopherol. This was confirmed by storing a sunflower oil sample, containing natural tocopherols (697 μg/g), with added citric acid (100 ppm) at 60°C, when quercetin did not show any antioxidant effect. This was shown by both measurements of PV (Fig. 5) and by headspace pentane levels (Fig. 6). Even increasing the quercetin concentration up to 5×10^{-4} M did not produce any significant antioxidant activity in this system (data not shown). Myricetin (10^{-4} M), however, was significantly effective ($P < 0.05$) at stabilizing sunflower oil, even when tocopherols and citric acid were present (Figs. 5,6), and this showed the stronger radical-scavenging activity of myricetin. Myricetin was similar in activity to BHT (0.02%)

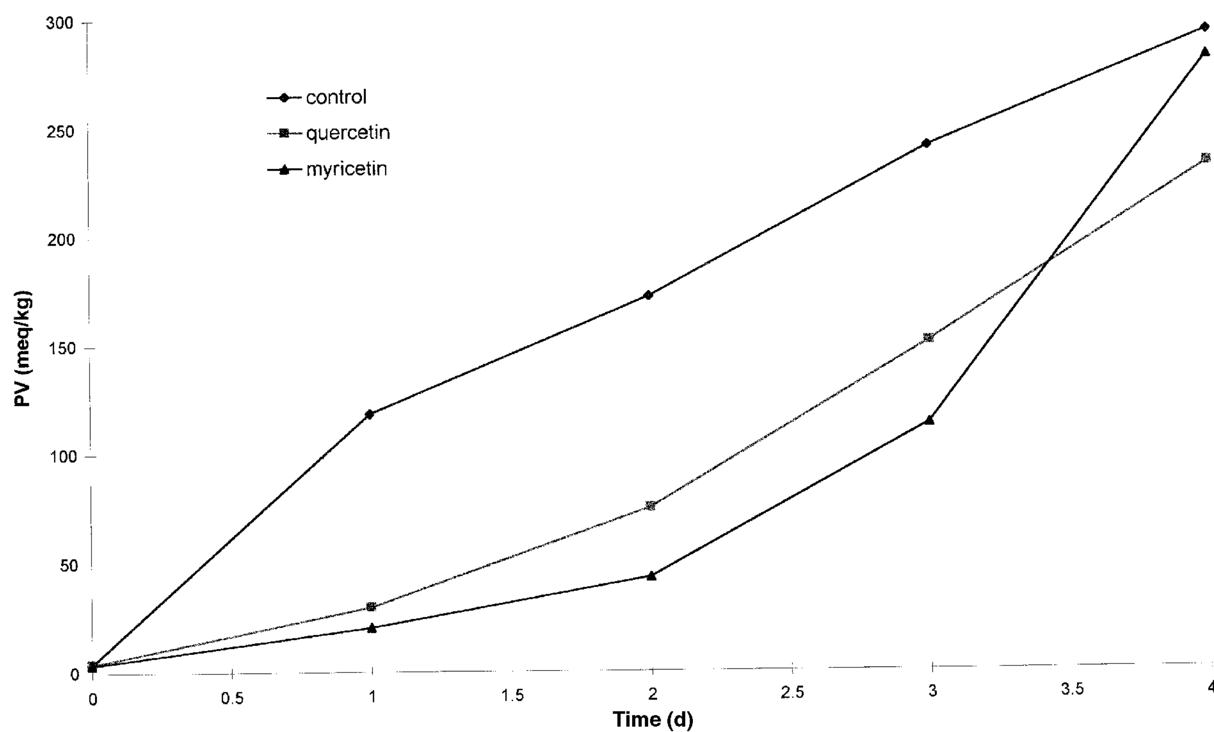

FIG. 1. Effect of quercetin (10^{-4} M)[a] and myricetin (10^{-4} M)[a] on the stability of stripped sunflower oil[b] at 60°C, assessed by peroxide value (PV) changes. (Different superscripts indicate samples with statistically different stability, $P < 0.05$.)

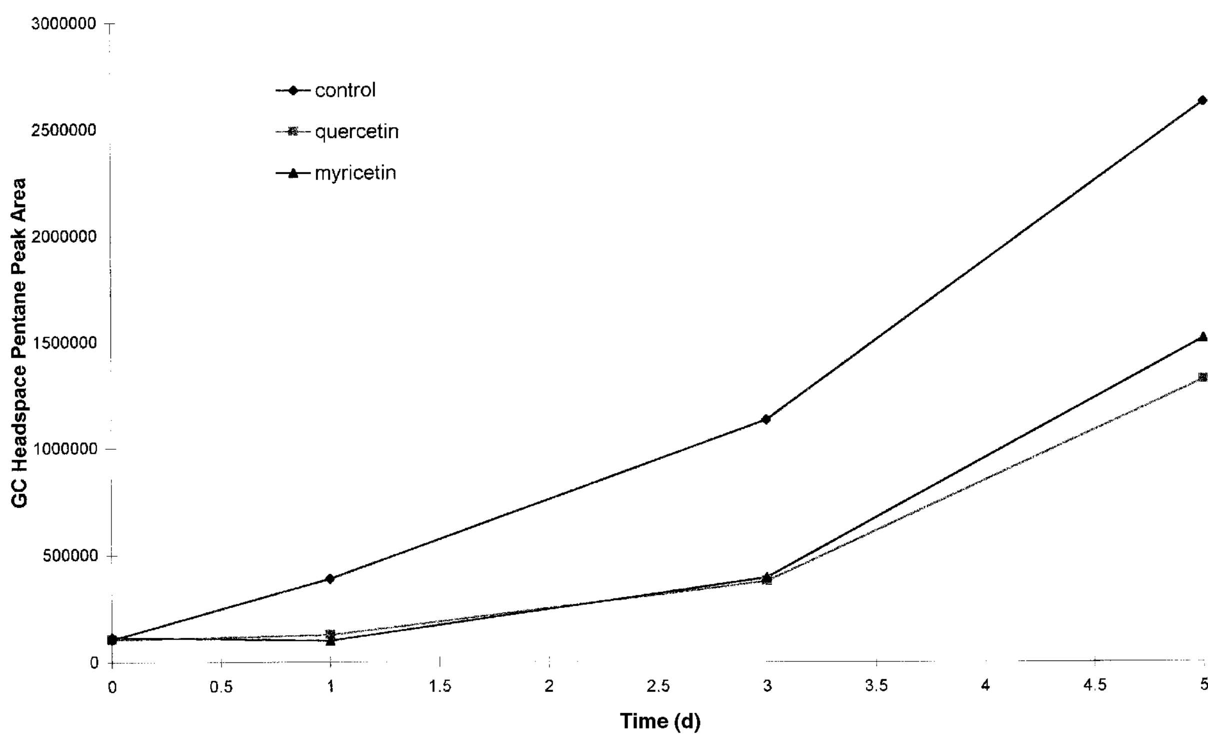

FIG. 2. Effect of quercetin (10^{-4} M)[a] and myricetin (10^{-4} M)[a] on the stability of stripped sunflower oil[b] at 60°C, assessed by gas chromatographic (GC) headspace pentane levels. See Figure 1 for statistics.

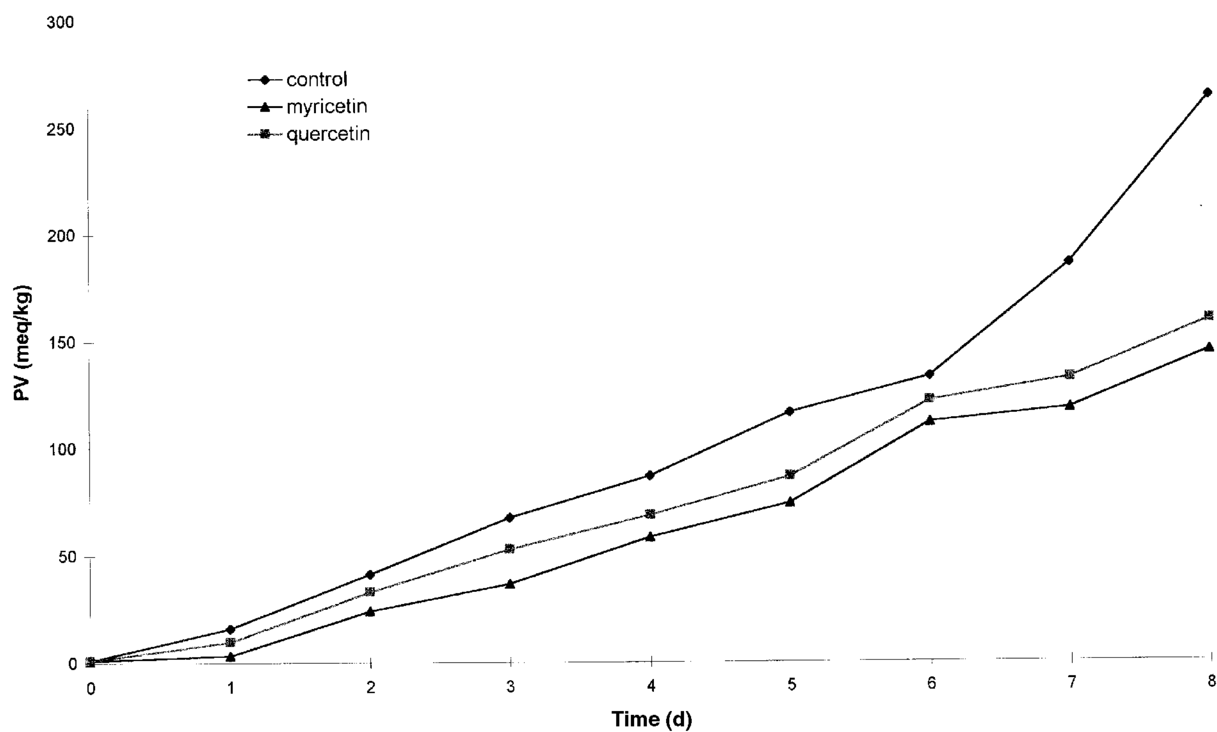

FIG. 3. Effect of quercetin (10^{-4} M)[a] and myricetin (10^{-4} M)[a] on the stability of sunflower oil[b] at 60°C, assessed by PV changes. For statistics and abbreviation see Figure 1.

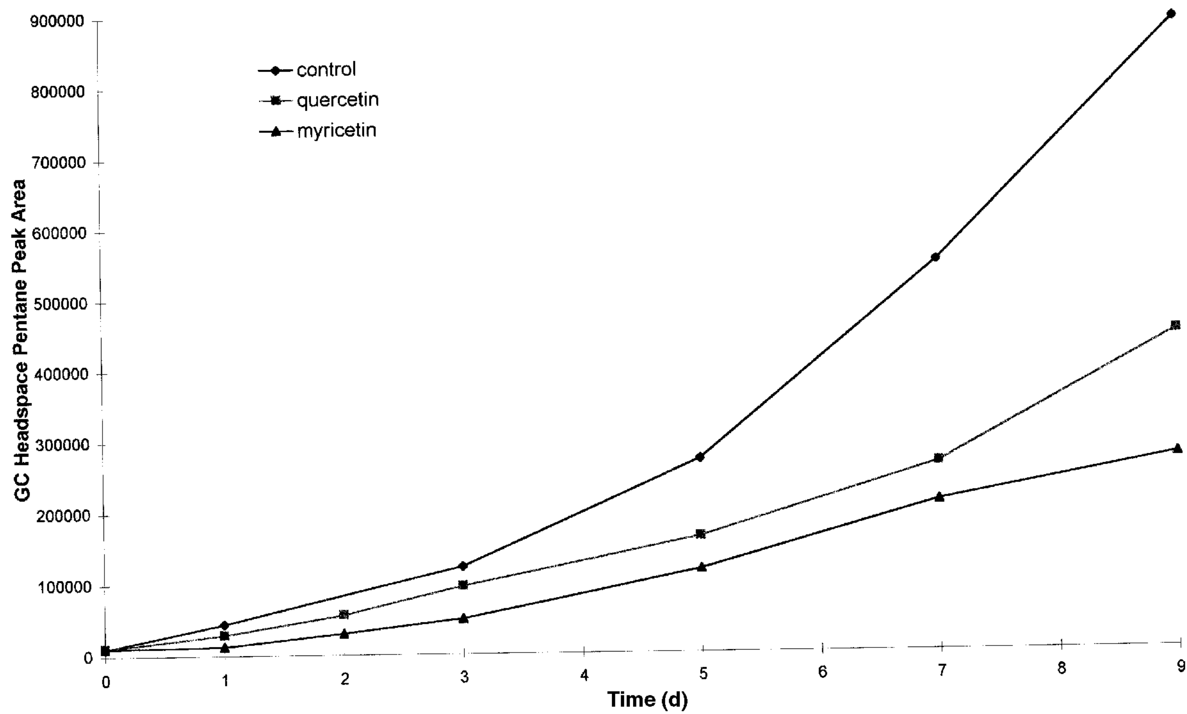

FIG. 4. Effect of quercetin (10^{-4} M)[a] and myricetin (10^{-4} M)[a] on the stability of sunflower oil[b] at 60°C, assessed by GC headspace pentane levels. For statistics and abbreviation see Figures 1 and 2.

TABLE 1
Time for Sunflower Oil Samples to Reach a Peroxide Value of 40 meq/kg at 60°C

Additive	Time (days) for stripped oil samples	Time (days) for oil samples with tocopherols (697 μg/g)
Control	0.3 (± 0.0)[a]	2.0 (± 0.1)
Quercetin (10–4 M)	1.2 (± 0.1)	2.4 (± 0.2)
Myricetin (10–4 M)	1.3 (± 0.6)	3.2 (± 0.1)

[a]Numbers in parentheses indicate range of duplicate stored samples.

in this system during storage at 60°C at a concentration of 10^{-4} M but significantly more active at 10^{-3} M ($P < 0.01$).

The strong radical-scavenging activity of myricetin was confirmed by storing sunflower oil that contained natural tocopherols and added citric acid (100 ppm) at 30°C while monitoring oxidation by PV (Fig. 7) and headspace pentane levels (Fig. 8). Myricetin (10^{-4} M) was similar in activity to BHT (0.02%), but it was significantly more active at a concentration of 3×10^{-4} M ($P < 0.05$). Quercetin in this system, again, had no significant ($P > 0.05$) antioxidant action at 10^{-4} and at 3×10^{-4} M concentrations.

Stable oil-in-water emulsions (pH 7.4) with myricetin or quercetin at 10^{-4} M in the oil phase were prepared and stored at 30°C. Neither myricetin nor quercetin showed antioxidant activity (data not shown), but it appeared likely that the iron-chelating effect of the phosphate buffer (39) would prevent any metal-chelating activity of the flavonols. Although the effects of quercetin and myricetin were studied in emulsions without a buffer present (data not shown), the pH of emulsions that contained different additives changed to different extents during storage, and oxidation appeared to depend more on the pH of the system than on the additives present. For example, the initial pH of 5.5 fell to 4.5 after 29 d for a sample that contained quercetin and to 2.2 for a sample that contained quercetin plus cupric chloride. Because acetate is known to be a weaker chelating agent than phosphate (40), the experiment was repeated with myricetin in an acetate buffer at pH 5.4, but with the concentration of the flavonol increased to 10^{-4} M in the whole emulsion. In this experiment, myricetin showed significant antioxidant activity as shown by both PV (Fig. 9) and conjugated diene measurements (Fig. 10). Gas chromatography (GC) headspace analysis of volatiles after 30 days' storage confirmed the antioxidant effect of myricetin; the sample that contained myricetin had a pentane peak area of 3.2×10^4, compared with 10.3×10^4 for the control.

Addition of ferric chloride (5×10^{-5} M) to emulsions that contained myricetin (10^{-4} M) produced a strong prooxidant effect at pH 5.4 ($P < 0.05$), as shown by both PV (Fig. 9) and conjugated dienes (Fig. 10). In the presence of the same concentration of cupric chloride, myricetin had neither an antioxidant nor a prooxidant effect. Analysis of headspace pentane levels by GC at day 30 confirmed these findings; the control that contained ferric chloride had a pentane peak area of 1.5 $\times 10^5$, compared with 1.6×10^6 for the sample that contained both ferric chloride and myricetin, whereas the control with cupric chloride had a pentane peak area of 7.0×10^5, compared with 6.6×10^5 for the sample that contained both cupric

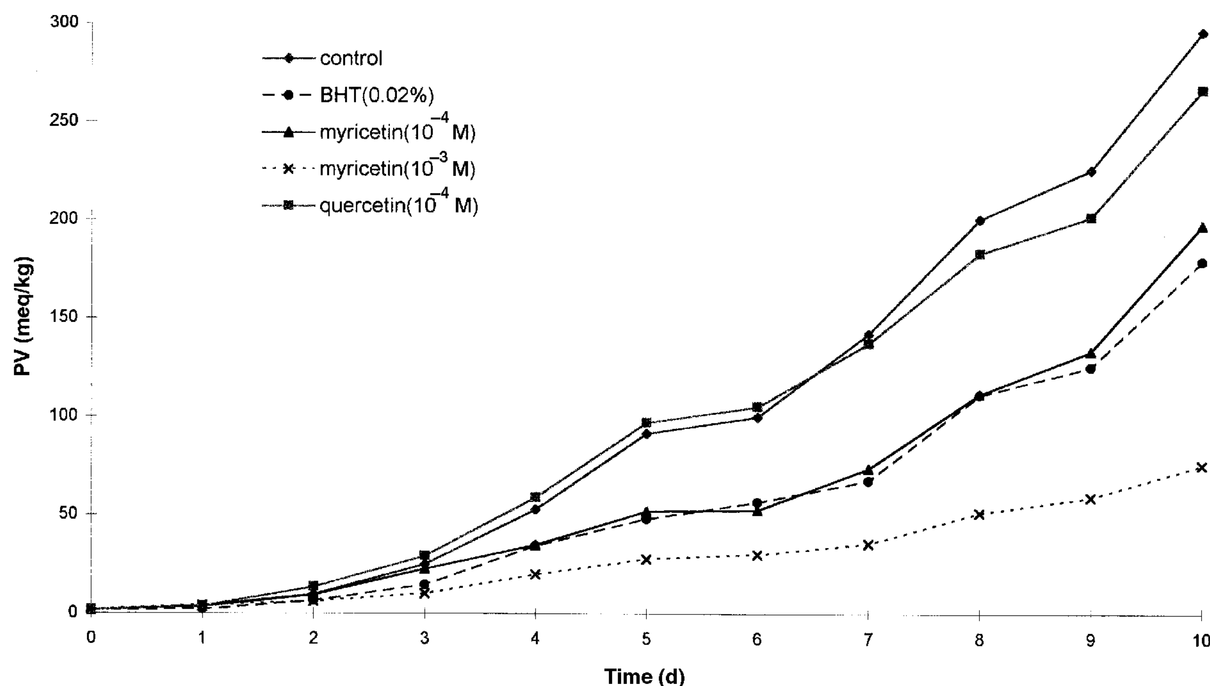

FIG. 5. Effect of myricetin (10^{-3} M)[a], myricetin (10^{-4} M)[b], quercetin (10^{-4} M)[c], and butylated hydroxytoluene (BHT) (0.02%)[b] on the oxidation of sunflower oil[c] that contained citric acid (100 ppm) at 60°C, assessed by PV changes. See Figure 1 for statistics and abbreviations.

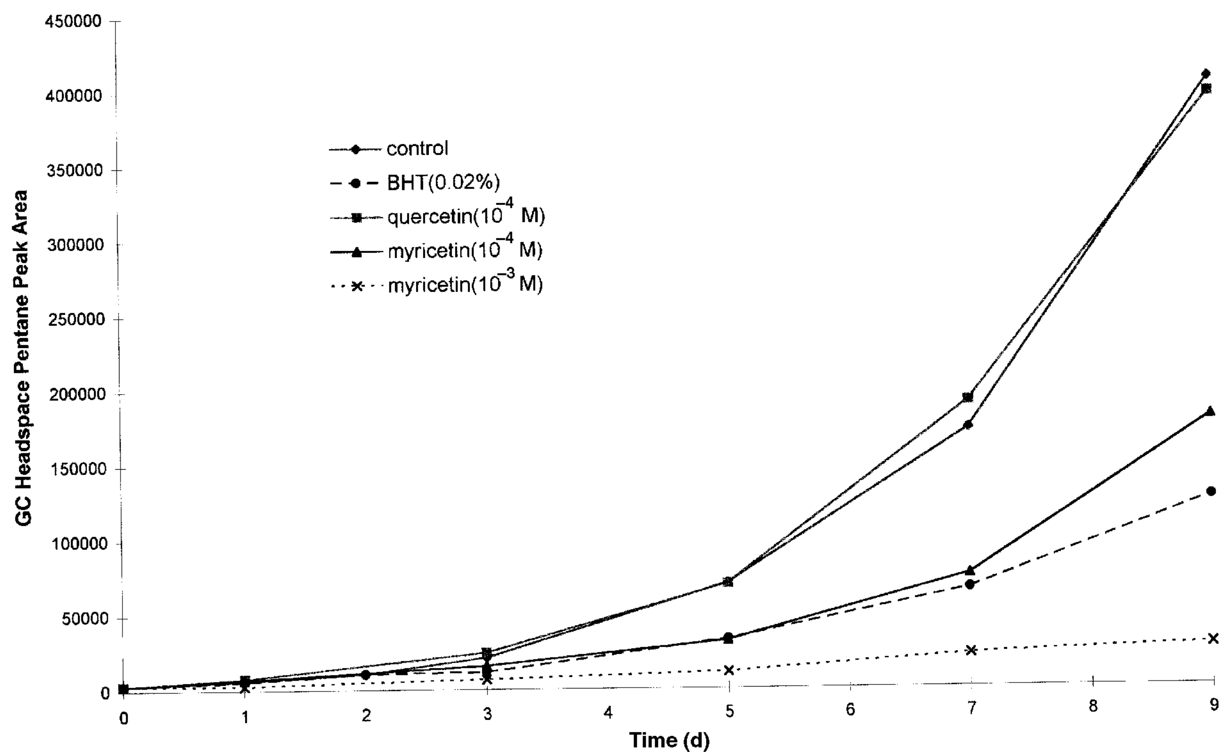

FIG. 6. Effect of myricetin (10^{-3} M)[a], myricetin (10^{-4} M)[b], quercetin (10^{-4} M)[c], and BHT (0.02%)[b] on the oxidation of sunflower oil[c] that contained citric acid (100 ppm) at 60°C, assessed by GC headspace pentane levels. See Figures 1, 2, and 5 for statistics and abbreviations.

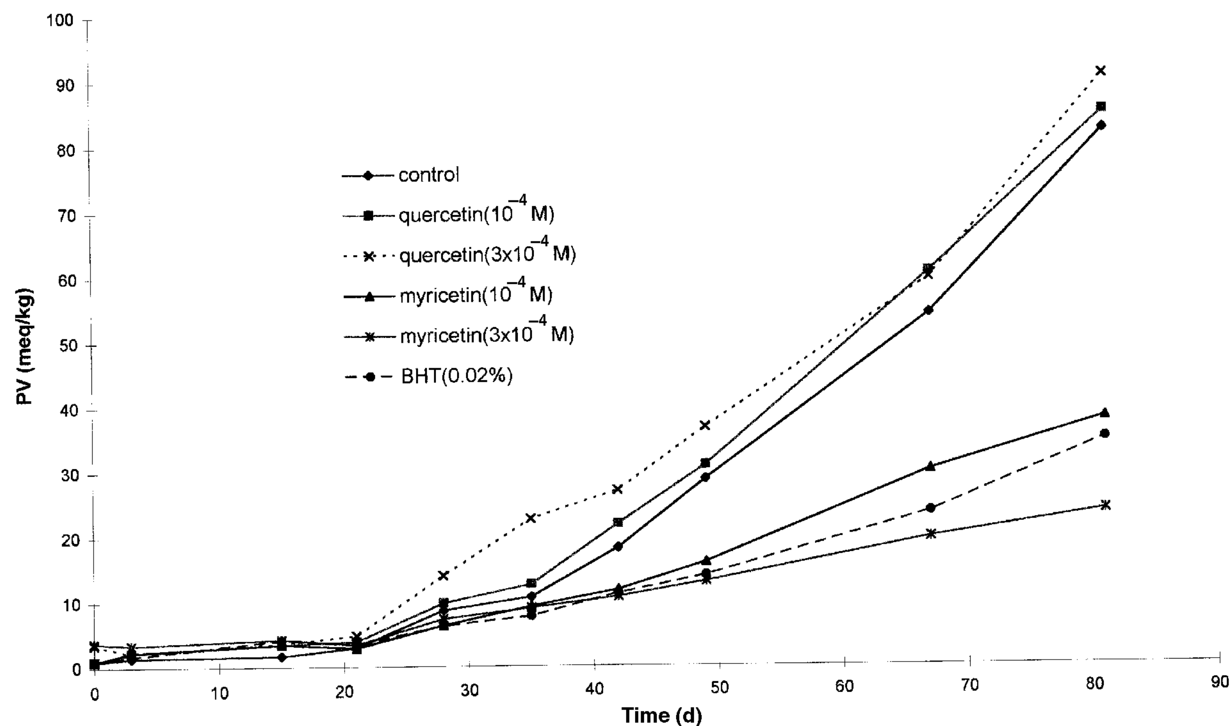

FIG. 7. Effect of myricetin (3×10^{-4} M)[a], myricetin (10^{-4} M)[b], quercetin (10^{-4} M)[c], quercetin (3×10^{-4} M)[c], and BHT (0.02%)[b] on the oxidation of sunflower oil[c] at 30°C, assessed by PV changes. For statistics and abbreviations see Figures 1 and 5.

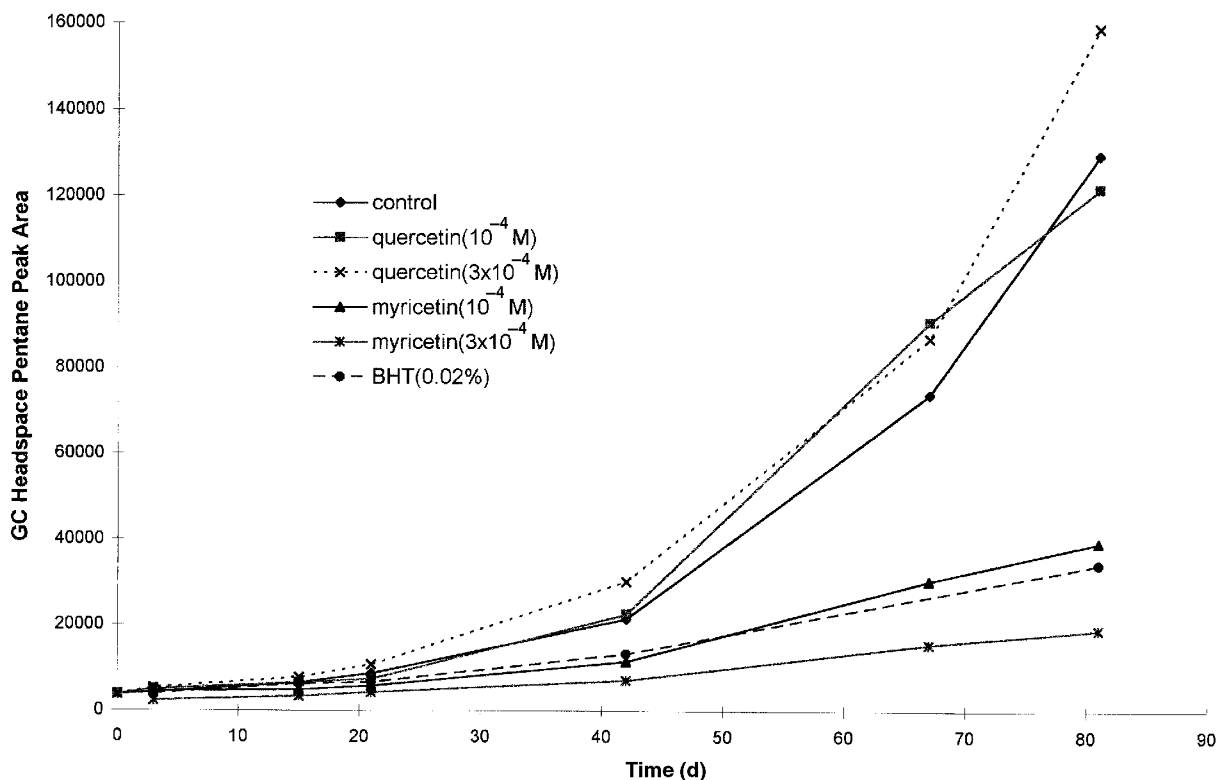

FIG. 8. Effect of myricetin (3×10^{-4} M)[a], myricetin (10^{-4} M)[b], quercetin (10^{-4} M)[c], quercetin (3×10^{-4} M)[c], and BHT (0.02%)[b] on the oxidation of sunflower oil[c] at 30°C, assessed by GC headspace pentane levels. For statistics and abbreviation see Figures 1 and 2.

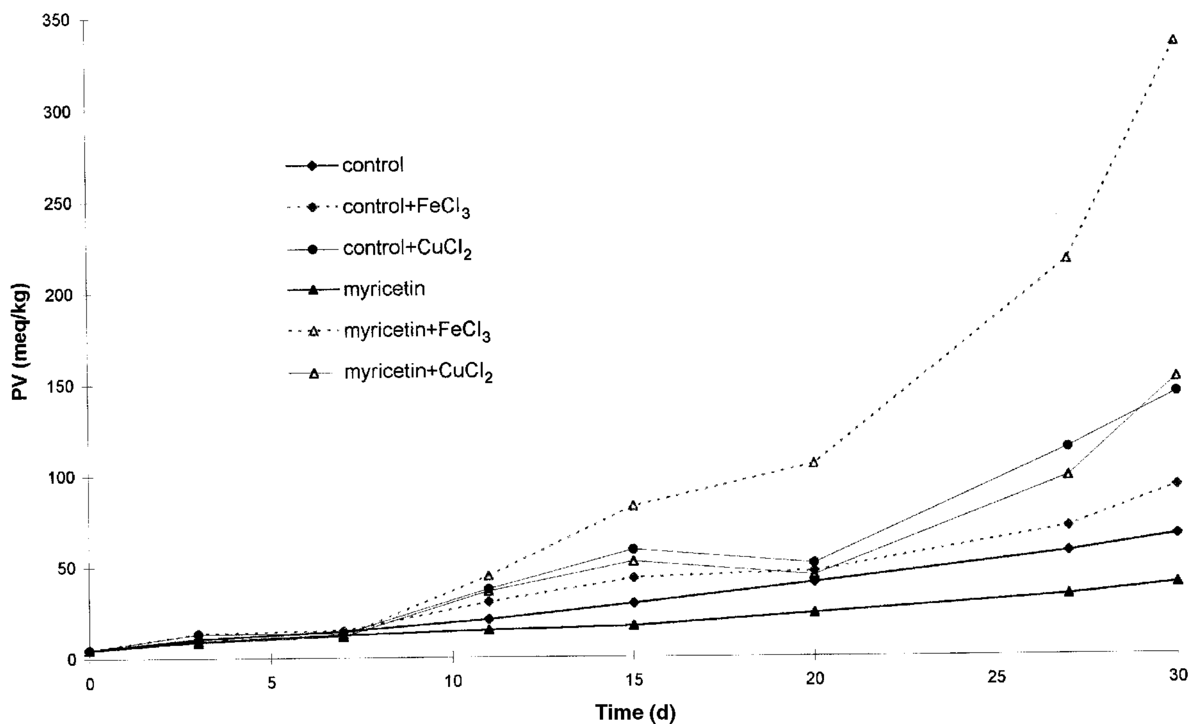

FIG. 9. Stability of sunflower oil-in-water emulsion[a] (pH 5.5) stored at 30°C, compared with samples that contained myricetin (10^{-4} M)[b], myricetin (10^{-4} M) + ferric chloride[e], cupric chloride[d], ferric chloride[c], and myricetin (10^{-4} M) + cupric chloride[d], assessed by PV changes.

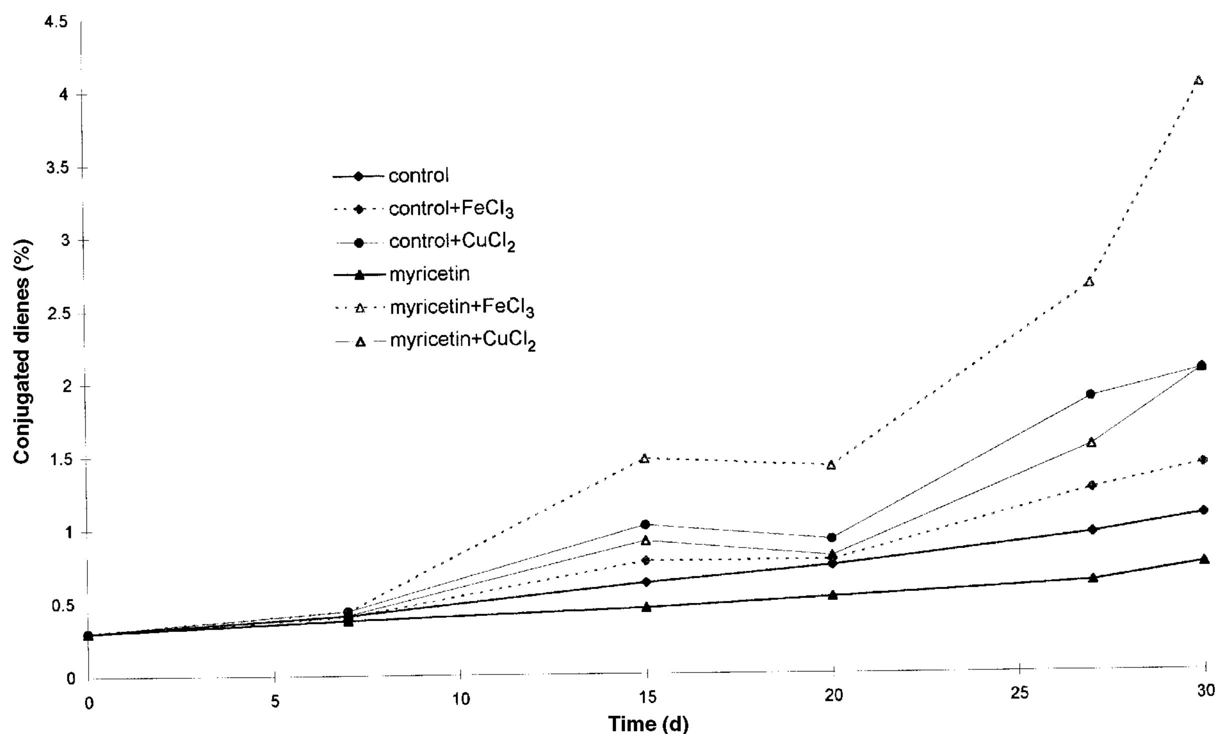

FIG. 10. Stability of sunflower oil-in-water emulsion[a] (pH 5.5) stored at 30°C, compared with samples that contained myricetin (10^{-4} M)[b], myricetin (10^{-4} M) + ferric chloride (5×10^{-5} M)[e], cupric chloride (5×10^{-5} M)[d], ferric chloride (5×10^{-5} M)[c], and myricetin (10^{-4} M) + cupric chloride (5×10^{-5} M)[d], assessed by conjugated diene changes. For statistics see Figure 1.

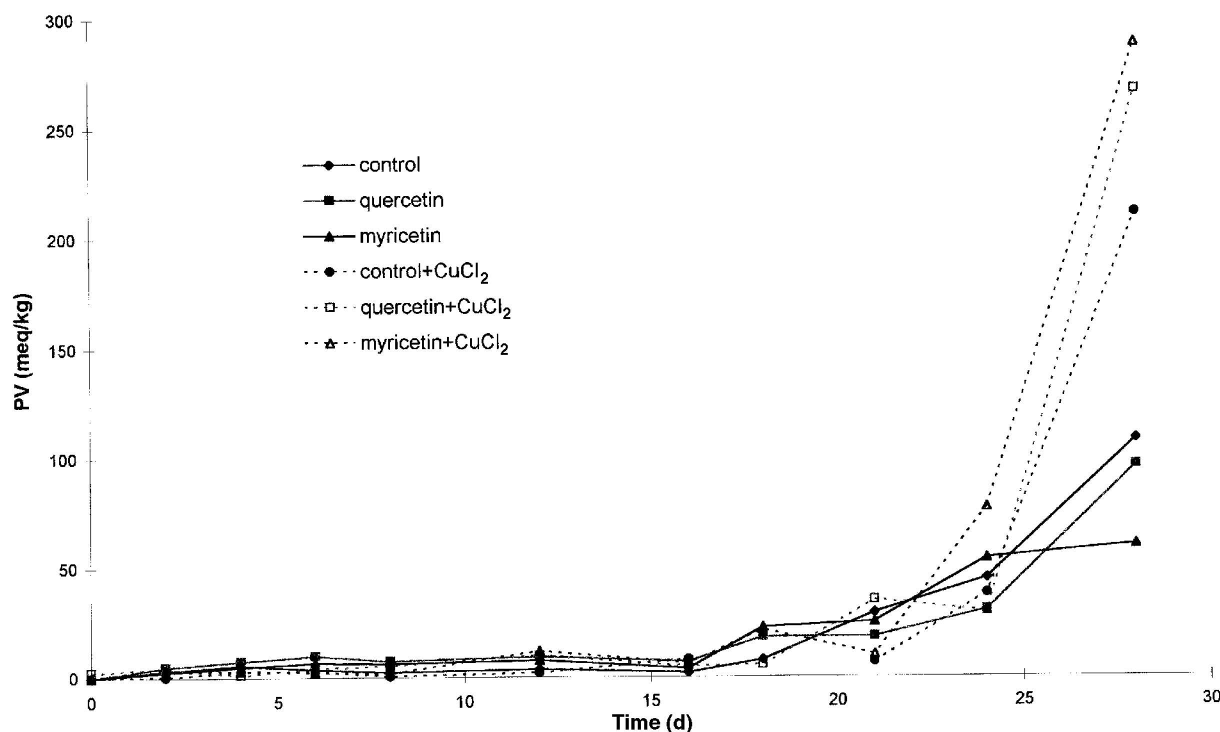

FIG. 11. Stability of sunflower oil-in-water emulsion[a] (pH 7.4), compared with samples that contained cupric chloride[c] (1.5×10^{-5} M), cupric chloride plus quercetin[d], cupric chloride plus myricetin[d], quercetin[a] (3×10^{-5} M), and myricetin[b] (3×10^{-5} M) stored at 30°C, assessed by PV changes. For abbreviation and statistics see Figure 1.

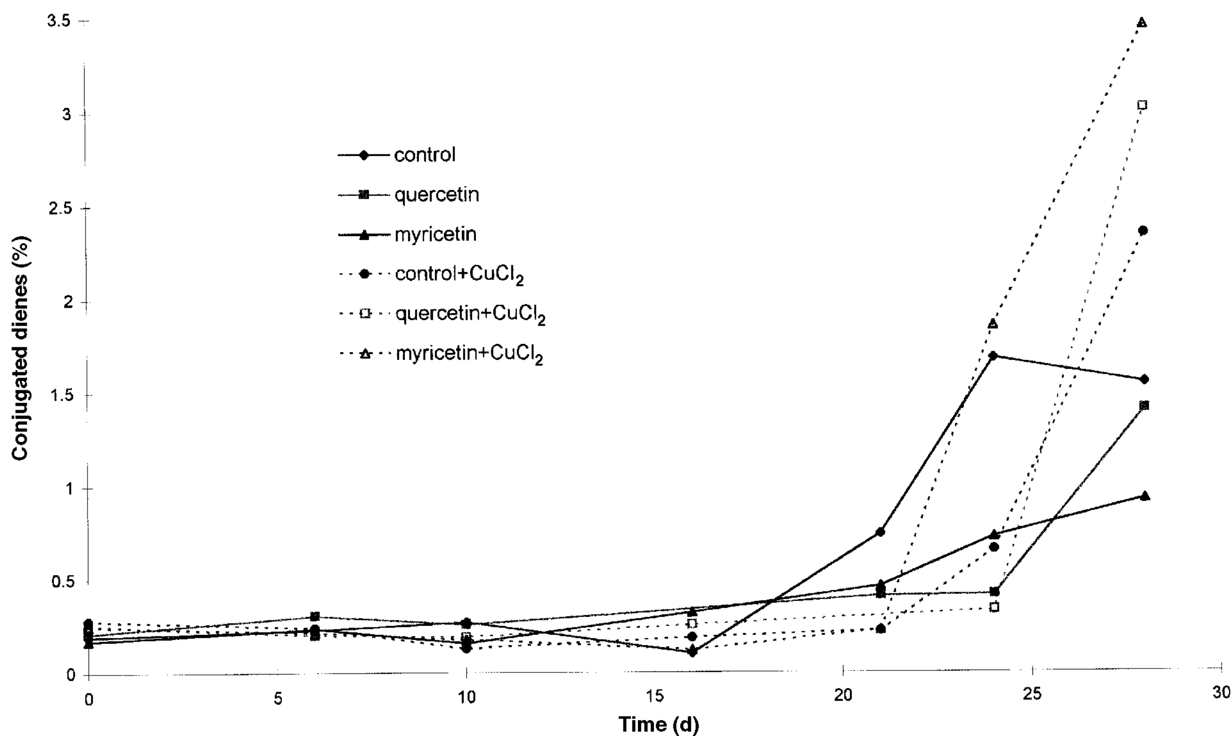

FIG. 12. Stability of sunflower oil-in-water emulsion[a] (pH 7.4), compared with samples that contained cupric chloride[c] (1.5×10^{-5} M), cupric chloride plus quercetin[d], cupric chloride plus myricetin[d], quercetin[a] (3×10^{-5} M), and myricetin[b] (3×10^{-5} M) stored at 30°C, assessed by conjugated diene changes. For statistics see Figure 1.

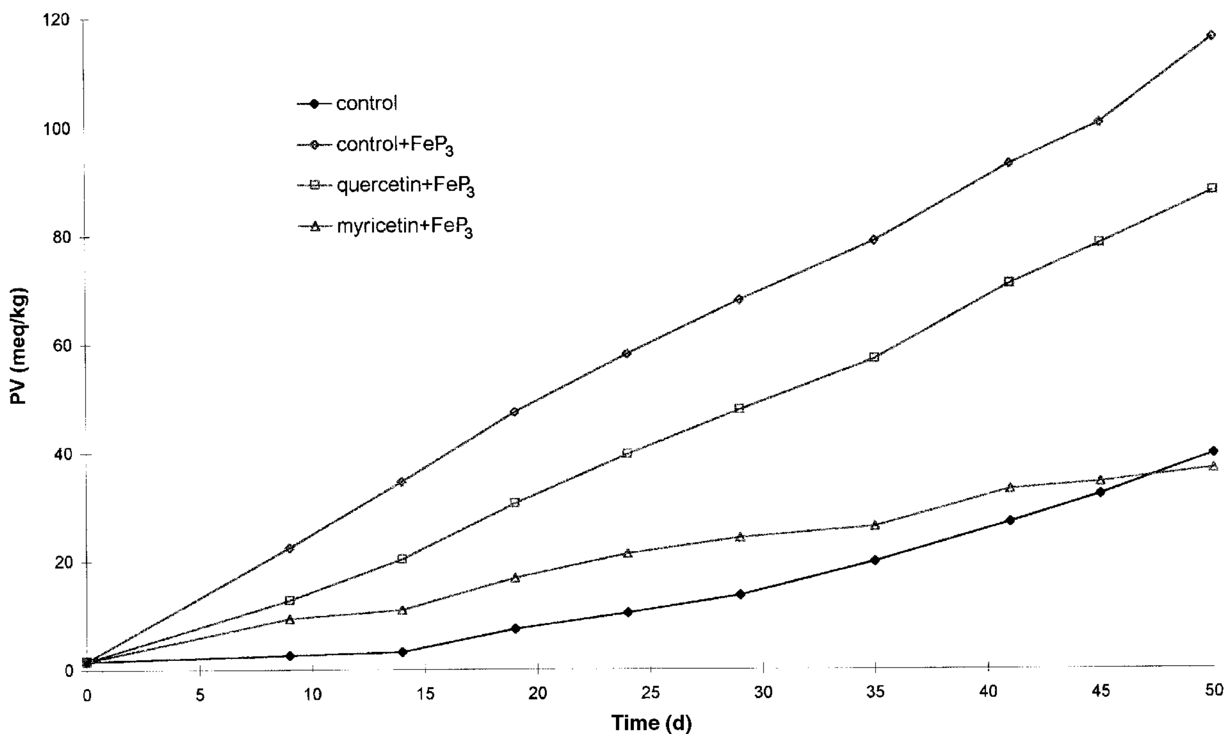

FIG. 13. Stability of sunflower oil[a], compared with samples that contained ferric palmitate[b] (FeP) (2×10^{-5} M), myricetin (10^{-4} M) plus FeP[c], and quercetin (10^{-4} M) plus FeP[d] stored at 30°C, assessed by PV changes. For other abbreviation and statistics see Figure 1.

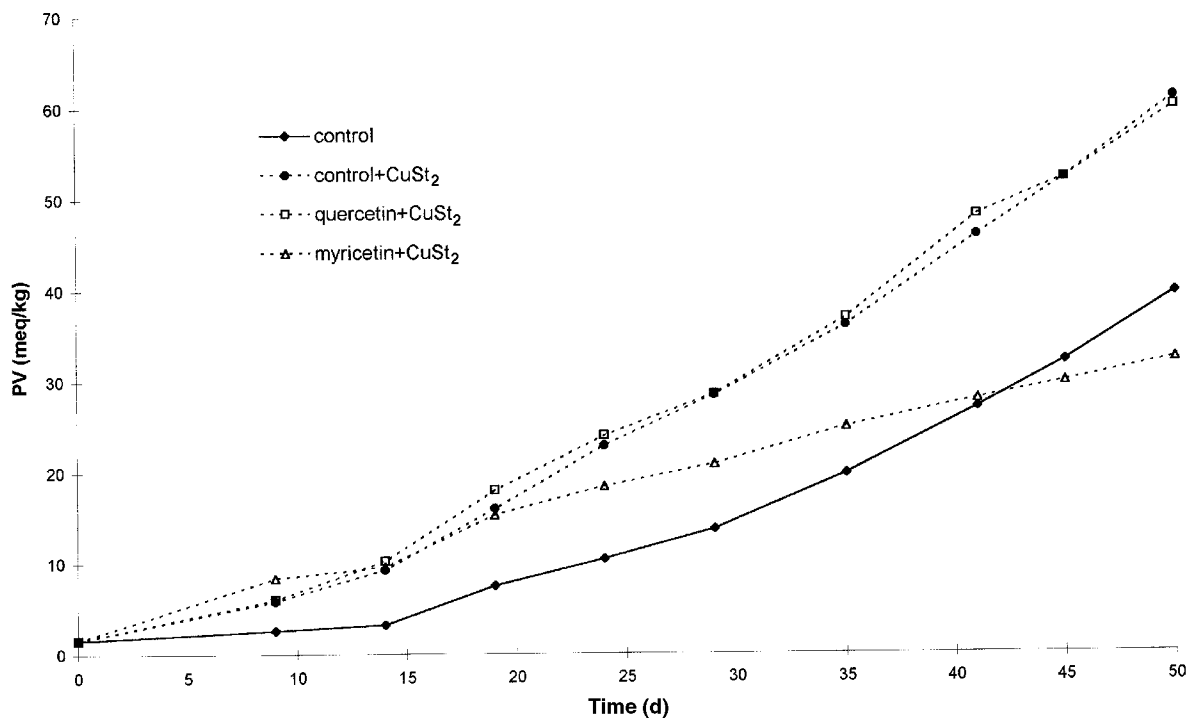

FIG. 14. Stability of sunflower oil[a], compared with samples that contained cupric stearate[b] (CuSt) (2×10^{-5} M), myricetin (10^{-4} M) plus CuSt[c], and quercetin (10^{-4} M) plus CuSt[b] stored at 30°C, assessed by PV changes. For other abbreviation and statistics see Figure 1.

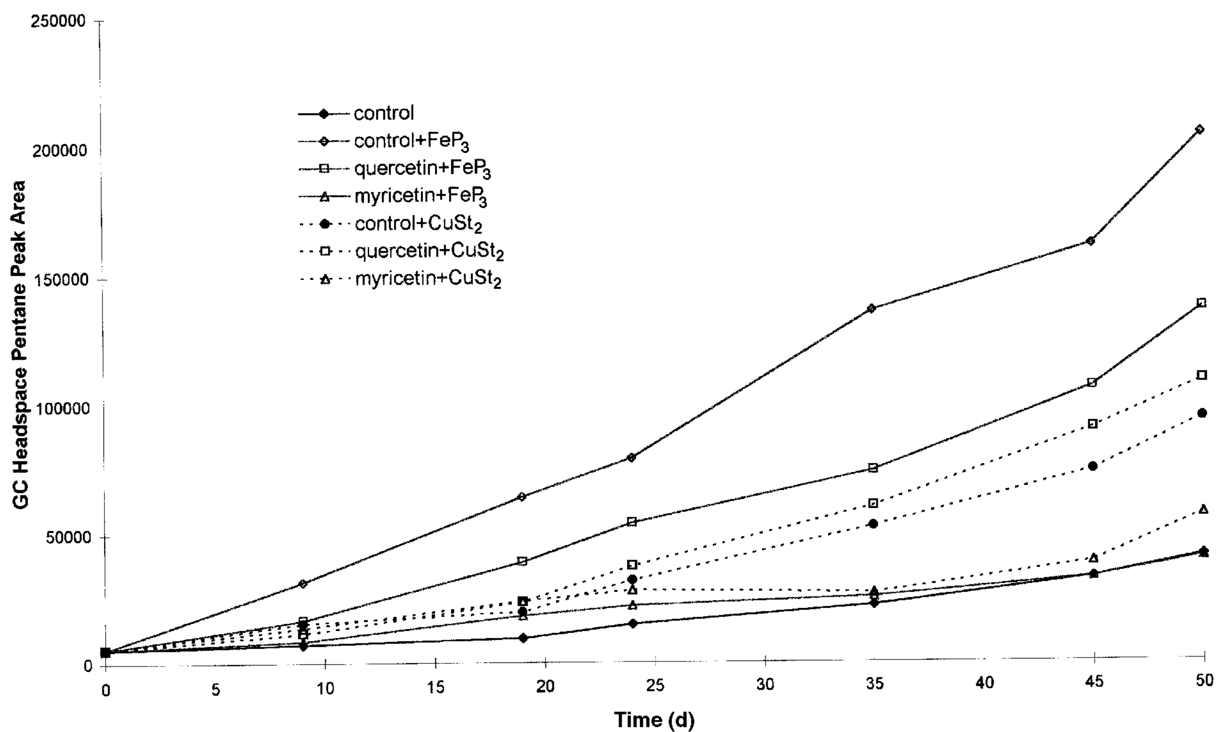

FIG. 15. Effects of myricetin and quercetin (10^{-4} M) on the oxidation of sunflower oil that contained FeP or CuSt (2×10^{-5} M) stored at 30°C, assessed by GC headspace pentane levels. For abbreviations see Figures 2, 13, and 14; for statistics, see Figure 1.

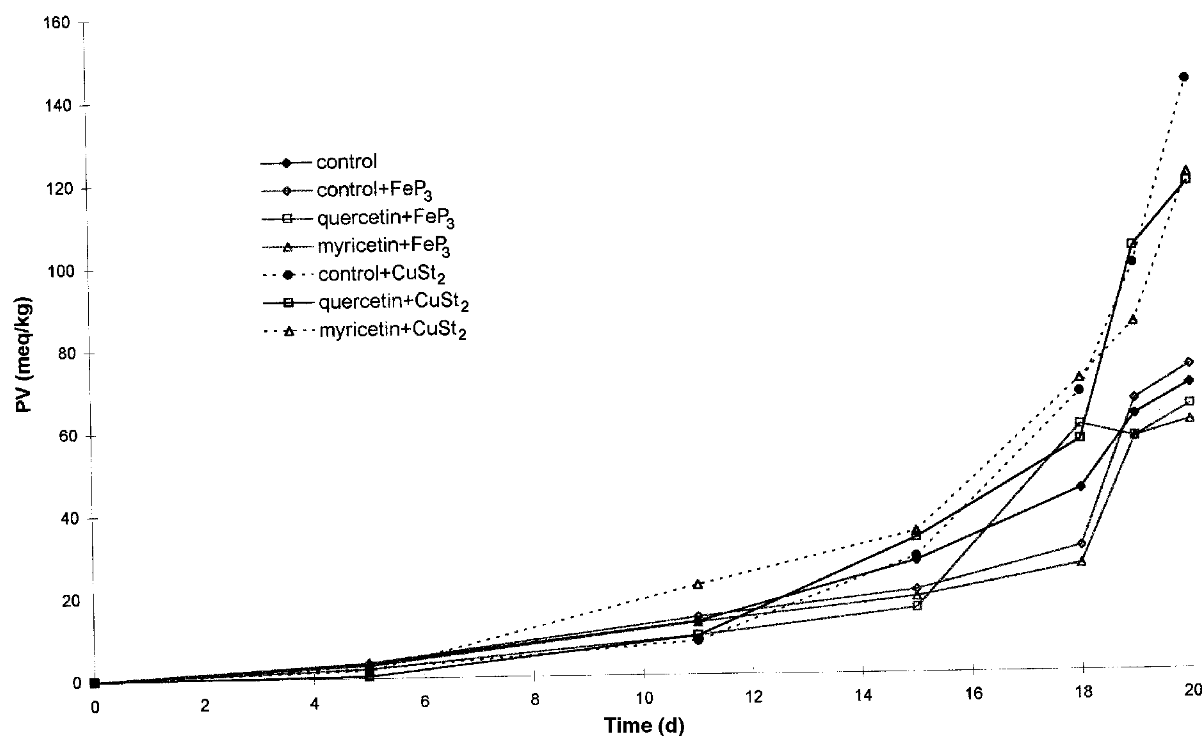

FIG. 16. Stability of sunflower oil[a] emulsion (pH 7.4), compared with emulsions that contained CuSt[b] (2×10^{-5} M), myricetin (10^{-4} M) plus cupric stearate[b], and quercetin (10^{-4} M) plus CuSt[b] and analogous emulsions that contained ferric palmitate[a] (2×10^{-5} M) stored at 30°C, assessed by PV changes. For abbreviations and statistics see Figures 1, 13, and 14.

chloride and myricetin. Both myricetin and quercetin (10^{-4} M) had a prooxidant effect ($P < 0.05$) in emulsions at pH 7.4 in the presence of cupric chloride (5×10^{-5} M), as shown by measurement of PV (Fig. 11) and conjugated diene values (Fig. 12) during storage. To assess the interactions between quercetin or myricetin with other metal salts, ferric palmitate and cupric stearate were synthesized and added to oils and emulsions, both of which were stored at 30°C. Myricetin (10^{-4} M) had a strong antioxidant effect in oil in the presence of both these metal salts, but quercetin only showed an antioxidant effect with ferric palmitate, and there was no significant effect of quercetin on the stability of an oil sample that contained cupric stearate. These conclusions were reached on the basis of PV (Figs. 13,14) , and headspace pentane levels (Fig. 15). In oil-in-water emulsions at pH 7.4, quercetin and myricetin did not increase the prooxidant effects of ferric palmitate or cupric stearate significantly (Fig. 16). Headspace pentane levels for samples that contained cupric stearate were 6.1×10^5 for the control, compared with 4.2×10^5 for samples containing either quercetin or myricetin.

The interaction of flavonols with ferric palmitate may have been prevented by the chelating effect of the phosphate buffer, but it appears that the tendency to prooxidant effects with copper salts is eliminated if the metal salts are not wholly water-soluble. This may reflect shielding of the copper or iron by the stearate or palmitate anion, which prevents interaction with a flavonol molecule, and therefore prevents the formation of reactive species, which occurs when a flavonal molecule reacts with cupric chloride or ferric chloride in an emulsion.

Thus, myricetin clearly has strong antioxidant activity owing to radical scavenging and metal-chelating properties in oils and emulsions. Quercetin has weaker radical scavenging activity, but it is active by metal chelation. Hence, it does not have significant activity in the presence of tocopherols and citric acid, but it does have significant activity in the presence of tocopherols alone. However, flavonols may show prooxidant effects in emulsions in the presence of added water-soluble ferric or cupric salts. Addition of flavonols to ferric or cupric salts of fatty acids did not increase the prooxidant activity of the metal salts in oils or emulsions at pH 7.4.

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