OXIDATIVE STABILITY OF SOME MAYONNAISE FORMULATIONS DURING STORAGE AND DAYLIGHT IRRADIATION

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ABSTRACT

The stability of various formulations of mayonnaise stored in commercial glass jars, at 20C in the dark was studied. Dijon mayonnaise made with sunflower oil and containing mustard paste can be stored up to 10 months in closed jars without serious oxidative damage due to the presence of high amounts of natural tocopherols in the oil and limited oxygen availability. However, in the absence of mustard, the oxidative degradation was somewhat faster and the amount of conjugated dienes was increased more quickly and to a higher degree than that in the mustard containing sample. Supplying oxygen by opening one time the jars to air increased the rate of degradation, even when the mayonnaise was stored at 4C. Exposing of glass jars of mayonnaise alternatively to daylight and darkness for 1 month produced only little conjugated dienes while hexanal appeared in significant amounts. Addition of antioxidant (rosemary extract and EDTA) or emulsifier (DATEM) decreased the level of photooxidative volatiles in the headspace.

INTRODUCTION

Mayonnaise is a relatively shelf-stable product that can be sold up to one year after its manufacturing date. However, in some cases, the product develops off-flavors in less than six months, leading to returns from consumers. These off-flavors are described as "rancid". The rancid descriptor is difficult to define even

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by trained panelists; these include different olfactory perceptions, arising from volatile degradation products of hydroperoxides, hydrolytic degradation of fats or fading taste. Thus, the term "rancid" may reflect a different sensory response in meat or in mayonnaise (Jacobsen 1999).

Emulsified lipids are often oxidized more quickly than bulk oil because of the larger exposure area with air; the mechanisms of flavor deterioration in emulsions are also more complex (Coupland *et al.* 1996). A full understanding of the oxidative reactions in emulsions remains to be important (Jacobsen *et al.* 2000). The headspace volatile analysis appears to provide the most appropriate instrumental method for studying and quantifying individual compounds responsible for rancid flavor (Robards *et al.* 1988; Snyder *et al.* 1988; Frankel 1998). Jacobsen *et al.* (2001) identified 148 compounds by GC-MS in fish oil enriched mayonnaise, many of which were derived from highly unsaturated fatty acids. Classically, pentane and aldehydes having 5 to 10 carbons are considered to be representative of the secondary products of lipid oxidation but many reports have measured only hexanal as the main oxidized volatile product of fats and oils rich in linoleic acid.

The goal of this study was to follow the chemical state of the mayonnaise during storage under "normal" conditions in order to explore if lipid oxidation could justify the "rancidity" term used by the consumers about returns of mayonnaise. At the same time, we analyzed different formulations to evaluate the composition and oxidation reaction rates of mayonnaise, particularly in the absence of mustard. Eight different formulations were prepared and evaluated during several months of storage. Finally, the samples were subjected to daylight photooxidation to test their resistance towards drastic conditions of storage.

MATERIAL AND METHODS

Materials

A first lot of four mayonnaise samples was prepared in a pilot scale under industrial manufacturing conditions. The reference mayonnaise (M1) was composed of sunflower oil (78%), egg yolk (9.2%), vinegar (5%), mustard (5%), salt, sugar, pepper, colorant (paprika and tagete extracts) and aromas citrus extract, A1, mustard aroma, A2. One or several ingredients were omitted in the other three samples (Table 1). A second lot of four formulations was constituted by the mayonnaise M1 alone or containing different additives (Table 1). Rosemary extract (Guardian GP) was from DANISCO (Trappers, France), ethylenediaminetetraacetic acid (EDTA), an efficient iron chelator, was from SIGMA (Saint Quentin – Fallavier, France) and the emulsifier DATEM Lamegin DWP 394 was from GRUNAU (Jllertissen, Deutchland). DATEM is not allowed for inclusion in commercial mayonnaise formulations.

TABLE 1.
FORMULATIONS OF MAYONNAISE IN THE TWO SERIES OF ASSAY

Series 1		Series 2	
M1	*Reference mayonnaise*	**M1**	*Reference mayonnaise*
M2	M1 without citrus aroma	**M5**	M1 + rosemary extract (0.03%)
M3	M2 without mustard	**M6**	M1 + EDTA (0.004%)
M4	M3 without mustard aroma	**M7**	M1 + DATEM (0.2%)
		M8	M1 + DATEM (0.2%)+ rosemary extract (0.03%)

Standards were used to identify volatile compounds by gas chromatography - mass spectrometry; tridecane (99%) was used as an internal standard for quantification. All other chemicals were purchased from Fluka-Sigma-Aldrich (Saint Quentin Fallavier, France); 2,2,4-trimethyl-pentane was used as a solvent in the conjugated dienes measurements.

Methods

Storage. The mayonnaises of the two series were stored in the dark, in 250 g filled and closed glass jars at 20C. One jar was taken out for analysis each month, in parallel with the control sample. Other jars were kept unopened. The samples of the first series (M1, M2, M3 and M4) that have been opened to take out a part of mayonnaise at T0 were stored at 4C. All the 10 months - aged jars stored at 20C (unopened) and 4C were analyzed and then placed in front of a window and turned each two days to be illuminated all over. Figure 1 shows the sample storage and analyses details.

Oil Extraction from Mayonnaise. The mayonnaise was gently mixed prior to sampling. Twenty grams of mayonnaise were poured into 50 mL polypropylene centrifuge tubes. According to the procedure of Min and Tickner (1982), the samples were frozen at – 30C for 24 h and thawed for 2 h at 5C to break the emulsion. Two milliliters of water were added and the mixtures centrifuged at 7500 g for 10 min. The oil phase separated from the emulsion residue was stored in closed glass flasks at –30C until analyzed. When the two phases were not well separated as it happened with some formulations, the procedure was repeated one more time. The recovery of the oil from 14 replicates was 62.3 ± 3.0 g oil /100 g

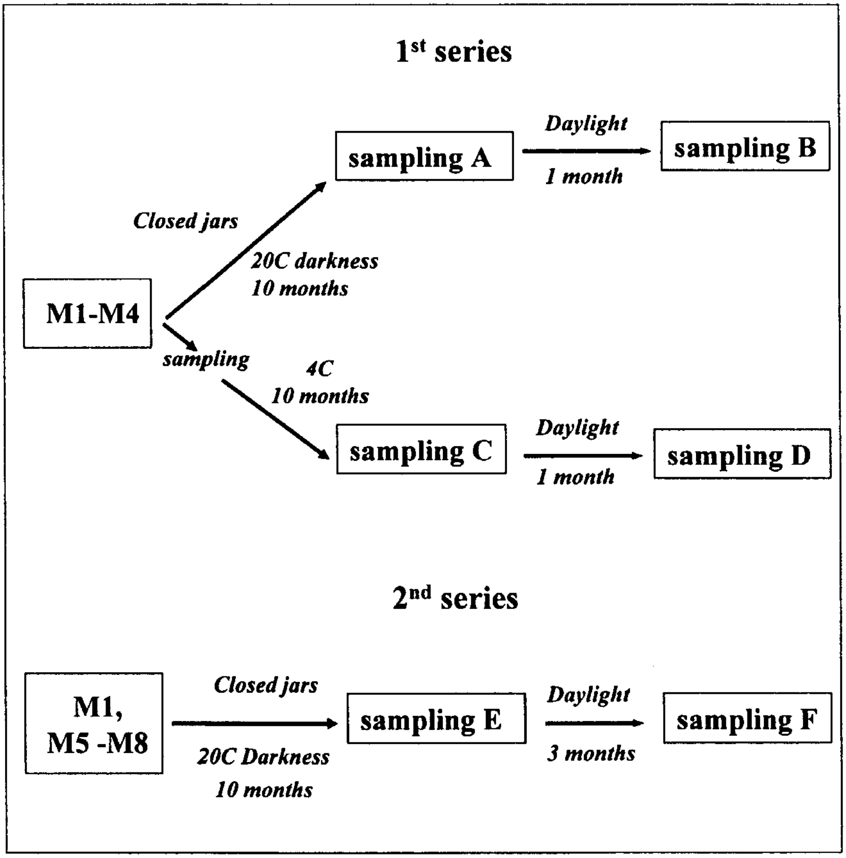

FIG. 1. CONDITIONS OF STORAGE OF THE MAYONNAISE IN THE TWO SERIES OF ASSAYS

mayonnaise. As mayonnaise contained 78% oil, the yield of extraction was around 80%.

The sunflower oil used in the formulations had the following composition: C14:0, 0.1%; C16:0, 6.1%; C16:1, 0.1%; C18:0, 4.0%; C18:1, 24.2%; C18:2, 63.5%; C18:3, 0.1%; C20:0, 0.3%; C20:1, 0.15%; C22:0, 0.7%; and C24:0, 0.2% (average of 4 lots). The oil contained 54.8 mg /100 g α- tocopherol, 2.4 mg/ 100 g β- tocopherol, 0.75 mg/100 g γ- tocopherol and 0.2 mg/100 g δ-tocopherol.

Determination of Conjugated Dienes. Ten to 20 mg of mayonnaise oil were dissolved in 10 mL of 2,2,4-trimethylpentane and mixed using a vortex shaker. The absorbance of the solutions was read at 234 nm and the specific absorbance $E_{1\%}^{1cm}$ was calculated using triplicate determinations.

Headspace Gas Chromatography Analyses (HS/GC). Two grams of oil samples were poured into 22 mL headspace vials (Perkin Elmer Co, Paris, France) and mixed with 100 mg of 5 g /L tridecane as an internal standard (IS). The vials were sealed with a silicon Teflon cap and placed in a Perkin-Elmer 40 XL headspace autosampler. After heating at 100C for 15 min and pressurization with helium carrier gas for 2 min, the volatiles were injected for 1 min and cryofocused at –20C at the top of a 30 m CARBOWAX™10 silica capillary column (Supelco). The following oven temperature set was then used: 40C during 4 min, increased at 4C/min to 200C and held there for 10 min. All analyses were performed in triplicate. Volatile compounds were detected by flame ionization and identified by comparison of their retention times with those of reference compounds and by solid phase microextraction-mass spectrometric (SPME-MS) analysis using the same column.

RESULTS AND DISCUSSION

Conjugated Dienes

Figure 2 shows the production of conjugated dienes (CD) in the oil and the mayonnaise dressings M1 to M4, stored for 10 months at 20C. At the beginning (T0) the level of CD in the four samples was the same as that in sunflower oil. No evidence of lipid oxidation was observed, as determined by conjugated diene analysis, either in the control mayonnaise or in oil, during storage. The high content of tocopherols in the sunflower oil (580 ppm) might explain the good stability of the fatty acids towards oxidation. Nevertheless it is noticeable that the level of conjugated dienes increased during the first month and then decreased in the M4 formulation. The same tendency can be seen in M3 but to a lesser extent. M3 did not contain mustard while M4 contained neither mustard nor mustard aroma. Thus, it seems that mustard serves as a stabilizing factor for mayonnaise.

The data for the second series (M1, M5-M8) are reported in Fig. 3. All samples were conventional Dijon mayonnaise, with or without additives (Table 1). As expected, no significant difference in CD was observed among the mayonnaises at T0 while their levels changed only marginally during storage for 10 months. Consequently, no protection by the additives could be seen at this step. To explain this low degree of oxidation, it could be inferred that oxygen would become rapidly limiting for oxidative reactions. Some researchers studied the influence of oxygen concentration on the rate of lipid oxidation. Marcuse and Fredriksson (1968) reported that lowering the partial pressure of oxygen from 2% to 1% in the headspace above an emulsion retarded oxidation more than lowering it from 21% to 2%. In the same way, production of aldehydes was reported to be highly dependent on oxygen concentration in the food products at low oxygen pressure (Andersson and Lingnert 1999). As observed, the amounts of CD were higher in

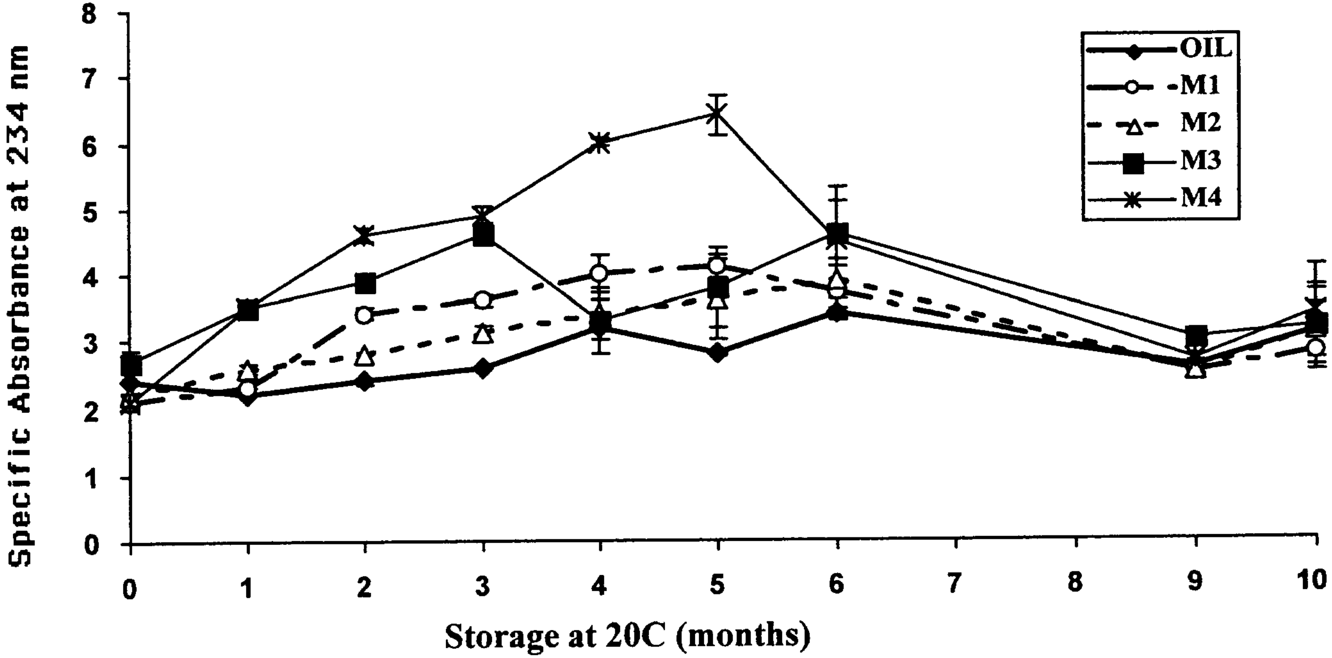

FIG. 2. EVOLUTION OF CONJUGATED DIENES IN SUNFLOWER OIL AND MAYONNAISE M1 – M4, DURING STORAGE AT 20C UNDER DARKNESS
(M1 = standard, M2 = M1 without citrus aroma, M3 = M2 without mustard, M4 = M3 without mustard aroma)

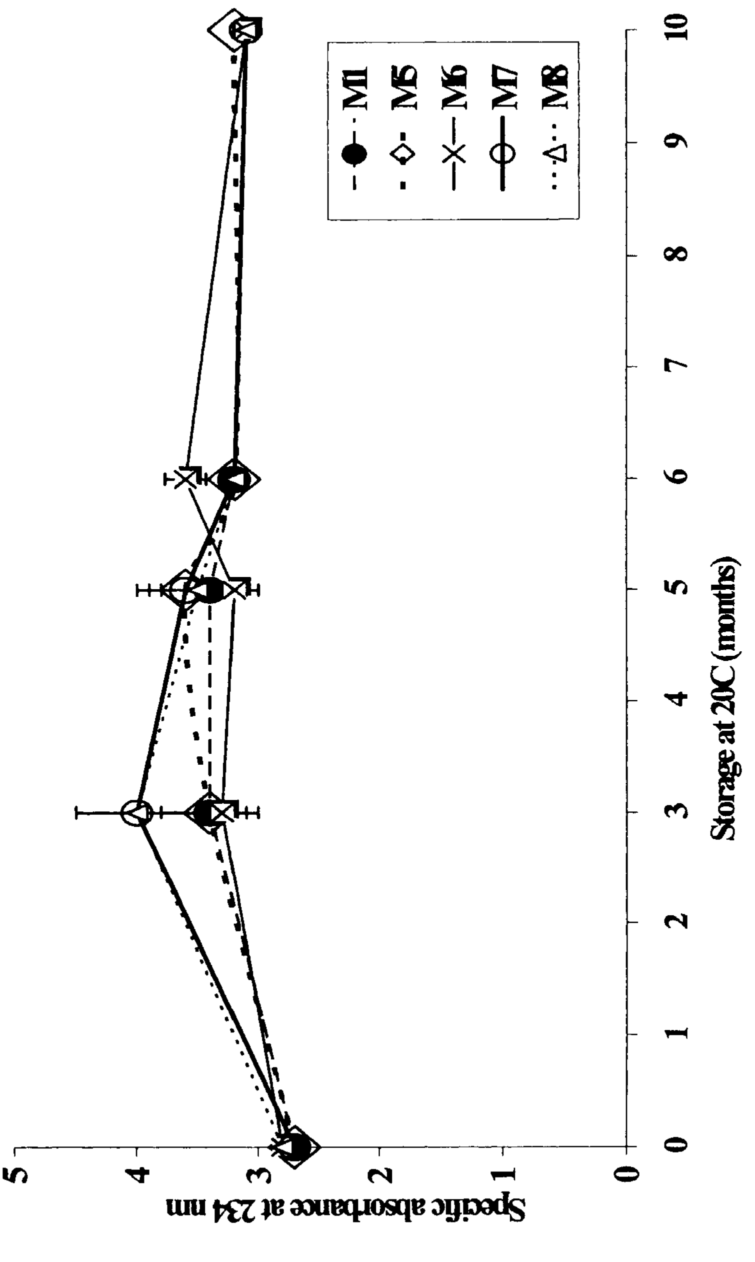

FIG. 3. EVOLUTION OF CONJUGATED DIENES IN MAYONNAISE OF THE SECOND SERIES DURING STORAGE AT 20C UNDER DARKNESS
(M1 = standard; M5 = M1 + antioxidant; M6 = M1 + metal chelator; M7 = M1 + emulsifier; M8 = M5 + antioxidant + emulsifier)

jars opened at T0 and then stored at 4C during 10 months, compared to jars unopened and stored at 20C (Fig. 4). Generally, consumers are advised to store mayonnaise in the refrigerator and to eat the product within one month after its opening, because each opening of the jar provides new oxygen supply that enhances oxidation. The greater instability of the samples without mustard and mustard aroma (M3, M4) was more evident in the jars that were opened, thus clearly confirming the protective role of mustard in mayonnaise. Meanwhile citrus aroma had no significant effect on the stability of mayonnaise.

In order to accelerate the oxidation, the mayonnaise was subjected to an intermittent lighting as it could be the case in the supermarket counters. This assay was conducted on the 10 month-aged jars stored at 20C (1st and 2nd series) or 4C (1st series) (Fig. 1). The results showed that a one-month daylight exposure increased the CD content in each mayonnaise marginally (Fig. 4 and 5) because of the absorption of the most energetic rays by the glass jar. Nevertheless, the mayonnaise samples which were subjected to light became bleached and paler. In the second series (with additives) the daylight exposure was extended for up to 3 months. The increase of CD was then much more pronounced, the specific absorbance reaching a value of 6.7 in the control (Fig. 5). This value was reduced by 25% in the presence of all additives, regardless of their nature. This result is not in accordance with those of Jacobsen et al. (2001) obtained on fish oil enriched mayonnaise which oxidized to a high degree. The authors found that EDTA reduced free radicals and lipid hydroperoxides much more efficiently than gallic acid or DATEM; this effect was attributed to the strong metal chelating ability of EDTA. The difference could be explained firstly by the high stability of sunflower oil that undergoes oxidative reactions at a slow rate and to a small extent. Secondly, rosemary extract could have a chelating effect as many plant extracts do, similar to that of EDTA.

Analyses of Volatile Compounds

To follow the profile of the volatile compounds in each mayonnaise, different headspace analyses conditions were compared. As the best results were obtained with a cryofocusing step of the volatiles at the top of the column, direct analysis of the emulsified product was not possible because of water trapping. Thus, the lipid phase was extracted by a series of steps involving freezing, thawing and centrifugation. Generally, equilibration of the vapor phase at 60C is carried out for 30 min or 1 h before headspace analysis, but under conditions employed in this work, it led to very small peaks of volatile products. Rorbaek and Jensen (1997) reported that above 75C, new volatile compounds may be formed in fish oils by degradation of the oxidized fatty acids. We did not observe such a phenomenon in the sunflower oil phase of mayonnaise, after an equilibration period of 15 min at 100C. The chromatographic profiles of the volatiles were similar at 60C and 100C, with only an increase in peak intensities at the higher temperature. In samples

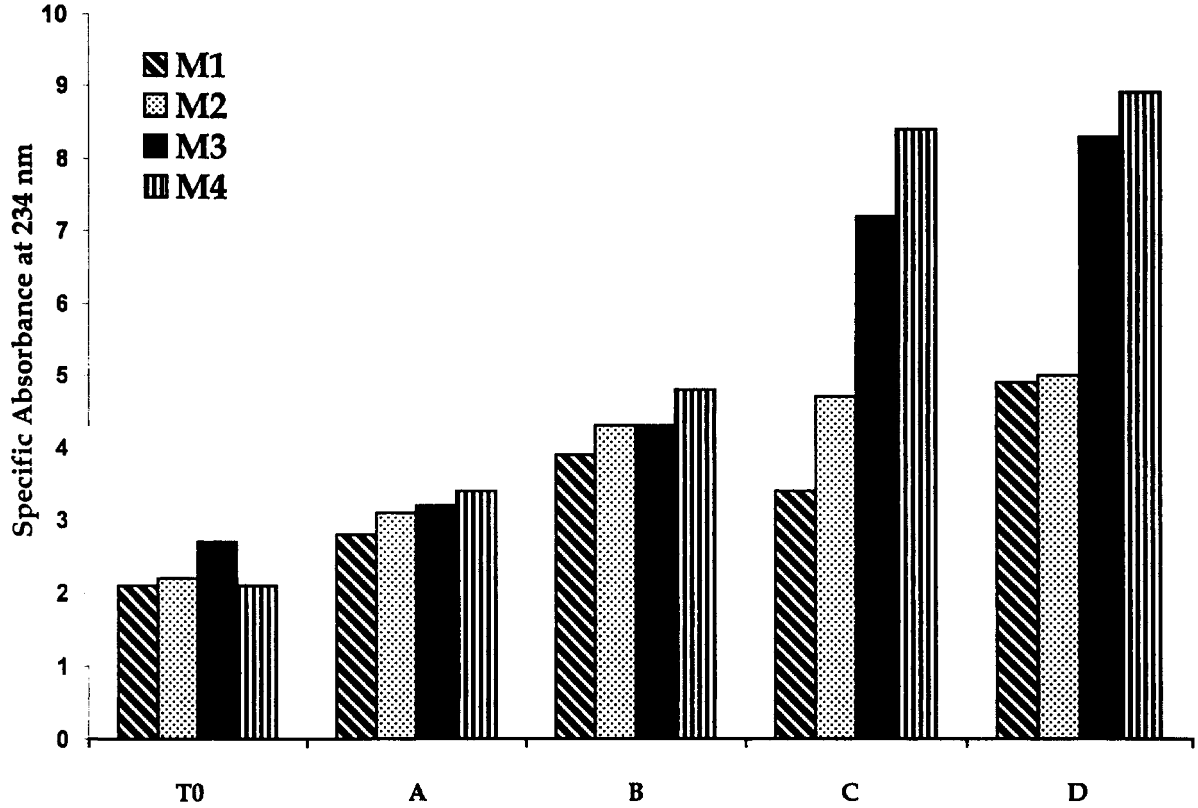

FIG. 4. CONTENT OF CONJUGATED DIENES IN MAYONNAISE SUBMITTED TO DIFFERENT CONDITIONS OF STORAGE
(Symbols A, B, C, D refer to the samplings described in Fig. 1. M1, M2, M3, M4 refer to the formulations of Fig. 2)

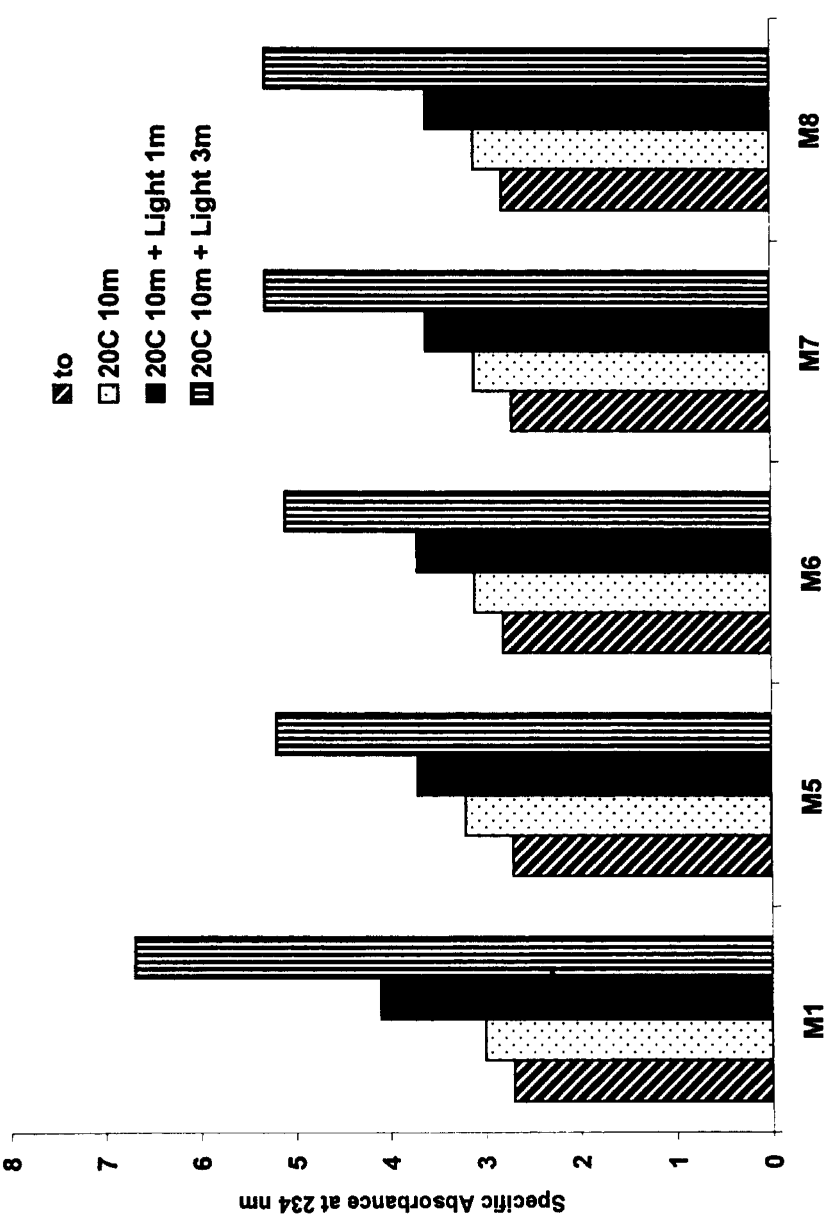

FIG. 5. EFFECT OF ADDITIVES ON THE FORMATION OF CONJUGATED DIENES IN MAYONNAISE STORED UNDER DAYLIGHT
(For the signification of symbols, see Fig. 3)

where oxidized compounds were absent at 60C, it was the same at 100C. So, an equilibration of the lipid phase at 100C for 15 min was selected in the present study. Nevertheless, the chromatograms were very poor compared to those obtained by Jacobsen *et al.* (2001) for fish oil enriched mayonnaise.

Minor changes in the aroma profile occurred during the storage of mayonnaise for 10 months at 20C. The main difference was a loss of volatiles originating from vinegar in the formulations. Fifteen standards of aldehydes, ketones and alcohols, identified as oxidation products of linoleic acid (Frankel 1998), were subjected to

TABLE 2.
OXIDATIVE VOLATILE COMPOUNDS PRODUCED IN MAYONNAISES AT T0 AND AFTER STORAGE UNDER DIFFERENT CONDITIONS

Volatile	To	Dark 20C 10 months	Dark 20C 10 m Light 1 m	Dark 4C 10 m	Dark 4C 10 m Light 1 m
Mayonnaise M1					
Pentanal	0.02	0.06	0.08	0.02	0.2
Hexanal	0.02	0.06	0.8	0.03	1.2
2 - heptenal		0.01	0.1	0.01	0.1
2 - octenal		tr	0.03		0.04
1 - pentanol			0.03		0.03
1 - octen 3 - ol			0.02		0.02
Mayonnaise M2					
pentanal	0.03	0.09	0.3	0.02	0.3
hexanal	0.03	0.08	2.3	0.05	2.1
2 - heptenal		0.02	0.15	0.01	0.1
2 - octenal		tr	0.03		
1 - pentanol			0.09		0.06
1- octen 3 - ol			0.03		
Mayonnaise M3					
pentanal	0.01	0.02	0.02	0.04	0.8
hexanal	0.02	0.03	1.8	0.2	6.9
2 - heptenal			0.09	0.01	0.1
2 - octenal			0.03		0.1
1 - pentanol			0.07		0.2
1 - octen 3 - ol			0.02		0.05
Mayonnaise M4					
pentanal	0.01	0.01	0.3	0.03	0.9
hexanal	0.02	0.02	2.7	0.09	6.9
2 - heptenal		0.01	0.1	0.01	0.2
2 - octenal		0.01	0.04		0.1
1 - pentanol			0.08		0.2
1 - octen 3 - ol			0.02		0.05

Data are the ratio of compound peak are/internal standard peak area. For symbols, see Table 1; m, month.

headspace conditions and their retention times measured. Only 6 of these compounds were detected, in small quantities, during the storage of mayonnaise, namely pentanal, hexanal, 2- heptenal, 2- octenal, 1- pentanol and 1- octen-3-ol, as identified by SPME at 60C followed by GC/MS. Table 2 summarizes the data for the first series of assays (M1 to M4) and Table 3 for the second series (M1, M5-M8). The data were calculated as the ratio of peak area of the compound/ peak area of the internal standard. As expected, during storage in the dark at 20C, only small quantities of volatiles were produced and the differences between samples were not significant. Hexanal and other aldehydes remained at a very low level in all mayonnaise samples (Tables 2 and 3). On the contrary, after the jars were stored under light, the peak of hexanal was more intense, simultaneously with the development of a rancid odor. In the unstable samples M3 and M4, after 10 months of storage at 4C followed by 1 month under light, the hexanal peak was nearly six times higher than the control peak. This result is in agreement with those of conjugated dienes and confirms the antioxidant effect of mustard.

In the second series (Table 3), the additives showed a protective activity; after three months of daylight exposure, M5-M8 produced 4 times less hexanal than M1. Once again, the nature of additives had little effect on their antioxidant effect; the iron chelator and the emulsifier had the same effect. However, these results must be considered with some caution. As reported above, the rosemary extract and EDTA could have a similar chelating activity. However, DATEM had an effect on oil-water partition coefficients of selected volatile off-flavors. Jacobsen *et al.* (1999) reported that the recovery of volatiles in the lipid phase of emulsions was lower when the fish oil mayonnaise contained this additive. Thus, it is possible that the composition of the headspace of samples M7 and M8 was not exactly representative and that the "antioxidant" effect was due to an incomplete recovery of the volatile compounds.

In conclusion, industrial mayonnaise made with sunflower oil is a stable product in spite of its high content of linoleic acid. We failed to find a noticeable level of oxidative compounds under usual storage conditions of the product. Therefore, there is no reason to add antioxidants in the mayonnaise formulations if the natural tocopherols in the oils are preserved. Nevertheless, mayonnaise must be consumed within a few weeks after opening of the jars and intensive lighting must be avoided to preserve the fresh taste of the products. Further investigations are warranted, in particular sniffing analysis, to be sure that some molecules, not detected by headspace chromatography, are not present at a very low level which could be perceived as "rancid" by the human nose.

TABLE 3.
OXIDATIVE VOLATILE COMPOUNDS PRODUCED IN MAYONNAISES STORED AT 20C IN THE DARK AND UNDER LIGHT

Volatile	Dark 6 m	Dark 10 m	Dark 20C 10 m Light 1 m	Dark 20C 10 m Light 3 m
Mayonnaise M1				
pentanal	0.03		0.08	0,6
hexanal	0.04	0.01	0.5	4,7
2 - heptenal	0.01		0.2	0,4
2 - octenal			0.02	0,1
1 - pentanol			0.01	0,2
Mayonnaise M5				
pentanal	0.02		0.02	0.2
hexanal	0.05	0.02	0.1	1.5
2 - heptenal	0.01	0.01	0.1	0.4
2 - octenal			tr	0.05
1 - pentanol				0.07
Mayonnaise M6				
pentanal	0.01	0.01	0.03	0.2
hexanal	0.04	0.06	0.15	1.5
2 - heptenal	0.01	0.02	0.2	0.5
2 - octenal			tr	0.05
1 - pentanol			tr	0.05
Mayonnaise M7				
pentanal	0.07	Tr	0.03	0.2
hexanal	0.15	0.03	0.15	1.1
2 - heptenal	0.03	0.01	0.1	0.3
2 - octenal			tr	0.04
1 - pentanol				0.05
Mayonnaise M8				
pentanal	0.03	0.03	0.03	0.2
hexanal	0.05	0.05	0.1	1.1
2 - heptenal	0.01	0.01	0.1	0.4
2 - octenal				0.04
1 - pentanol				0.04

Data are the ratio of compound peak are/internal standard peak area. For symbols, see Table 1; m, month.

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