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QUALITY CHARACTERISTIC ANDVOLATILES OF COOKIES AS AFFECTED BY ADDITION OF SOY PROTEIN ISOLATE.

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ABSTRACT

The effectiveness of replacing different concentrations of soy protein isolate (SPI) on improving the overall quality of cookies was evaluated. The cookies were prepared by replacing wheatflour with 5, 10, 15 and 20% SPI. The chemical composition and sensory characteristics of these products were studied during storage for three months. The volatiles of each cookie sample were isolated and subjected to gas chromatography – mass spectrometry (GC – MS) analysis. Results showed that addition of SPI caused an increase in moisture and protein content and a decrease in fat and carbohydrates, while the energy level was in the required range.

Sensory evaluation showed insignificant differences ($P > 0.05$) in colour among all cookies whereas the other sensory qualities showed significant ($P < 0.05$) increase up to 10% SPI fortification. The GC – MS analysis revealed qualitative and quantitative variations among the cookie samples. The Maillard reaction products increased as the level of SPI increased. The lipid derived products showed a remarkable increase after storage for 3 months in all cookies, however, their increased ratios decreased with increasing SPI level. Fortification with 10% SPI produces the most preferred cookies that comprised the highest yield of the volatiles responsible for the pleasant cookies aroma.

Keywords: Cookies, volatiles, sensory evaluation, and soy protein isolate.

INTRODUCTION

Cookies are widely accepted and consumed in many developing countries. Biscuits and cookies represent the largest category of snack items among baked foods overall the world Akubor and Onimawo (2003); Hooda and Jood (2005). The main ingredient of cookies dough is soft wheatflour Tsen (1976). Soft wheatflour is low in protein (7 – 14%) and deficient in some amino acids Claughton and Pearce (1989). Over the years, a number of studies have been reported on high-protein cookies using soy flour Tsen *et al.* (1973), gluten – soy protein blends Singh and Mohamed (2007), sunflower kernels Bajaj *et al.* (1991), pulse flours Singh *et al.* (1993), chickpea, broad bean or isolated soy protein. Kaur *et al.* (1999) Found that cookies made with 30% pigeon peaflour were acceptable. Bajaj *et al* (1991) substituted 30% flour with wheat germ without affecting the acceptability. Giami *et al.* (2005) found that up to 15% substitution of wheatflour with fluted pumpkin flour produced acceptable cookies with spread ratio, hardness, colour and flavour similar to the control (100% wheatflour) cookies. There were no significant ($P > 0.05$) differences between the values obtained for protein efficiency ratio, net protein ratio and true digestibility of cookie diets containing 15–20% fluted pumpkin flour, and casein when fed to rats.

James *et al.* (1989) found that cookies containing soy protein isolate (SPI) were acceptable in color, crispiness and flavor. Lee and Brennand (2005) reported that up to 15% of wheatflour could be replaced by soy protein isolate without diminishing acceptability of fried cookies. Soy protein provides several functionalities such as water-holding, binding and emulsifying properties Arrese *et al.* (1991); Liu (1997). Soy protein substitution, therefore, affects the food quality Taha *et al.* (2006). Besides it is associated with significant decreases in serum cholesterol and LDL cholesterol concentrations Anderson *et al.* (1995). In 1999, the FDA authorized the use of health claims about the role of soy protein in reducing the risk of Coronary heart disease (CHD) on labeling of foods containing soy protein FDA talk paper (1999).

During baking process of cereal products such as bread, cakes and cookies, many structural (textural), physico – chemical and organoleptic changes occur Sabalni *et al.* (1998). All these cooking – induced changes are important for digestibility and sensorial acceptance by the consumers. The Maillard reaction (MR), caramelization (CR) and lipid peroxidation (LP) explain most of these changes, although the complex mixture of compounds formed are poorly characterized. In particular, the proportion of chemical compounds formed in the dough which is released in the vapours and contributing to the specific aroma of the cereal product have not been examined Brauss *et al.* (1999).

No studies have been reported so far concerning the effect of soy protein isolate (SPI) addition on the cookie volatiles. Therefore, the objective of the present study was to evaluate the addition effect of SPI at different levels to wheat flour cookies on their overall qualities. Besides, the effect of such addition on the volatiles of the final cookies during storage.

MATERIAL AND METHODS

I-Cookies ingredients

Soy protein isolate (SPI), a product of Qingdao, Crown Lmp-Exp. LTD – KIEL/Cyprus, contained: 5.5% moisture, 90.5% protein, 0.5% fat, 4% ash and 0.5% fiber was used. The amino acid composition is shown in Table 1.

Table 1.Amino acid compositions of soy protein isolate (SPI)

Amino acid composition	g AA/ 100g product	g AA/ 100g protein	Amino acid composition	g AA/ 100g product	g AA/ 100g protein
Analnine	3.70	4.20	Leucine	6.90	7.80
Arginine	7.10	8.00	Lysine	5.70	6.50
Aspartic acid	10.70	12.10	Methionine	1.20	1.40
Glutamic acid	18.00	20.40	Phenylalanine	4.80	5.40
Cystine	1.20	1.40	Proline	4.70	5.30
Glycine	3.70	4.20	Serine	5.00	5.70
Histidine	2.40	2.70	Threonine	3.20	3.60
Isoleucine	3.80	4.30	Tryptophan	0.90	1.00
Valine	4.00	4.50	Tyrosine	3.60	4.10

-The other ingredients i.e. sugar (granulated sucrose), wheat flour (72% extraction), butter, egg (whole, fresh), baking powder (Cook's – Tag EL-Melok, Co) were purchased from local market, Cairo, Egypt.

II - Authentic compounds and Standard n-paraffin (C8 – C22) were purchased from Sigma-Aldrich Co. (St.Louis, MN, USA) and Merck (Darmstadt, Germany). All other chemicals were of analytical grade.

III- Cookies formulation and preparation:

The cookies were prepared according to the method described by Akubor and Onimawo (2003), as follows; the basic formulation contained wheatflour 44.5%, butter 25%, sucrose 20%, beaten whole egg 10% and baking powder 0.5%. SPI was added to wheat flour dough at levels 5, 10, 15 and 20% by mixing with wheatflour and baking powder. The finished dough was shaped into cookie form (5 x 30mm) and baked in an electric oven (Electra, model EK-450-OT, China) at 150°C ± 5°C for 17min ± 3 min. The cookie pieces were cooled to room temperature, packed in plastic bags and stored at room temperature for three months until analysis.

IV- Chemical composition of cookies:

Moisture, crude protein, crude fat, total ash and crude fiber contents of fresh and stored cookie samples were determined according to AOAC (1984). Carbohydrate content was calculated by difference. Energy values (kcal) were calculated applying the factors 4, 9 and 4 for each gram of protein, fat and carbohydrate, respectively Greenfield and Southgate (1992).

V- Sensory evaluation:

The different sensory qualities (colour, aroma, taste, crispiness and appearance) of the fresh and stored cookies were estimated and scored by 20 panelists (Food Technology & Nutrition Division, National Research Centre, Cairo. Egypt).

The grading system was based on total score of 100 of which 35 was awarded for aroma, 35 for taste, 10 for colour, 10 for mouth feel and 10 for appearance.

VI- Statistical analysis:

Data were analyzed using the analysis of variance (ANOVA) by the Statgraphics package (Statistical Graphics Corporation, 1993, Manugistics Inc., USA). The multiple range test L.S.D (Duncan multiple range test), with significant level at $p < 0.05$, was applied to the results to test the significant difference.

VII- Isolation of cookie volatiles:

Simultaneous distillation extraction (SDE) method was used for isolation of the volatiles of cookie samples Prost et al. (1993) by using Likens and Nickerson apparatus. The ground cookie (100g) of each sample was mixed with 400 ml of distilled water and subjected to (SDE) extraction using diethyl ether – pentane (1:1, v/v). The solvents containing volatiles were dried over anhydrous sodium sulphate for 12h and concentrated using rotary evaporator at 40°Cunder reduced pressure, then to final volume (100 µl) under a flux of nitrogen before GC and GC – MS analysis.

VIII- Gas chromatographic (GC) analysis:

GC analysis was performed by using a Perkin Elmer Auto System XL equipped with flame ionization detector (FID). A fused silica capillary column

DB5 (60m x 0.32mm i.d.) was used. The oven temperature was maintained initially at 45°C and programmed to 60°C at a rate of 1°C/min, then programmed from 60 to 240°C at a rate of 3°C/min. Helium was used as the carrier gas, at flow rate 1.1 ml/min. The injector and detector temperatures were 220 and 250°C, respectively. The retention indices (Kovats index) of the separated volatiles components were calculated with hydrocarbons (C8 – C22, Aldrich Chemical Co.) as references.

X- Gas chromatographic – mass spectrometric (GC – MS) analysis:

The analysis was carried out by using a coupled gas chromatography Hewllet-Packard (5890)/mass spectrometry Hewllet-Packard-MS (5970). The ionization voltage was 70eV, mass range m/ z 39-400 amu. The GC conditions carried out as mentioned earlier. The isolated peaks were identified by matching with data from the library of mass spectra (NIST) and comparison with those of authentic compounds and published data Adams (1995) the quantitative determination was carried out based on peak area integration.

RESULTS AND DISCUSSION

Chemical composition of fresh and stored cookies:

The chemical composition of the fresh and stored cookies supplemented with SPI is shown in Table (2). Concerning the fresh cookies the moisture content showed gradual increase by increasing the SPI level reaching its highest value (6.30 ± 0.08 %) in sample contained 20% SPI. This increase could be attributed to the high water binding properties of SPI Liu (1997). Addition of SPI at 5 – 20% caused an increase in protein content of the final product, whereas, reductions in fat, carbohydrate and ash contents were noted in the baked cookies as a result of SPI addition. These results are in a quite agreement with those of Lee and Brennand (2005) who evaluated the physicochemical characteristics of Korean cookies supplemented with SPI.

Table 2: Chemical composition of fresh and stored cookies fortified with Soy protein isolate (SPI).

Samples / Properties	Cookie samples									
	Control		SPI 5%		SPI 10%		SPI 15%		SPI 20%	
	Fresh	Stored	Fresh	Stored	Fresh	Stored	Fresh	Stored	Fresh	Stored
Moisture %	5.24* ± 0.03	2.77 ± 0.35	5.55 ± 0.11	3.21 ± 0.19	5.69 ± 0.03	3.88 ± 0.08	5.87 ± 0.06	3.97 ± 0.08	6.30 ± 0.08	4.10 ± 0.05
Protein %**	12.35 ± 0.28	10.19 ± 0.52	14.89 ± 0.35	12.52 ± 0.56	19.25 ± 0.54	18.71 ± 0.59	19.67 ± 0.85	19.12 ± 0.42	20.43 ± 0.84	20.10 ± 0.18
Fat %**	22.16 ± 0.11	21.08 ± 0.19	20.78 ± 0.30	20.52 ± 0.41	20.66 ± 0.14	20.21 ± 0.18	20.57 ± 0.16	20.11 ± 0.29	20.42 ± 0.29	19.42 ± 0.21
Carbohydrate %**	63.28 ± 0.43	66.58 ± 0.21	62.43 ± 0.11	64.97 ± 0.20	58.00 ± 0.23	59.13 ± 0.08	58.86 ± 0.11	58.88 ± 0.23	57.32 ± 0.20	58.66 ± 0.24
Ash %**	1.56 ± 0.20	1.52 ± 0.03	1.41 ± 0.04	1.39 ± 0.01	1.39 ± 0.01	1.37 ± 0.02	1.35 ± 0.02	1.34 ± 0.02	1.32 ± 0.01	1.31 ± 0.02
Fiber %**	0.65 ± 0.02	0.63 ± 0.01	0.61 ± 0.01	0.60 ± 0.02	0.58 ± 0.02	0.58 ± 0.01	0.55 ± 0.03	0.55 ± 0.01	0.51 ± 0.02	0.51 ± 0.03
Total energy kcal/100g product	501.96 ± 0 .27	493.80 ± 7.16	495.22 ± 8.38	494.64 ± 5.90	496.01 ± 3.97	493.24 ± 3.20	495.24 ± 4.60	493.00 ± 4.60	494.78 ± 0.21	489.62 ± 2.61

* Values are the mean of three determinations ± SD.

** On dry base

The protein content of all samples in the present study was higher than the protein level (6 – 12 %) reported for conventional cookies Shrestha and Noomhorm (2002). Taha et al. (2006) reported that moisture content of cookies was significantly increased by increasing protein content resulted from replacing wheatflour with chickpea, broad bean and ISP. They attributed this increase to the presence of polar amino acids and the positive influence of increasing levels of protein on water holding capacity. The results also revealed that consumption of about 100g of each sample would provide more than half of the recommended daily requirement for protein (25 – 30g day -1) and about one fifth of the requirement for energy (1790 – 2500 kcal day -1) as recommended by FAO/WHO (1973) for children aged between 5 and 19 years.

Storage for three months revealed a significant (P<0.05) decrease in moisture of all cookie samples. The protein, fat content and energy value were decreased, whereas carbohydrate content was increased with different ratios.

Sensory evaluation of cookies:

The mean sensory scores of fresh and stored cookies are shown in Table (3).In general, the total quality score of the freshly prepared cookies increased with addition of different SPI levels. No significant (P>0.05) differences was found in colour among all cookie samples under investigation. However, supplementation of cookies with SPI up to 10% increased all other sensory attributes Table (3).

Storage for three months showed considerable reduction in overall acceptability and other evaluated attributes in all investigated cookie samples. However, cookie sample supplemented with 10% ISP was most preferred with respect to colour, aroma, taste and crispiness. The differences in aroma and taste among the cookie samples could be correlated to the generated volatiles during baking process as will be discussed below.

Volatile compounds in cookies:

About 80 volatile components could be separated and identified in the cookie samples by using GC/MS analysis, however only the most potent components for cookies aroma with their relative area percentages were listed in Table (4). These compounds were related to different chemical classes such as strecker aldehydes(4), diketones(2), carbonyls(14), pyrazines(4), furans(6), pyrroles(2), lactones(2), pyranone(2), acids(2), alcohols(2) and esters(2). Most of them were previously identified in baked cereal products Fadel and Hegazy (1993); Grosch and Shieberle (1997); Pozo-Bayyone et al. (2006) and Taha et al. (2006).

It is appropriate to consider the volatiles in relation to their mode of formation either from Maillard reaction (MR) or lipid degradation Ledl and Schleicher (1990) and Mottram (1994). Some of the most common volatile products of the Maillard reaction are Stercker aldehydes, formed by the decarboxylation and deamination of amino acids. Typical sugar dehyderation products are furfural and furanones, whereas pyrrole and pyrazines, heterocyclic nitrogen compounds formed from the reaction of these sugar degradation products with ammonia or amino acids.

Table 3: Sensory evaluation of fresh and stored cookies fortified with Soy protein isolate (SPI).

Properties / Samples	Color		Aroma		Taste		Crispiness		Appearance		Total quality score	
	Fresh	Stored	Fresh	Stored	Fresh	Stored	Fresh	Stored	Fresh	Stored	Fresh	Stored
Control	9.08 ^{a} ± 0.41	9.36 ^{a} ± 0.49	26.83 ^{a} ± 0.52	24.22 ^{a} ± 0.20	27.42 ^{a} ± 0.75	24.77 ^{a} ± 0.20	7.50 ^{a} ± 0.55	7.00 ^{a} ± 0.32	7.32 ^{a} ± 0.52	6.92 ^{a} ± 0.20	78.15 ± 0.76	68.91 ± 0.49
SPI 5%	9.08 ^{a} ± 0.75	9.36 ^{a} ± 0.49	28.89 ^{ab} ± 0.42	26.25 ^{b} ± 0.45	28.58 ^{a} ± 0.41	27.42 ^{b} ± 0.26	8.32 ^{b} ± 0.52	7.67 ^{b} ± 0.41	8.32 ^{b} ± 0.41	7.58 ^{b} ± 0.38	83.19 ± 0.56	78.28 ± 0.45
SPI 10%	9.17 ^{a} ± 0.61	9.59 ^{a} ± 0.49	32.98 ^{c} ± 0.49	29.75 ^{c} ± 0.45	32.39 ^{b} ± 0.42	30.33 ^{c} ± 0.41	9.00 ^{b} ± 0.55	8.67 ^{c} ± 0.41	9.26 ^{c} ± 0.42	8.83 ^{c} ± 0.26	92.80 ± 0.58	87.17 ± 0.49
SPI 15%	9.13 ^{a} ± 0.82	9.26 ^{a} ± 0.51	29.48 ^{ab} ± 0.38	27.14 ^{b} ± 0.27	29.17 ^{a} ± 0.41	28.00 ^{b} ± 0.32	8.32 ^{b} ± 0.41	8.07 ^{b} ± 0.38	8.32 ^{b} ± 0.26	8.00 ^{d} ± 0.32	84.42 ± 0.49	80.47 ± 0.41
SPI 20%	8.89 ^{a} ± 0.75	9.12 ^{a} ± 0.49	27.72 ^{ab} ± 0.67	24.89 ^{b} ± 0.46	28.58 ^{a} ± 0.75	26.09 ^{b} ± 0.27	8.24 ^{b} ± 0.81	7.64 ^{b} ± 0.32	7.64 ^{b} ± 0.79	7.74 ^{b} ± 0.27	81.85 ± 0.76	75.48 ± 0.39

- Values are score average of 10 panelist's ± SD.
- Values in the same column followed by different superscript letters are significantly different ($P < 0.5$).
- Control no soy protein isolate (SPI) added, and 5, 10, 15 and 20% are the soy protein isolate substitution levels.

Table 4: Volatile Compounds of Fresh and Stored Cookies Fortified with Different Levels of Soy Protein Isolate (SPI).

Peak No.	K.I[a]	Components	Percentage of (SPI) g/100g wheat flour										Method of Identification[b]
			control		5% SPI		10% SPI		15% SPI		20% SPI		
			Fresh	Stored 3 month	Fresh	Stored 3 month	Fresh	Stored 3 month	Fresh	Stored 3 month	Fresh	Stored 3 month	
1	600	2-Methylpropanal	0.15[c]	0.58	0.43	0.12	1.33	5.91	0.63	0.32	0.31	0.13	KI, MS
2	618	2-Butandione	24.74	14.62	24.41	15.49	10.75	26.77	29.90	18.52	21.79	17.35	KI, MS,St
3	642	2-Methylbutanal	4.56	1.50	5.97	3.04	7.82	5.35	4.97	12.99	4.39	3,47	KI, MS
4	667	3-Methylbutanal	18.52	8.07	18.20	5.37	15.62	11.26	3.24	2.98	9.86	6.12	KI, MS
5	698	2-Pentanal	0.52	0.57	0.29	0.44	1.52	0.26	1.30	10.30	0.51	5.51	KI, MS
6	702	2-Pentanone	0.40	0.32	0.50	0.80	— —	— —	0.69	1.75	0.70	1.84	KI, MS
7	705	2,3-Pentandione	0.87	0.34	0.32	0.20	0.84	0.24	0.54	0.85	— —	— —	KI, MS
8	724	Pyrazine	0.72	0.65	0.45	1.90	0.59	2.04	9.34	15.58	14.78	17.48	KI, MS,St
9	750	1-Hpyrrole	0.88	— —	0.20	0.50	0.92	2.16	9.37	14.86	12.64	15.23	KI, MS
10	766	2-Pentenal	0.12	0.15	— —	0.12	0.73	0.58	2.54	4.87	1.91	2.34	KI, MS
11	798	2-Ethyl-5-methylfuran	0.28	0.16	0.22	0.40	0.84	0.34	0.87	— —	0.88	0.41	KI
12	808	Hexanal	0.55	0.60	1.74	0.95	0.52	0.79	2.35	0.71	0.97	0.59	KI, MS,St
13	813	3-Hexenal	0.57	0.35	— —	0.30	0.53	— —	0.54	0.45	— —	— —	KI, MS
14	819	Butyric acid	0.83	0.20	0.51	— —	0.65	— —	0.56	— —	1.81	— —	KI, MS
15	823	Dihydro-2-methyl(2H)furanone	0.16	— —	0.88	0.16	0.61	0.21	0.88	— —	2.35	1.85	KI, MS,St
16	832	2-Methylpyrazine	0.20	— —	2.96	0.85	5.80	3.52	5.50	0.90	10.64	8.94	KI, MS,St
17	844	2-Furfural	28.44	4.51	4.46	3.00	3.53	0.40	— —	0.61	0.66	0.11	KI, MS,St
18	858	2-Hexenal	0.47	44.8	0.80	42.35	0.74	10.13	0.26	— —	0.56	9.47	KI, MS
19	865	Hexanol	— —	— —	— —	2.41	2.39	3.00	0.38	— —	— —	— —	KI, MS
20	891	Heptanone	0.12	— —	0.26	— —	0.29	— —	0.32	— —	— —	— —	KI, MS
21	900	4-Heptenal	1.59	1.51	3.96	1.61	2.65	2.91	3.56	1.83	2.30	1.38	KI, MS
22	914	2-Acetyl-1-pyrroline	0.20	0.31	0.75	0.58	0.41	0.09	0.61	0.35	1.10	0.69	KI, MS
23	993	2-Pentylfuran	0.71	5.23	0.76	3.56	0.46	0.57	0.24	0.79	— —	— —	KI, MS
24	1003	2-Ethyl-5-methylpyrazine	0.34	— —	0.75	0.46	2.36	1.53	0.81	0.56	— —	— —	KI, MS,St
25	1011	Octanal	0.72	3.35	0.24	1.76	0.34	0.27	0.26	— —	— —	— —	KI, MS,St
26	1017	2,4-Heptadienal (ZZ)	1.01	3.49	0.76	1.64	2.58	0.21	0.50	— —	— —	— —	KI, MS
27	1040	Phenylacetaldehyde	0.05	— —	0.09	[illegible]	[illegible].69	0.75	0.57	— —	— —	— —	KI, MS
28	1070	2-Ethyl-2,5-dimethylpyrazine	0.35	1.37	[illegible]	[illegible]	[illegible]50	0.47	0.26	0.15	— —	— —	KI, MS,St
29	1093	4-Hydroxy-2,5-dimethylfuranone	0.65	— —	0.48	— —	0.69	0.11	0.75	0.35	0.62	0.32	MS,St
30	1098	Nonanal	0.92	1.20	4.90	2.67	3.00	2.63	1.15	1.58	1.56	1.35	KI, MS
31	1100	1.5-octadiene-3-one	— —	— —	0.70	— —	1.89	0.81	0.90	— —	1.10	0.54	KI, MS
32	1111	3-hydroxy-2- methyl -4(H)-pyran-4-one	1.72	0.25	2.64	0.70	2.00	3.47	2.19	1.64	0.88	0.58	MS,St
33	1120	3-Hydroxy 4,5-dimethylfuranone	— —	— —	0.60	0.50	2.07	0.50	1.00	— —	0.07	— —	KI, MS
34	1130	2,3dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one	0.50	— —	0.62	— —	11.57	3.90	0.82	0.60	0.07	— —	KI, MS
35	1185	2-Nonanol	0.29	0.06	0.50	— —	— —	— —	— —	0.37	— —	— —	KI, MS
36	1213	Nonadienal (ZZ)	0.32	0.25	0.32	0.26	— —	— —	— —	— —	— —	— —	KI, MS
37	1300	γ - Butyrolactone	3.98	1.79	8.20	1.86	6.51	4.96	6.10	1.99	3.64	2.19	KI, MS
38	1324	2,4-Decadienal (EE)	0.38	0.51	0.26	— —	— —	— —	— —	— —	— —	— —	KI, MS
39	1376	Decanonic acid	0.46	0.45	0.85	0.68	— —	— —	— —	— —	— —	— —	KI, MS
40	1397	Ethyldecanoate	0.51	0.11	0.53	0.13	— —	— —	— —	— —	— —	— —	KI, MS
41	1496	Methyllaurate	0.37	0.14	0.47	0.21	0.30	— —	— —	— —	— —	— —	KI, MS
42	1501	δ - Decalactone	2.83	2.56	8.96	4.10	4.27	3.95	6.10	4.12	4.10	2.13	MS,St

- Compounds listed according to their elution on DB5 column. - [a] Kovats Index.

- [b] Compounds identified by GC – MS (MS) and/or by Kovats Index on DB5 (KI) and/or by comparison of MS and KI of standard compounds (St) run under similar GC – MS conditions.

- [c] Values are the average of two experiments and expressed as relative area percentages to total identified compounds

Concerning the fresh cookies it is obvious from Table (4) that addition of SPI revealed variations in number and content of most of the identified volatiles. The increased protein level may indirectly influence the rate of Maillard reaction either by hydrolysis or by deamination of the bound amino acids Izzo et al. (1993); Riha and Ho (1996); Pozo-Bayyone et al. (2006).

The four Stercker aldehydes identified in the present study, 2-methyl -propanal, 2/3-methylbutanal and phenylacetaldeyde Table (4) may be derived from amino acids valine, isoleucine, leucine and phenylalanine, respectively. The increase in SPI level up to 10% in cookie samples revealed a slight increase in the stercker aldehydes content (Fig. 1a) followed by a remarkable decrease in samples contained 15 and 20% SPI. This decrease in the sterecker aldehyde contents might indicate that they became involved in further condensation reaction with amines producing heterocyclic and/or polymeric substances Bredie et al. (1998) and Fadel et al. (2006). The diketone compounds identified in cookies aroma were 2,3-butandione and 2,3-pentandione(as sugar degradation compounds) Ledl and Schleicher (1990) and can undergo condensation reaction via MR Table (4) and Fig.1b showed that 10% SPI sample comprised the least content of these compounds (11.59%). The Furans comprised the highest level in volatiles of fresh control sample (30.24%). Among them 2-furfural was the predominant compound (28.44%), however, it showed dramatic decrease by increasing the SPI content in cookie samples Table (4). Furfural is a pungent and sweet but does not have a cookie like, caramelic aroma. The two furans, 2-ethyl-5-methylfuran and 2-pentylfuran are lipid derived products as will be discussed bellow. Three furanones were identified in the present study, Furanones are mainly associated with caramel-like, sweet, fruity, nutty and burnt odour impression Flament (1991). The fresh cookie sample SPI 10% comprised the highest yield of these compounds (3.37%). These results confirm those of the odour sensory analysis Table (3).

Four pyrazines were identified in the cookie samples Table (4). Pyrazines have previously received attention in thermally treated cereals because of their roasted, nutty flavour properties Bredie et al. (2002). It is clear that the increase in the added concentration of SPI gave rise to a remarkable increase in total pyrazines content. The pyrazines level in sample SPI 20% was more than fifteen times greater than that in control sample (Fig. 1c).

Many studies have shown that a number of amino acids readily react with sugar to form alkyl pyrazines Whitfield (1992). In present study the soy protein isolate contains substantial amounts of these amino acids Table (1). Biscuit like, burnt odour was noted for 2-ethyl-5-methylpyrazine Bredie et al. (1998) it showed the highest concentration in sample SPI 10%. This result confirms those of odour sensory evaluation Table (3). The increased relative concentration of pyrazines revealed the development of increased roasted / toasted flavour in thermally treated cereal products Bredie et al. (1998) and Fadel et al. (2006).

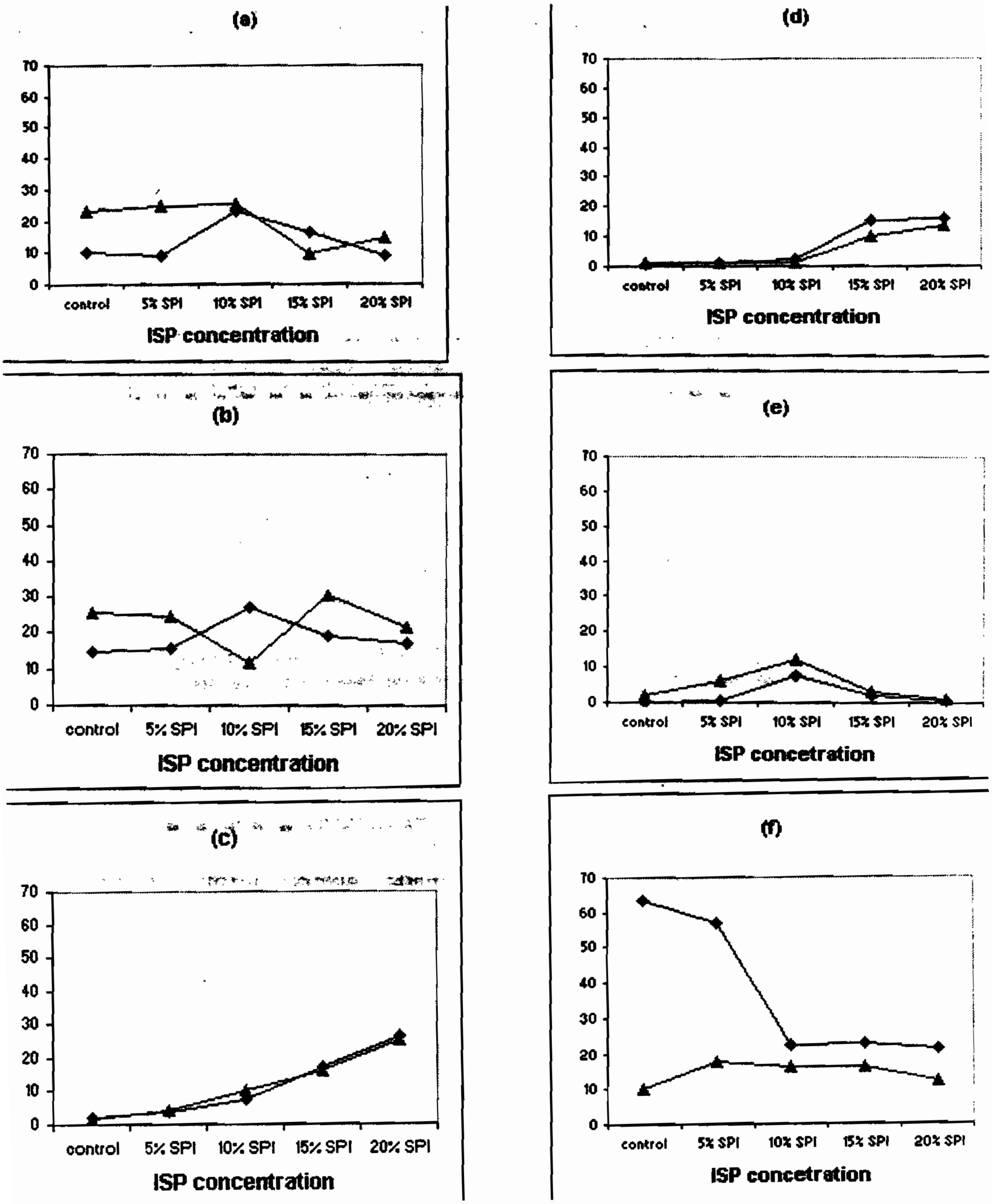

Fig 1 : Effect of SPI supplementation (5-20%) on the main chemical classes in volatiles of fresh stored cookies (▲ fresh & ■ stored).
(a) Strecker aldehydes, (b) Diketones, (c) Pyrazines, (d) Pyrroles, (e) Pyranones and (f) Lipid degradation products.

The identified pyrroles were,1-H-pyrrole and 2-acetyl-1-pyrroline, they followed the same pattern as the pyrazines Table (4) and Fig.1d, 1-pyrrole was the most abundant species in volatiles of fresh sample SPI 20%. Popcorn like aroma was noted for 2-acetyl-1-pyrroline Pozo -Bayyone et al. (2006). Proline is the precursor of 2-acetyl-1-pyrroline Schieberle (1991). It comprised 4.7% of the total amino acids in SPI Table (1). 3-Hydroxy-2- methyl -4(H)-pyran-4-one (maltol) and .2,3-dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one (DDMP) were the identified pyranone in cookies. These compounds possessing sweet – caramel note Nishibori et al. 1999 and Pozo -Bayyone et al. (2006). Their total yield increased with addition of SPI up to 10% where it exhibited more than 10 folds that in control sample (Fig. 1e). Pozo et al, 2006 stated that the addition of protein source to cookie dough promote the formation of some pyranones with a pleasant sweet aroma. DDMP was dominated in sample SPI 10%, it showed a sudden decrease in sample SPI 15% associated with a considerable increase in maltol Table (4).

In a series of studies, Nishibori and Kawakishi (1990, 1991, 1992) and Nishibori et al. (1999). Stated that the generation of DDMP in baked cookies enhanced by addition of some proteins and amino acids. DDMP was isolated and identified in Maillard type browning reaction Mills and Hodge (1976) it may be dehydrated to give maltol Mills et al. (1970) by extensive heating. DDMP is well known as an indicator of the 2, 3-enolisation pathway in Maillard reaction Davidek et al. (2000) and is a precursor of maltol, a key odorant in cereal products. In additlon to maltol, 2-butandione, 2-methyl pyrazine, 2-furfural and δ-decalactone were reported amongst the volatile compounds used in model system of cookies flavour Prost et al. (1993).

Most of the lipid degradation products found in the cookie samples are derived from the oxidation of oleic acid, linoleic acid and small amount of linolenic acid which are found in wheatflour and SPI Bredie et al. (2002); Solina et al. (2005). Typically, lipid oxidation products that are odour/flavour – active are short chain carbonyl components (aldehydes and ketones), fatty acids and alcohols derived from unsaturated fatty acids Whitfield (1992). 2-Ethyl-5-methylfuran and 2-pentylfuran are oxidative and/or thermal degradation of unsaturated lipids Grosch (1982). Pentanal, hexanal, pentylfuran, heptanone, 2-alkenal and 2,4-alkadienal are the major lipid derived compounds in SPI Solina et al. (2005).

As shown in (Fig. 1f) the fortification of the cookie samples with 5% SPI revealed a considerable increase in the lipid derived volatiles followed by gradual decrease by increasing ISP content. This apparent decrease in lipid – derived volatiles may be attributed to an increased formation of Maillard – derived products. Intermediates from Maillrad reaction have been shown to act as free radical scavengers, inhibiting propagation of radical reaction Elizalde et al (1991); Fallico et al. (2003).

The total content of the two identified lactones, γ-butyrolactone and δ-decalactone increased in sample 5% SPI to more than twice that in control, however the increase in the level of SPI in the cookie samples up to 10 – 20% revealed considerable decrease in the total yield of these lactone compounds Table (4). γ-Butyrolactone possess sweet – caramel note, it is most widely distributed γ-lactone Flament (1991). δ-Decalactone is described as sweet, creamy and nut like note Flament (1991). Besides δ-decalactone, 2-butandione, 3-hexenal, butyric acid and 2,4-decadienal were reported amongst the potent odorants of butter oil Widder et al. (1991).

Effect of storage for three months on the main chemical classes in the cookie sample volatiles was investigated (Table 4 and Fig 1). In general, the strecker aldehydes and diketones showed a noticeable decrease in comparison to their yields in fresh cookie samples (Fig. 1a, b). Mayer and Grosch (2001) correlated the decrease in the intensity of the sweetish/caramel like odour quality of fresh ground coffee powder to the decrease of these two chemical classes. These results were recently confirmed in previous study concerning the effect of storage on the volatiles of cocoa Fadel et al. (2006) and coffee substitutes (Fadel et al. (2007). Lactones showed the same trend Table (4). In general, pyrazines and pyrroles showed similar trend, their total yields showed slight increases (Fig.1c, d) especially for cookies containing high SPI levels (15, 20%). The formation of these Maillard reaction products during storage is not likely, but their increase may be attributed to some physical process taking place during water dehydration process Stöllman (1985); Fadel and Hegazy (1993). Pyranones, the key odorants of cookies, showed remarkable decrease after storage for 3 months. These results are consistent with those of odour sensory analysis Table (3). An opposite trend was observed for the lipid degradation products (Fig 1f). The stored control sample comprised the highest level of these compounds. Their total yield was more than six folds higher than fresh control sample (Fig 1f).

2-Hexenal, the lenoleic derived compound, was the dominant compound contributing to this increase Parker et al. (2000). The rate of increasing lipid derived compounds in the stored cookies showed a remarkable decrease by increasing the added amounts of SPI (Fig.1f). This may be attributed to the increased formation of Maillard-derived products that can act as free radical scavengers Elizalde et al. (1991).

CONCULUSION

- The present study showed that wheatflour supplemented with SPI at different levels (5 – 20%) produced high quality cookies with an increased nutrition value.
- Cookies fortified with 10% SPI possessed the highest yield of the volatiles that are considered as markers of cookies aroma.
- A quite agreement was found between the generated volatiles and aroma sensory attributes of each cookie sample.

REFERENCES

Adams, R. P.(1995) Allured Publishing, Carol Steam Illinois, USA.

Akubor, P. I. and I. A. Onimawo (2003) Functional properties and performance of soy bean and maize flour blends in cookies. Plant Foods for Human Nut., 58: 1 - 12.

Anderson, J. W.; B. M. Johnstone and M. E. Cook-Newell (1995) Meta-analysis of the effect of soy protein intake on serum lipid. New England Journal of Medicine, 333: 276–282.

AOAC (1984) Official Method of Analysis, 14th edn. Washington, DC, USA: Association of Official Analytical Chemists.
Arrese, E. L.; D A. Sorgentini; J. R. Wagner and M. C. Anon (1991) Electrophoretic, solubility and functional properties of commercial soy protein isolates. J Agric. Food Chem., 39: 1029–1032.
Bajaj, M.; A. Kaur and J. S. Sidhu (1991) Studies on the development of nutritious cookies utilizing sunflower kernels and wheat germ. Plant Food for Human Nutrition, 41: 381–387.
Brauss, M.; B. Balders; R. S. T. Linforth; S. Avison and A. Taylor (1999) Fat content, baking time, hydration and temperature affects flavour release from biscuits in model-mouth and real systems.Flavour Fragr. J., 14: 351–357.
Bredie, W. L. P.; D S. Mottram; G. M. Hassell and R. C. E. Guy (1998) Sensory characterization of the aromas generated in extruded maize and wheat flour. J. Cereal Sci., 28: 97 – 109.
Bredie, W. L. P.; D. S. Mottram and R. C. E. Guy (2002) Effect of temperature and pH on the generation of flavour volatiles in extrusion cooking of wheat flour. J Agric. Food Chem., 50: 1118.
Claughton, S. M. and R.J. Pearce (1989) Protein enrichment of sugar snap cookies with sunflower protein isolate. Journal of Food Science, 54: 354.
Davídek, V.; M. Laipert and M. Vl_ek (2000) Analogové a _íslicové filtry (337 s.), Vyd. _VUT.
Elizalde, B. E.; M. Dalla Rosa and C. R. Leici (1991) Effect of Maillard reaction volatile products on lipid oxidation. J.Am. Oil Chem. Soc., 68: 758 – 762.
Fadel, H. M. M. and N. A. Hegazy (1993) Improvement and stabilization of white bread flavour. Die Nahrung, 37: 386 – 394.
Fadel, H. M. M.; E. E. Ragheb and M. A. Abd El-Mageed (2006) Effect of amino acid and protein addition on the flavour extruded corn flavour. Egypt J Sci., 34:21 – 36.
Fadel, H. M. M.; M. A. Abd El-Mageed; A. M. E. Abdel Samad and S. N. Lotfy (2007) Cocoa substitutes: evaluation of sensory qualities and flavour stability. In Press.
Fallico, B.; E. Arena and M. Zappalà (2003) Roasting of hazelnuts. Role of oil in colour development and hydroxymethylfurfural formation. Food Chemistry, 81: 569-573.
FAO/WHO (1973) Energy and Protein Requirements. Food and Agriculture Organization Nutrition meeting report Series 52, Rome: World health organization Technical Report Series, 522.
FDA talk paper (1999) FDA approves new health claim for soy protein and coronary heart disease. US Food and Drug Administration Web site. Available at: http://vm.cfsan.fda.gov:80/ lrd/tpsoypr2.html. Accessed November 08, 2004.
Flament, I. (1991) Coffee, Cocoa and Tea Ch 17. In: Volatile Compounds. In: Food and Beverages, H. Maarse, Ed., Marcel Delker Inc., New York, pp 617 – 669.
Giami, S. Y.; S. C. Achinewhu and C. Ibaakee (2005) The quality and sensory attributes of cookies supplemented with fluted pumpkin (Telfairia occidentalis Hook) seed flour. Int. J Food Sci. Tech., 40: 613–620.
Greenfield, H. and D. A. T. Southgate (1992) Food composition Data: Production, Management and Use. Barking, UK: Elsevier Applied Science.
Grosch, W. (1982) Lipid degradation products and flavour. In Food Flavours. Part A: Introduction; Morton I D, MacLeod A J. Eds., Elsevier: Amsterdam, pp 325 – 398.
Grosch, W. and P. Shieberle (1997) Flavor of cereal products-A Review. Cereal Chem., 74: 91–97.

Hooda, S. and S. Jood (2005) Organoleptic and nutritional evaluation of wheat biscuits supplemented with untreated and treated fenugreek flour. J Food Chem., 90:427–35.
Izzo, H. V.; M. D. Lincoln and C. T. Ho (1993) Effect of temperature, feed moisture and pH on protein deamunation in an extruded wheat flour. J Agric. Food Chem., 41:199 – 202.
James, C.; D. L. D. Courtney and K. Lorenz (1989) Rice bran-soy blends as protein supplements in cookies. International Journal of Food Science and Technology, 24: 495–502.
Kaur, H.; B. Kaur and S. Sharma (1999) Studies on the baking properties of wheat: pigeon pea flour blends. Plant Food for Human Nutrition, 54: 217–226.
Ledl, F.and E. Schleicher (1990) New aspects of the Maillard reaction in food and the human body. Angew. Chem. Int. Ed. Engl., 29: 565 – 706.
Lee, K. A. and C. P. Brennand (2005) Physico-chemical, textural and sensory properties of a fried cookie system containing soy protein isolate. International Journal of Food Science and Technology, 40: 501–508.
Liu, K. (1997) Soybeans: Chemistry, Technology and Utilization. Pp. 393–399. New York: Chapman & Hall.
Mayer, F. and W. Grosch (2001) Aroma simulation on the basis of the odourant composition of roasted coffee headspace. J Flavour and Fragrance, 16: 180–190.
Mills, F. D.; D. Weisleder and J. E. Hodge (1970) 2,3-Dihydro-3,5-dihydroxy-6-methyl-4H—pyran-4-one, a novel nonenzymatic browning products. Tetrahedron Lett. 1243.
Mills, F. D. and J. E. Hodge (1976) Amadori compounds vacuum thermolysis of 1-deoxy-1-L-prolino-D-fructose. Carbohydr. Res., 51:9.
Mottram, D. S. (1994) Flavour compounds formed during the Maillard reaction. In Thermally Generated Flavour: Microwave and Extrusion Processes, Parliament T H, Morello M J and McGorrin R J., Eds., American Society: Washington, DC, pp 104 – 126.
Nishibori, S. and S. Kawakishi (1990) Effects of Dough Materialson Flavor Formation in Baked Cookies. J. Food Sci.,55: 409-412.
Nishibori, S. and S. Kawakishi (1991) Formation of 2,3-Dihydro-3,4-dihydroxy-5-acetylfuran in the Reaction between D-Fructose and ß-Alanine. Agric. Biol. Chem., 55: 1159-1160.
Nishibori, S. and S. Kawakishi (1992) Effect of Various Sugars on the Quality of Baked Cookies. Cereal Chem., 69, 160-164.
Nishibori, S.; T. Osawa and S. Kawakishi (1999) Volatile components formed from various sugars with ß-alanine in actual cookies. Flavor Chemistry of Ethnic Foods. 23: 239 – 249.
Parker, J. K.; G. M. E. Hassell; D. S. Mottram and R. C. E. Guy (2000) Sensory and instrumental analysis of volatiles generated during extrusion cooking of oat flour. J. Agric. Food Chem., 48: 3497 – 3506.
Pozo-Bayyone, M. A.; E. Guichard and N. Cayot (2006) Flavor control in baked cereal products. Food Reviews International, 22: 335 – 379.
Prost, C.; C. Y. Lee; P. Giampaoli and H. Richard (1993) Extraction of Cookie Aroma Compounds from Aqueous and Dough Model System. J. Food Sci. 58 (3): 586–588.
Riha, W. E. and C.-T. Ho (1996) Formation of flavors during cooking. Food Rev. Int., 12: 351 – 373.
Sablani, S. S.; M. Marcotte; O. D. Baik and F. Castaigne (1998) Modeling of simultaneous heat and water transport in the baking process. Lebensmittel–Wissenschaft und–Technologie, 31: 201–209.
Schieberle, P. (1991). Primary odorants in popcorn. J Agric. Food Chem.,39: 1141–1144.
Shrestha, A. K. and A. Noomhorm (2002) Comparison of physico-chemical properties of biscuits supplemented with soy and Kinema flours. International Journal of Food Science and Technology, 37: 361–368.

Singh, M. and A. Mohamed (2007) Influence of gluten – soy protein blends on the quality of reduced carbohydrates cookies. LWT 40: 353-360.

Singh, B.; M. Bajaj; S. Sharma and J. S. Sidhu (1993) Studies on the development of high-protein biscuits from composite flours. Plant Food for Human Nutrition, 43: 181–189.

Solina, M.; P. Baumgartner; R. L. Johnson and F. B. Whitfield (2005) Volatile aroma components of soy protein isolate and acid-hydrolysed vegetable protein. Food Chem., 90: 861–873

Stöllman, U. (1985). Flavour changes in white bread during storage. SIK Rapport, 537:1 -10.

Taha, M. R.; A. A. Majdi and I. E. Khalil (2006) Effect of Chickpea, Broad Bean, or Isolated Soy Protein Additions on the Physicochemical and Sensory Properties of Biscuits. J Food Sci., 71: 438 – 442.

Tsen, C. C.; E. M. Peters; T. Schafter and W. J. Hoover (1973) High protein cookies. Effect of soy fortification and surfactants. Baker's Digest, 47: 34–38.

Tsen, C.C. (1976) Regular and protein fortified cookies from composite flours. Cereal Food World, 21:633–8.

Whitfield, F. B. (1992) Volatiles from Maillard reactions and lipids. Crit. Rev. Food Sci. Nutr., 31: 1 – 58.

Widder, S.; A. Sen and W. Grosch (1991) Changes in the flavour of butter oil during storage. Z. Lebensm. Unters. Forsch. 193:32-35.

تأثير إضافة بروتين فول الصويا المعزول علي خواص الجودة ، والمركبات الطيارة في الكوكيز.

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****قسم كيمياء مكسبات الطعم والرائحة – شعبة الصناعات الغذائية والتغذية – المركز القومي للبحوث.**

تم تقدير تأثير إحلال تركيزات مختلفة من بروتين فول الصويا المعزول علي تحسين خواص الجودة في الكوكيز (بسكوتات). تم إعداد كوكيز بإحلال نسب مختلفة من بروتين فول الصويا المعزول (٥، ١٠ ، ١٥ ، ٢٠%) محل دقيق القمح.

تم دراسة التحليل الكيميائي و الصفات الحسية لهذه المنتجات أثناء التخزين لمدة ثلاثة أشهر، وقد تم عزل وتحليل المركبات الطيارة بجهاز التحليل الغازي الكروماتوجرافي – طيف الكتلة.

أوضحت النتائج أن إضافة بروتين فول الصويا المعزول أدت إلي زيادة في المحتوي الرطوبي ونسبة البروتين، نقص في نسبة الدهون والكربوهيدرات ، بينما كان محتوي الطاقة في المستوي المطلوب.

لم يظهر التقييم الحسي أي اختلافات معنوية في لون الكوكيز لكل العينات، بينما أظهرت الصفات الحسية الأخري اختلافات معنوية وذلك عند تدعيم الكوكيز ببروتين فول الصويا المعزول بنسبة أعلي من ١٠%.

تم تحليل عينات الكوكيز كميا وكيفيا بجهاز التحليل الغازي الكروماتوجرافي – طيف الكتلة.

وجد أنه بزيادة معدلات بروتين فول الصويا المعزول زادت نواتج تفاعل ميلارد. أظهرت نواتج تكسير الليبيدات زيادة واضحة بعد التخزين لمدة ثلاثة أشهر في كل العينات وهذه الزيادة نقصت بزيادة معدل بروتين فول الصويا المعزول.

وجد أن تدعيم الكوكيز ببروتين فول الصويا المعزول بنسبة ١٠% أدت إلي انتاج كوكيز ذات محتوي عالي من المركبات الطيارة المسؤلة عن رائحة الكوكيز المرغوبة.