

FATTY ACIDS COMPOSITION OF FATS USED IN SOME EGYPTIAN BISCUITS

Hassan, R. A.*; Safaa M.A. Hassan * and Sh. M. M. El-Shehawey **

*** Agricultural Chemistry Dept., Faculty of Agriculture, Mansoura University, Egypt**

**** Food Industries Dept., Faculty of Agriculture, Mansoura University, Egypt**

ABSTRACT

The composition of fatty acids and trans C_{18:1} fatty acid contents of fat used in five Egyptian biscuit samples were determined using GLC. The results revealed that total saturated fatty acids (SFA) ranged between 64.35% to 85.43% of total fatty acids, while total monounsaturated fatty acids varied from 0.393% to 31.44%. As for polyunsaturated fatty acids (PUFA), it ranged from 0.461% to 17.93% of total fatty acids. Trans fatty acid (C_{18:1}) was detected in lower values ranged from 0.042% in sample D to 0.176% in sample E, however this fatty acid was absent in sample C. GLC chromatogram revealed also the presence of Docosahexaenoic acid, DHA, (C_{22:6} ω-3) in low amounts ranged from 0.294% in sample A to 0.474% in sample C. Comparing fatty acids composition of the investigated biscuit samples with those of lard fat, all samples were free from lard fat as it is not permissible in Muslim foods.

Keywords: Biscuit , SFA , PUFA , DHA , TFA, Lard fat.

INTRODUCTION

Fats are one of the most important ingredients used in the manufacture of biscuits. They are the third largest component, after flour and sugar. Fat quality is determined by its fatty acids composition. The reduction of saturated fat in the diet will eventually help in lowering blood cholesterol (Grundy, 1990; Koletzko, 1992). Fatty acids with medium chain length have a greater adverse effect on lowering blood cholesterol, such as Luric C12:0, Myristic C14:0 and Palmitic C16:0, than those with longer chain ones.

Determination of the total fatty acid profile allows calculating the type and concentration of each fatty acid present in an original lipid sample (Carapelli *et al.*, 2004).

Trans fatty acids are produced during industrial hydrogenation of edible fats and oils to produce dietary fats with improved texture and other commercially desirable physical properties. During partial hydrogenation, some double bonds remain but may shift to a different position along a chain and alter their configuration (Spiller, 2004). Small amounts of trans-fatty acids are also formed from heat-induced isomerization during deodorization under high temperature. The extent of isomerization is more serious in polyunsaturated oils. Depending on the type of unsaturated acids, different trans-isomers can be formed from the original cis unsaturated fatty acids (Tang, 2002).

Tavella *et al.* (2000) found that cookies and crackers in Argentina contained trans fatty acid (2.85%) as elaidic acid (C_{18:1}).

Martin *et al.* (2005) indicated that total trans fatty acids (TFA) ranged from 12.2% to 31.2% of total fatty acids in Brazilian cream cracker biscuits. Trans 18:1 isomer was the major group of TFA present in all the analyzed

brands, representing 83.2% of total trans isomers. The mono-trans 18:2 isomer content ranged from 1.6% to 4.2% of total fatty acids, this being the most common group of trans polyunsaturated acid. The di-trans 18:2 isomer (9t, 12t) was found at very low levels (0.10–0.15% of total fatty acids). Trans 18:3 isomer content ranged from 0.11% to 0.75% of total fatty acids representing 24.4–75.0% of total α -linolenic acid. These results indicate that Brazilian cream cracker biscuits contain considerable proportions of trans fatty acids, both monounsaturated and polyunsaturated.

Neo *et al.* (2007) found that total saturated fatty acids (SFA) in five Malaysian biscuits samples ranged from 48.90% to 54.87% of total fatty acids. As for the polyunsaturated fatty acids (PUFA), the total PUFA in the samples ranged from 9.97% to 11.73% of total fatty acids. Total trans fatty acids (TFA) ranged from 0.17% to 0.77% of total fatty acids. The monotrans 18:2 tc or 18:2 ct isomer content ranged from 0.07% to 0.10% of total fatty acids and the ditrans 18:2 isomer (9t, 12t) was not detected. The results indicated that all fat sources of the five biscuit brands were palm oil based.

The objectives of this study were: (1) to identify the fatty acids composition of fats used in five types of Egyptian biscuit; and (2) to assess the quality of these biscuit types using some fat properties like acid value, free fatty acids percentage, peroxide value and thiobarbituric acid. The results of this study can be a valuable source to differentiate between hydrogenated vegetable oil in white and chocolate creamed wafer biscuits and lard fat using fatty acids composition and fat constants.

MATERIALS AND METHODS

Materials:

Five types of most common Egyptian white and chocolate creamed wafer biscuits were brought from local market of Mansoura City, Egypt, during the shelf life of these products.

Chemical analysis:

Acid value (AV), peroxide value (PV) and iodine value (IV) were determined as described in A.O.A.C. (2000).

Free fatty acids content (FFA%) were calculated from acid value as follows:

$$\text{FFA \%} = \text{acid value} \times 0.503.$$

Thiobarbituric acid value (TBA) was determined as described by Tarladgis *et al.* (1960). TBA value was expressed as mg malonaldehyde/kg oil using the following equation:

$$\text{TBA} = 7.8 \times \text{O.D.}$$

Where: O.D. = optical density at 538 nm.

Fatty acids composition of fat samples were analyzed out in The Central Laboratory Unit, High Institute of Public Health, Alexandria University, Egypt. Fatty acid methyl esters were prepared according to the procedure of Radwan (1978). About 50 mg of fat sample was transferred into screw-cap vial. Two ml of benzene and 10 ml of 1% H₂SO₄ in absolute methanol were added. The vial was covered under a stream of nitrogen before heating, in an oven, to 90°C for 90 min. Ten ml of distilled water were added to the cooled

vial and the methyl esters in each vial were extracted with 5 ml of petroleum ether for three times. The three petroleum ether extracts were combined and concentrated to its minimum volume by using a stream of nitrogen.

The different fatty acid methyl esters (FAMES) were determined and identified using a gas chromatography (HP 6890) equipped with a flame ionization detector (FID). A HP-5 column (30 m) [5% dimethyl 95% diphenyl polysiloxane] was used. The detector and injector temperatures were 250°C and 220°C, respectively. Sample size was 1 µl. Helium was used as a carrier gas at a flow rate of 0.8 ml/min. Oven temperature was programmed as:

- set point (initial temperature) 150°C for 1 Min.
 - rate 10°C/Min. to 200°C.
 - rate 5°C/Min. to 250°C and hold for 4 Min.
- A standard mixture of methyl esters was used.

RESULTS AND DISCUSSIONS

Fatty Acids composition of Egyptian biscuit fat:

Fatty acids composition of five types of Egyptian biscuit fat was shown in Table (1). In all samples, saturated and polyunsaturated fatty acids represented the largest and lowest contents, respectively, except in case of sample B and C where polyunsaturated fatty acids were higher than monounsaturated ones. The most abundant saturated fatty acid in most biscuit samples was luric acid (C_{12:0}) except for sample E, where, palmitic acid (C_{16:0}) was the most common one while, the most prevailing monounsaturated fatty acid in all samples was oleic acid (C_{18:1cis}). Among polyunsaturated fatty acids, linoleic acid (C_{18:2} ω-6) was the major fatty acid in three samples (A, B and C). Docosahexaenoic acid (DHA, C_{22:6} ω-3) was detected in all samples under investigation but in small amounts.

From data presented in Table (1) and Fig. (1), it could be observed that total saturated fatty acids ranged from 64.35% in sample E to 85.43% in sample B. The most predominant fatty acids were luric, myrastic and palmitic. The highest value of luric acid was in sample B (38.52%), while the least one was in sample E (15.68%). Myrastic acid (C_{14:0}) ranged from 5.48% in sample E to 13.15% in sample B. On the other hand, palmitic acid (C_{16:0}) was found to be 13.99% in sample B and 28.85% in sample E. Concerning stearic acid (C_{18:0}) content, it was nearly similar in all samples but the highest value was in sample B (14.47%). These results agreed with those of Neo *et al.* (2007) who reported that saturated fatty acids have the highest of fats extracted from Malaysian biscuit samples, but the present results gave higher percentage values of saturated fatty acids than those mentioned by the same authors. Martin *et al.*, (2005) found that total SFA were significantly higher in Brazilian cracker biscuits than the present results. This may be due to the use of lard in production of Brazilian samples.

Data presented in Table (1) and Fig. (2) show that total monounsaturated fatty acids content ranged between 0.393% to 31.44% in fats of five Egyptian biscuit samples. Oleic acid (C_{18:1cis}) was the main monounsaturated fatty acid detected in samples A, D and E where, it represented 12.77%, 21.31% and 30.84% of total fatty acids, respectively.

Table (1): Fatty acids composition of five Egyptian biscuit fat as percentage of total fatty acid methyl esters:

Fatty acids	Biscuit Samples				
	A	B	C	D	E
C _{4:0}	0.014	0.034	0.015	0.004	0.025
C _{6:0}	1.44	2.37	1.53	1.10	1.16
C _{8:0}	0.002	0.004	0.045	0.007	1.69
C _{10:0}	1.95	2.71	2.45	1.93	1.16
C _{12:0}	26.49	38.52	34.72	30.11	15.68
C _{13:0}	0.022	0.035	0.000	0.023	0.000
C _{14:0}	9.16	13.15	11.63	10.73	5.48
C _{15:0}	0.025	0.022	0.000	0.000	0.000
C _{16:0}	23.71	13.99	18.22	21.77	28.85
C _{17:0}	0.052	0.040	0.045	0.048	0.060
C _{18:0}	11.75	14.47	12.71	11.88	10.24
C _{23:0}	0.241	0.087	0.064	0.076	0.000
Σ(Saturated)	74.86	85.43	81.43	77.68	64.35
C _{15:1}	0.016	0.019	0.024	0.013	0.000
C _{16:1}	0.077	0.045	0.000	0.000	0.000
C _{17:1}	0.019	0.025	0.029	0.019	0.020
C _{18:1 trans}	0.083	0.090	0.000	0.042	0.176
C _{18:1 cis}	12.77	0.029	0.034	21.31	30.84
C _{20:1}	0.286	0.271	0.256	0.270	0.340
C _{22:1}	0.060	0.050	0.050	0.057	0.065
Σ(Monounsaturated)	13.31	0.529	0.393	21.71	31.44
C _{18:2 ω-6}	11.15	13.11	17.33	0.00	0.00
C _{20:3}	0.108	0.088	0.101	0.079	0.148
C _{22:2}	0.022	0.016	0.026	0.049	0.000
C _{22:6 ω-3}	0.294	0.397	0.474	0.333	0.343
Σ(Polyunsaturated)	11.57	13.61	17.93	0.461	0.491
Total	99.74	99.57	99.75	99.85	96.28
Total unsaturated	24.88	14.14	18.32	22.17	31.93
Biological Value*	0.33	0.17	0.23	0.29	0.50

* Biological value means total unsaturated fatty acids / total saturated fatty acids.

However, samples B and C gave lower percentage values (0.029% and 0.034% of total fatty acids, respectively). Trans Oleic acid was found in all samples in small amounts (0.042% to 0.176% of total fatty acids) except in sample C where it was absent. These results are not inline with those of Martin *et al.* (2005) who stated that Brazilian cream cracker biscuits contain considerable proportions of trans fatty acids, both monounsaturated and polyunsaturated. The amount of trans monounsaturated and polyunsaturated fatty acids in all the investigated samples were very low or even undetectable. Therefore, it could be postulated that palm oil was only fat sources for making such biscuits. Results of other authors revealed that trans fatty acids content was 12.7% for USA (Enig *et al.*, 1984), 11.1% for Argentina (Tavella *et al.*, 2000), 9.1% for Greece (Van Erp-baart *et al.*, 1998) and 2.0% for New Zealand (Lake *et al.*, 1996). The high level of trans fatty acids content could be due to the use of hydrogenated polyunsaturated fat in making such biscuits (Neo *et al.*, 2007). This means that the fat of present Egyptian biscuit fat samples were nearly free from trans fatty acids which play negative effects on human health.

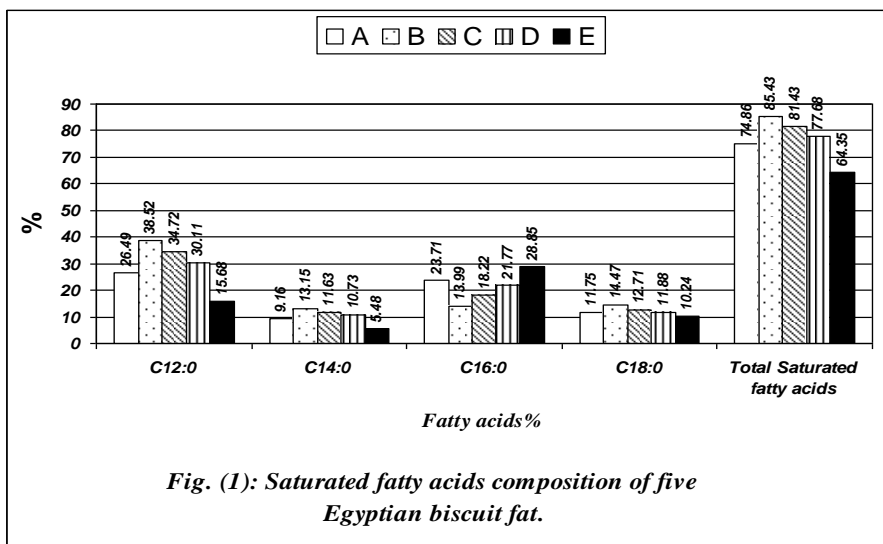


Fig. (1): Saturated fatty acids composition of five Egyptian biscuit fat.

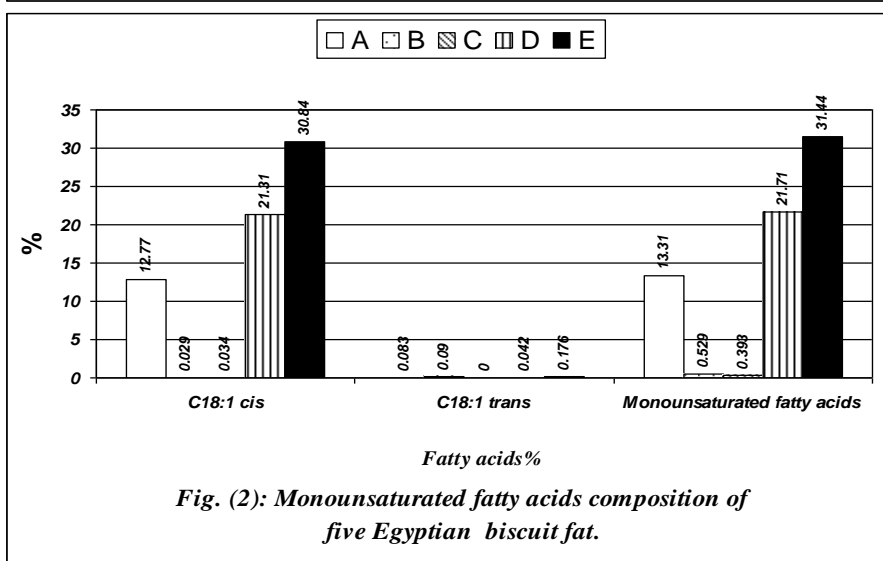


Fig. (2): Monounsaturated fatty acids composition of five Egyptian biscuit fat.

The data presented in Table (1) and Fig. (3) indicate that polyunsaturated fatty acids (PUFA) ranged from 0.461% in sample D to 17.93% in sample C. Linoleic acid (C_{18:2}) was the main polyunsaturated fatty acid which ranged from 11.15% in sample A to 17.33% of fatty acids in sample C while, this fatty acid was not detected in samples D and E. From Table (1), it could be seen that docosahexaenoic acid, DHA (C_{22:6} ω-3), varied from 0.294% in sample A to 0.474% in sample C. PUFA group includes essential fatty acids which are very important for the biological and nutritional values of these biscuit types. Although, sample E showed to contain high amount of trans fatty acids, it had a lower level of essential fatty acids.

It should be mentioned that the Department of Health (UK) (HMSO, 1994) recommended a minimal PUFA/ SFA ratio of 45%. The obtained results gave a lower value of 22% for sample C.

Total unsaturated fatty acids content in five Egyptian biscuit fat samples were shown in Fig. (4) where, it was 14.14% in sample B and 31.93% in sample E. These results were the sum of mono and polyunsaturated fatty acids in biscuit fat samples.

Biological value of biscuits fat (total unsaturated fatty acids/ total saturated fatty acids) indicated the nutritive value of these fats. It reached the highest value in sample E (0.50) while reached the least value in sample B (0.17).

Some chemical properties of Egyptian biscuit fat:

Similarly, Iodine number which express the degree of unsaturation of fatty acids, ranged from 5.36 in sample C to 17.25 in sample E as shown in Fig. (4).

It is well known that acid value could hardly be considered a constant value characteristic of edible oils since it changes, more or less according to a certain extent, during storage of such oils or when subjected to severe treatments (Zein El-Din, 1999).

Acid value of five Egyptian biscuit samples (Table 2) ranged from 0.44 in sample E to 3.38 in sample B. Similarly, percentage of free fatty acids ranged from 0.221 % to 1.700 %. These results indicate that there was a lipolytic rancidity. However, it can be confirmed that all fat samples are suitable except sample B but it was in range.

It is well established that initial and primary products of lipid oxidation are hydroperoxides, which are hydrolyzed and break down by further reactions to ketones and aldehydes. Peroxide value is generally listed among the characteristics of edible oil. It is a measure of the deleterious effects and oxidation happened of oil during the storage period. It could serve in detection some intermediate steps in the oxidation process (Mahmoud, 1998).

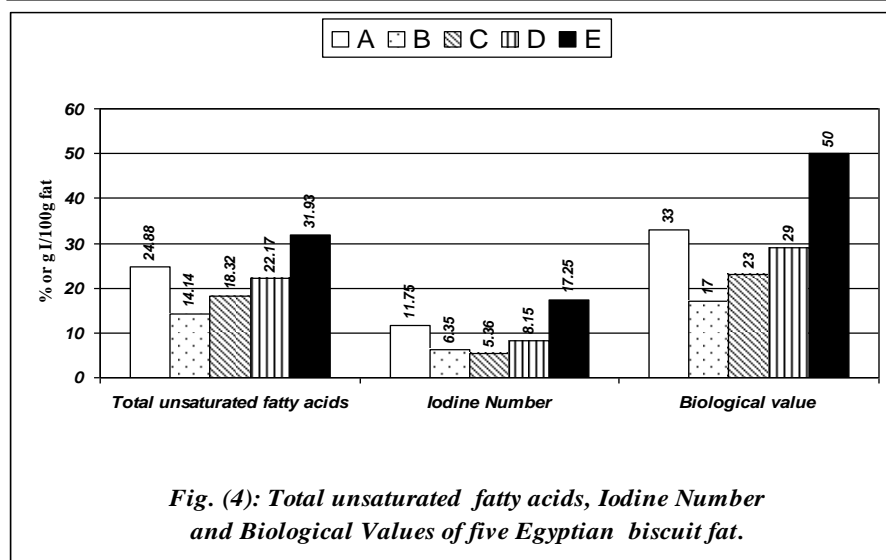
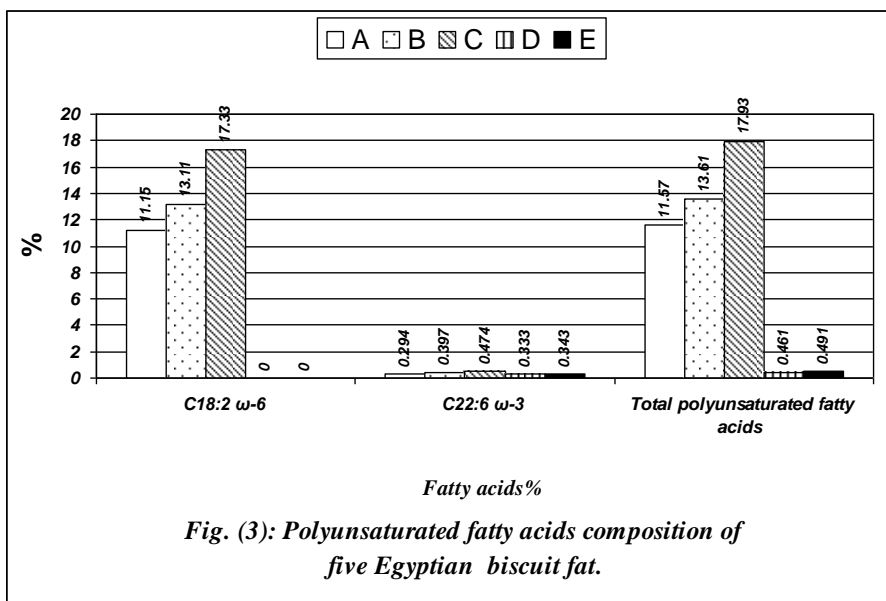
Peroxide values of the investigated samples were ranged from 1.00 to 1.65 meq/kg oil. These values are in the permissible limits. On the other hand, thiobarbituric acid (TBA) value was reported to be a good index for fat oxidation and the undesirable changes in the products quality. From the obtained data (Table 2), it could be seen that TBA values of all samples ranged from 0.686 to 5.13 mg/kg. These results indicated that Egyptian biscuit samples contained a good quality fatty matter with least level of deterioration.

Table (2): Some chemical properties of fats used in five Egyptian biscuit samples:

Constants	Biscuit Samples				
	A	B	C	D	E
AV (acid value)	1.03	3.38	2.82	0.74	0.44
FFA % (Free fatty acids)	0.518	1.700	1.420	0.372	0.221
PV (peroxide value)	1.00	1.10	1.20	1.58	1.65
TBA (Thiobarbituric acid value)	2.3	0.686	2.34	5.13	1.16

PV: meq. peroxide / Kg oil.

TBA: mg malonaldehyde / Kg oil



Ripoche and Guillard (2001) stated that saturated, monounsaturated and polyunsaturated fatty acids percentage of lard fat were 38.60%, 49.90% and 11.60%, respectively. The most common fatty acids were C_{18:1}, C_{16:0}, C_{18:0}, and C_{18:2} represented 46.90%, 23.80%, 3.30% and 10.60%, respectively.

So, when we compared fatty acids composition of Egyptian biscuit fat samples with those of lard fat, we found some remarkable notices may help to differ between vegetable oils and lard fat. For example, vegetable oil contained short chain fatty acids i.e. C_{12:0} and C_{14:0} which appeared in biscuit

fat samples. In other study when we compared fatty acids composition of both palm oil and lard fat, palmitic acid (C_{16:0}) showed a higher percentage value of 43.50% represented twice times than that detected in lard fat (23.80%). Also, stearic acid in lard fat (13.30%) was triple of that found in palm oil (4.30%) (Tan *et al.*, 2000).

CONCLUSION

So, it could be easily concluded that the fats of investigated Egyptian biscuit samples are nearly free from trans fatty acids and lard fats, i.e. contained only vegetable oil, thus, it become safe and healthy for Muslims human nutrition. It could say that, it is possible to differentiate between hydrogenated vegetable oil and lard fat using fatty acids composition and fat constants but we need further research in this area.

REFERENCES

- A.O.A.C. (2000). Official Methods of Analysis, 17th Ed. Association of Official Analytical Chemists, Washington, D.C., USA.
- Carapelli, R.; Martin, C. A.; Matsushita, M.; Souza, N. E. and Visantainer, J. V. (2004). Trans fatty acid content of Brazilian biscuits. *Journal of Maringa State University, Food Chemistry*, 10.022.
- Enig, M. G.; Pallansch, L. A.; Sampugna, J. and Keeney, M. (1984). Fatty acids composition of the fat in selected food items with emphasis on trans components. *Journal of American Oil Chemist Society*, 60: 1788-1795.
- Grundy, S. M. (1990). Trans monounsaturated fatty acids and serum cholesterol levels. *New England Journal of Medicine*, 323: 480 - 487.
- HMSO, UK. (1994). Department of Health. Nutritional aspects of cardiovascular disease (pp. 37–46). London (Report on Health and Social Subjects, 46).
- Koletzko, B. (1992). Fats for brains. *European Journal of Clinical Nutrition*, 46:51- 62.
- Lake, R., Thomson, B., Devane, G., and Scholes, P. (1996). Trans fatty acids content in New Zealand foods. *Journal of Food Composition and Analysis*, 9: 365–374.
- Mahmoud, H.A. (1998). Comparative studies on the use of some agricultural by-products and chemical antioxidants in the storage of foods. M.Sc. thesis, Agricultural Biochemistry, Faculty of Agriculture, Ain Shams University, Egypt.
- Martin, C.A.; Jesui, R.C.; Visantainer, V.L.; Matsushita, M. and De Souza, N.E. (2005). Trans fatty acid content of Brazilian biscuits. *Food chemistry*, 93:445-448.
- Neo, Y.P., Tan, C.H. and Ariffin, A. (2007). Fatty Acid Composition of Five Malaysian Biscuits (Cream Crackers) With Special Reference to trans-Fatty Acids. *ASEAN Food Journal* 14 (3): 197-204.
- Radwan, S.S. (1978). Coupling of two dimensional thin layer chromatography with gas chromatography for the quantitative analysis of lipid classes and their constituent fatty acids. *J. Chromatog. Sci* 16:538-542.

- Ripoche, A. and Guillard, A.S. (2001). Determination of fatty acids composition of Pork fat by Fourier transform infrared spectroscopy. *Meat Science* 58:299-304.
- Spiller, G. A. (2004). The trans fats dilemma and natural palm oil. pp. 27-49. Rocklin, California: Pascoe Publishing Inc.
- Tan, Y.A. ; Kuntom, A. ; Siew, W.L. ; Yusof, M. and Chong, C.L. (2000). PORIM Tech. Palm Oil Research Institute of Malaysia, No. 22.
- Tang, T. S. (2002). Fatty acids composition of edible oils in the Malaysian market, with special reference to trans-fatty acids. *Journal of Oil Palm Research*, 14: 1-8.
- Tarladgis, B.G.; Watts, B.H. and Jounathan (1960). A distillation method for the quantitative determinate of malonaldehyde in rancid food. *J.A.O.C. S.*, 37:44-49.
- Tavella, M.; Peterson, G.; Espeche, M.; Cavallero, E.; Cipolla, L.; Perego, L. and Caballero, B. (2000). Trans fatty acid content of a selection of foods in Argentina. *Food chemistry*, 69: 209-213.
- Van Erp-baart, M. A., Couet, C., Cuadrado, C., Kafatos, A., Stanley, J., and van Poppel, G. (1998). Trans fatty acids in bakery products from 14 European countries: the TRANSFAIR study. *Journal of Food Composition and Analysis*, 11:161-169.
- Zein El Dein, G.E.E. (1999). Chemical and technological studies on oils and oil products and some of its preservation and stability. Ph.D. thesis, Food Industries Dept., Faculty of Agriculture, Mansoura University, Egypt.

تركيب الأحماض الدهنية للدهون المستخدمة في البسكويت المصري

رمضان أحمد حسن* ، صفاء محمد علي حسن* و شادي محمد محمود الشهاوي**
* قسم الكيمياء الزراعية – كلية الزراعة – جامعة المنصورة – مصر
** قسم الصناعات الغذائية – كلية الزراعة – جامعة المنصورة – مصر

تم تقدير تركيب الأحماض الدهنية و كذلك محتوى الأحماض الدهنية الترانس في خمس عينات من البسكويت المصري باستخدام الفصل الكروماتوجرافي السائل الغازي GLC. أشارت النتائج إلى أن الأحماض الدهنية المشبعة الكلية تراوحت بين 64.35% إلى 80.43% بينما تفاوتت نسبة الأحماض الدهنية أحادية عدم التشبع بين 0.393% و 31.44%. أما عن الأحماض الدهنية عديدة عدم التشبع فقد تراوحت بين 0.461% إلى 17.93%. و لقد ظهر حمض الأوليك الترانس بكميات قليلة تمثلت في 0.294% في العينة A و 0.474% في العينة C. و بمقارنة تركيب الأحماض الدهنية في عينات البسكويت المختبر بالموجودة بدهن الخنزير نجد أن عينات البسكويت المصري خالية من الأحماض الدهنية المميزة لدهن الخنزير الغير مصرح به في أغذية المسلمين.

قام بتحكيم البحث

كلية الزراعة – جامعة المنصورة
كلية التربية النوعية – جامعة طنطا

أ. د/ مسعد عبد العزيز أبو رية
أ. د/ عادل عبد الحميد الباجوري

