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Photooxidative stability of stripped and non-stripped borage and evening primrose oils and their emulsions in water

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Abstract

Minor components in edible oils affect both their autooxidative and photooxidative stabilities. Thus, stripping of minor components may influence stability of oils being studied. The impact of natural endogenous pigments on photooxidative stability of stripped and non-stripped borage and evening primrose oils and their emulsions in water was studied. Peroxide values (PV) of non-stripped borage and evening primrose oils and their emulsions in water were significantly ($P < 0.05$) higher than corresponding values for stripped oils and their emulsions in water. A similar trend was observed when considering hexanal contents of bulk oils and their corresponding oil-in-water emulsions. These results indicate that minor components, especially endogenous chlorophylls, play a major role in the photooxidation of borage and evening primrose oils and their emulsions in water. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Borage oil; Evening primrose oil; Nutritional oils; Oil-in-water emulsion; Photooxidation; Stripped oil

1. Introduction

Borage and evening primrose oils have been used for the treatment of a wide range of nutritional and clinical disorders. Anti-diabetic and anti-ulcerogenic properties of evening primrose oil were reported by Garland, Forshaw, and Sibley (1997) and Andreassi, Forleo, Dilorio, Masci, Abate, and Amerio (1997), respectively. Recently, Engler and Engler (1998) have reported that dietary borage oil lowers blood pressure in spontaneously hypertensive rats. Moreover, Munoz, Lopez, Valentich, and Eynard (1998) have observed that omega-6 rich diets, such as corn and evening primrose oils, exhibit anticarcinogenic activity.

The omega-3 and omega-6 polyunsaturated fatty acids (PUFA) emulsions have been used in the treatment of different clinical disorders (Zadak & Cervinkova, 1997). However, studies on the oxidative stability of borage and evening primrose oils have been limited. Therefore, the aim of this work was to examine the impact of minor components, including chlorophylls in borage and evening primrose oils on their photooxidative stability. To achieve this, stabilities of stripped and non-stripped borage and evening primrose oils and their emulsions in water under fluorescent light were examined.

2. Materials and methods

2.1. Materials

Cold-pressed borage oil was obtained from Bioriginal Food & Science Co. (Saskatoon, SK). The evening primrose oil was obtained from Scotia Pharmaceuticals (Kentville, NS) and was also prepared via cold-pressuring. Samples used were pooled from several bottles of each oil received within a week of processing. All other chemicals were of ACS grade or better.

2.2. Methods

2.2.1. Preparation of minor component-stripped oils

Borage and evening primrose oils were stripped of their minor components as described previously (Khan

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& Shahidi, 1999). A chromatographic column (3.4 cm i.d.×40 cm) was connected to a water pump and packed sequentially with four adsorbents. The bottom layer consisted of activated silicic acid (40 g); the next layers were a 1:2 (w/w) mixture of Celite 545- activated charcoal (20 g), a 1:2 (w/w) mixture of Celite 545-powdered sugar (80 g) and a top layer of activated silicic acid (40 g). Oil (100 g) was diluted with an equal volume of n-hexane and passed through the chromatographic column. The solvent in the eluent (stripped oil) was evaporated under vacuum at 30 °C and any remaining traces of solvent were removed by flushing with nitrogen. The volume of oil recovered from 100 g was approximately 80 g. Oils used in subsequent experiments were pooled samples obtained from different stripping runs.

2.2.2. Preparation of oil-in-water emulsions

Ten percent (w/v) borage and evening primrose oil-in-water emulsions were prepared as described by Frankel, Huang, Kanner, and German (1994) with modifications. Oil (5 g) was weighed into a 125 ml Pyrex flask. Then, exactly 45 ml of distilled water were added to the flask and the mixture was subsequently emulsified with 0.5 g of Tween 40. The emulsions were mixed gently for 5 min using a magnetic stirrer; flasks containing emulsions were then sonicated at maximum power for 25 min in an ultrasonic Sonicator, Model 6 QT (NEYO, Yucaipa, CA) filled with crushed ice.

2.2.3. Preparation of samples for accelerated photooxidation tests

Stripped and non-stripped oil samples (5 g in 25 ml flasks) and oil-in-water emulsions (50 g in 125 ml flasks) were used to study their stability under intense fluorescent light. The samples were placed in a box (70 cm length × 35 cm width × 25 cm height) equipped with two 40 W cool white fluorescent lights which were suspended approximately 10 cm above the surface of the oil containers. The remaining open space was covered with aluminium foil. The fluorescent radiation was at a level of 2650 Lux and the temperature inside the container was maintained at 27±1 °C. Oil and emulsion samples were removed from the box after 12, 24, 48 and 72 h for stability tests.

2.2.4. Oxidative stability tests

The oxidative stabilities of stripped and non-stripped oil and oil-in-water emulsions were evaluated by determining peroxide value (PV) (AOCS, 1990, method Cd-8-35), and hexanal content, as described by a gas chromatography-headspace analysis according to Shahidi, Amarowicz, Abou-Gharbia, and Shehata (1997). Prior to oxidative stability tests, except for headspace analysis, the oil was extracted from the emulsion (50 g) by adding 50 ml methanol and 50 ml hexane in a 250 ml Pyrex separatory funnel (Frankel et al., 1994).

2.2.5. Chemical and instrumental analyses

Fatty acid compositions of the oils were determined following transmethylation and subsequent gas chromatographic analysis of fatty acid methyl esters, according to the method described by Wanasundara and Shahidi (1997). The absorbance of the pigments present in the stripped and non-stripped oil samples was measured for carotenoids and chlorophylls and their derivatives (Blekas, Tsimidou, & Boskou, 1995). Oil samples (3 ml) were transferred into Hellma glass cells and the absorbance was read using a Hewlett-Packard 8452A diode array spectrophotometer (Palo Alto, CA). Furthermore, the absorption spectra were recorded between 430 and 710 nm. Olive oil, which contains carotenoids and chlorophylls, was used as a reference. Tocopherol contents in the stripped and non-stripped oils were determined according to the high performance liquid chromatography procedure described by Shahidi et al. (1997).

2.2.6. Statistical analysis

All experiments and/or the measurements were replicated three times. Mean±standard deviation was reported for each case. Analysis of variance and Tukeys' studentized test were performed at a level of $P<0.05$ to evaluate the significance of differences between mean values. Data presented as percentages were transformed, prior to statistical analysis, using the following formula: transformed $x = \arcsin\sqrt{x/100}$

3. Results and discussion

3.1. Chemical characteristics of stripped and non-stripped borage and evening primrose oils

Chemical characteristics and fatty acid composition of stripped and non-stripped borage oils are presented in Table 1. Non-stripped borage oil (NBO) was stripped from its minor components effectively, using a modified multi-layer column chromatographic technique. No peroxides, conjugated dienes, hexanal, pigments, tocopherols, phospholipids or glycolipids were detected in the stripped borage oil (SBO). However, some primary and secondary oxidation products, as well as γ-tocopherol (84 ppm), were retained in the stripped evening primrose oil (SEPO). Similar difficulties were experienced by Lampi, Hpoia, Ekholm, and Piironen (1992) in removing all of the γ-tocopherol from vegetable oils, when present at more than 300 ppm, using a similar technique. Moreover, Finnish rapeseed oil, stripped by this procedure, showed a reduction in its γ-tocopherol content from 700 to 24 ppm (Lampi, Piironen, Hopia, & Koivistoinen, 1997). EPO contained higher amounts of primary and secondary products which may interfere with the stripping process. Thus, the use of small

Table 1
Chemical characteristics and fatty acid composition of non-stripped and stripped borage and evening primrose oils[a]

Characteristic		Borage oil		Evening primrose oil	
		Non-stripped	Stripped	Non-stripped	Stripped
Oxidative status	Peroxide value (meq/kg)	1.65±0.27[c]	0[a]	3.16±0.11[d]	1.0±0.23[b]
	Hexanal (mg/kg)	1.92±0.06[b]	0[a]	4.14±0.11[c]	0[a]
Tocopherols[b] (mg/kg)	α	0[a]	0[a]	16[b]	0[a]
	δ	52[b]	0[a]	0[a]	0[a]
	γ	659[d]	0[a]	335[c]	84[b]
	Total	711[a]	0[a]	341[c]	84[b]
Pigments absorbance	430 nm	0.07±0[c]	0[a]	0.62±0.01[d]	0.01±0[b]
Fatty acid composition (%)	16:0	11.3±0.09[b]	11.0±0.77[b]	6.77±0.33[a]	6.54±0.29[a]
	18:0	4.00±0.21[b]	4.28±0.13[b]	1.84±0.11[a]	1.80±0.01[a]
	18:1	16.9±0.42[b]	16.5±0.13[b]	8.67±0.28[a]	8.31±0.71[a]
	18:2	36.3±1.33[a]	37.0±0.11[a]	73.6±1.81[b]	75.8±0.27[b]
	18:3 ω6	22.1±0.92[c]	22.3±1.26[c]	9.16±0.58[b]	7.6±0.75[a]
	20:1	4.58±0.03[a]	4.68±0.02[a]	–	–
	22:1	2.85±0.05[a]	2.59±0.01[a]	–	–
	24:1	1.85±0.07[a]	1.67±0.01[a]	–	–
	PUFA	58.4±0.29[a]	59.2±0.81[a]	82.7±0.39[b]	83.4±0.81[b]

[a] Values are means of three determinations±standard deviations. Values with different letters in each row are different ($P<0.05$) from one another. Values equal to zero are those below their detection limits (approximately 0.1 meq/kg for peroxide values, 0.001 mg/kg for hexanal, 1–2 mg/kg, for tocopherols and 0.0001 for absorbance of pigments).
[b] Average of duplicate analysis.

Table 2
Peroxide values (meq/kg) of stripped and non-stripped borage and evening primrose oil and emulsion systems[a]

System	Oxidation time (h)				
	0	12	24	48	72
SBO	0a	4.1±0.19a	10.3±0.24a	11.6±0.03a	23.3±0.06a
NBO	1.65±0.27d	15.1±1.29c	19.4±0.85c	28.3±0.11e	29.2±1.52c
SBE	0a	4.41±0.05b	10.4±0.04a	19.5±1.09b	30.5±1.91c
NBE	1.65±0.27d	15.0±0.0c	22.8±2.49d	30.8±1.07f	26.2±1.36b
SEPO	1.0±0.23c	19.3±0.28e	15.0±1.85b	24.0±0.08c	28.8±0.32e
NEPO	0.33±0.17b	16.6±0.65d	41.4±1.62f	39.4±0.03g	52.9±2.79d
SEPE	0.98±0.06c	18.9±0.04e	25.5±0.02e	26.0±1.25d	57.1±1.46e
NEPE	3.16±0.11e	38.2±1.53f	91.9±4.33g	133.5±5.38h	164±4.87f

[a] Values are means of three determinations±standard deviations. Values followed by different letters in each column are different ($P<0.05$) from one another. Abbreviations are: SBO, stripped borage oil; NBO, non-stripped borage oil; SBE, stripped borage oil emulsion; NBE, non-stripped borage oil emulsion, SEPO, stripped evening primrose oil; NEPO, non stripped evening primrose oil; SEPO, stripped evening primrose oil emulsion; NEPE, non stripped evening primrose oil emulsion.

amounts of EPO might provide a useful means of improving the efficiency of removal of minor components. Distillation and/or short path fractionation techniques, prior to column chromatography, might also prove beneficial when stripping the oils. The main tocopherol classes, as determined by high performance liquid chromatography (HPLC), in NBO were 52 ppm of δ- and 659 ppm of γ-tocopherols, while NEPO contained only 16 ppm of α- and 335 ppm of γ-tocopherols. Thus, NBO had higher amounts ($P<0.05$) of total tocopherols than NEPO.

Pigments, such as carotenoids, with absorbances between 430 and 460 nm, and chlorophylls, which absorb light between 400 and 500 nm and again between 600 and 710 nm (Blekas et al., 1995), were significantly ($P<0.05$) higher in NEPO than NBO. According to Sensidoni, Bortolussi, Orlando, and Fantozzi (1996), borage oil contains 0.8–3.3 ppm of chlorophylls.

Non-stripped evening primrose oils (NEPO) contained higher amounts ($P<0.05$) of PUFA than stripped and non-stripped borage oils. The main PUFA in both oils was linoleic acid which constituted more than 70% of the stripped and non-stripped evening primrose oils, but was present only at 36% in stripped and non-stripped borage oils. Borage oil had up to 22% of γ-linolenic acid (18:3 ω6) while evening primrose oil contained only 8–9% of it.

3.2. Photooxidative stability

The peroxide values (PV) of stripped and non-stripped borage and evening primrose oils and their oil-in-water emulsions under fluorescent light are presented in Table 2. Since the oils were obtained from two different suppliers, the initial qualities, as reflected in their PV and hexanal contents were somewhat different. Meanwhile, stripping conditions of the oils and the subsequent oxidative stability test performed on them, were identical. Thus minor residual effects for initial differences in oil quality cannot be discounted. Photooxidation of NBO and NBE, in the initial stages, progressed rapidly compared to that of SBO and SBE. Thereafter, the photooxidation, as reflected in PV, progressed gradually for NBO and NBE. The PV of SBO and SBE were lower ($P<0.05$) than those of their corresponding non-stripped counterparts. Therefore, NBO and NBE are more susceptible to photooxidation than their stripped counterparts. Both NEPO and NEPE were more ($P<0.05$) susceptible to photooxidation than SEPO and SEPE. This may be explained when considering the presence of photosensitizing pigments, mainly chlorophylls, in non-stripped borage oil. The visible spectra of pigments in non-stripped and stripped olive, borage and evening primrose oils are presented in Fig. 1. It is well documented that olive oil contains naturally-occurring pigments, such as chlorophylls and pheophytins, as well as carotenoids (Rahmani & Csallany, 1991; Salvador, Aranda, & Fregapane, 1998). The characteristic absorbance peaks, occurring below 500 nm, correspond to carotenoids with a contribution from chlorophylls, while the absorbance peaks beyond this wavelength correspond characteristically to different types of chlorophylls. Thus, the latter peaks confirm the presence of chlorophylls in non-stripped olive, borage and evening primrose oils. Meanwhile, NEPO appeared to contain more pigments than NBO. It has been reported that edible oils containing natural pigments, such as chlorophylls and pheophytins, are highly susceptible to light-induced oxidation (Hall & Cuppett, 1993; Lee, Jung, & Kim, 1997). The presence of higher levels of chlorophylls and linoleic acid, as well as lower amounts of tocopherols in evening primrose oil and its emulsion in water, than in in borage oil and its emulsion made them more susceptible to photooxidation when compared to NBO and NBE. The NEPO contained only 16 ppm of α- and 335 ppm of γ-tocopherols compared to 659 ppm of γ- and 52 ppm of δ-tocopherols in NBO. Jung, Choe, and Min (1991) have reported that α-, γ-, and δ-tocopherols reduce the photooxidation of soybean oil. Moreover, Kamal-Eldin and Appelqvist (1996) have reported that the quenching efficiency of tocopherols for singlet oxygen was in the decreasing order of α- > β- > γ- > δ-. However, γ- and δ-tocopherols may prove to be more effective than α-tocopherol during the latter stages of photooxidation due to their higher resistance to destruction by singlet oxygen. Meanwhile, pigments that act as initiators of photooxidation in edible oils may be destroyed by light (Kiristsakis & Dugan, 1985) and this might explain the decrease of PV of NBE during the latter stages of photooxidation.

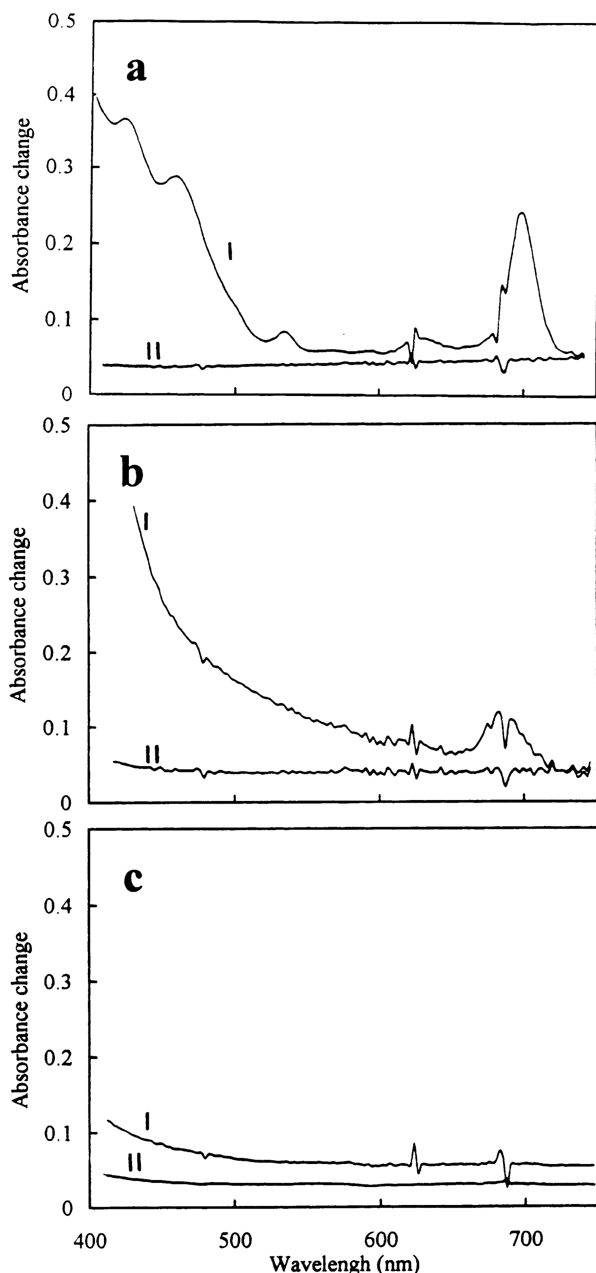

Fig. 1. Visible spectra of pigments in oil/hexane (1:1, v/v) of non-stripped (I) and stripped (II) olive, (a); evening primrose, (b); and borage, (c) oils. (Peaks between 400 and 500 nm represent carotenoids with a contribution from chlorophylls while peaks from 500 to 700 nm represent chlorophylls only.).

Photosensitizers such as chlorophylls, absorb light and transform to an excited state, which in turn might convert them to a less stable triplet state sensitizer. The sensitizer can transfer its energy to the most stable triplet

state oxygen, thus converting it to a higher energy level, singlet oxygen, that would then attack the double bonds in unsaturated fatty acids. The primary products of photooxidation, namely hydroperoxide, are subsequently decomposed to off-flavour volatiles (Warner & Frankel, 1987; Jung et al., 1991). The role of photosensitizer in light-induced oxidation has also been demonstrated in non-stripped borage and evening primrose oil-in-water emulsions. The PV of NEPE were higher ($P < 0.05$) than those of NBE (Table 1).

The endogenous pigments were substantially removed from the stripped borage oil and therefore the photooxidation was not affected to the same degree. The gradual increase in PV of SBO and SBE can be attributed to free radical chain reactions that occur at room temperature. Meanwhile, residual pigments in SEPO and SEPE may be responsible for the rapid increase in PV during the earlier stages of storage under fluorescent lighting.

The emulsions prepared (average droplet size 0.1 μm) and stored at 27 °C under fluorescent light for 72 h were

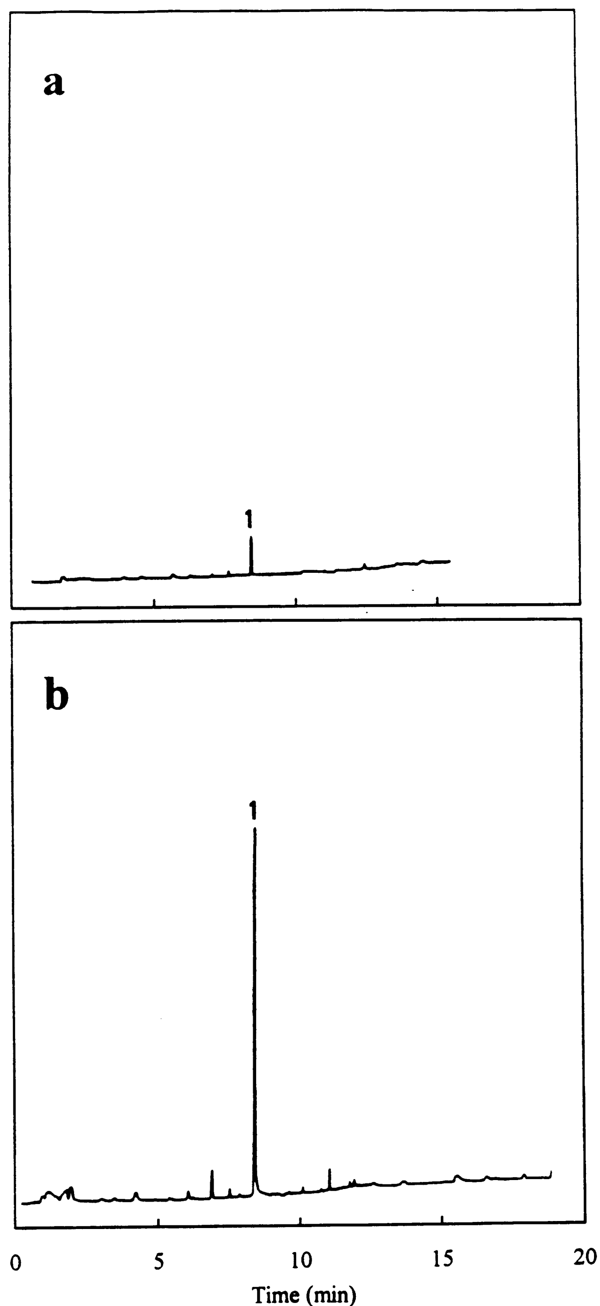

Fig. 2. Gas chromatogram of headspace volatiles of stripped (a) and non-stripped (b) borage oil illuminated with fluorescent light at 27 °C for 72 h. Peak (1), hexanal.

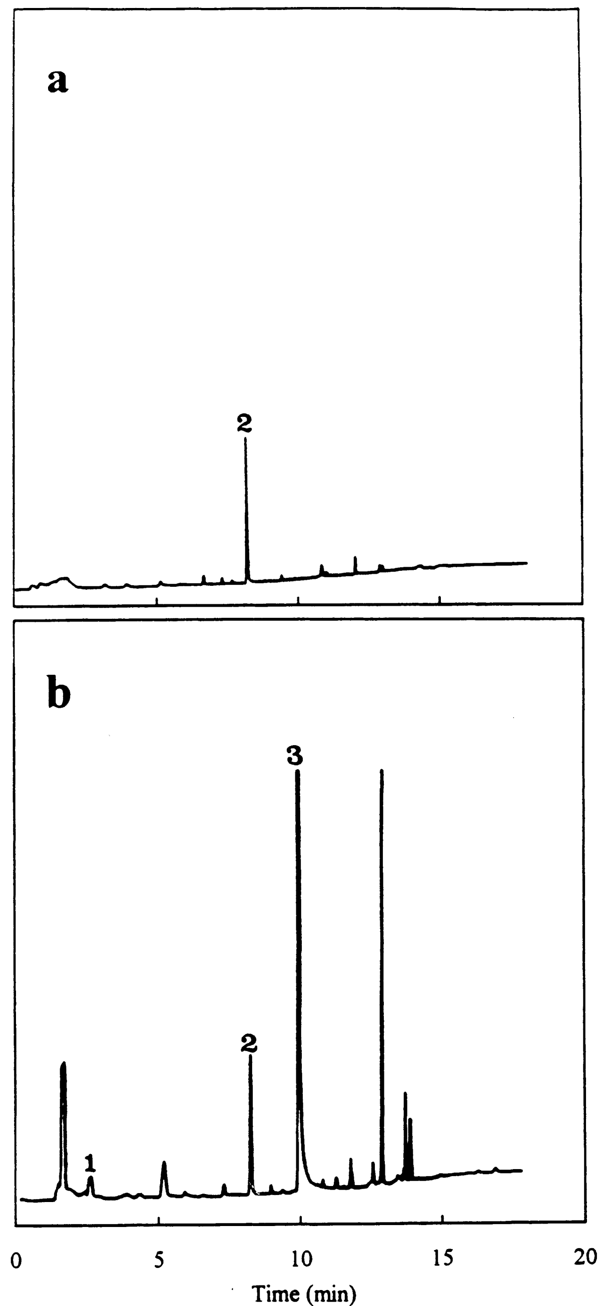

Fig. 3. Gas chromatogram of headspace volatiles of stripped (a) and non-stripped (b) evening primrose oils illuminated under fluorescent light at 27 °C for 72 h. Peaks (1), pentanal; (2), hexanal; (3) 2-heptenal.

Table 3
Hexanal content (mg/kg) of stripped and non-stripped borage and evening primrose oil and emulsion systems[a]

System	Oxidation time (h)				
	0	12	24	48	72
SBO	0a	0a	0a	0.9±0.03a	1.09±0.22a
NBO	0.16±0.06c	1.28±0.08b	1.91±0.08c	3.47±0.28b	4.34±0.21b
SBE	0a	1.47±0.03c	1.5±0.07b	7.59±0.85c	44.9±0.14c
NBE	0.09±0.04d	2.52±0.03f	4.46±0.04c	13.0±0.07d	55.1±2.19e
SEPO	0c	1.58±0.12d	3.23±0.04d	3.59±0.08b	4.6±0.01b
NEPO	0.41±0.11d	2.31±0.2e	8.29±0.01f	13.5±0.57e	79.4±2.11f
SEPE	0c	3.73±0.22g	10.1±0.04g	17.0±1.46f	51.2±9.79d
NEPE	0.14±0.01c	9.96±0.29h	15.0±0.41h	70.6±0.02g	129.5±1.09g

[a] Values are means of three determinations±standard deviations. Values followed by different letters in each column are different ($P<0.05$) from one another. Abbreviations are: SBO, stripped borage oil; NBO, non-stripped borage oil; SBE, stripped borage oil emulsion; NBE, non-stripped borage oil emulsion, SEPO, stripped evening primrose oil; NEPO, non stripped evening primrose oil; SEPO, stripped evening primrose oil emulsion; NEPE, non stripped evening primrose oil emulsion.

physically stable. No creaming, flocculation, coalescence or oil separation was observed in the emulsions examined. These criteria may be used as indicators of emulsion stability (Roedig-Penman & Gordon, 1997). The peroxide values of NBO and NEPO were lower ($P<0.05$) than those of NBE and NEPE, respectively. Therefore, NBO and NEPO, are more stable than their corresponding oil-in-water emulsions (Table 2). These results appear to be in contrast with the polar paradox theory proposed by Porter, Black, and Drolet (1989) for autooxidation of oils, if only the presence of tocopherols is considered. According to this theory, the non-polar lipophilic antioxidants, such as tocopherols, are sufficiently surface-active to be oriented at the oil–water interface in oil-in-water emulsions and thus form a protective membrane around oil droplets. Therefore, free radicals, which are generated in the aqueous phase, will be prevented from crossing the emulsion droplet membrane and oxidizing the oil in the interior of the droplet (Coupland & McClements, 1996). Meanwhile, the polar antioxidants, such as ascorbic and carnosoic acids, both water-soluble natural antioxidants, will be markedly diluted by moving to the water phase and therefore being less effective in preventing the oil oxidation (Frankel, 1996; Huang, Frankel, & German, 1996). The opposite trend was observed in bulk oil systems. In this dry system, the lipophilic antioxidants will remain in the oil, while the hydrophilic antioxidants will be oriented in air–oil interface, thus being more effective in reducing or preventing oxygen accessibility for oil oxidation (Huang et al., 1996). Although the polar paradox theory was originally proposed for autooxidation of food lipids, its potential use in explaining photooxidative changes in fats and oils, which follow a different mechanism, has not been explored. Based on this theory, it may be expected that NBE and NEPE should be more stable than their corresponding bulk oil samples, due to the presence of tocopherols. However, the reverse trend was observed. The most likely explanation for this observation is that the droplets of the emulsions have taken a configuration that is more susceptible to photooxidation than the bulk oil (Miyashita, Hirao, Nara, & Ota, 1995), as explained for marine and soybean oils, or that the effect of photosensitizers overwhelmed the effects exerted by the hydrophobicity/hydrophilicity of the antioxidants involved.

The primary hydroperoxides generated in photooxidation of unsaturated fatty acids are decomposed to volatiles, which in turn have detrimental effects on flavour stability of edible oils (Shahidi & Wanasundara, 1998). The major volatile detected, using headspace gas chromatographic analysis of photooxidized stripped and non-stripped borage (Fig. 2) and evening primrose oils and emulsions (Fig. 3), was hexanal, which has been shown to cause undesirable flavour effects in lipids (Shahidi & Wanasundara, 1998). The compound 2-heptenal was also detected as another major volatile in non-stripped evening primrose oil and its emulsions in water. Hexanal and 2-heptenal may be formed via photooxidation of linoleic acid (the major fatty acid in borage and evening primrose oil), which initially gives 4 isomers, 2 conjugated 9- and 13-diene hydroperoxides and 2-unconjugated 10- and 12- diene hydroperoxides, which in turn may be converted to alkoxy radicals. Carbon–carbon cleavage on either side of this radical can produce different types of aldehydes (Frankel, 1984). Hexanal, a dominant aldehyde, can also be formed via the oxidation of γ-linolenic acid. The hexanal content of all samples kept under light increased gradually throughout the storage period (72 h). Based on hexanal contents (Table 3), NEPO and NEPE, as well as NBO and NBE, were more ($P<0.05$) susceptible to photooxidation than SEPO and SEPE as well as SBO and SBE. Meanwhile, NEPO and NEPE were more ($P<0.05$) susceptible to photooxidation than NBO and NBE. This trend is similar to that observed for PV.

4. Conclusions

Minor constituents of borage and evening primrose oils had a considerable effect on their photooxidative stability. The effects were primarily dictated by the chlorophylls present which overwhelmed the influence of antioxidative tocopherols and carotenoids. Similar effects were operative in both bulk and oil-in-water emulsion systems.

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