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Effect of Type of Oil and Addition of δ-Tocopherol on Model Flavor Compound Stability during Storage

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The objective of this study was to investigate approaches to protect selected flavor compounds from deterioration when stored in an oil matrix. An aroma compound model mixture was prepared in a medium-chain triglyceride (MCT) or sunflower oil (SfO) matrix and stored under either an ambient air or argon atmosphere containing, respectively, ca. 20 and <0.5% residual oxygen as controls or containing a natural antioxidant, δ-tocopherol (0.01%). Samples were analyzed by static headspace GC/FID to determine the stability over time of the compounds in mixture. It was found that the type of oil had the greatest effect ($P < 0.01$) on overall compound stability. A low-oxygen atmosphere also had a significant ($P < 0.05$) protective effect on the aroma compounds in both oils. The addition of δ-tocopherol generally offered little additional protection. No significant relationship could be determined between the oxidation of the lipid matrix and the loss of oxidation-sensitive thiol compounds.

KEYWORDS: Aroma stability; oxidation; storage; matrix effect; tocopherol

INTRODUCTION

One of the major causes of quality deterioration in food products during storage is oxidation. The effects of oxygen and oxidation have been intensively studied for their influence on quality of meat products (*1, 2*), fats and oils (*3, 4*), and citrus beverages (*5*). Oxidation of a food product most commonly implies the appearance of off-flavors. However, it is most probable that the loss of flavor quality is caused not only by the formation of undesirable sensory notes but also by the disappearance of desirable ones.

The loss of desirable flavorings due to oxidation has been extensively studied in citrus oils, particularly for limonene, mostly in dry flavorings (*5–8*). In the area of wines several investigations have provided evidence of the formation of phenolic polymers as a result of oxidation. The polymeric phenolics alter mouthfeel and the flavor profile of wine (*9*). These studies document that the oxidation of desirable flavor components produces undesirable changes in flavor profile. Recently we have shown (*10*) that the presence of oxygen can be detrimental to the stability of flavor compounds also in various oil matrices. A faster degradation was found for ethanethiol, diacetyl, and acetaldehyde in an air versus a low-oxygen environment both in water and in oil model systems. These results are concordant with the findings of Williams et al. (*11*), which showed the increased loss of desirable flavors over time for peanut flavor when stored in an oxygen-containing environment.

To slow the negative effects of oxygen on food quality, antioxidants can be employed. A variety of food antioxidants have been studied and classified according to their action mechanism or their origin (*12, 13*). The main category belongs to "chain-breaking compounds" or primary antioxidants. In lipid oxidation reactions they end the free radical chain reaction by donating either an electron or a hydrogen radical to the fatty acid free radicals. A diversity of antioxidants belong to this group, including naturally occurring compounds such as tocopherols, flavonoids, and vanillin, and synthetic antioxidants such as BHA, BHT, and TBHQ. These antioxidants are extensively used in the food industry (*12, 14*). Vitamin E (tocopherols) can function as an oxidation inhibitor either by donating their hydrogen from hydroxyl group to the radical or by scavenging singlet oxygen molecules (*14*). Various tocopherol isomers have been used in the food industry to stabilize essential oils in encapsulated materials (*15*) and in beverages (*16, 17*). α-Tocopherol is used typically as supplementation in vitamin E for food products and as antioxidant, whereas the other isomers (β-, γ-, δ-tocopherol) are used exclusively as antioxidants. Abundant literature is available on the specific activity of tocopherol isomers in vegetable or animal oils, in bulk oil or in emulsions (*18, 19*). δ-Tocopherol is considered to have a high antioxidant activity in bulk oil and to show a pro-oxidant activity only at very high concentration (*20, 21*); it is therefore easy to incorporate into food products (*19*).

The ability of antioxidants to slow lipid oxidation has been well documented. Despite a lack of literature demonstrating that flavor compounds are protected by antioxidants, we assumed

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that antioxidants could also slow their oxidation. Thus, the first objective of the work presented here was to investigate the use of a natural antioxidant (δ-tocopherol) to better preserve flavor compounds in oil systems. The second objective was to determine if the type of oil matrix in which the aroma compounds were diluted influenced aroma compound stability. Finally, it was of interest to investigate if the oxidation of the compounds was correlated to the oxidation of the lipid matrix they were present in.

MATERIALS AND METHODS

Aroma Compounds. A mixture of 10 flavor compounds was prepared using acetaldehyde, dimethyl sulfide, propanethiol, butane-2-thiol, diacetyl, *N*-methypyrrole, 2-ethylpyrazine, furfuryl mercaptan, 3-mercapto-3-methylethyl formate, and furfuryl acetate. The following will focus on data collected for four of these compounds, representative of the variety of degradation patterns observed for the different compounds: diacetyl, dimethyl sulfide, *N*-methylpyrrole, and furfuryl mercaptan. All chemicals were purchased from Aldrich Chemicals at the highest purity available and used at equal molar concentration (7.5×10^{-3} mol/L). The four compounds were selected as representing several different chemical classes and differing in loss mechanism. Furfuryl mercaptan has been shown to be very reactive, degrading rapidly in an oxidative environment such as Fenton-type conditions (*22*). Dimethyl sulfide has also been reported to degrade due to oxidative reactions (*10*). Diacetyl, on the other hand, was equally stable in these two systems. Finally, *N*-methylpyrrole was found to polymerize under mild or strong oxidative conditions and can be used as biopolymer (*23, 24*).

Oils Used for Dispersion of the Model Aroma Compounds. In our primary study two oils were selected as flavor solvents: medium-chain triglycerides (MCT, Delios V, Cognis/Grünau; fully saturated, initial peroxide value = 0.5 mequiv/kg) and sunflower oil (SfO; high oleic content, Nutriswiss, Morges, initial peroxide value = 0.5 mequiv/kg). A third oil, soybean oil (Crisco Pure Vegetable Oil), was used in a secondary short study to determine if the oxidation state of the oil was an important factor influencing the stability of our model flavor compounds during storage.

Preparation of Oxidized Oil. To investigate the effects of lipid oxidation on our model flavor compounds, our volatiles were diluted individually in both fresh and oxidized soybean oil (polyunsaturated, SbO) and then stored. The "fresh" oil was purchased from a local grocery store. The oxidized oil was prepared from the fresh oil by placing 150 mL of the oil in a 200 mL flask and heating it in a water bath (75 °C) for 24 h while compressed air was bubbled through it at a flow rate of 50 mL min^{-1}. Samples were stored only under ambient O_2 levels. Oxidation state of the oils was monitored via peroxide value (PV, AOCS method, as cited in ref *25*). In this analysis, 5 mL of stored sample was analyzed each time. Each storage time was analyzed in duplicate, and the results were averaged and are presented in milliequivalents per kilogram. PV was determined for all oils.

Antioxidants Used. A natural antioxidant, δ-tocopherol (Aldrich Chemical; DTOC), was added to aliquots of both MCT and SfO at 100 ppm (ppm) by weight. The δ-tocopherol isomer was chosen as the antioxidant for study on the basis of published literature (*19–21*) suggesting a high antioxidant capacity. Results and conclusions reported are specific to this isomer.

The controls used in the experiment consisted of a group of positive controls (matrix and flavor mix only, low-oxygen environment) and a group of negative controls (matrix and flavor mix only, ambient air environment). A summary of the samples prepared is given in **Table 1**.

Sample Packaging for Storage and Analysis. Five milliliters of each aromatized oil matrix was dispensed in 20 mL GC headspace sampling vials. Vials containing sample to be stored in ambient air were immediately closed with septa, previously baked to avoid any odor contamination, and then sealed. Vials containing sample to be stored in a low-oxygen environment were taken quickly to an anaerobic glovebox for gas flushing and closure similar to that as described in ref *10*.

Table 1. Summary of Samples Prepared for Storage, Each Containing a Mixture of 10 Compounds at Equimolar Concentration

	air atmosphere	low-oxygen atmosphere	addition of δ-tocopherol (air atmosphere)
medium-chain triglyceride (MCT)	X	X	X
sunflower oil (SfO) soybean oil (SbO)	X	X	X
fresh	X		
oxidized	X		

Storage of Vials. Samples were stored standing upright in an incubator at 30 °C. Sampling times were 0, 1, 2, 4, and 8 weeks of storage. At each sampling time, samples were transferred to a −46 °C freezer until analysis. Samples were prepared in triplicate and analyzed once each.

In the lipid oxidation experiment, aromatized fresh and oxidized soybean oil samples were stored at higher temperature (50 °C) to accelerate degradation reactions; sampling times were 0, 3, 5, 7, 10, 14, and 20 days.

Analytical Method for Volatile Analysis. *Extraction Method.* A static headspace autosampler (Agilent 7694) with a 3 mL loop was used in this study. The extraction parameters were as follows: 45 min of equilibration of the sample at 55 °C; 0.75 min pressurization of the vial at 4 psi; loop filling time, 1.5 min; injection time, 1.5 min.

Separation and Identification. A Hewlett-Packard gas chromatograph (HP-5890) equipped with a DB-Wax column 20 m × 0.1 mm × 0.2 μm (J&W Scientific, Folsom, CA) was used. The following instrument operating parameters were used: column head pressure, 45 psi; 3 mL min^{-1} carrier flow (helium) from the autosampler; 50 mL min^{-1} total split flow; splitless mode for 5 min; oven program, 45 °C/1 min/10 °C min^{-1} /125 °C/5 °C min^{-1}/160 °C/20 °C min^{-1}/190 °C/5 min. A flame ionization detector (FID) was used, and HP ChemStation software was used for data collection.

To identify possible degradation products, sample headspace was analyzed by GC-MS in full-scan mode (ions 29–450). The gas chromatograph (HP model 6890) was equipped with the same column and used with similar operating parameters as above. A mass spectrometer (Hewlett-Packard model 5972 mass selective detector) was used in compound identification coupled with Hewlett-Packard ChemStation software. The parameters were set with 0.5 min solvent delay and 1.84 scan/s. A Wiley library was used for tentative identification.

Quantification. Calibration curves were prepared to ensure aroma compound concentrations were within the method linear range for detection and quantification. Quantification was based on the peak area at an elution time corresponding to that of the pure reference compound. The losses of model volatiles were expressed in terms of percentage of remaining fraction compared to the initial peak area value of week 0, after the triplicate values obtained for each week point were averaged.

Method for Gas Analysis. The gas analysis in pouches and vials was performed using a gas chromatograph (GC, HP-5890) equipped with thermal conductivity detector (TCD) and a HP-Molesieve column 30 m × 0.53 mm × 50 μm (J&W Scientific). The GC operating parameters were as follows: injection port, 150 °C; isothermal run at 40 °C; detector, 175 °C; column head pressure, 5 psi; and column flow, 5 mL min^{-1}. Ten microliter gas samples were taken with a gastight syringe (Hamilton) from either pouches or vial headspace.

Data Analysis. Statistical analyses were performed with the R software (R 2.0.1 Software, www.r-project.org) on the fraction remaining after 8 weeks in the different systems. *t*-Tests were performed for each compound to evaluate (i) the effect of atmosphere type, that is, between the two controls; (ii) the effect of type of oil matrix; and (iii) the effect of δ-tocopherol in a given oil ($P < 0.05$). For each compound, an analysis of variance (ANOVA) was performed with the R package to determine the combined effects of oil, the presence of δ-tocopherol, and one-way interaction ($P < 0.05$).

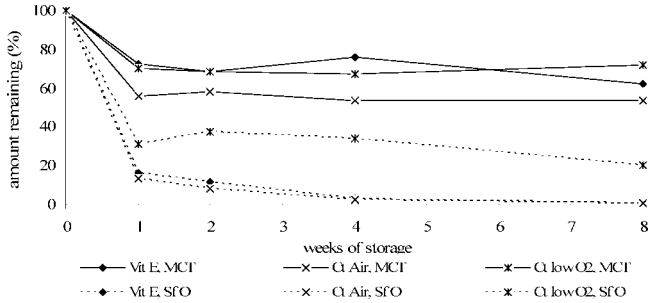

Figure 1. Amount (percent) remaining of diacetyl during storage (30 °C) when diluted in the presence of DTOC or controls, in MCT or SfO.

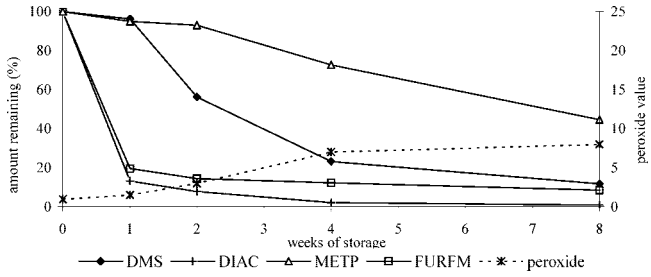

Figure 2. Amount (percent) remaining of model compounds during storage (30 °C) when diluted in SfO in ambient air environment and corresponding peroxide value of the oil matrix (milliequivalents per kilogram).

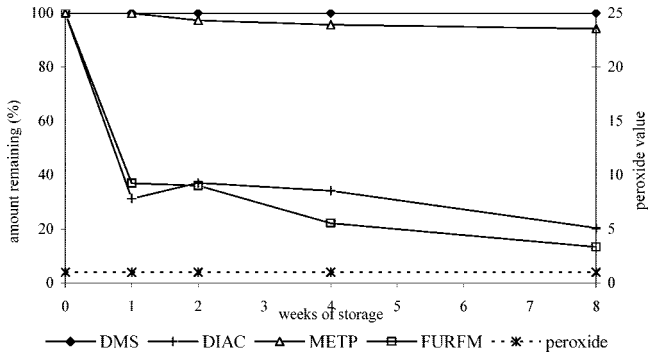

Figure 3. Amount (percent) remaining of model compounds during storage (30 °C) when diluted in SfO in low-oxygen environment and corresponding peroxide value of the oil matrix (milliequivalents per kilogram).

RESULTS AND DISCUSSION

In the primary study we have monitored the retention of selected flavor compounds during storage when diluted in a "stable", highly saturated oil (MCT) and a potentially oxidizable oil (unsaturated), sunflower oil (SfO). The study involved adding the model flavor system to each oil and then storing the oils under different conditions including ambient and low-oxygen samples, as well as a sample sets containing an antioxidant (δ-tocopherol, DTOC) as shown in **Table 1**. The results of this first study showed that the flavor compounds were less stable in the SfO than in the MCT. We hypothesized that the SfO may have become oxidized and the free radicals formed may have contributed to the degradation of the model flavor system. Therefore, we intentionally oxidized a second oil and added our model flavor system to this fresh and oxidized oil. We stored both oils at an elevated temperature to determine if the oxidation state of the oil had an influence on the stability of our model flavor system. For reporting purposes, the fractions of each model compound remaining in each sample treatment during storage are presented (**Figures 1**–**10**). The results presented are organized by model flavor compound.

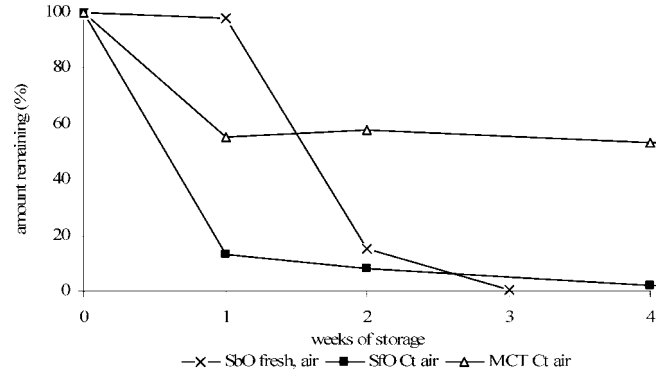

Figure 4. Amount (percent) remaining of diacetyl during storage when diluted in MCT (air, 30 °C), SfO (air, 30 °C), and SbO fresh (air, 50 °C).

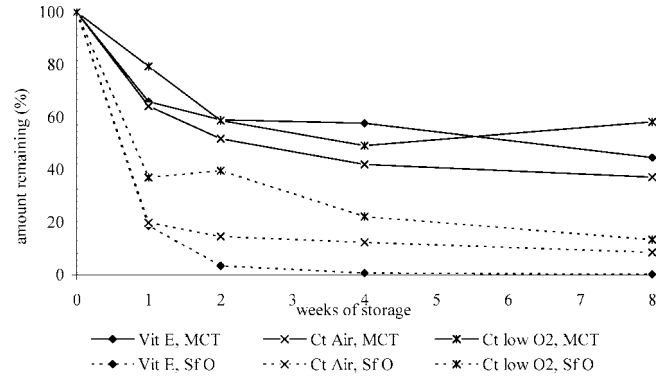

Figure 5. Amount (percent) remaining of furfuryl mercaptan (FM) during storage (30 °C) when diluted in the presence of DTOC or controls, in MCT or SfO.

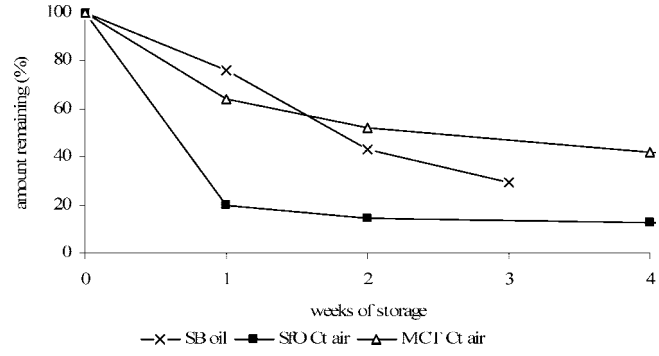

Figure 6. Amount (percent) remaining of furfuryl mercaptan during storage when diluted in MCT (air, 30 °C), SfO (air, 30 °C), and SbO fresh (air, 50 °C).

Diacetyl. When stored under ambient O_2 level, diacetyl was very unstable in SfO (Ctl) with only 10% remaining after 2 weeks of storage (**Figure 1**). A reduced O_2 environment improved the retention of diacetyl: 40% remained after 2 weeks of storage and 20% after 8 weeks of storage. Although diacetyl was not very stable in any of the SfO systems, the absence of oxygen slowed its degradation. The presence of DTOC in SfO did not significantly improve ($P > 0.05$) the stability of diacetyl compared to the Ctl.

Diacetyl was substantially more stable in MCT: About 50% of it remained in the Ctl samples after 8 weeks of storage, and about 70% remained in low-O_2 sample. In these two systems, the major loss occurred within the first week of storage and then losses stabilized. This is in contrast to the loss profile in SfO, for which losses continued throughout the whole storage

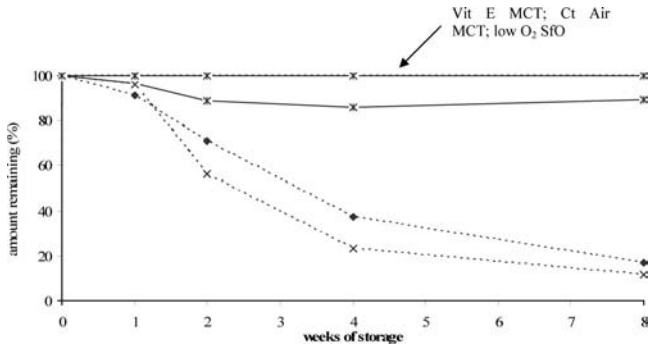

Figure 7. Amount (percent) remaining of dimethyl sulfide (DMS) during storage (30 °C) when diluted in the presence of DTOC or controls, in MCT or SfO.

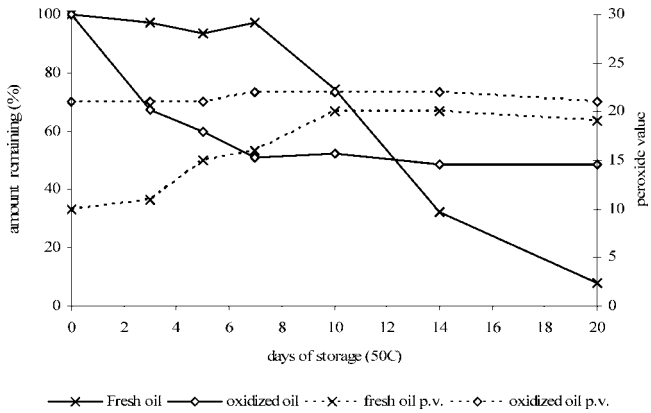

Figure 8. Amount (percent) remaining of dimethyl sulfide (DMS) during storage when diluted in SbO fresh and SbO oxidized (air, 50 °C) and corresponding peroxide value of the oil matrix (milliequivalents per kilogram).

period. Reducing O_2 or adding DTOC significantly improved the retention of diacetyl in MCT ($P < 0.05$).

On the basis of the above data it would appear that diacetyl may be at least partially lost via oxidation, being more stable in MCT than in SfO. Considering the data presented in **Figure 2**, we see that diacetyl losses occurred in the SfO and the oil clearly was oxidizing (increasing PV with time). However, the PV of the SfO at low O_2 (**Figure 3**) was virtually unchanged during storage, suggesting no significant oxidation of the SfO occurred, and yet substantial amounts of diacetyl were lost. This suggests that diacetyl losses appear to be independent of oil oxidation. This was also observed in SbO when losses of diacetyl could not be correlated with changes in PV (data not presented). In addition, substantially different degradation patterns could be observed in the three oils, but could not be related to the saturation level of the oil matrix (**Figure 4**; data presented over 4 weeks). It is possible that diacetyl interacted with other components in the systems, which resulted in apparent losses.

Furfuryl Mercaptan (FM). Similar degradation patterns as for diacetyl were observed for FM (**Figure 5**): ca. 17% of FM remained after only 2 weeks of storage in SfO Ctl compared to about 33% in low O_2. However, after 8 weeks, the final losses in the two systems were similar. The addition of DTOC did not significantly reduce losses of FM in SfO.

Again similar to diacetyl, FM degrades less quickly and to a lower extent when dissolved in MCT compared to SfO [37% left after 8 weeks in MCT versus 8% left in SfO (ambient O_2)].The effect of oil type was found to be highly significant ($P < 0.01$) after the total storage period. Low O_2 versus Ctl provided a significant benefit ($P < 0.05$) for FM in MCT. Whereas the addition of DTOC in this oil may have slowed early losses of FM, it did not provide significant protection during continued storage. Our findings are in agreement with those of Blank et al. (*22*) that oxidative conditions induce rapid and complete degradation of FM. The low-O_2 environment or added tocopherol showed limited protection for FM and were not efficient in avoiding its losses.

Overall, the oil type has a greater effect on compound stability than added antioxidant or reduced-O_2 storage. According to data collected on FM losses in fresh soybean oil (**Figure 6**), it seems that the more unsaturated the oil matrix, the more FM degraded during storage, at least on a long-term basis (>2 weeks of storage). Additional work would be needed to confirm this observation.

Similar to diacetyl losses, FM losses occurred whether the SfO was undergoing oxidation or was stable to oxidation (**Figures 2** and **3**, respectively). Poor stability of FM was found when stored under low O_2 even though the PV of the SfO was stable over the storage period.

Dimethyl Sulfide (DMS). This study included a second sulfur-containing compound, DMS (**Figure 7**). The retention profiles of DMS are very different from those observed for diacetyl and FM. DMS losses from SfO were substantial (70% remaining after 2 weeks of storage with antioxidant; 54% remaining in ambient O_2 samples) except for the sample stored in the reduced-O_2 environment, which had no detectable losses even after up to 8 weeks of storage). Although the presence of DTOC may have initially slowed DMS losses, the difference between the treatment sample and the control was not significant after 8 weeks of storage (12% remaining in Ctl versus 17% remaining with DTOC). DMS was quite stable when added to MCT (**Figure 7**). It appears that DMS was lost to a greater extent in the low-O_2 sample, but this difference was not statistically significant. Despite this lack of statistical significance, this result is consistent with a previous study (*10*) in which DMS was found to undergo equal or greater loss when stored in a reduced-O_2 environment than at ambient O_2 levels in MCT.

As can be seen in **Figures 2** and **3**, DMS tended to be inversely related to the change in PV of the samples: DMS levels in the sample undergoing oxidation (increased PV value) decreased, whereas there was no DMS loss in the sample with a stable PV value. This suggests a relationship between oxidation of the oil (free radical formation or the formation of reactive oxidative products?) and DMS stability. When DMS was added to fresh and oxidized SbO and stored (**Figure 8**), the initial losses of DMS were higher in the oxidized oil than in fresh oil. Losses stabilized in the oxidized oil but continued at a slow rate in the fresh oil sample to reach similar overall loss after 8 weeks of storage. It appears that losses increased when PV > ≈15. However, this trend could not be confirmed in the two other oils.

Similar to FM and diacetyl, DMS stability was significantly influenced by oil type ($P < 0.01$), which led us to conclude here again that in these experimental conditions, the effect of the matrix (MCT versus SfO) is greater than the effect of adding vitamin E antioxidant.

***N*-Methylpyrrole (NMP).** NMP degraded substantially in SfO Ctl (45% remaining after 8 weeks of storage), whereas no loss was detectable in low O_2 in the same matrix (**Figure 9**). This suggests that oxygen may be involved in NMP loss. Similar trends and relative differences were found for NMP in MCT (75% remaining after 8 weeks in Ctl versus 88% in low O_2).

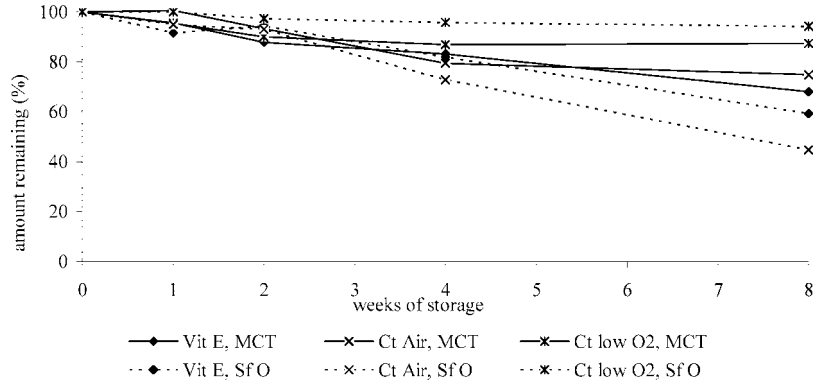

Figure 9. Amount (percent) remaining of *N*-methylpyrrole (NMP) during storage (30 °C) when diluted in the presence of DTOC or controls, in MCT or SfO.

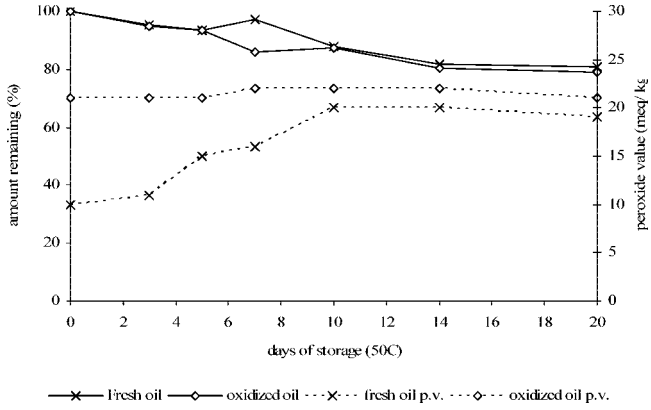

Figure 10. Amount (percent) remaining of *N*-methylpyrrole (NMP) during storage when diluted in SbO fresh and SbO oxidized (air, 50 °C) and corresponding peroxide value of the oil matrix (milliequivalents per kilogram).

NMP losses were significantly lower in the low-O_2 systems compared to Ctl systems ($P < 0.01$) in the two oils. In addition, losses were reduced in SfO when DTOC was added to the system compared to Ctl (60% versus 45% in Ctl), but there was no effect of DTOC when added to the MCT system. The observation that losses were reduced by lowering the O_2 but not as effectively by the addition of antioxidant suggests that molecular oxygen might be involved in the degradation process.

Data on NMP losses when added to fresh and oxidized SbO (**Figure 10**) also support this hypothesis because the same degradation pattern and losses were observed regardless of the oxidation state of the oil. The fact that NMP is degraded under oxidative conditions is in agreement with the use of oxidation to polymerize this compound to form conducting biopolymers in biotechnologies (*23*). Because we used a headspace method in this study, we would not detect polymerized NMP. It would be interesting to conduct further studies using C-14-labeled compounds to help in determining loss mechanisms.

Similar to the other model compounds, the type of oil had a highly significant effect ($P < 0.01$) on NMP stability after 8 weeks of storage. This effect was found to surpass the effects of oxygen or antioxidant in terms of long-term stability.

Although the presence of DTOC was found to be significant for the stability of some compounds in a given matrix, as well as the type of matrix, no significant interaction could be determined statistically (ANOVA) for any of the four model compounds studied.

In addition to measuring peroxide values, sample headspace was analyzed by GC-MS in full-scan mode (ions 29–450) to identify possible degradation products. Hexanal, heptanal, and octanal could be detected and identified in SfO Ctl after 8 weeks of storage, whereas none of these aldehydes could be detected in SfO DTOC or low-O_2 control, nor in any of the MCT systems. These findings are in agreement with the PVs in the various systems (Ctl versus low O_2 versus DTOC). The addition of antioxidant or reduced O_2 levels effectively limited SfO oxidation. Assuming oxidation is a loss mechanism for some of our model compounds, it appears that DTOC does not protect all oxidizable compounds equallyl that is, it might preferentially target the fatty acids rather than the flavor compounds. Hras et al. (*26*) found a pro-oxidant activity of α-tocopherol when added to sunflower oil (0.01%). In the present study, δ-tocopherol was added at 100 ppm (0.01%) and an opposite effect was observed. This contradiction may be explained by the work of Huang et al. (*18*), who studied the influence of α- and γ-tocopherol on lipid oxidation in corn oil emulsions. They found different optimal levels for each type of tocopherol.

Because lowering the O_2 in the sample environment often led to reduced losses of our model volatiles, we expected that the addition of DTOC might also offer similar protection. However, of our model compounds only diacetyl in MCT benefited from added DTOC under the conditions of our experiments.

Overall, this study showed that DTOC provided little protection to the model volatiles studied. In one case the addition of DTOC (NMP in MCT) had a detrimental effect on stability (over 8 weeks). Reduced oxygen in the sample atmosphere generally provided a better protection. This suggests that oxidation is involved in the loss of our model volatiles but that a free radical acceptor such as DTOC may not be the right choice of antioxidant. The major factor influencing the stability of our model compounds over time was the type of oil matrix used as flavor solvent. Overall, MCT offered substantially greater stability to the volatile compounds than SfO or SbO. However, the data gathered could not provide sufficient evidence that either the saturation level or the oxidation level of the oil matrices was the key factor. The influence of other oil characteristics such as fatty acid composition or the presence of trace components would need to be investigated to make definitive conclusions.

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