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Quality Evaluation and Discrimination of Flavouring Process of Garlic Flavoured Vegetable Oils

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ABSTRACT

In this study, the effects of two garlic flavouring processes on quality parameters and the organosulphur compound profile were investigated. The results showed that the addition of fresh garlic increased acidity and peroxide values in all flavoured vegetable oils. Mono-, di- and trisulphides were mainly present in aromatized oils, while allicin, ajoene and vinyldithiins were found in macerated oils. Analyses of the principal components demonstrate that flavoured oils could be discriminated according to the flavouring processes. The experiments carried out in this study would allow one to predict the results of a flavouring procedure on an unknown sample and, consequently, its potential beneficial effects.

KEYWORDS: garlic, flavouring process, flavoured vegetable oil, quality parameters, organosulphur compounds

Running title: Quality properties of garlic flavoured oils

INTRODUCTION

Currently, consumers are increasingly concerned about the quality attributes of food products. They are even willing to pay a higher price when quality is guaranteed. The requirements for quality in food include sensorial attributes as well as chemical, physical and microbiological characteristics. In addition, the concept of quality is expanding and also includes aspects related to the influence nutrition and human health. Consequently, the market is turning toward diversification from traditional products. Among the possibilities for new products and development, there is a branch focused on the introduction of gourmet products. Flavoured oils are a good example. A flavoured oil can be defined as oil

that has been processed with vegetables, herbs or fruits to improve nutritional value, enrich sensory characteristics and increase shelf life (1). The assortment is wide, since it is possible to choose among different vegetable oils (olive, soybean, canola, sunflower and corn oils) with the addition of different aromatic ingredients. There is extensive literature on the flavouring of olive, canola, sunflower and corn oils with different aromatic ingredients (2, 3, 4, 5). Two main types of flavouring processes have been recognized. The first consists of the infusion or maceration of aromatic ingredients with oil, where the mixture is left at room temperature for a defined time and is subjected to periodic shaking (6). The alternative to this method is the use of essential oils or vegetable extracts as flavouring agents (1, 3, 7).

The present work focused on the study of oils flavoured with garlic due to the particular characteristics of this ingredient. Garlic (*Allium sativum* L.) has long been used as a food seasoning and a medicinal agent (8). Diverse biological activities, including anticarcinogenic, antiatherosclerotic, antithrombotic, antimicrobial, antiinflammatory and antioxidant effects, are usually assigned to its constituents (9). The organosulphur compounds (OSCs) are responsible for the characteristic flavour and the physiological activities of garlic mentioned above (10). These compounds include allicin, which represents 70-80% of the thiosulfinate (TS) in garlic. Allicin is a reactive molecule and can undergo a number of transformations depending on the temperature, pH and polarity of the medium (11, 12). Those variables could lead to the formation of sulphides (diallyl, methyl allyl, and diethyl mono-, di-, tri-, tetra-, penta- and hexasulphides), the vinyldithiins, and (E)- and (Z)-ajoene.

In recent years, garlic-derived products and health pharmaceutical preparations have become popular and are widely available on the market. Regarding their OSC profiles, the therapeutical products have been well documented (11-13), while edible preparations have not been sufficiently studied. Given that OSCs are responsible for different biological activities, it seems necessary to explore them. Thus, a reliable analytical methodology should be used (14). Garlic flavoured oils are considered a product that satisfies the consumer's preferences due to both their sensorial and health-related properties (7). Indeed, there are different ways to flavour oil, and the chosen method can affect the quality of the resulting flavoured oil (2).

Few studies evaluated the effects of the garlic flavouring processes on OSCs (14, 15). Moreover, to our knowledge, there are no reports about the influence of flavouring processes on the quality of garlic flavoured oils, considering both aromatization process and vegetable oil used. The purpose of this study is to evaluate these subjects in depth. The aim of this study was to evaluate the effects of two garlic flavouring processes on both quality parameters and bioactive compounds profiles. In the present study, garlic flavoured oils were prepared following an experimental design considering two factors, aromatization processes and vegetable oil, with three and two levels, respectively, to reveal differences in quality parameters. In addition, a comparison was made by studying the same variables on flavoured oils acquired from the local market. To our knowledge, this is the first report about the influences of aromatization process on OSC profiles and consequently on the potential health beneficial effects

MATERIALS AND METHODS

Reagents

Garlic Oil Blend (DAS 5-13%; DADS 30-50% and DATS 10-13%) and two sulphides, diallyl sulphide (DAS, 97%) and diallyl disulphide (DADS, 80%), were purchased from Sigma Aldrich (Buenos Aires, Argentina). Diallyl trisulphide (DATS, 98%) was acquired from LKT Laboratories, Inc. (St. Paul, MN, United States). Allicin was synthesized as previously reported by our group (16). Ajoene and vinyldithiin isomers were synthesized as previously described (3, 17). UV and mass spectra of all synthesized OSCs were determined as previously described (14). Chromatography grade acetonitrile (ACN), methanol (MeOH), acetone, hexane, isopropanol and dichloromethane (DCM) were purchased from Merck (NY, United States). Ultrapure water (18 MΩcm) was obtained from a Milli-Q water purification system (Millipore, France). Sodium hydroxide, acetic acid, chloroform, potassium iodine, distilled water, sodium thiosulphate, starch solution, ethyl alcohol, diethyl ether, and phenolphthalein, the chemical and reagents used to determine peroxide and acidity values, were of analytical grade and purchased from local laboratories.

Samples

All flavoured oils were prepared in triplicate. Vegetable oils of canola, sunflower and olive without garlic were used as blank oil samples. Aromatized oils (AO) were prepared by the direct addition of 200 ppm Garlic Oil Blend to canola, sunflower and olive oils (18). The samples were homogenized, placed in closed amber glass bottles and stored for 4 days

until analysis. Macerated oils (MO) were prepared following the method from Iberl et al. (11). Fresh garlic cloves (Rubi INTA cultivar) were crushed and left standing for 30 min in order to promote allicin formation. Then, 2.5 g of this crushed garlic was added per 10 mL of canola, sunflower and olive oil. Then, the samples were homogenized, placed in closed amber glass bottles and stored at room temperature for 9 days. After that, the oils were filtered and analysed. Commercial garlic-flavoured oils available locally were purchased.

Determination of quality parameters

Peroxide Value (PV) was determined using the AOAC 965.33 method (19). The results were expressed in meq O_2 kg^{-1} vegetable oil. Acidity Value (AV) was determined, in triplicate, by the AOAC 969.17 titration method (19). The results were expressed as g oleic acid g^{-1} vegetable oil. CIELab coordinates (L, a and b) were read directly with a Minolta Colourimeter. In this coordinate system, the 'L' value is the measure of lightness, ranging from 0 (black) to 100 (white), the 'a' value ranges from -a (greenness) to +a (redness) and the 'b' value ranges from -b (blueness) to +b (yellowness). Total colour difference (ΔE) was calculated by:

$$\Delta E = \left[(L - L_{(blank\ oil\ sample)})^2 + (a - a_{(blank\ oil\ sample)})^2 + (b - b_{(blank\ oil\ sample)})^2\right]^{0.5}$$

where blank oil sample refers to canola, sunflower or olive oil without garlic.

Determination of OSC profiles

Sample Extraction: the OSCs were quantitatively extracted from flavoured oil with 2 mL acetonitrile per 2 g of sample (12). The resulting extract was centrifuged at 14000 rpm fr 5 min, and the acetonitrile layer was filtered through a 0.22-µm nylon membrane before injection. Operating conditions for HPLC: this analysis was performed as previously described (11). A Konik KNK-500-series liquid chromatograph coupled with a UV-Vis 200 detector (scan wavelength 190-380 nm) was used (Konik, Barcelona, Spain). The chromatography was achieved by an isocratic elution on a Waters Spherisorb ODS2 column (250 mm x 4.6 mm, 5 µm). The mobile phase consisted of acetonitrile:water:methanol (50:41:9 v/v/v). The flow rate was 1 mL min^{-1}, and the injection volume 10 µL. The detector was adjusted to 254 nm. The data were collected and processed by EZChrom Chromatography Data System Version 6.8 software. Peak identification of OSCs was done by comparing retention times with reference standards. The samples were tested in triplicate, and each was injected in duplicate.

Statistical analysis

The results were expressed as the mean ± standard deviation (SD) and subjected to analysis of variance (ANOVA), Tukey's HSD test and Analysis of Principal Component (PCA) using the commercially available software Infostat version 2012e. A P value < 0.05 was considered significant.

RESULTS AND DISCUSSION

Effects of aromatization processes on the quality parameters of prepared flavoured garlic oils

Table 1 shows the effects of flavouring processes on the quality parameters of different vegetable oils flavoured with garlic. To evaluate the effect of flavouring processes on the quality parameters, new indices were determined (ΔPV, ΔAV, ΔL, Δa, Δb). Each of them was obtained from the subtraction between indices obtained of the values of control oils minus those of garlic flavoured oil. The results indicated that the flavouring process significantly affected the quality parameters evaluated.

Concerning changes in acidity values (ΔAV), the addition of fresh garlic increased the AV for all the vegetable oils significantly compared with their controls ($P < 0.05$). Although AO showed an increase in AV, their values were lower than MO. Even aromatized olive oil (OAO) showed less acidity than the control olive oil. The formation of primary compounds of oxidation was determined by the PV. We found significant differences ($P < 0.05$) with olive MO and canola AO, presenting a lower variability in PV. With respect to colour parameters, the main change was observed in L values, which represent the relative lightness of oil. In general, both flavouring processes studied resulted in a decrease of lightness. The negative 'a' value is related to the greenish cast. The obtained results show that the 'a' values changed significantly during flavouring ($P <0.05$), becoming more positive in the case of canola oil and more negative in sunflower oil, which indicates that they were more reddish and greenish, respectively. In the case of the 'b' values, all oils

showed positive values, resulting a more yellowish colour compared with the blank sample oils (Table 1).

The variability observed in quality parameters agrees with previous reports. Sousa et al. (20) and Da Costa (21) explained that the rise in the AV of fresh macerates could be related to an enzymatic activity promoting lipolytic reactions in the vegetable oil or simply to the water content in fresh garlic. Our results provide evidence that the flavouring of vegetable oils through maceration with fresh garlic was detrimental to the quality parameters.

OSC profiles in flavoured oils

Table 2 shows the composition of OSCs in flavoured oils obtained following the procedures described in the Materials and Methods. Clearly, qualitative and quantitative differences were observed in the OSC profiles for both flavouring processes and for the different vegetable oils used ($P < 0.05$). Figure 1 is a comparative graph of the percentage composition of OSCs for all samples analysed. In the AO samples, only DAS, DADS and DATS were detected. Although all aromatized oils were prepared using the same concentration of garlic oil blend, the percentage compositions of OSCs found after flavouring were significantly different. As mentioned in the Materials and Methods, the garlic oil blend label indicated DADS 30-50%, DATS 10-13% and DAS 5-13%. The percentage composition of DADS in the prepared OAO was found in a range of 17 to 22%, with olive garlic oil recording the highest DADS content. DAS was present only in SAO (sunflower aromatized oil), in a similar proportion to that of the garlic oil blend. DATS

was higher than in the garlic oil blend, varying from 72 to 82%, and had the highest value observed in CAO (canola aromatized oil).

According to Lawson and Hughes (1992), a typical distilled garlic oil contains 26% DADS, 19% DATS, 3% monosulphides, 4% pentasulphides and 1% hexasulphides, while others consider it to contain mainly diallyl trisulphide (22, 23). In this work, although DADS is the major component in the garlic oil blend used, DATS turns out to be the main compound in all the aromatized vegetable oils. In contrast, the OSCs found in MO samples were allicin, ajoene, the vinyldithiins, and the sulphides DAS and DADS. It can be noted from Figure 1 that although all MOs were prepared under the same conditions, their OSC profiles were significantly different. This fact indicates a matrix effect related to the vegetable oils used. The major differences were related to the amounts of DADS, ajoene and vinyldithiins. The DADS content was very high in all macerated oils (25 to 45%), while DAS was only present in SMO (sunflower macerated oil) and OMO (olive macerated oil) in a proportion of 25%. DATS was not detected in any of the aromatized oils. Low levels of allicin were quantified in SMO (25.79%) and COM (canola macerated oil) (2.7%). Ajoene (1-10%) and 2-VD (16-70%) were also found in all the flavoured oils. The isomer 3-VD was present only in SMO (16%). These data agree with the previous knowledge of allicin transformation in non-polar mediums (11). The rate of formation of OSCs was influenced by each type of vegetable oil. The remaining allicin levels detected in SMO and CMO indicate a matrix effect of sunflower and canola oils on the rate of formation of OSCs. In those cases, the allicin transformation rate was lower than in olive oil, where allicin could not be detected. With regards to the concentrations of sulphides found, the DAS and DADS levels were similar to previous reports (4, 24).

After comparing the profiles for both flavouring procedures, it is evident that allicin-derived compounds, such as ajoene and vinyldithiins, only appear when fresh garlic is present. This is characteristic of oils flavoured by maceration. In oils flavoured using garlic oils or garlic extracts, the OSC profile is mainly characterized by the presence of sulphides, in agreement with previous reports (13). Due to the dependency of the health benefits on OSC composition, we could estimate that the compounds we found in AOs (mainly polysulphurs) can exhibit antioxidant and anti-carcinogenic effects, while MOs, according to their composition, could present hypolipidaemic and hypocholesterolaemic effects.

Commercial flavoured oils: quality parameters and OSC profile

To compare flavoured garlic oils acquired locally, they were subjected to the same analytical determinations. Table 3 presents the physicochemical characteristics of flavoured oils acquired locally. In all cases, the PV and AV were within the limits set for edible oils by the Argentine Food Code (Chapter XVI, Article 1279).

Table 4 includes the OSC profile of commercial flavoured oils. The results showed significant differences by Tukey's HDS test at $P < 0.05$. Diallyl disulphide was the only OSC present in all commercial flavoured oils analysed. Its content ranged from 10.34 ppm to 27.83 ppm (C1 and C4, respectively). DAS and DATS were found in commercial flavoured oils C1, C2, C3 and C5. DAS values fell within a broad range from 0.37 ppm to 28.75 ppm. DATS was found to be the dominant sulphide detected in all flavoured oils. Its values ranged from 28.57 ppm to 68.07 ppm. Allicin was found only in C2; none of the other oils contained this OSC, and its concentration was 14.31 ppm, representing 5% of the total OSC content.

Other OSCs detected were the products of allicin transformation, such as ajoene and vinyldithiins. Ajoene was present in all flavoured oils, except in C1. Its content varied from 1.51 ppm to 29.97 ppm. Both isomers of vinyldithiins were detected in C2 and C5, but 2-vinyldithiin was more dominant. Traces of the 3-vinyldithiin isomer, below LOQ, were identified in C2. Iberl et al. (11) reported that with maceration of garlic cloves in soybean oil, the main OSCs found were DADS, DATS and 2-VD. This profile agrees with the results found in C2, C4 and C5. Similar results were also obtained by other studies (13, 24). However, content variations were especially noticeable regarding the vinyldithiin isomers. These authors detected both isomers, with 2-VD as the main component, at a concentration ranging from 12 to 8300 ppm, while 3-VD ranged from 10 to 3800 ppm. In contrast, we found significantly lower levels of 2-VD and 3-VD in all the flavoured oils. Regarding DATS and DADS, quantitative differences were also observed. The values of both sulphides were similar to previous reports from macerated oils but significantly lower than aromatized oils. None of these authors found DAS. Variations in flavouring processes and storage time may explain the differences in composition (including ajoene, vinyldithiin and sulphide content) of commercially available garlic flavoured oils.

Commercial flavoured oils vs. prepared flavoured oils

The OSC data gathered were subjected to Principal Component Analysis (PCA) in an attempt to elucidate the relationship between OSC profiles and flavouring processes. The results yielded five principal components (PCs). The first three explained 81% of the total variability. The first PC (PC1) provided 39.9% and the second (PC2) provided 23.6%, together accounting for 63.56% of the total variance. The data structure obtained and the

model efficiency reached are shown in the graphs of scores and loadings, which were based on PC1 and PC2 (Figure 2). At a cursory glance, a clear distinction between flavoured oils becomes evident in relation to the negative and positive scores of PC1 and PC2. The group in the negative area of both PC2 and PC1 (aromatized garlic oils and C1) has a high content of DATS and lower content of DADS and DAS. In contrast, the group that stands out in the upper left quadrant, which is the positive area of PC2 and negative area of PC1, is characterized mainly by low ajoene and 3-VD content. Macerated oils seem to be very distinct from aromatized garlic oils due to the significant content of allicin decomposition products, such as ajoene, 2-VD, and aliphatic sulphides. From this analysis, we can conclude that there are two clearly distinguishable groups: oils aromatized with garlic oil, in which only sulphides are present, and oils macerated with fresh garlic, in which mostly decomposition products of allicin are present.

It should be noted that commercially flavoured oils were also incorporated into the model. Figure 2 shows the analysis of commercial flavoured oils based on the first two principal components, and from their distribution, it was possible to establish the flavouring process employed to obtain these oils. We estimate that C1 was obtained by the addition of garlic oil, whereas C2, C3, C4 and C5 were obtained through maceration.

CONCLUSION

The results obtained in this study show that different flavouring processes significantly affect the quality parameters of flavoured oils. We have also demonstrated that the quality and quantity of bioactive compounds present in vegetable oils depend on the flavouring process. The best OSC profile (regarding qualitative and quantitative compounds) was

obtained by maceration with fresh garlic. Differences in the OSC profiles allow us to distinguish between flavouring processes through PCA analysis. In addition, our work provides a conceptual framework for future studies and can be applied to discriminate garlic products obtained under different conditions.

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Figure 1. Percentage composition of OSCs found in prepared flavoured oils.

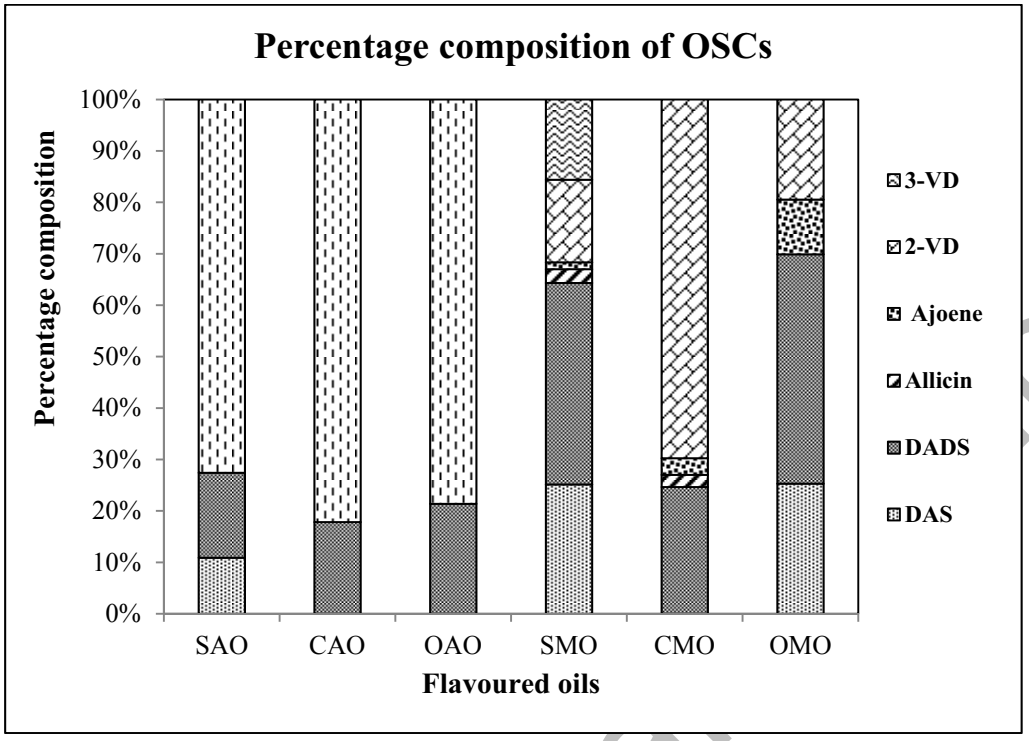

Figure 2. Graph of the principal components (PCs) belonging to the flavoured oils analysed.

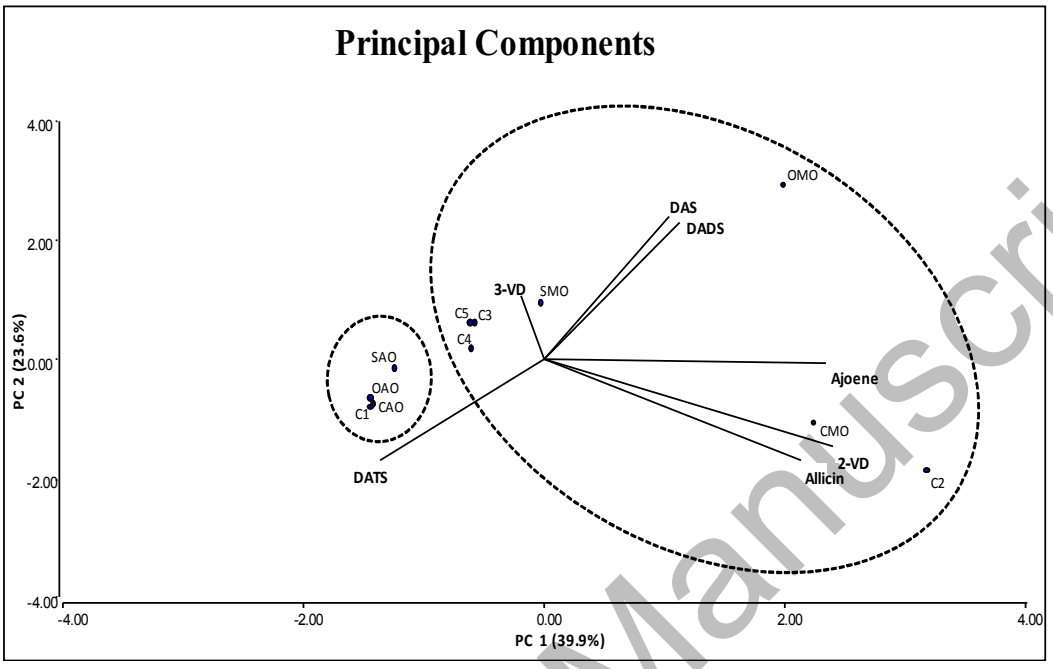

Table 1. Effects of flavouring processes on quality parameters

		Quality parameters								
		AV[c]	**ΔAV**[d]	**PV**[e]	**ΔPV**[f]	**L**[g]	**ΔL**	**a**	**Δa**	**b**	**Δb**
Canola	**CMO**[a]	2.70 ± 0.04c	1.7	14.7 ± 0.5c	12.7	24.0± 0.1c	-12.7	2.80 ± 0.01a	-0.4	13.4 ± 0.1a	-0.9
	CAO[b]	1.10 ± 0.02b	0.1	1.1 ± 0.1a	-1.0	25.2 ± 0.3ab	-1.0	3.8 ± 0.1c	0.6	16.4 ± 0.4b	2.0
	Control	1.00 ± 0.02a		2.0 ± 0.1b		26.1 ± 0.9b		3.2 ± 0.2b		14.4 ± 0.7a	
Olive	**OAM**	1.8 ± 0.1c	1.1	9.4 ± 0.4a	-0.1	23.1 ± 0.2a	-1.0	-0.04 ± 0.01a	-0.6	14.6 ± 0.3a	-1.2
	OAO	0.4 ± 0.0a	-0.2	14.10 ± 0.01b	4.8	25.30 ± 0.04b	1.4	0.2 ± 0.0b	-0.5	14.50 ± 0.03a	-1.3
	Control	0.60 ± 0.01b		9.3 ± 0.1a		24± 1a		-0.6 ± 0.1c		15.9 ± 0.7b	
Sunflower	**SMO**	1.30 ± 0.07b	1.3	16.7 ± 0.1c	15.0	28.4 ± 0.04a	-6.1	-0.40 ± 0.01a	-0.2	5.60 ± 0.04a	0.2
	SAO	0.1 ± 0.0a	0.05	3.0 ± 0.2b	1.3	30 ± 1a	-5.3	-0.9 ±	0.3	6.9 ± 0.5b	1.4

Control	0.1 ± 0.0a	1.7 ± 0.7a	34.5 ± 0.4b	0.1b -0.6 ± 0.0a	5.5 ± 0.1a

Values are mean ± standard deviation within each column followed by different letters that denote significant differences ($P < 0.05$), according to Tukey's test.

[a]MO: macerated oil

[b]AO: aromatized oil

[c]AV: acidity values expressed as g oleic acid g^{-1}.

[d]ΔAV: delta acidity value difference.

[e]PV: peroxide values expressed in meq O_2 kg^{-1}.

[f]ΔPV: delta peroxide value difference.

[g]Colour: L: lightness; 'a': redness to greenness; 'b': yellowness to blueness.

Table 2. OSC profiles of prepared flavoured oils

OSCs[a]	Macerated oils			Aromatized oils		
(µg/g)	**Canola**	**Olive**	**Sunflower**	**Canola**	**Olive**	**Sunflower**
DAS	nd	46.5 ± 0.2b	17 ± 4a	nd	nd	18 ± 1a
DADS	46 ± 1b	82 ± 2c	25.8 ± 0.2a	19.5 ± 0.1a	31.8 ± 0.6c	26.7 ± 0.1bc
DATS	nd	nd	nd	90 ± 3a	117 ± 3b	117 ± 3b
Allicin	4 ± 3a	nd	1.7 ± 0.2a	nd	nd	nd
Ajoene	6 ± 2b	20 ± 3c	0.90 ± 0.02a	nd	nd	nd
2-VD	131 ± 10c	35.8 ± 0.5b	10.60 ± 0.02a	nd	nd	nd
3-VD	nd	nd	10 ± 1	nd	nd	nd

Values are mean ± standard deviation within each column followed by different letters that denote significant differences ($P < 0.05$), according to Tukey's test

[a]OSCs: DAS: diallyl sulphide; DADS: diallyl disulphide; DATS: diallyl trisulphide; 2-VD and 3-VD: isomers of vinyldithiins. nd: not detected (LOD/LOQ: DAS = 2.02/11.09; DADS = 0.01/4.51; Allicin = 1.38/4.44; E/Z ajoene = 0.01/0.62; 2-VD = 3.16/6.03).

Table 3. Physicochemical analysis of commercial flavoured garlic oils

	PV[d]	AV[e]	Colour[f]		
			L	a	b
C1[a]	2.8 ± 0.1b	0.40 ± 0.01a,b,c	34.1 ± 0.2b,c	-0.9 ± 0.1a,b,c	5.9 ± 0.1a
C2[a]	2.7 ± 0.6b	0.2 ± 0.0a,b	35.6 ± 0.2c	-0.50 ± 0.03b,c	7.1 ± 0.1b
C3[b]	0.7 ± 0.1a	1.40 ± 0.01c	29.5 ± 0.1a,b	0.80 ± 0.03c	19.4 ± 0.2d
C4[c]	1.5 ± 0.3a	0.5 ± 0.0b,c	30.2 ± 0.9a,b,c	-1.4 ± 0.1a	8.2 ± 0.4c
C5[c]	2.40 ± 0.03b	0.10 ± 0.02a	26.6 ± 0.3a	-1.10 ± 0.03a,b	19.6 ± 0.4d

Values are mean ± standard deviation within each column followed by different letters that denote significant differences (P< 0.05), according to Tukey's test.

[a]C1 and C2: commercial flavoured sunflower oils

[b]C3: commercial aromatized canola oils

[c]C4 and C5: commercial aromatized olive oils.

[d]PV: peroxide values expressed in meq O_2 kg^{-1}

[e]AV: acidity values expressed as g oleic acid g^{-1}

[f]Colour: L: lightness; 'a': redness to greenness; 'b': yellowness to blueness

Table 4. OSC profiles of commercial flavoured oils

	OSCs (µg/g)						
	DAS[b]	**DADS**	**DATS**	**Allicin**	**Ajoene**	**2-VD**	**3-VD**
C1[a]	4 ± 1b	10 ± 2a	29 ± 8a	nd	nd	nd	nd
C2	16.0 ± 0.2c	19 ± 5b	68 ± 3b	14.3 ± 0.8	30 ± 1b	154 ± 7b	traces
C3	29 ± 3d	14.2 ± 0.1a,b	28.9 ± 0.5a	nd	1.5 ± 0.6a	nd	nd
C4	nd	28 ± 5c	nd	nd	2.70 ± 0.01a	nd	nd
C5	0.37 ± 0.05a	12 ± 4a,b	66.6 ± 0.3b	nd	2.4 ± 0.2a	22 ± 2a	7 ± 2

Values are mean ± standard deviation within each column followed by different letters that denote significant differences ($P < 0.05$), according to Tukey's test

[a]Commercial flavoured oils: C1 and C2: commercial flavoured sunflower oils; C3: commercial flavoured canola oil; C4 and C5: commercial flavoured olive oils

[b]OSCs: DAS: diallyl sulphide; DADS: diallyl disulphide; DATS: diallyl trisulphide; 2-VD and 3-VD: isomers of vinyldithiins. nd: not detected (LOD/LOQ: DAS = 2.02/11.09; DADS = 0.01/4.51; Allicin = 1.38/4.44; E/Z ajoene = 0.01/0.62; 2-VD = 3.16/6.03).