**TITLE:** Influence of rapeseed and sesame oil on crystallization and rheological properties of cocoa cream fat phase and quality of final product

**AUTHORS:** Ivana Lončarević, Biljana Pajin, Marijana Sakač, Danica Zarić, Marica Rakin, Jovana Petrović, Aleksandra Torbica

Journal of Texture Studies ISSN 1745-4603

# INFLUENCE OF RAPESEED AND SESAME OIL ON CRYSTALLIZATION AND RHEOLOGICAL PROPERTIES OF COCOA CREAM FAT PHASE AND QUALITY OF FINAL PRODUCT

IVANA LONČAREVIĆ[1], BILJANA PAJIN[1], MARIJANA SAKAČ[2], DANICA ZARIĆ[3], MARICA RAKIN[4], JOVANA PETROVIĆ[1,5] and ALEKSANDRA TORBICA[2]

[1]Faculty of Technology, University of Novi Sad, Bul. cara Lazara 1, Novi Sad, Serbia
[2]Institute of Food Technology, University of Novi Sad, Bul. cara Lazara 1, Novi Sad, Serbia
[3]IHIS Tehno Experts d.o.o., Rresearch Development Center, Belgrade, Serbia
[4]Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia

**KEYWORDS**
Crystallization, rapeseed and sesame oil, rheology, shelf life, spreadable cocoa cream

[5]Corresponding author. J. Petrović, Faculty of Technology, Carbohydrate Food Engineering, University of Novi Sad, Bul. cara Lazara 1, 21000 Novi Sad, Serbia.
TEL: +381/646438001;
FAX: +381/21450413;
EMAIL: jovana@tf.uns.ac.rs

Received for Publication September 2, 2015
Accepted for Publication February 5, 2016
Published online Article Accepted on Month 0, 2016

doi:10.1111/jtxs.12179

## ABSTRACT

This research examined spreadable cocoa cream in which fat phase has been modified and analyzed regarding its crystallization and rheological properties and further influence on final product quality. Vegetable fat and refined sunflower oil, as fat phase of spreadable cocoa cream, have been partially substituted with rapeseed and sesame oil, having nutritional and sensory benefits in mind.

Substitution of sunflower oil with rapeseed or sesame oil had no influence on cream fat phase viscosity but increased cream viscosity up to 1.7 times and decreased its yield stress up to 2.7 times. Substitution of 70 wt % and total amount of sunflower oil with rapeseed or sesame oil resulted in lower crystallization rate in cream fat phase and the highest sensory scores of final products. Rapeseed and sesame oil have changed and improved the taste of spreadable cocoa cream making it sustainable for use in new products, but with shorter shelf life.



## PRACTICAL APPLICATIONS

Spreadable cocoa cream is a confectionery product having a high amount of sugar and fat. In recent decades, confectionary industry in Serbia has used hydrogenated fats in spreadable cocoa cream production and also refined sunflower oil, to improve spreadability of the final product. Today, the development of functional foods imposes the use of edible fats with no undesirable *trans* fatty acids, instead of those obtained by common hydrogenation process. As manufacture of cream product in the ball mill does not require high temperatures during its production, refined sunflower oil can also be substituted with less resistant unrefined oils with different distinctive flavor and health benefits, such as rapeseed and sesame oil.

## INTRODUCTION

Spreadable cocoa cream is a confectionery product based on powdered sugar, vegetable fat, cocoa powder, milk powder and other ingredients. It ideally features good spreadability across a wide temperature range (ranging between ambient to fridge temperature), a rich creamy taste, smooth homogeneous structure and good oxidative stability. Unlike chocolate, spreadable cocoa cream products do not contain cocoa butter, but contain cheaper vegetable fats and may also contain vegetable oil to improve spreadability of final product (Lončarević *et al.* 2016).

As the quality of fat-based confectionery products are strongly influenced by the behavior of its fat phase, which amount is often above 30%, the fat selection depends on its physical–chemical and crystallization characteristics and complex processes that may occur during manufacture and later in storage (Pajin *et al.* 2007). Conversely, new confectionery products have been developed to satisfy requirements for both being tasty and healthy. In addition to physical and chemical characteristics, sensory acceptance, stability, and price of the final product, it is of great importance to be also focused on its functional properties (Betoret *et al.* 2011).

Sesame oil has a mild odor and a pleasant taste and, as such, is used as a natural salad oil, as cooking oil, in shortening and margarine (Döker *et al.* 2010). Although sesame oil contains nearly 85% unsaturated fatty acids, its oxidative stability is provided by the presence of unique unsaponifiable constituents, namely lignans and tocopherols, possessing strong antioxidant activity and having an important role on health-promoting effects (Abou-Gharbia *et al.* 2000; Graca Costa do Nascimento 2012). Also, sesame oil is excellent source of phytosterols and may contain as high as 1.9% of total sterols with only a trace amount of cholesterol (Hwang 2005). The use of sesame oil as edible oil is, however, largely limited to the areas of production because of the high cost of the seed. This is due to the low yield of the crop and difficulties in mechanized harvesting because of the uneven ripening of the capsules (Mirghani *et al.* 2003). Conversely, yields of rapeseed oil range from 940 to 1,880 l per hectare and are among the highest of any conventional oil crop (Calisir *et al.* 2005). Low erucic acid rapeseed oil is classified as one of the healthiest vegetable oils because of its fatty acid composition. Rapeseed oil contains low levels of saturated fatty acids (5–10%), high amounts of monounsaturated fatty acids (44–75%), linoleic acid (18–22%) and alpha-linolenic acid (9–13%) (Yang *et al.* 2013a,b).

Sowmya *et al.* (2009) studied the partial and total replacement of fat with sesame oil in cakes, in combination with additives. However, no scientific literature sources have so far published any results that involve testing the physical properties of spreadable confectionery products with the addition of rapeseed or sesame oil. Therefore, this research examined crystallization and rheological properties of cocoa cream fat phase as well as physical properties and shelf life of spreadable cocoa cream with partial and total substitution of refined sunflower oil, which is exclusively used in Serbia in the production of spreadable cocoa cream, with unrefined rapeseed and sesame oil.

# MATERIALS AND METHODS

## Materials

Cocoa-cream mass that passed through three roll mill in industrial conditions: mixture of powdered sugar (Crvenka, Crvenka, Serbia), cocoa powder (Centroproizvod, Beograd, Serbia), milk powder (Imlek, Beograd, Serbia), vegetable fat NTFCP (non trans fat intended for cream production) (Dijamant, Zrenjanjin, Serbia). Refined sunflower oil (Dijamant, Zrenjanin, Serbia)

Unrefined rapeseed oil and sesame oil (Suncokret, Hajdukovo, Serbia), Native fluid sunflower lecithin (Victoriaoil, Sid, Serbia), Hazelnut and vanilla flavor (VK Aromatics, Novi Sad, Serbia). AQ2

## Plan of Experiments

As spreadable cocoa cream contains big amount of fat phase, the crystallization and rheological properties of fat phase were examined first. Fat and oil ratio was calculated from the composition of spreadable cocoa cream, meaning that in the control sample 100 g of fat was homogenized with 50 g of sunflower oil (FP/control). Other samples were obtained by substitution of 50 wt %, 70 wt % and 100 wt % (25 g, 35 g and total amount) of sunflower oil with rapeseed/sesame oil.

The control sample of spreadable cocoa cream (C/control) was produced with refined sunflower oil, while other samples were obtained using mixtures of sunflower oil with rapeseed/sesame oil (50:50, 30:70) or just rapeseed or sesame oil.

The following scheme represents the spreadable cocoa cream formulation and the plan of experiments.

## Preparation of Fat Samples

The mixture of fat and oil was homogenized at room temperature (21 ± 1C) in a homogenizer Ultraturrax T-25 (Janke Kunkel, Staufen, Germany) with a rotation speed of 6,000 rpm for 5 min.

## Preparation of Spreadable Cocoa Cream Samples

Raw materials were added into a laboratory ball mill (Masino Produkt, Crvenka, Serbia) with a capacity of 5 kg. The temperature in the ball mill was 40C, with a speed of 50 rpm. Retention time in a ball mill was 40 min and temperature of cream dosing into sterile plastic cups was 35C.

## The Fatty Acid Composition of Sunflower, Rapeseed and Sesame Oil

The fatty acid composition in oils was determined by gas chromatography (ISO 5508:1990), using gas chromatograph Becker 409 (Packard, Zurich, Switzerland), equipped with a packed steel column (3 m × 3 mm) coated with 10% SP 2330 stationary phase immobilized on a Chromosorb W/ AQ3

AW of 60–80 mesh particle size. Nitrogen was used as an inert carrier (15 mL/min), whereas for the detection of eluted compound flame ionization detector was used. Methyl-esters were separated under isothermal regime applying the oven temperature of 170C, while detector temperature was 250C.

## Crystallization Rate Under Static Condition

The crystallization rate under static conditions of cocoa cream fat phase was followed by measuring the changes of solid fat content (SFC) as a function of time by Bruker minispec mq 20 NMR Analyzer pulse device (Bruker, Rheinstetten, Germany). Approximately 3 g of melted fat sample was put into the glass NMR tube and heated for 30 min at 60C to destroy the crystals. Then, the sample was placed directly in a water bath at a crystallization temperature of 20C. SFC measurements were taken at 1 min intervals within duration of 1 h.

## Rheological Properties of Cocoa Cream Fat Phase and Spreadable Cocoa Cream Product

Rheological properties of fat samples and spreadable cocoa cream samples were determined by a rotational rheometer Rheo Stress 600 (Haake, Karlsruhe, Germany).

The flow curves were performed at 35C using a concentric cylinder system (sensor Z20 DIN). The shear rate was first increased from 0/s to 100/s, then kept constant at a maximal speed of 100/s and eventually reduced from 100/s to 0/s, each time within 240 s.

## Color on the Surface of Spreadable Cocoa Cream

Color of the surface of spreadable cocoa cream samples was monitoring by instrumental method and by sensory evaluation 24 h after cream production and every 2 months in the period of 6 months of storage in the dark at room temperature (21 ± 1C).

Color measuring was performed using a Minolta Chroma Meter CR-410 (Minolta Co., Ltd., Osaka, Japan) colorimeter (8 mm Ø contact area). The instrument was calibrated using a standard light white reference tile and the measurements were performed under standard illuminant D65. The obtained results were expressed in terms of $L^*$ (lightness), $a^*$ (redness to greenness – positive to negative values, respectively), and $b^*$ (yellowness to blueness – positive to negative values, respectively) values.

Color was also sensory assessed. A group of 10 experienced panelists, who had been trained to evaluate the sensory properties of spreadable cocoa cream, evaluated the following attributes using seven point rating scale: color of the surface (1 – extremely bright, 4 – optimal, 7 – extremely dark), and surface gloss (1 – mat, 4 – optimal; 7 – separation of oil on the surface). The samples were kept at room temperature (21 ± 1C) and served in the plastic cups in laboratory for sensory analysis with 10 boxes in which each panelist tested all samples at room temperature (21 ± 1C).

## Oxidative Stability of Spreadable Cocoa Cream

Oxidative stability of spreadable cocoa cream samples was monitoring using static headspace gas chromatography (SHS-GC) method for quantification of 5 aldehydes (propanal, pentanal, hexanal, heptanal and octanal) developed by Mandić *et al.* (2013), and using sensory evaluation as well. The aldehydes content is expressed as a sum of 5 aldehydes (total aldehydes). Samples were investigated 24 h after cream production and every 2 months in the period of 6 months of storage in the dark at room temperature (21 ± 1C).

Static headspace gas chromatographic analyses were performed on Agilent 7890A GC System (Agilent, Paolo Alto, CA) equipped with a capillary split/split less inlet, total electronic pneumatic control of gas flow, headspace autosampler and FID. Chromatographic data were collected and analyzed using Agilent ChemStation Software.

Static headspace sampling was performed with the headspace sampler, CombiPAL System (CTC Analytics, Zwingen, Switzerland). A 2.5-mL headspace syringe for CombiPAL was used for the injection of 2.0 mL from the 10 mL headspace vials. The auto sampler conditions were set as follows: incubation temperature, 90C; incubation time, 10 min; syringe temperature, 100C; agitator speed, 500 rpm; fill speed, 100 μL/s; pullup delay, 1 s; injection speed, 500 μL/s; pre- and post-inject delay, 500 ms; flush time, 10 s. After each injection, carryover in the syringe was eliminated by automatic flush of the syringe with carrier gas.

The sensory parameters important for oxidative stability evaluation (flavor and taste) were assessed by a group of 10 experienced panelists, who were familiar with sensory analysis techniques. They used seven point rating scale to evaluate flavor (1 – extremely bad; 7 – extremely good) and taste (1 – extremely bad; 7 – extremely good). The samples were kept at room temperature (21 ± 1C) and served in the plastic cups in laboratory for sensory analysis with 10 boxes in which each panelist tested all samples at room temperature (21 ± 1C).

## Statistical Analysis

Results were expressed as mean of triplicate analyses. The results were statistically tested using ANOVA method and the means were compared by one-factor analysis at variance

**TABLE 1.** FATTY ACID COMPOSITION OF SUNFLOWER, RAPESEED AND SESAME OIL

| Fatty acid (%) | Sunflower oil | Rapeseed oil | Sesame oil |
|---|---|---|---|
| 14:0 | 0.15 ± 0.01 | n.d.[a] | n.d.[a] |
| 16:0 | 6.91 ± 0.17 | 5.84 ± 0.14 | 9.38 ± 0.20 |
| 16:1 | n.d.[a] | 0.51 ± 0.04 | 0.20 ± 0.01 |
| 18:0 | 4.00 ± 0.15 | 2.03 ± 0.07 | 5.71 ± 0.13 |
| 18:1 | 31.68 ± 0.36 | 53.25 ± 0.62 | 40.88 ± 0.39 |
| 18:2 | 56.79 ± 0.52 | 24.61 ± 0.32 | 42.60 ± 0.46 |
| 18:3 | n.d.[a] | 10.95 ± 0.24 | 1.23 ± 0.10 |
| 20:0 | n.d.[a] | 2.57 ± 0.06 | n.d.[a] |
| SFA | 11.06 | 10.44 | 15.09 |
| MUFA | 31.68 | 53.76 | 41.08 |
| PUFA | 56.79 | 35.56 | 43.83 |

[a]Not detected.
Values are means of three determinations ± standard error. SFA, saturated fatty acid(s); MUFA, monounsaturated fatty acid(s); PUFA, polyunsaturated fatty acid(s).

with subsequent comparisons by Duncan's test at a significance level at 0.05 using software Statistica 12.0 (Statsoft).

# RESULTS AND DISCUSSION

## Fatty Acid Composition of Sunflower, Rapeseed and Sesame Oil

Our previous research (Lončarević *et al.* 2013) showed fatty acid composition of fat NTFCP, containing 0.11% of *trans* fatty acids. Composition of fatty acids in examined oils is given in Table 1. Sunflower oil being used in Serbian confectionery industry for spreadable cocoa cream production is rich in ω-6 fatty acids (56.79% of linoleic) and contains 31.68% of ω-9 fatty acids (oleic). Conversely, α-linolenic (ω-3 fatty acids) was not detected, which is known to exert a strong positive influence on human health (Arab-Tehrany *et al.* 2012). Conversely, rapeseed oil contains the highest proportion of monounsaturated fatty acids (53.25% of ω-9), a significantly lower amount of ω-6 fatty acids (24.61%) and a high proportion of ω-3 fatty acids (10.95%). This approximate relation between linoleic and linolenic of 2:1 in this oil is proven to be extremely beneficial from the nutrition point of view (Tynek *et al.* 2012). Sesame oil containes approximately the same proportion of ω-6 (42.60%) and ω-9 fatty acids (40.88%) and a small amount of ω-3 fatty acids (1.23%). All examined oils contain saturated palmitic acid, which is most present in sesame oil (9.38%) and least present in rapeseed oil (5.84%).

## Crystallization Kinetics

An investigation of Foubert *et al.* (2002) and Pajin *et al.* (2007) showed that the fat crystallization kinetics under isothermal conditions can be described by the Gompertz mathematical model:

**TABLE 2.** PARAMETERS OF GOMPERTZ'S MATHEMATICAL MODEL

| Sample | *a* (%) | $\mu$ (%/min) | $\lambda$ (min) | $R^2$ |
|---|---|---|---|---|
| FP/control | 15.04 | 0.92 | 0.31 | 0.99 |
| FP/R/50 | 15.19 | 0.92 | 0.15 | 0.99 |
| FP/R/70 | 15.41 | 0.89 | 0 | 0.99 |
| FP/R/100 | 15.31 | 0.83 | 0 | 0.99 |
| FP/S/50 | 15.38 | 0.98 | 0.52 | 0.99 |
| FP/S/70 | 15.18 | 0.89 | 0 | 0.99 |
| FP/S/100 | 15.38 | 0.89 | 0.17 | 0.99 |

$$S(t)=a\cdot\exp\left(-\exp\left[\frac{\mu\cdot e}{a}(\lambda-t)+1\right]\right)$$

where $S$ is the SFC (%) at time $t$ (min), $a$ is the value for $S$ when $t$ is approaching infinity (%), $\mu$ is the maximum crystallization rate (%/min), and $\lambda$ is a parameter proportional to inductive time (min). The parameters of this model were determined on the basis of experimental data of fat crystallization under isothermal conditions by means of nonlinear regression for all fat samples. Coefficient of determination ($R^2$) indicates how well experimental data fit a Gompertz's mathematical model. The obtained parameters, including the estimates of the 95% confidence interval, are shown in Table 2. During 1 h crystallization at 20C approximately the same quantity of solid phase was formed in all fat samples, meaning that modification of fat phase does not seem to have any influence on final SFC which amounts from 15.04% in FP/control to 15.41% in FP/R/70. The samples with 50 wt % substitution of sunflower oil with rapeseed or sesame oil have the highest values of maximum crystallization rate (0.92%/min and 0.98%/min, respectively).

Increasing the amount of rapeseed or sesame oil lowers crystallization rate meaning that samples with 70 and 100% of rapeseed or sesame oil contain less solid triglycerides during one hour crystallization under isothermal conditions. Parameter $\lambda$ is near zero and may be assumed that induction period is negligible, indicating that the crystallization centers were formed very quickly. High values of the coefficient of determination ($R^2$) (0.99 for all samples) indicate that the application of the Gompertz's mathematical model for describing experimental data by a theoretical curve of fat crystallization during 1 h at 20C is justified.

## Rheological Characteristics

Flow curves of pure oils and fat samples, determined at 35C, are presented in Fig. 1a,b, respectively. The viscosity values of sesame and rapeseed oil (0.036 Pa s and 0.037 Pa s, respectively) are higher but not statistically significantly ($P < 0.05$) different in comparison with the viscosity value of sunflower

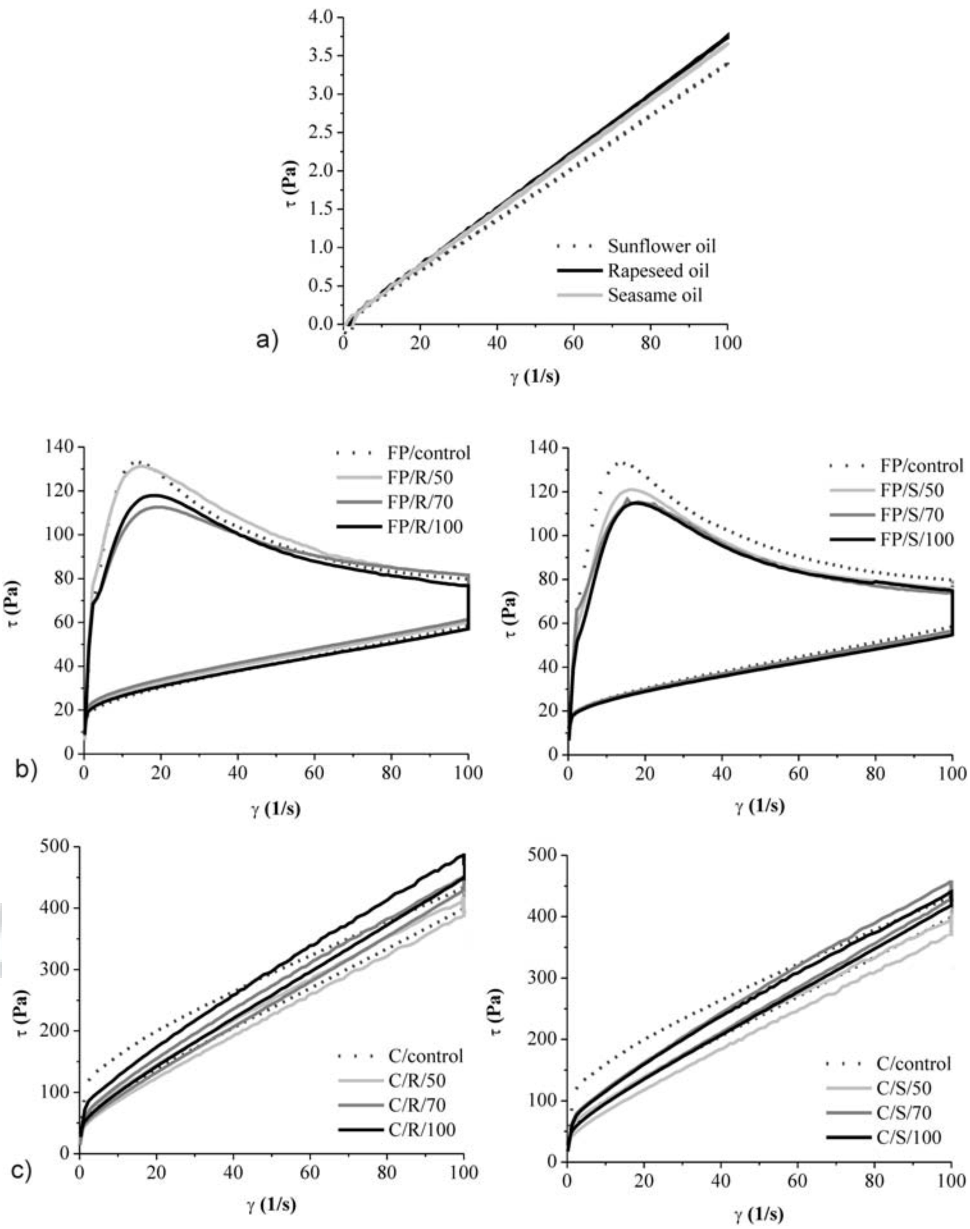


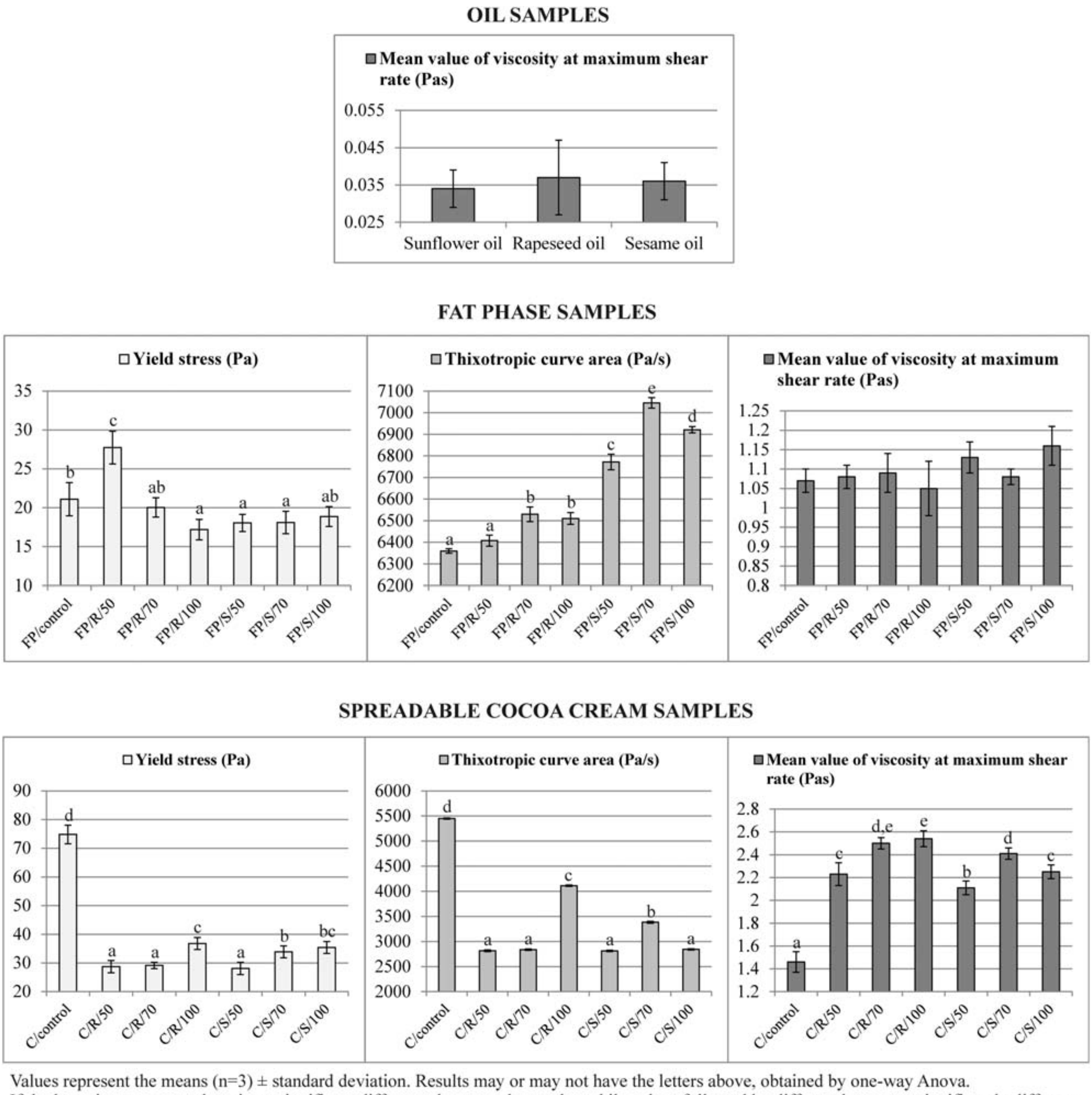

**FIG. 1.** FLOW CURVES OF: (A) PURE OILS, (B) COCOA CREAM FAT PHASE, C) SPREADABLE COCOA CREAM

oil (0.034 Pa s), as shown in Fig. 2. The mentioned oils do not affect the viscosity of the cocoa cream fat phase, which values range from 1.05 to 1.16 Pa s, and do not differ statistically significantly in the 95% confidence interval of the mean value of three measurements, also showed in Fig. 2. As our previous investigation (Lončarević *et al.* 2013) showed that the viscosity of NTFCP fat was 5.14 Pa s, it may be assumed that the addition of oil in cocoa cream production reduce fat phase viscosity up to five times, improoving its spreadability. Thixotropic curve area of fat phase having rapeseed or sesame oil has higher values compared to the control sample of fat phase with pure sunflower oil. Substitution of sunflower oil with sesame oil causes an increase in the complexity of the system, where fat phase samples with sesame oil have a statistically significant higher values of thixotropic curve area in comparison to fat phase of control sample and samples with rapeseed oil. This indicates that increasing the shear rate led to more energy loss due to gradual destruction of the fat phase structure with sesame oil.

Figure 1c shows the rheological properties of spreadable cocoa cream samples with the substitution of 50, 70 and 100 wt % of sunflower oil with rapeseed and sesame oil. All samples show a thixotropic flow, wherein the control sample with sunflower oil has a higher complexity of the system at lower shear rates, compared to samples of spreadable cocoa cream with the addition of sesame and rapeseed oil. This

J_ID: JTXS Customer A_ID: JTXS12179 Cadmus Art: JTXS12179 Ed. Ref. No.: JTS-1981.R1 Date: 19-February-16 Stage: Page: 6





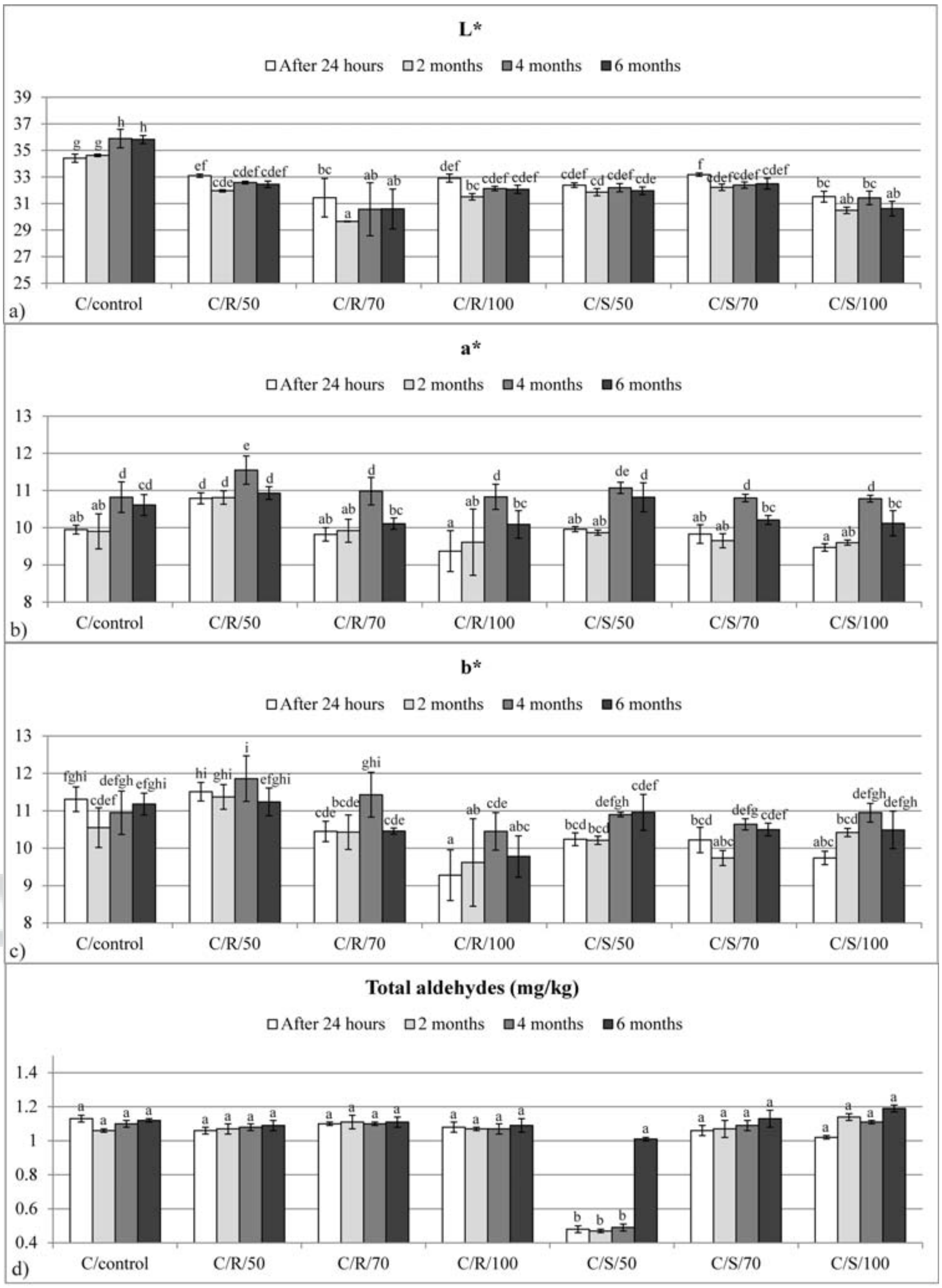

Values represent the means (n=3) ± standard deviation. Results may or may not have the letters above, obtained by one-way Anova. If the letter is not present there is no significant difference between the results, while values followed by different letters are significantly different from each other (p<0.05).

**FIG. 2.** VISCOSITY OF SUNFLOWER, RAPESEED AND SESAME OIL AND RHEOLOGICAL PARAMETERS OF CREAM FAT PHASE AND FINAL PRODUCT

manifests to the statistically significant ($P < 0.05$) highest values of thixotropic curve area (5449 Pa s) and Casson yield stress (74.83 Pa) of C/control. This sample has higher initial force that must be applied to the system to begin to flow which later may contribute to lower spreadability of the final product. Conversely, control sample has the lowest value of Casson viscosity at maximum shear rate (1.46 Pa s) which is statistically significant ($P < 0.05$) compared to other samples of spreadable cocoa cream and where, in practice, proved to be too low while dosing the cream samples during production. Increasing the concentration of rapeseed oil results in an increase in the complexity and viscosity of system. Increasing the concentration of rapeseed oil from 50 to 70 and 100 wt % increases the values of thixotropic curve area and viscosity at the maximum shear rate. Sample with 100 wt % of rapeseed oil has the highest value of thixotropic



ID: vijayalakshmi.s Time: 14:35 I Path: //10.18.11.53/Home$/vijayalakshmi.s$/JW-JTXS160006




Values in each chart represent the means of three measurements ± standard error. Values followed by different letters, obtained by one-way Anova, are significantly different from each other ($p<0.05$).

**FIG. 3.** COLOR (CIE *L*A*B** SYSTEM) ON THE SURFACE: (A) *L**, (B) *A**, (C) *B** VALUES AND (D) TOTAL ALDEHYDES CONTENT OF SPREADABLE COCOA CREAM IN A PERIOD OF 6 MONTHS OF STORAGE

curve area and Casson viscosity (4111 Pa s and 2.54 Pa s, respectively), which are statistically significantly different from the other samples within 95% interval of mean value of three measurements. Increasing the concentration of sesame oil from 50 to 70 wt % also increases the values of thixotropic curve area, yield stress and viscosity. However, the substitution of the entire amount of sunflower oil with sesame oil decreases the values of the above mentioned rheological parameters, compared to samples with the substitution of 70 wt % of sunflower oil with sesame oil.

## Color

The values of lightness (*L**), *a** (red tone) and *b** (yellow tone) measured on the surface of spreadable cocoa cream

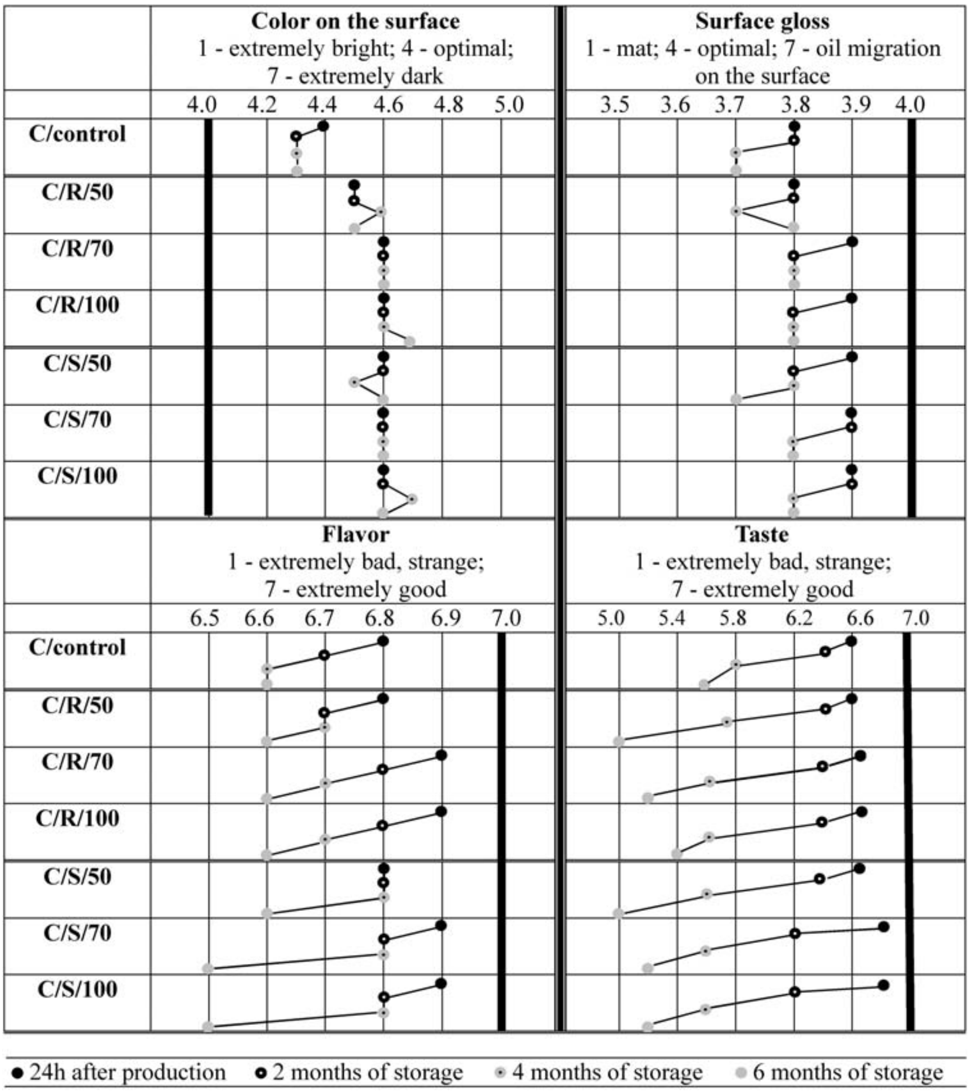



**FIG. 4.** SENSORY EVALUATION OF THE SURFACE COLOR AND GLOSS, FLAVOR AND TASTE OF SPREADABLE COCOA CREAM

with substitution of 50, 70 and 100 wt % of sunflower oil with rapeseed or sesame oil during 6 months of storage are presented in Fig. 3.

The control sample with sunflower oil had the highest $L^*$ value or the brightest color of the surface, while its other values are not significantly different ($P < 0.05$) compared to other samples, both 24 h after production and during the whole storage period. Samples with the addition of rapeseed or sesame oil had darker surface color and their values do not significantly differ ($P < 0.05$) during the storage period. Substitution of 50 wt % of sunflower oil with rapeseed and sesame oils increased the red ($a^*$) and yellow ($b^*$) value comparing to the control sample 24 h after production. However, increasing the proportion of these oils decreased the red ($a^*$) and yellow ($b^*$) value, whereby the sample with addition of 100 wt % of rapeseed oil had significantly different ($P < 0.05$) $a^*$ (9.37) and $b^*$ value (9.28) compared to other spreadable cocoa cream samples. Sensory evaluation of color (Fig. 4) showed that all samples had intrinsic color of cocoa 24 h after production, without the presence of white and gray color on the surface. The control sample had a slightly darker color than the optimum, while the samples with the addition of rapeseed or sesame oil had even more darker color. After 6 months, significantly color changes on spreadable cocoa cream samples were not registered and, therefore, their sensory scores did not differ (Fig. 4). All samples had a shiny surface, with no oil separation at the surface. On standing for 6 months of storage there was a minor loss of intensity of gloss, with no oil migration to the surface of cocoa spread cream samples.

## Oxidative Stability

During the processing and storage, fats and oils undergo oxidative changes that could lead to the development of off-flavors causing rancidity, which is followed by decreasing the nutritional quality of the final product (Li *et al.* 2012). Off-flavors in fat-based food occur mainly as a result of the formation of volatile compounds, representing a small proportion of the formed lipid oxidation products. Some of them, such as aldehydes, are highly specific to the oxidative degradation of particular polyunsaturated fatty acids. Hexanal is the most frequently used marker which indicates the level of lipid oxidation (Mandić *et al.* 2013). In addition, some other aldehydes were also used as markers for lipid deterioration. Viscidi *et al.* (2004) used heptanal for the mentioned purpose, while Yang *et al.* (2013a,b) measured 2,4-decadienal and 2,4-heptadienal to monitore buiscuits rancidity.

Oxidative stability of spreadable cocoa cream samples is presented in Fig. 3. The obtained data showed that there are no significant differences ($P < 0.05$) in aldehydes content, which ranged between 0.48 and 1.19 mg/kg during 6 months of storage. The exception are spreadable cocoa cream samples containing 50 wt % of sesame oil in the formulation, which showed significantly lower content of aldehydes in the first 2 months of storage comparing to other samples. The results indicate that the investigated spreadable cocoa cream samples were stable concerning lipid oxidation processes during the storage period. It is in line with the statement that much higher hexanal content of 5.39 mg/kg in crackers corresponded with their lipid deterioration (Berenzon and Saguy 1998).

All spreadable cocoa cream samples were well scored by the panelists during the first sensory session (24 h after production) (Fig. 4). During the storage the flavor became worse, whereby it was less pronounced, especially in samples with 70 and 100 wt % of sesame oil. These observations resulted in decreased flavor scores during storage. The addition of rapeseed or sesame oil improved the taste of spreadable cocoa cream samples 24 h after production in comparison to the control sample containing sunflower oil. Samples with 70 and 100 wt % of sesame oil had the most aromatic taste and were assessed with the highest taste scores (Fig. 4), followed by those containing 70 and 100 wt % of rapeseed oil. Assuming crystallization kinetics it is evident that fat phase samples containing 70 and 100 wt % of rapeseed or sesame oil had lower crytallization rate (%/min) compared to the control sample and samples with 50 wt % of rapessed and sesame oil, indicating the presence of more liquid triglycerides during crystallization of creams fat phase after the production. This is in accordance with literature data indicating that liquid triglycerides bind much more aroma compounds than solid fat triglycerides (Ghosh *et al.* 2006). After 2 months of storage there were no significant changes in spreadable cocoa cream taste, where the fat was emphasized, especially in samples C/S/70 and C/S/100. However, after 4 months of storage the taste became more worsened, where both sweetness and fat were emphasized. After 6 months of storage, the taste of the control sample remained with emphasizing sense of sweetness and fatty taste. However, the beginning of rancidity was noticed in samples with rapeseed and sesame oil, mostly pronounced in samples with 50% of rapeseed and sesame oil.

The obtained results indicate the necessity of sensory evaluation in assessing spreadable cocoa cream shelf life, because total aldehyde contents, which do not correlate with sensory scores, would not be chosen as appropriate marker of lipid oxidation in spreadable cocoa creams in investigated storage period. It seems that this parametar might be used for cocoa cream samples stored longer at higher temperatures.

# CONCLUSION

Substitution of sunflower oil with rapeseed or sesame oil in spreadable cocoa cream production did not have a significant impact either on solid phase that was formed during the crystalization of cream fat phase at 20C or on fat phase rheological properties. However, samples in which sunflower oil was substituted with 70 and 100 wt % of rapeseed or sesame oil had lower crystallization rate which later influenced the taste of final products. These samples had the most pronounced aromatic taste 24 h after the production. The composition of rapeseed and sesame oil also affected physical properties of cream by increasing its viscosity and reducing yield stress, compared to the control sample with sunflower oil. However, using these unrefined oils in cream production caused a shorter shelf life of this type of product, which was not determined by the instrumental determination of total aldehydes content during the investigated storage period, but was assessed by sensory evaluation.



# ACKNOWLEDGMENT

This research has been supported by the COST Action CM1402 “From molecules to crystals – how do organic molecules form crystals (Crystallize).”

# CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

## REFERENCES

ABOU-GHARBIA, H.A., SHEHATA, A.A.Y. and SHAHIDI, F. 2000. Efect of processing on oxidative stability and lipid classes of sesame oil. Food Res. Int. *33*, 331–340.

ARAB-TEHRANY, E., JACQUOT, M., GAIANI, C., IMRAN, M., DESOBRY, S. and LINDER, M. 2012. Beneficial effects and oxidative stability of omega-3 long-chain polyunsaturated fatty acids. Trends Food Sci. Technol. *25*, 24–33.

BERENZON, S. and SAGUY, I.S. 1998. Oxygen absorbers for extension of crackers shelf-life. LWT - Food Sci. Technol. *31*, 1–5.

BETORET, E., BETORET, N., VIDAL, D. and FITO, P. 2011. Functional foods development: Trends and technologies. Trends Food Sci. Technol. *22*, 498–508.

CALISIR, S., MARAKOGLU, T., OGUT, H. and OZTURK, O. 2005. Physical properties of rapeseed (*Brassica napus oleifera* L.). J. Food Eng. *69*, 61–66.

DÖKER, O., SALGIN, U., YILDIZ, N., AYDOGMUS, M. and ÇALIMLI, A. 2010. Extraction of sesame seed oil using supercritical CO2 and mathematical modeling. J. Food Eng. *97*, 360–366.

FOUBERT, I., VANROLLEGHEM, P.A., VANHOUTTE, B. and DEWETTINCK, K. 2002. Dynamic mathematical model of the crystallization kinetics of fats. Food Res. Int. *35*, 945–956.

GHOSH, S., PETERSON, D.G. and COUPLAND, J.N. 2006. Effects of Droplet Crystallization and melting on the aroma release properties of a model oil-in-water emulsion. J. Agric. Food Chem. *54*, 1829–1837.

GRAÇA COSTA DO NASCIMENTO, E.M., PILER CARVALHO, C.W., TAKEITI, C.Y., CASTRO FREITAS, D.G. and RAMIREZ ASCHERI, J.L. 2012. Use of sesame oil cake (*Sesamum indicum* L.) on corn expanded extrudates. Food Res. Int. *45*, 434–443.

HWANG, L.S. 2005. Sesame oil. In *Bailey's Industrial Oil and Fat Products, 6th Ed., Vol 6*, (F. Shahidi ed.) Wiley–Interscience, New Jersey.

ISO 5508:1990 Animal and vegetable fats and oils. Analysis by gas chromatography of methyl esters of fatty acids. AQ5

LI, C., TANG, Z., HUANG, M., TAO, N., FENG, B. and HUANG, S. 2012. Antioxidant efficacy of extracts produced from pickled and dried mustard in rapeseed and peanut oils. J. Food Sci. *77*, 394–400.

LONČAREVIĆ, I., PAJIN, B., OMORJAN, R., TORBICA, A., ZARIĆ, D., MAKSIMOVIĆ, J. and ŠVARC GAJIĆ, J. 2013. The influence of lecithin from different sources on crystallization and physical properties of non trans fat. J. Texture Studies *44*, 450–458.

LONČAREVIĆ, I., PAJIN, B., PETROVIĆ, J., ZARIĆ, D., SAKAČ, M., TORBICA, A., LLOYD D.M. and OMORJAN, R. 2016. The impact of sunflower and rapeseed lecithin on the rheological properties of spreadable cocoa cream. J. Food Eng. *171*, 67–77.

MANDIĆ, A., SEDEJ, I., SAKAČ, M. and MIŠAN, A. 2013. Static headspace gas chromatographic method for aldehyde determination in crackers. Food Anal. Methods *6*, 61–68.

MIRGHANI, M.E.S., CHE MANA, Y.B., JINAP, S., BAHARINA, B. and BAKARA, J. 2003. Application of FTIR spectroscopy in determining sesamol in sesame seed oil. J. Am. Chem. Soc. *80*, 1–4.

PAJIN, B., KARLOVIĆ, Đ., OMORJAN, R., SOVILJ, V. and ANTIĆ, D. 2007. Influence of filling fat type on praline products with nougat filling. Eur. J. Lipid Sci. Technol. *109*, 1203–1207.

SOWMYA, M., JEYARANI, T., JYOTSNA, R. and INDRANI, D. 2009. Effect of replacement of fat with sesame oil and additives on rheological, microstructural, quality characteristics and fatty acid profile of cakes. Food Hydrocolloid. *23*, 1827–1836.

TYNEK, M., PAWŁOWICZ, R., GROMADZKA, J., TYLINGO, R., WARDENCKI, W. and KARLOVITS, G. 2012. Virgin rapeseed oils obtained from different rape varieties by cold pressed method – their characteristics, properties, and differences. Eur. J. Lipid Sci. Technol. *114*, 357–366.

VISCIDI, K.A., DOUGHERTY, M.P., BRIGGS, J. and CAMIRE, M.E. 2004. Complex phenolic compounds reduce lipid oxidation in extruded oat cereals. LWT - Food Sci. Technol. *37*, 789–796.

YANG, N., HORT, J., LINFORTH, R., BROWN, K., WALSH, S. and FISK, I.D. 2013a. Impact of flavor solvent (propylene glycol or triacetin) on vanillin, 5-(hydroxymethyl)furfural, 2,4-decadienal, 2,4-heptadienal, structural parameters and sensory perception of shortcake biscuits over accelerated shelf life testing. Food Chem. *141*, 1354–1360.

YANG, M., ZHENG, C., ZHOU, Q., HUANG, F., LIU, C. and WANG, H. 2013b. Minor components and oxidative stability of cold-pressed oil from rapeseed cultivars in China. J. Food Compost. Anal. *29*, 1–9. AQ6

# AUTHOR QUERY FORM

Dear Author,
During the preparation of your manuscript for publication, the questions listed below have arisen. Please attend to these matters and return this form with your proof.
Many thanks for your assistance.

| Query References | Query | Remarks |
|---|---|---|
| AQ1 | Please check whether edit made in unit (70 wt %) is OK as typeset. | |
| AQ2 | Please check whether sentence „Unrefined rapeseed oil" is OK as typeset. | |
| AQ3 | Please note that trade mark symbol has been deleted as per style. Please check. | |
| AQ4 | Please spell out NTFCP. | |
| AQ5 | Please provide complete details for reference ISO 5508:1990. | |
| AQ6 | Please check whether insertion of "a" and "b" in reference Yang *et al*. (2013) is OK as typeset. | |
| AQ7 | Please confirm that given names (red) and surnames/family names (green) have been identified correctly. | |