



OXIDATIVE STABILITY AND SOME FUNCTIONAL PROPERTIES OF GOAT AND CAMEL MILK FAT FRACTIONS

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Awad^{1*}, R.A.; L.F. Hamzawi¹; Marwa. M. Desouky² and K.A.Soryal²

1- Food Sci. Dept., Fac. Agric., Ain Shams Univ., Shoubra Kheima, Cairo, Egypt

*e-mail: rezkawad@hotmail.com

2- Desert Research Center, Matariya, Cairo, Egypt

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ABSTRACT

Goat and camel milk fat were fractionated into liquid and solid fractions by crystallization at 15, 25 for goat and 30, 40 °C for camel milk fat. Fatty acid profile and functional properties (slip melting point, specific gravity, refractive index, cholesterol content, iodine value, and yield) were analysed for original butter oil and obtained fractions. Stability of fat to oxidation during induction & acceleration periods using TBA and polymorphism using x-ray diffraction pattern were also characterized. Fatty acid profile of camel milk fat indicated lower values of total short chain (TSC) and higher values of total long chain (TLC) and unsaturated fatty acids (USFA) compared to goat milk fat. The short chain and unsaturated fatty acids migrate to the liquid fractions being higher at lower fractionation temperature whereas, long chain saturated fatty acids concentrated in solid fractions being increased with increasing the fractionation temperature. Slip melting points were statistically significantly differed among all fractions being higher in camel fractions. Goat milk fat fractions showed higher specific gravity, with lower refractive index, cholesterol content and iodine values compared to camel fat being lowest in solid fractions. Camel milk fat and its fractions were highly stable against oxidation (up to 20 days) and longer shelf-life especially its solid frac-

tions, as compared to goat fat. The liquid fractions of both goat and camel fat exhibited lower stability to oxidation (higher TBA) than their butter oil or solid fractions. The X-ray diffraction pattern of camel milk fat fractions showed different peaks compared to goat fat fractions. Liquid fractions of camel fat showed both β and β' polymorphs while liquid goat fat fractions showed only β polymorph. The magnitude of X-ray diffraction peaks increased with increasing the fraction melting point being more pronounced in camel fractions which indicate higher crystallization and stability of camel fat.

INTRODUCTION

Milk fat is a very complex mixture containing more than 473 fatty acids, having wide melting range from -40 °C to 40 °C (Boudreau and Arul, 1993). This heterogeneity can be used to the advantages of dairy industry to separate out these different melting components into fractions that are more functional in food as individual fractions than as intact milk fat. Nevertheless, milk fat has several undesirable attributes that limit its uses and thus have caused a world wide surplus of this important food ingredient. Among these attributes are the negative health aspects represented in the high content of saturated fatty acids, cholesterol with the low content of polyunsaturated fatty acids and poor spreadability due to its high solid fat content at refrigeration temperature (Viatte, 1997).

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Milk fat is traditionally supplied to the food industry as butter or anhydrous milk fat, which may not be the forms best suited to some applications. The functional requirements of fats vary greatly depending on the application. Different types of fractionation processes have been developed, which include melting (Deffense, 1993), solvent (Hartel, 2001), detergent (Rajah, 1996), supercritical fluid extraction (Rizvi and Bhaskar, 1995) and short path distillation (Campos *et al* 2003). The most common process is cold or dry fractionation, in which the separation of triacylglycerol takes place on the basis of their melting points. Dry fractionation or melt crystallization of milk fat is a simple physical process that separates milk fat into fractions that have different physical and chemical properties. The process is termed 'dry' as no chemicals are used, which matches with the consumer demand for foods devoid of any chemical treatments. Dry fractionation as well offers benefits such as, the reasonable cost of scale-up and processing alongside with the relatively simple equipments required (Laakso *et al* 1992). Specialty milk fat ingredients are tailored for specific end uses and designed to optimize the functional characteristics that are desirable and important to a given application. The most common changes that can be made to modify milk fat are melting profile and melting point, plasticity, and total fat content. Technologies used to make these modifications are fractionation, blending, and texturizing (Kaylegian, 1999). Milk fat can be modified to improve its functional and expand its usage for traditional and nontraditional application. New applications include the use of intact milk fat and milk fat fractions in the production of structured lipids, sucrose polyesters, edible films, emulsifiers, and cosmetics. Other nontraditional functionality associated with milk lipids includes the antioxidant and anticarcinogenic properties of conjugated linoleic acid and the antimicrobial properties of lauric acid (Kaylegian and Lindsay, 1995).

Camel and goat milk fat have unique different functional properties. Turags belief that camel milk is especially healthy for sick and old people probably because of its fat composition and vitamin content. Goat milk fat exceeds cow milk in monounsaturated (MUFA), polyunsaturated fatty acids (PUFA), and medium chain triglycerides (MCT), which all are known to be beneficial for human health. Goat and camel butter, ghee and related products have not studied much nor produced commercially which would have new human health benefits (Alferez *et al* 2001).

Since cow milk is the predominant source of milk fat in most of world countries, therefore cow milk fat has gained more interest to be subjected for fractionation and properties of its fractions. Scanning of literature revealed that studies on camel and goat milk have been mainly conducted on its gross chemical composition, while little work has been done on milk fat and nearly nothing on the detailed fractions. However, this work was planned to spot some light on the properties of goat and camel milk fat fractions with emphasis on fractions stability and functional properties.

MATERIALS AND METHODS

Materials

Preparation of goat and camel butter oil (BO)

Collected goat and camel milk samples were separated using a separator (Alfa-Laval, Sweden). The resultant cream was churned into butter using stainless steel butter churner. Obtained butter was melted at 60°C and the top layer was decanted, then the melted butter was filtered through four layers of cheese cloth to obtain clear butter oil (BO) with approximately 99.5 %pure milk fat.

Preparation of fat fractions

BO samples of both goat and camel were separately placed in beaker and held at 80°C for 10 min using water bath to destroy all crystal nuclei. Each sample was then slowly cooled at a rate of 1°C/min using the same water bath to the initial fractionation temperature (15°C for goat and 30°C for camel). After 9 hr of total cooling and holding time the resultant solid fraction at 15 or 30°C was separated from the liquid fraction (liquid 15 or 30°C for goat and camel butter oil respectively) using centrifuge under cooling. Both solid and liquid fractions were weighed and the yield of each was calculated. A similar process was used for fractionation of solid goat or camel milk fat fraction at 25 or 40°C in order to obtain the solid and liquid fraction at the same temperatures.

Method of analysis

Slip melting point, specific gravity and refractive index were measured in both goat and camel milk fat and their various fractions as described in AOAC, (2000). Cholesterol content was determined by the method of Gilliland *et al* (1985).

Iodine value was determined by the method of AOCS, (1998). Fatty acid profiles of both goat and camel milk fat and their various fractions were determined after conversion of the fatty acids into the corresponding methylesters as described by the method of Amer *et al* (1985). Keeping quality of both goat and camel milk fat fractions and their original butter oil was carried out by determining the accelerated stability test by placing open tubes containing the samples in an oven set at $63 \pm 0.5^\circ\text{C}$ using the thiobarbituric acid (TBA) value at regular intervals according to Keeney and Smith, (1971).

Polymorphism of both goat and camel milk fat fractions and their original butter oil were characterized by following the method of Fomuso and Akoh, (2001) using X-ray diffraction pattern (Shimadzu, X-D-1, X-ray diffractometer, Japan). The X-ray source generation power was set at 40Kv and 30mA. The 2 θ range used was from 10-35° which contains the different patterns characteristics for the different triacylglycerol crystal polymorphs (Aken *et al* 1999). Sample as melted and poured into rectangular mold, then allowed to solidify at room temperature and kept at refrigerator temperature for 12 h. Short spacing of the major polymorphs are as follows β' a strong spacing at 4.2; and β a very strong spacing at 4.6 and another one at 3.80 Å (Man, 1992).

Statistical analysis

The data (mean of three replicates) were analysed by the General Linear Models procedure of SAS (1994). Least significant difference test was performed to determine differences in means at $p \leq 0.05$.

RESULTS AND DISCUSSION

The fatty acid composition of goat and camel milk fat and its fractions are depicted in Table (1). Fatty acid profile of goat fat and its fractions indicated that all fatty acids are present except $C_{16:1}$, $C_{18:3}$ and C_{20} , while in camel fat only short chain C_4 was not shown. These notices were also confirmed with total short chain (TSC) and total long chain (TLC) fatty acid values as well as the ratio of both (TSC/TLC). Goat milk fat exhibited higher values of TSC while camel milk fat had higher values of TLC and unsaturated fatty acid (USFA). Therefore, the ratio of TSC/TLC was very low in camel fat compared to goat fat. It can be also noticed that, saturated fatty acids (SFA) were most abundant in all samples. With increasing fractiona-

tion temperature, saturated fatty acids gradually increased, while unsaturated fatty acids gradually decreased. Unsaturated fatty acids of liquid goat milk fat fractions were higher than that of solid fractions and the original butter oil. These findings are in agreement with the results obtained by Grall and Hartel, (1992), who indicated that the short chain fatty acids and unsaturated fatty acids migrate to the liquid fractions, whereas the long chain saturated fatty acids remain with the crystalline fraction. It can be inferred also from the data that, the fatty acids composition of the various fractions differed appreciably from one to another as well as from the original butter oil. Short chain saturated fatty acids $C_{4:0}$ to $C_{8:0}$ were found to be in higher concentration of the liquid fractions. The liquid fraction (L15) had greater content of short chain fatty acids than L25, whereas myristic ($C_{14:0}$) and palmitic ($C_{16:0}$) were more in solid fractions than liquid fractions and S25 had greater content of these long chain fatty acids than S15. The unsaturated fatty acids, oleic $C_{18:1}$ and linoleic $C_{18:2}$ were mostly concentrated in the liquid fractions and the concentration of these fatty acids was related to the fractionation temperature. Our results are in close agreement with the results obtained by Bindal and Wadhwa, (1993) and Arora and Rai, (1998).

From fatty acid profile of camel milk fat and its fractions it could be also observed that liquid camel fractions showed the highest levels of unsaturated fatty acids and the ratio of USFA / SFA decreased from 0.632 to 0.597 for L30 and L40, respectively. Gnan and Sheriha, (1986) showed that, in Libyan camel milk fat, C_{14} , $C_{16:0}$, $C_{16:1}$, $C_{18:0}$, $C_{18:1}$ contributed more than 85 % of the fatty acids. Sawaya *et al* (1984) showed comparable results for some individual fatty acids and pointed out that short chain fatty acids ($C_{6:0}$ - $C_{10:0}$) were present in very small amounts. However, camel milk fat contained high levels of linoleic and poly unsaturated fatty acids, which are essential for human nutrition. Moreover, Farah *et al* (1989) indicated that camel milk fat contains less short chain fatty acids but relatively high concentration of $C_{14:0}$ and $C_{16:0}$ acids. The results obtained of fatty acids profile are concised with general trends of Badings *et al* (1983); Amer *et al* (1985); Fouad *et al* (1990); Abd El-Rahman *et al* (1998) and Aken *et al* (1999). There were no information on fatty acid composition of camel milk fat fractions, and no research has been done concerning the effect of thermal fractionation on fatty acid composition of each fraction (solid and liquid).

Table 1. Fatty acid profile (as %) of the main fatty acid groups for goat and camel milk fat and their fractions

Fatty acid	NO. of carbon	% Fatty acid									
		Goat milk fat					Camel milk fat				
		BO	L15	S15	L 25	S 25	BO	L30	S30	L40	S40
Butyric	C4	5.95	4.98	3.57	3.29	2.48	-	-	-	-	-
Caproic	C6	6.96	2.85	2.24	2.17	1.88	0.38	0.29	0.12	0.28	0.08
Caprylic	C8	3.39	3.29	2.28	2.43	1.78	0.55	0.43	0.27	0.38	0.22
Capric	C10	12.99	11.47	11.25	10.87	10.08	1.34	0.72	0.51	0.69	0.46
Lauric	C12	4.49	5.98	5.33	5.24	4.25	2.52	0.07	1.94	2.01	1.82
Myristic	C14	11.26	12.48	14.62	14.52	16.19	14.43	13.03	11.31	11.54	9.89
Palmitic	C16	22.76	23.53	26.19	24.22	28.24	28.34	28.98	33.48	30.34	33.67
Palmitoleic	C16 :1	-	-	-	-	-	8.50	9.79	9.67	11.48	10.64
Stearic	C18	10.35	8.43	9.99	11.49	13.64	15.44	14.57	19.81	16.24	21.43
Oleic	C18 :1	19.49	23.09	22.11	22.86	19.58	22.11	24.26	18.34	22.00	17.58
linoleic	C18 :2	1.98	3.39	1.89	2.41	1.61	2.88	3.46	2.91	2.75	2.69
linolenic	C18 :3	-	-	-	-	-	1.18	1.15	0.96	1.11	0.88
Arachidonic	C20	-	-	-	-	-	2.31	1.06	0.41	1.03	0.34
Total short chain	C ₄ - C ₈	16.30	11.12	8.09	7.89	6.14	0.93	0.72	0.39	0.66	0.30
Total long chain	C ₁₀ - C ₂₀	83.32	88.37	91.38	91.61	93.59	99.05	99.09	99.34	99.19	99.40
USFA	C _{16:1} - C _{18:3}	21.47	26.48	24.00	25.27	21.19	34.67	38.66	31.88	37.34	31.79
SFA	C ₄ - C ₂₀	78.15	73.01	75.47	74.23	78.54	65.31	61.15	67.85	62.51	67.91
USFA / SFA		0.275	0.363	0.318	0.340	0.269	0.531	0.632	0.469	0.597	0.468
TSCFA/TLCFA		0.196	0.133	0.089	0.086	0.066	0.0093	0.0073	0.0039	0.0065	0.0030

BO, Butter oil; S, L solid and liquid fractions. Number following the type of fraction corresponds to the temperature at which the fraction separated.
USFA, unsaturated fatty acids; SFA, saturated fatty acids.

Functional properties of fat fractions

Slip melting point, specific gravity, refractive index, cholesterol content, iodine value and yield of goat and camel milk fat fractions obtained by thermal fractionation at 15, 25 and 30, 40°C for goat and camel milk fat, respectively are presented in **Table (2)**. It could be noticed from the data that, camel milk fat and its fractions had a significantly higher melting point ($p \leq 0.05$) than goat milk fat fractions, which was 21.4 and 40.9°C for goat and camel butter oil, respectively. Whereas, **Farah et al (1989)** and **Fatouh et al (2004)** showed that, camel butter melted at a comparable range of 40.6 – 42.5°C with a mean melting point of 41.4°C which is 8°C higher than the corresponding values in cow milk butter oil and 6.2°C higher than the buffaloes milk fat. The higher melting point of camel milk fat and its various fractions than goat milk fat fractions could be due to the higher percentages of solid fat (long chain fatty acids) in camel milk fat fractions. The high melting point for camel milk fat produces butter not usually eaten and often used as a base of medicines. The highest slip melting point of goat milk fat and its fractions was observed for S25°C followed by S15°C, while, the lower slip melting point were observed for L15°C. Solid fractions of both goat and camel fat generally indicated higher slip melting point than liquid fractions being highest for camel S40. Thus, it can be concluded that higher slip melting point of solid than liquid fractions might be due to a greater content of high melting triglycerides in solid fractions (**Table, 1**). **Lakshminarayana and Murthy, (1985)**; **Ramesh and Bindal, (1987)**; **Bindal and Wadhwa, (1993)** recorded similar trend for cow and buffalo milk fat fractions. Changes in slip melting point of the fractions are mainly due to changes that occurred in proportions of palmitic C_{16:0}, and stearic C_{18:0} acids, which have melting points of 62.9 and 69.6°C, respectively (**Formo, 1979**). Slip melting point of S25°C was significantly higher by 14.63°C than that of the original butter oil (21.44°C) due to the increase in both C_{16:0} (From 22.76 to 28.24 mg / 100mg) and C_{18:0} (From 10.35 to 13.64 mg/100mg). **Lakshminarayana and Murthy, (1985)** reported melting points of 37.5, 14.5 and 35.8°C for S31°C, L15°C and buffaloes milk fat, respectively. It is noteworthy that, the substantial differences in the melting properties among fractions were not reflected as much as in their fatty acids composition. **Saada et al (1983)** reported that, after five successive crystallization process,

there was no clear cut difference among the fractions, which maintained an overall similarity in gross fatty acid composition. This is due to the fact that the process is based on the different melting points of the triacylglycerol in the mixture and only indirectly on the melting points of the individual fatty acids. The melting point of triacylglycerol is a function of the chain length of its three fatty acids residues, their type of unsaturation and their distribution on the glycerol backbone (**Laakso et al 1992 and Deffense, 1993**).

Specific gravity (Sp gr) of both goat and camel butter oil and their various fractions are given in **Table (2)**. It can be noticed that, specific gravity decreased with increasing slip melting point of the fractions which may be ascribed to the decrease in the unsaturated fatty acids content (**Table 1**). Sp gr of camel milk fat and its fractions was significantly lower than that of goat milk fat and its fractions. Moreover, solid fractions showed lower Spgr values compared to liquid fractions. This would be attributed to the content of USFA, SFA and the chain length of fatty acids in the fraction (**Formo, 1979**). Camel milk fat is generally characterized with its higher solidification due to higher content of TLC and lower TSC (**Table, 1**) which lead to lower Sp gr and this is confirmed with obtained results. Fraction L15 of goat milk fat had the highest Sp gr while the fraction S40 of camel milk fat possessed the lowest. The trend found in our results is in agreement with data obtained by **Badings et al (1983)** and **Lakshminarayana and Murthy, (1985)**. Unfortunately, there were no available data in the cited literature for comparison to the results obtained of camel milk fat fractions. Statistical analysis of Sp gr among all fat fraction was significantly different.

Refractive index (RI) values of butter oil and its fractions of goat and camel milk fat are presented in **Table (2)**. The greater the degree of unsaturation, the higher the refractive index. Goat fat fraction L15 content of unsaturated fatty acids was highest among all the obtained goat fat fractions. Consequently, RI of L15 was higher than the original butter oil which has lower content of unsaturated fatty acids (**Table, 1**). Refractive index of high melting fat fractions L25, S25 of goat and L40, S40 of camel were lower than the original butter oil and other fractions. Generally, the refractive index value for the original camel milk fat is higher than the corresponding values of both cow milk fat (1.449) and buffaloes milk fat (1.452) as determined by **Sankhla and Yadava, (1981)** and **Fatouh et al (2004)**.

Table 2. Some functional properties of goat and camel milk butter oil (BO) and its fat fractions.

Characteristics	Goat BO	Goat milk fat fractions				Camel BO	Camel milk fat fractions			
		L15	S15	L25	S25		L30	S30	L40	S40
Slip melting point (°C)	21.43 ^g	16.80 ⁱ	31.27 ^f	20.73 ^h	36.07 ^e	40.9 ^c	38.2 ^d	42.9 ^b	41.4 ^c	45.9 ^a
Specific gravity	0.9113 ^c	0.9140 ^a	0.9092 ^d	0.9126 ^b	0.9082 ^e	0.9058 ^f	0.9054 ^f	0.9019 ^h	0.9039 ^g	0.8979 ⁱ
Refractive index	1.4517 ^b	1.4549 ^{ab}	1.4516 ^b	1.4519 ^b	1.4448 ^c	1.4558 ^{ab}	1.4577 ^a	1.4547 ^{ab}	1.4559 ^{ab}	1.4525 ^b
Cholesterol content (mg/100g fat)	244.9 ^g	262.9 ^e	240.7 ^h	249.84 ^f	233.97 ^f	321.97 ^c	343.5 ^a	289.44 ^d	328.51 ^b	239.31 ^b
Iodine value (gI ₂ absorbed/100g fat)	31.64 ^g	35.87 ^f	29.44 ⁱ	30.46 ^h	27.41 ^j	42.22 ^a	41.20 ^b	39.25 ^d	39.76 ^c	37.73 ^e
Yield (g/100g)	100	8.4	91.6	16.48	75.12	100	4.9	95.1	8.46	86.64

S, L, solid and liquid fractions. Number following the type of fraction corresponds to the temperature at which the fraction separated.

a, b, c: Means with same letter among various fractions are not significantly different ($P \leq 0.05$)

The distribution of cholesterol content among various goat and camel milk fat fractions indicated that liquid fractions of goat and camel were higher in cholesterol content than solid fractions. Low melting fractions (L15, L30) for goat and camel milk fat showed significantly higher cholesterol content than their original butter oil and solid fractions. The higher concentration of cholesterol in low melting fractions may be attributed to the high affinity of cholesterol for short chain and unsaturated fatty acids, which were predominate in low melting fraction as compared to high melting fraction. Values of cholesterol returned to decrease with increasing the fractionation temperature reaching its lowest value of 233.97 mg / 100g fat in goat fraction S25. Same trends of cholesterol distribution were found between liquid and solid camel milk fat fractions. Generally, cholesterol content was significantly higher in camel milk fat and its fractions than goat milk fat. This is mainly due to the high affinity of cholesterol for USFA, which were predominate in camel milk fat fractions (34.67 % in BO, Table, 1) as compared to (21.47) in goat BO. This could also be explained by the ratio of USFA/SFA which was higher in camel milk fat and its fractions than goat milk fat. The results obtained are in agreement with general trends observed by Arul *et al* (1988) and Bhaskar *et al* (1998). Unfortunately, there were no available data in the cited literature for total cholesterol for goat and camel milk fat fractions.

Iodine value (IV) of various fat fractions (Table, 2) revealed substantial alterations in the chemical composition of the resultant fractions caused by multi-step fractionation. It is well known that (IV) is a measure of unsaturation in fat, the higher proportion of unsaturated fatty acids the higher the IV. Camel milk fat fractions showed significantly higher iodine value IV than goat milk fat fractions. Iodine value of goat L15, which was entirely liquid at room temperature, was the highest among all the obtained goat fractions while S25 was the lowest. Similar trend was found in camel milk fat since L30 had the highest IV value while S40 which was solid with waxy appearance showed lower IV. The higher iodine value of low melting fractions is readily explained by the chemical composition and distribution of fatty acids. Low melting fractions L30, L15 were enriched in USFA, while depleted in SFA content and the trend was vice versa in high melting fractions. Farah *et al* (1989) and Hamzawi *et al* (1998) reported that camel butter had higher IV than cow butter with an average of 48.96 g I₂ ab-

sorbed /100 g fat. The trend of the obtained data confirmed other reported studies and it was in agreement with Amer *et al* (1985), and Sherbon *et al* (1972).

The proportional yield of solid and liquid fractions varied with increasing fractionation temperature. The ratio between liquid and solid goat milk fat fractions at 15 and 25°C was 8.4: 91.6 and 16.48: 75.12, respectively. However, at 30°C the ratio between liquid and solid camel milk fat fractions was 4.9: 95.1, but when the fractionation temperature increased to 40°C, the liquid fraction yield increased from 4.9 to 8.46%, while the solid fraction yield decreased from 95.1 to 86.64%. Nevertheless, crystallization at lower temperature of 15 or 30°C for goat and camel milk fat yielded higher amount of solid fraction. At these lower temperature degrees, more crystallization of medium and high melting triglycerides was occurred, thus increasing the yield of solid fraction. In addition, at lower crystallization temperature the mass of solid fraction also includes a mass of liquid oil entrapped within the crystal lattice, which has been noted as a major problem associated with melt crystallization (Grall and Hartel, 1992).

Stability of fat to oxidation

Oxidation of milk fat is one of the most important changes limiting the palatability, nutritional quality and different uses of fat and fatty products. The compositional properties of milk fat and the concentration of natural antioxidants are the main factors affecting the degree of stability to oxidation. Autoxidation of cow and buffalo milk fat was extensively studied before (Bhat *et al* 1980; Nath and Murthy, 1983; AL-Tahiri *et al* 1987), whereas there are rare information on camel and goat BO and nearly none concerning goat and camel milk fat fractions. The development of thiobarbituric acid (TBA) readings (as OD) at 63°C of goat (A) and camel (B) milk fat fractions, during induction and acceleration periods are demonstrated in Fig. (1). Chemical composition of fat fraction has great influence on their susceptibility to oxidation. The higher the degree of unsaturation, the lower the oil stability. At lower fractionation temperature the fraction contains higher ratio of USFA especially polyunsaturated fatty acids which are highly susceptible to oxidation. Therefore, L15 which is liquid at room temperature showed the highest TBA values among all goat and camel fractions. Thus, it is expected to undergo a faster rate of oxidation with significantly

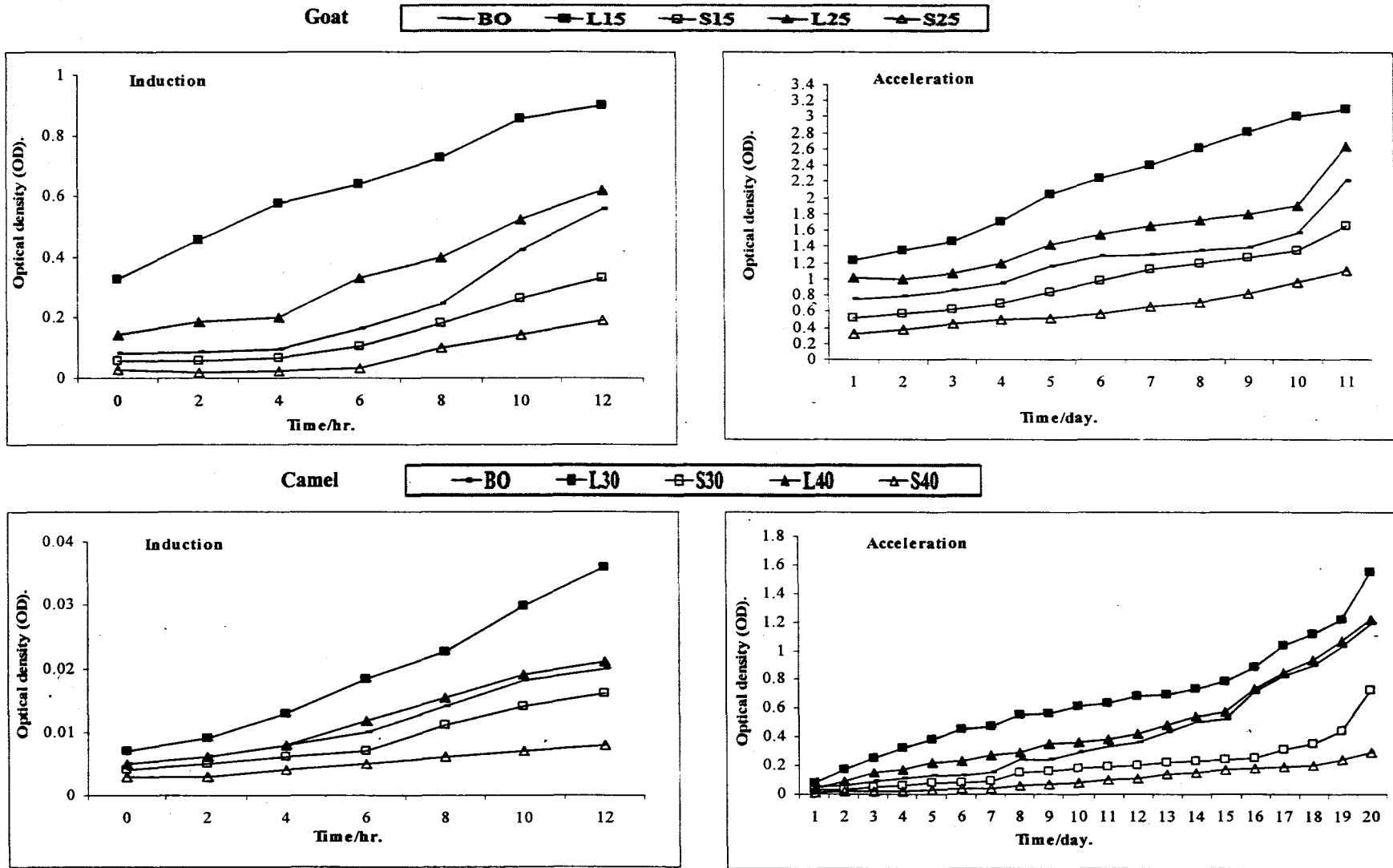


Fig. 1. Oxidative stability of goat and camel milk fat at 63°C during induction and acceleration periods using thiobarbituric acid (TBA) test.

lower fat stability and keeping quality. Goat BO and its fat fractions exhibited higher TBA values during induction and acceleration compared to camel BO and its fractions. This means that camel fat is generally more stable to oxidation and has higher keeping quality than goat milk fat. It is also observed from Fig. (1) that the liquid fractions of both goat and camel fat exhibited lower stability to oxidation (higher TBA values) than BO or solid fractions. On the other hand, solid fractions showed more stability to oxidation than BO in both goat and camel fats. The previous trend was noticeable during induction and acceleration periods. The acceleration period continued up to 11 days for goat fat fractions when sharp increase was noticed. For camel fat, the acceleration period continued up to 20 days when the sharp increase in TBA values was noticed. The extended period of acceleration in camel fat would also confirm the higher stability to oxidation and longer shelf-life of this fat especially its solid fractions, even compared to buffalo or cow fat. It could be also noticed that, TBA readings were null at zero time being 0.08, 0.32, 0.14, 0.06 and 0.03 for goat BO, L15, L25, S15 and S25°C, respectively. TBA showed gradual increase during induction and acceleration period at 63°C being highest in L15 among all fractions and original butter oil. Generally, liquid fractions had higher TBA values than solid fractions due to the higher content of unsaturated fatty acids at liquid fraction which apparently involved in the formation of malondialdehyde that reacts with thiobarbituric acid. More oxidation resulted in more accumulation of malondialdehyde; also the acceleration temperature is responsible for the formation rate of such aldehyde. (Sonntag, 1979; Richardson and Korycka, 1983). It was also observed from Fig. (1) for camel fat that, low melting fraction L30°C showed significantly higher autoxidation rates as compared to original milk fat and other fractions, whereas S40 fraction showed lesser autoxidation rate as compared to the camel butter oil. The presence of higher concentration of unsaturated fatty acids had a greater influence on accelerating rates. Based on chemical composition, the great resistance exhibited by camel fat toward oxidation could be attributed to its significantly higher content of high melting fat and long chain fatty acids. The unsaturation in fractions mainly due to triglycerides containing oleic acid and polyunsaturated fatty acids which have been transferred to liquid fractions than solid fractions. It is known that autoxidation markedly increase with increase-

ing the number of double bounds in the fatty acids (Lakshminarayana and Murthy, 1986 and Mahran *et al* 2000).

Polymorphism

The x-ray diffraction pattern of both goat and camel milk fat and its liquid and solid fractions is shown in Fig. (2). The two polymorphs detected were β and β' , the absence of α polymorph attributed to its rapid transformation to the more stable polymorph β and β' . The x-ray diffraction pattern of liquid goat fat fractions showed only β polymorph at 3.9 Å and were less resolved than solid fractions because the sample softened considerably during the x-ray analysis (Fomusa and Akoh, 2001). β and β' polymorphs were pronounced for both butter and solid fractions. β polymorph was detected at 3.9 Å and 4.3 Å of S 15°C and S 25°C while, β' polymorph showed at 4.5 Å for goat butter oil. The inherent BO of goat or camel and its solid fractions revealed similar pattern of polymorphism of β and β' polymorphs. It was also noticed that, the magnitude of x-ray diffraction peaks gradually increased with increasing the fraction melting point which is consistent with the alteration in their chemical composition. Milk fat crystallize in the β' polymorph together with a little β polymorph. β' is attributed to low and medium melting fat, while β polymorph is attributed to higher melting fat (Schaap *et al* 1975). The x-ray diffraction pattern of camel milk fat and its solid and liquid fractions. (Fig. 2, B) showed different peaks in comparison to goat milk fat and its various fractions. All camel milk fat and its solid and liquid fractions showed the two polymorphs β and β' with absence of α - polymorphs. The high melting camel fat fraction (S40) showed β polymorph at 2.9 Å and β' polymorph at 4.8 Å, while β' polymorph detected at 4.4 Å for camel butter oil (BO). Liquid camel milk fat showed different peaks of x-ray diffraction than solid fractions. The liquid fractions of camel fat were also different than liquid fractions of goat fat. The x-ray diffraction pattern of camel liquid fractions showed both β and β' polymorphs at 3.9, 4.6 Å for L30 and 3.9, 4.4 Å for L40 in order. Moreover, camel solid fractions showed different x-ray pattern than goat solid fractions. The peak intensity was more pronounced in camel fractions and β' was showed at 2.9 Å in both S30 and S40 fractions. This means that the crystalline and stability were higher in camel milk fat than that in goat milk fat.

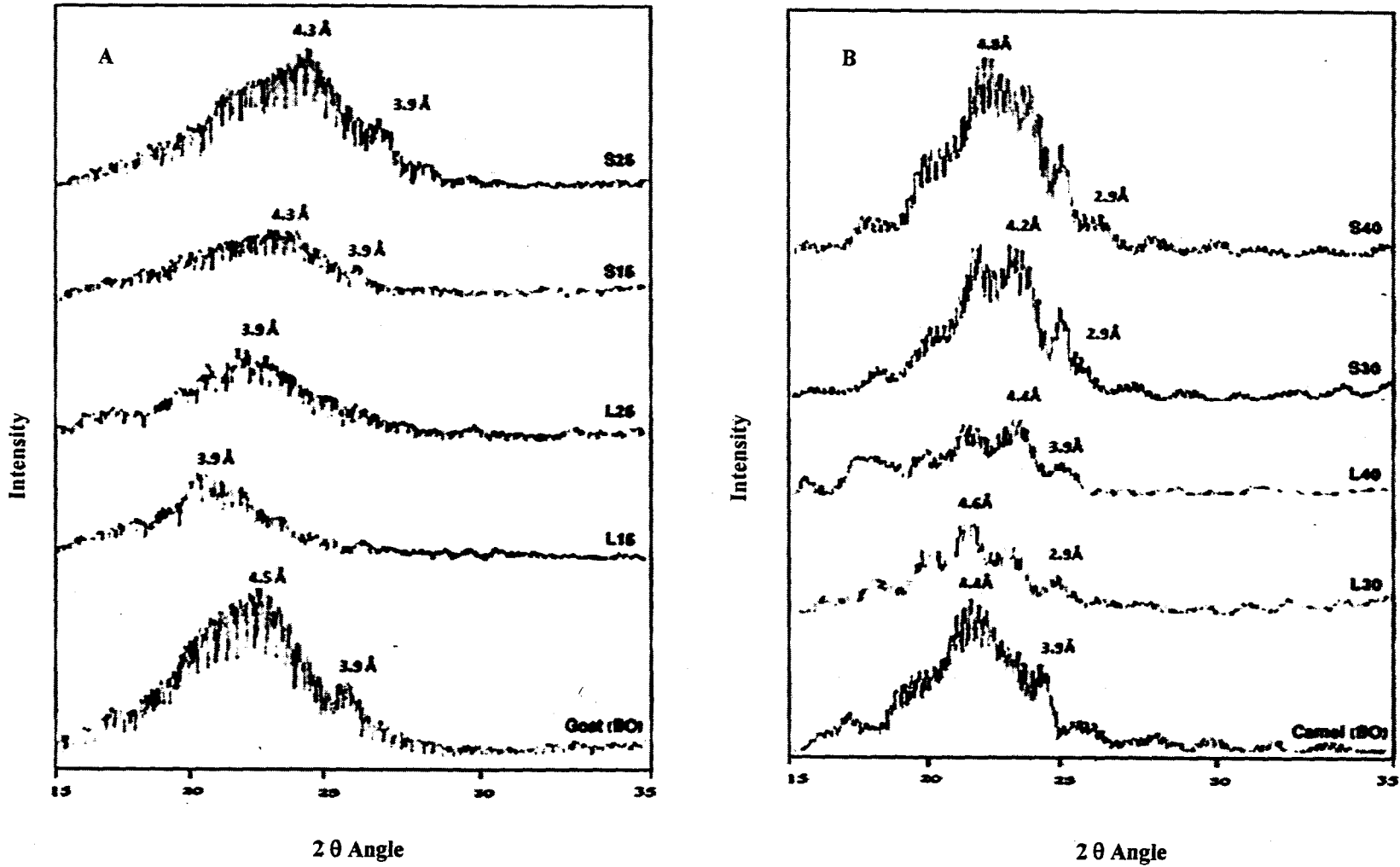


Fig 2. X-ray diffraction pattern of goat (A) and camel (B) milk fat fractions compared to original butter oil (BO)

CONCLUSION

Fractionation of goat or camel milk fat to different liquid and solid fractions can be a good process to produce various fats with various functional properties. The process can give liquid fat at low temperature (15°C) and also solid fat at higher temperature (40°C). It was interesting to find that camel milk fat contains higher amount of TLC, USFA and cholesterol content than goat fat. Camel milk fat fractions were found to be more stable against oxidation and therefore, have longer shelf-life and keeping quality compared to buffalo, cow or goat fats. The X-ray diffraction pattern of camel fat fractions indicated different crystallization behavior than that of goat fat fractions.

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REFERENCE

- Abd El-Rahman, A.M.; S.I. Shalabi and A. Kilara (1998). Chemical and physical properties of anhydrous milk fat, low and very high melting milk fat fractions obtained by a commercial fractionation process. *Milchwissenschaft*, 53: 77-81.
- Aken, G.A.; E. Grotenhuis; A.J. Langevelde and H. Schenk (1999). Composition and crystallization of milk fat fractions. *J. American Oil Chemists' Society*, 76: 1323-1331.
- Alferez, M.J.M.; M. Barrionvevo; A. Lopez; I. Sanz; M.R. Sampelayo; F. Lisbona; J.C. Robles and M.S. Compos (2001). Digestive utilization of goat and cow milk fat in malabsorption syndrome. *J. Dairy Res.* 68: 451-461.
- AL-Tahiri, R.A.; V.N. Wade and R.J.M. Crawford (1987). Peroxide production during the storage of anhydrous milk fat with and without antioxidants. *Egypt. J. Dairy Sci.* 15: 193-207.
- Amer, M.A.; D.B. Kupranycz and B.E. Baker (1985). Physical and chemical characteristics of butter fat fractions obtained by crystallization from molten fat. *J. American Oil Chemists' Society*, 62: 1551-1557.
- AOAC (2000). *Official Methods of Analysis*. Association of Official Analytical Chemists, AOAC International. 17th Ed., Horwitz, H. (ed); Gaithersburg, MD, USA.
- AOCS (1998). *Official Methods and Recommended Practices*. 5th Ed., American Oil Chemists' Society, Firestone, D. (ed.), Champaign, IL, USA.
- Arora, S. and T. Rai (1998). Fatty acids profile and physico-chemical properties of goat milk fat fractions. *Indian J. Dairy Sci.* 51: 20-25.
- Arul, J.; A. Boudreau; J. Makhlof; R. Tardif and B. Grenier (1988). Distribution of cholesterol in milk fat fractions. *J. Dairy Res.* 55: 361-371.
- Badings, H.T.; J.E. Schaapde; C. Jong and H.G. Hagedoorn (1983). An analytical study of fractions obtained by stepwise cooling of melted milk fat. I. Methodology. *Milchwissenschaft*, 38: 95-97.
- Bhaskar, A.R.; S.S.H. Rizvi; C. Bertoli; L.B. Fay and B. Hug (1998). A comparison of physical and chemical properties of milk fat fractions obtained by two processing technologies. *J. American Oil Chemists' Society*, 75: 1249-1264.
- Bhat, G.S.; M.K.R. Murthy and M.B. Rao (1980). Autoxidation of milk fat. I-development of peroxides and carbonyl compounds during storage of cow and buffalo milk. *Milchwissenschaft*, 35: 248-286.
- Bindal, M.P. and B.K. Wadhwa (1993). Compositional differences between goat milk fat and that of cows and buffaloes. *Small Ruminant Res.* 12: 79-88.
- Boudreau, A. and J. Arul (1993). Cholesterol reduction and fat fractionation technologies of milk fat: An overview. *J. Dairy Sci.*, 76: 1772-1781.
- Campos, R.J.; J.W. Litwinenko and A.G. Marangoni (2003). Fractionation of milk fat by short-path distillation. *J. Dairy Sci.*, 86: 735-745.
- Deffense, E. (1993). Milk fat fractionation today: A review. *J. American Oil Chemists' Society*, 70: 1193-1201.
- Farah, Z.; T. Streiff and M.R. Bachmann (1989). Manufacture and characterization of camel milk butter. *Milchwissenschaft*, 38: 412-414.
- Fatouh, A.E.; R.K. Singh; P.E. Koehler; G.A. Mahran and A.E. Metwally (2004). Physical, chemical and stability properties of buffalo butter oil fractions obtained by multi-step dry fractionation. *J. Food Chemistry*, 89: 243-252.
- Fomuso, L.B. and C.C. Akoh (2001). Enzymatic modification of high-laurate canole to produce margarine fat. *J. Agric Food Chemistry*, 49: 4482-4487.
- Formo, M.W. (1979). Physical Properties of Fats and Fatty Acids. In: *Bailey's Industrial Oil and*

- Fat Products; Vol. I, 4th Ed., pp. 177-232.** Swern, D. (ed.); John Wiley & Sons, NY, USA.
- Fouad, F.M.; F.R. Voort; W.D. Marshall and P.G. Farrell (1990).** A critical evaluation of thermal fractionation of butter oil. *J. American Oil Chemists' Society*, 67:981-988.
- Gilliland, S.E.; C.R. Nelson and C. Maxwell (1985).** Assimilation of cholesterol by lactobacillus acidophilus. *Appl Environ Microbiol.* 49: 377-381.
- Gnan, S.O. and A.M. Sheriha (1986).** Composition of Libyan camel's milk. *Aust. J. Dairy Technol.* 41:33-35.
- Grall, D.S. and R.W. Hartel (1992).** Kinetics of butter fat crystallization. *J. American Oil Chemists' Society*, 69:741-747.
- Hamzawi, L.F.; G.A. Mahran; A.A. Askar and A.E. Akasha (1998).** Effect of stage of lactation on some physical and chemical properties of camel milk fat. *Proc., the 3rd Saudi Symposium on Food & Nutrition, Riyadh, Saudi Arabia*, pp. 205-215.
- Hartel, R.W. (2001).** *Crystallization in Foods.* pp. 238-240 and 265-270. Aspen Publications, Gaithersburg, MD, USA
- Kaylegian, K.E. (1999).** The production of the specialty milk fat ingredients. *J. Dairy Sci.* 82: 1433-1439.
- Kaylegian, K.E. and R.C. Lindsay (1995).** *Handbook of Milk Fat Fractionation Technology and Applications.* pp. 208-214. AOAC Press, Champaign, IL, USA
- Keeney, P.G. and P.W. Smith (1971).** *A Guide to Controlling Oxidation in Butter Creams. Candy Industry & Snack.* 136: 68-73.
- Laakso, P.H.; K.V.V. Nurmela and D.R. Homer (1992).** Composition of the triacylglycerol of butter fat and its fractions obtained by an industrial melt crystallization process. *J. Agric. Food Chem.* 40: 2472-2482.
- Lakshminarayana, M. and M.K. Murthy (1985).** Cow and buffalo milk fat fractions. Part I: Yield, physico-chemical characteristics and fatty acid composition. *Indian J. Dairy Sci.*, 38: 256-264.
- Lakshminarayana, M. and M.K. Murthy (1986).** Cow and buffalo milk fat fractions. Part III: Hydrolytic and autoxidative properties of milk fat fractions. *Indian J. Dairy Sci.* 39: 251-255.
- Mahran, G. A.; A. A. Askar; L. F. Hamzawi and A. E. Akasha (2000).** Autoxidation of camel milk fat. *Proc., of the 2nd Scientific Conference of Agric. Sci., Assiut Univ. Egypt*, pp. 997-1002.
- Man, J.M. (1992).** X-ray diffraction spectroscopy in the study of fat polymorphism. *Food Res. International*, 25: 471-476.
- Nath, B.S. and M.K. Murthy (1983).** Autoxidative stability of cow and buffalo milk triglycerides as influenced by the other minor lipid constituents. *Indian J. Dairy Sci.* 36: 151-156.
- Rajah, K.K. (1996).** *Fractionation of Fat Separation Processes in the Food and Biotechnology Industries: Principles and Applications.* pp. 207-210. Grandison A.S. and M.J. Lewis, eds. Lancaster, PA, USA.
- Ramesh, B. and M.P. Bindal (1987).** Softening point, melting point and fatty acid composition of solid, liquid fractions of cow, buffalo and goat ghee. *Indian J. Dairy Sci.* 40: 303-308.
- Richardson, T. and M. Korycka (1983).** Lipid oxidation. In: *Development in Dairy Chemistry-2: Lipids.*, pp. 241-364. (ed. Fox P.F) App. Sci., Pub., London and New York.
- Rizvi, S.S.H. and A.R. Bhaskar (1995).** Supercritical fluid processing of milk fat: Fractionation, scale-up and economics. *Food Technol.* 49: 90-100.
- Saada, M.Y.; F. Addeo and S. Kuzdzal (1983).** Fractional crystallization of water-buffalo milk fat. In: *Progress in Food Engineering. Proceedings of a European Symposium of the Food.* pp. 489-493. Working Party of the EFCE, Cantarelli, C. and C. Peri, (eds.), Foster Publishing L td., Kusnacht, Switzerland,
- Sankhla, A.K. and F.K. Yadava (1981).** A comparison of unsaponifiable matter and physico-chemical constants of milk fat from various species. *Indian J. Dairy Sci.* 34: 327-330.
- SAS User's Guide Statistics (1994).** *Statistical Analysis System (SAS), SAS Institute Inc., Cary, NY, USA.*
- Sawaya, W.N.; J.K. Khalil; A.F. AL-Shalhat and H. AL-Mohammad (1984).** Chemical composition and nutritional quality of camel milk. *J. Food Sci.* 49: 744-747.
- Schaap, J.E.; H.T. Badings; D.G. Schmidt and E. Frede (1975).** Differences in butter fat crystals, crystallized from acetone and from melt. *Netherlands Milk and Dairy Journal.* 29: 242-252.
- Sherbon, J.W.; R.M. Dolby and R.W. Russell (1972).** Melting properties of milk fat fractions obtained by double fractionation using a commercial process. *J. Dairy Res.* 39: 325-333.
- Sonntag, N.O.V. (1979).** Reactions of fats and fatty acids. In: *Bailey's Industrial Oils and Fat Products.* pp. 99-176. (ed. Swern D.) John Wiley and Sons Inc., New York.

Vlatte, G. (1997). Major issues facing the world dairy economy. In: *Milk Composition, Production and Biotechnology*. pp. 1-11. Welch, R.A.S.;

D.J.W. Burns; S.R. Davis; A.I. Popay and C.G. Prosser, (eds.); CAB International, Wallingford, UK.



حوليات العلوم الزراعية
جامعة عين شمس، القاهرة

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الثبات ضد الأكسدة والخواص الوظيفية لشقوق دهن ألبان الماعز والإبل

[١٩]

رزق عزب عواد^١ - لطفى فهمى حمزاوى^١ - مروه محمد دسوقى^٢ - كمال أسعد سوريال^٢

١- جامعة عين شمس - كلية الزراعة - قسم علوم الأغذية - حدائق شبرا - شبرا الخيمة - القاهرة

٢- مركز بحوث الصحراء - المطرية - القاهرة

طويلة السلسلة المشبعة في الشقوق الصلبة و تزداد نسبتها مع زيادة درجة حرارة الفصل. كانت هناك فروق معنوية في نقطة الانصهار بين كل الشقوق وكانت أكثر ارتفاعا في شقوق دهن لبن الإبل. أظهر دهن لبن الماعز إرتفاع في الوزن النوعي، انخفاض في قيم كل من معامل الإنكسار، محتوى الكوليستيرول، الرقم اليودي بالمقارنة مع دهن الإبل. أظهر دهن الإبل وشقوقة ثباتا أكبر ضد الأكسدة (حتى ٢٠ يوم) ومدة حفظ أطول مقارنة بالدهن الجاموسي أو البقري أو حتى الماعز. أظهر استخدام المسح بأشعة إكس إختلاف بين دهن الإبل والماعز خصوصا الشقوق السائلة حيث ظهرت الصور البلورية β' ، β في دهن الإبل بينما ظهرت الصورة β فقط في دهن الماعز وكانت درجة التبلور أكثر وضوحا وأكثر ثباتا في دهن الإبل خصوصا مع زيادة نقطة الانصهار.

تم تجزئة دهن لبن الماعز و الإبل الي شقوق سائلة و صلبة بإستخدام البلورة علي (١٥، ٢٥) ، (٣٠، ٤٠م) لكل من الماعز و الإبل علي الترتيب وتم تحليل الشقوق الناتجة من حيث محتواها من الأحماض الدهنية و خواصها الطبيعية (نقطة الإنصهار، الوزن النوعي، معامل الإنكسار، محتوى الكوليستيرول، الرقم اليودي، التصافي). كذلك تم دراسة ثبات الدهن ضد الأكسدة و تعدد الصور البلورية . أظهر تركيب الأحماض الدهنية لدهن لبن الإبل قيم منخفضة من الأحماض الدهنية قصيرة السلسلة و مرتفعة لكل من الأحماض الدهنية طويلة السلسلة والأحماض الدهنية غير المشبعة بالمقارنة بدهن لبن الماعز. الأحماض الدهنية قصيرة السلسلة والأحماض الدهنية غير المشبعة تكون نسبتها مرتفعة في الشقوق السائلة خصوصا المفصولة علي درجات حرارة منخفضة ، بينما تتركز الأحماض الدهنية

تحكيم: أ.د عبد الحميد أبو الحسن عسكر أ.د أبو السمح محمد محرز