

## Effect of Deep-Fat Frying on Phytosterol Content in Oils with Differing Fatty Acid Composition

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Received: 28 November 2006 / Revised: 2 August 2007 / Accepted: 5 September 2007 / Published online: 5 October 2007  
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**Abstract** The objective of this study was to determine the fate of phytosterols in vegetable oils with varying fatty acid composition used for frying. High oleic sunflower (HOSun), corn (Corn), hydrogenated soybean (HSBO), expeller pressed soybean (ESBO), and expeller pressed low-linolenic acid soybean oil (ELLSBO) were used for frying potato chips in a pilot plant-scale continuous fryer. The same oils, and regular soybean oil (SBO) were also used in intermittent batch frying of tortilla chips. Phytosterols were measured in oils collected at various times during frying by GC to determine their loss. The formation of polymerized triacylglycerides (PTAGs) and total polar compounds (TPC) were analyzed to determine the extent of oil degradation. In the continuous frying system, phytosterol loss ranged between 4 and 6% in ESBO, ELLSBO, HOSun, and Corn, with no loss in HSBO. PTAGs and TPC were highest in ESBO and ELLSBO, followed by Corn, HOSun, and HSBO. In the batch frying experiment, phytosterol loss ranged from 1 to 15%, and was highest in Corn followed by SBO and HSBO. There was no significant loss of phytosterols in ESBO, ELLSBO, and HOSun. Formation of PTAGs and TPC during batch frying was highest in SBO and ESBO, followed by Corn, ELLSBO, HOSun, and HSBO. In

conclusion, phytosterol loss in both the continuous fryer and in the batch frying system appeared to be unrelated either to fatty acid composition, or to the extent of oil degradation.

**Keywords** Deep-fat frying · Phytosterols · Polymerized triacylglycerides · Expeller pressed oils · Soybean · Vegetable oils

### Introduction

Phytosterols and phytostanols are triterpene compounds, similar in structure to cholesterol, that are found ubiquitously in plants [1]. They are found in the form of free sterols, or with the  $3\beta$ -OH group esterified to a fatty acid, glycoside, acylated glycoside, or to ferulic or  $p$ -coumaric acid. In vegetable oils, phytosterols are the dominant class of unsaponifiables and are found mainly in either their free form or as steryl-fatty acid esters [1, 2]. The amount of phytosterols in vegetable oils varies by source, but ranges between  $\sim 70$  mg/100 g in palm oil to over 1,000 mg/100 g in evening primrose oil [3, 4]. While there are over 100 different phytosterol structures, the most predominant phytosterols in vegetable oils are campesterol,  $\beta$ -sitosterol, stigmasterol and  $\Delta 5$ -avenasterol [1–3]. Brassicasterol is also a predominant phytosterol in oils from plants in the *Brassicaceae* family, such as canola. The saturated stanols, sitostanol and campestanol are found in corn oil and oils from grains such as wheat and rice.

Phytosterols have received widespread attention recently due to their ability to block cholesterol reabsorption in the gut, and thus lower blood cholesterol levels [5]. The US Food and Drug Administration recently approved a health claim for certain foods containing at least 0.65 g or 1.7 g/serving of plant steryl or plant stanyl esters, respectively [6].

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Phytosteryl and phytostanyl esters have been added to vegetable oil-based spreads, margarines, and salad oils, and new products are continually being developed [7]. In addition to their cholesterol-lowering properties, some phytosterols have also been investigated for antioxidant or anti-polymerization activity during the high temperature heating of oils [8–11]. Thus far, it has been observed that sterols with an ethylidene group in their side-chain, such as  $\Delta^5$ - and  $\Delta^7$ -avenasterol and citrostadienol, seem to have antioxidant or anti-polymerization activity, while others, such as sitosterol, stigmasterol, and campesterol had either no effect or a slightly prooxidant effect [8–11].

With the growing use of phytosterols as functional ingredients in foods it is important to understand their stability under the conditions that they might undergo in these systems. Deep-fat frying represents an extreme food-processing system where oils are subjected to high temperature, aeration, and moisture from food products. These interactions can lead to a multitude of chemical reactions taking place, which can degrade triacylglycerides as well as other components. Phytosterols can undergo oxidation reactions when heated, leading to a variety of polar and nonpolar compounds [12]. Oxidized phytosterols may be less biologically active, and could potentially have negative physiological effects similar to cholesterol oxidation products [12]. Several studies have looked at the formation of phytosterol oxidation products and loss of phytosterols in model heating systems [13–16] to try to understand the effects of temperature, structure, and the degree of saturation of the medium on phytosterol oxidation. We are only aware of a few published studies that have measured the stability of phytosterols under actual frying conditions [17–19]. These studies have mainly focused on the quantitation of phytosterol oxidation products in oils used for frying and in fried foods. The analysis of sterol oxidation products does not always account for total sterol losses [13], so not much is known about the fate of phytosterols in oils subjected to standard frying conditions. Thus, the aim of this study was to follow the loss of phytosterols in vegetable oils of various origins under two different types of frying conditions, pilot-plant scale continuous frying and batch (intermittent) deep-fat frying. The oil stability was monitored by measuring triacylglyceride polymer (PTAG) formation and total polar compounds (TPC).

## Experimental Procedures

### Materials

Stigmasterol, and  $5\alpha$ -cholestane were purchased from Matreya, Inc. (Pleasant Gap, PA, USA); campesterol was purchased from Steraloids (Newport, Rhode Island, USA);

$\beta$ -sitosterol and sitostanol were from Sigma-Aldrich (St. Louis, Missouri, USA). Each standard was  $\geq 97\%$  purity. All other chemicals and solvents were obtained from Sigma-Aldrich, unless otherwise stated, and were ACS grade or better. Hexane extracted, alkali refined, bleached and deodorized oils including soybean oil (SBO), high oleic sunflower oil (HOSun), corn oil (Corn) and hydrogenated soybean oil (HSBO) were obtained from commercial processors. Expeller pressed soybean oil (ESBO) and expeller pressed low linolenic acid soybean oil (ELLSBO) that were physically refined, bleached and deodorized were also obtained from commercial processors. All oils contained citric acid as the only additive.

### Pilot Plant-scale Fry Study

The Dakota Pearl potato variety used in the potato chip study were stored for 9–10 months at 9 °C before being used for frying. The potatoes were cut from stem end to bud end and placed in a Knotts rotary slicer, set at 18 slices per inch. From the slicer, the potato slices dropped into a rotating cold water bath for 10–15 s, then proceeded up a shaker chain to remove some of the water before entering the small-scale chipper, which is 1/20 scale of an industry chipper and capable of processing 60 pounds of raw product per hour. The oil entered the chipper at 188 °C and exited the chipper at 180 °C. The potato chips were fried in the oil for 90 s. After exiting the chipper, the potato chips dropped onto a de-oiling table to drain excess oil before being bagged. For this study, oil samples were collected at 0, 1, 5 and 9 h. Fresh oil was added periodically to replenish the oil absorbed by the potato chips.

### Batch Scale Fry Study

The white corn tortillas used in the tortilla chip portion of the study were obtained in a local grocery store. Each tortilla was cut into six equal wedges. Each 50 g batch was fried for 1 min, 30 s at 180 °C  $\pm$  2 °C in a 2 L capacity fryer (National Presto Industries, Eau Claire, WI) containing 1,200 g oil initially. One tortilla chip batch was fried every 15 min for 7 h per day, for a total of 35 h. Tortilla chips and oil samples were collected at 5, 15, 25, and 35 h. Fresh make-up oil (120 g) was added after the oil samples were collected.

### Phytosterol Analysis

Each oil sample was analyzed in triplicate for quantitation of phytosterols [20]. To 13  $\times$  100 mm screw cap test tubes,

5 $\alpha$ -cholestane (internal standard) dissolved in chloroform was added and the solvent evaporated under nitrogen. Approximately 20–25 mg oil was added to each tube and saponified with 2 mL 2N KOH in ethanol at 60 °C for 45 min. After cooling the tubes to room temperature, 0.1 mL ethanol and 1 mL H<sub>2</sub>O were added and mixed by vortexing. Phytosterols were extracted twice with 2 mL hexane. The combined hexane fractions were dried under N<sub>2</sub>. Trimethylsilyl (TMS) derivatives of the phytosterols were made by adding 100  $\mu$ L each pyridine and *N,O*-bis(trimethylsilyl)-fluoroacetamide with 1% trimethylchlorosilane (Regis Tech., Morton Grove, IL, USA) and heating at 60 °C for 1 h on a heating block. Samples were injected by autosampler into a Varian 3800 GC equipped with an FID, and a Supelco (Bellefonte, PA) SPB<sup>TM</sup>-1701 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m capillary column. Helium was used as a carrier gas, with a 1:50 injector split. Injector temperature was 270 °C, and detector temperature was 290 °C. The column oven initial temperature was 250 °C for 0.5 min, increased at 10 °C/min to 270 °C and held for 27 min, then increased at 10 °C/min to 280 °C and held for 3.5 min GC control, data collection and integration were performed using Varian Star Chromatography Software Ver. 5.3. Phytosterols were identified by comparison of their retention times (relative to 5 $\alpha$ -cholestane) with those of commercially available standards. Phytosterols without commercially available standards such as  $\Delta$ 5-avenasterol,  $\Delta$ 7-avenasterol, and  $\Delta$ 7-stigmasterol were identified by their relative retention time compared to literature, and by comparison with samples known to contain those phytosterols [17, 20]. For phytosterols with commercially available standards, quantitation was carried out by determining the response factor relative to the internal standard. For those phytosterols without available standards, phytosterols were quantified using the same response factor of the standard with the nearest retention time. Only demethylsterols were quantified in all samples; no attempt was made to identify or quantify the other minor constituents of mono- or dimethylsterols.

#### Analysis of Polymerized Triacylglycerides

PTAGs in the oil samples were determined using the AOAC Official Method 993.25 [21] with the exception that an ELSD (Sedex model 55, Sedex, Inc., New Jersey) was used rather than a refractive index detector. Samples were dissolved in THF and injected into a Shimadzu HPLC (model LC20AT) equipped with an autosampler, membrane degasser, and a size exclusion column (PLGel 5  $\mu$ m, 100 Å pore size, 300  $\times$  7.5 mm Polymer Labs, Amherst, MA). The ELSD was operated at a temperature of 40 °C with the nebulizer gas (ultra-pure N<sub>2</sub>) pressure set to

2.5 bar, and the Gain set at 4. HPLC control, data collection and analysis were performed by Shimadzu EZStart Chromatography Software Version 7.3. All samples were analyzed in triplicate.

#### Analysis of Total Polar Compounds

Total polar compounds (TPC) were determined in duplicate using the AOCS official method Cd 20–91 [22].

#### Analysis of Fatty Acid Composition of Oils

FAMEs were separated using a Varian 8400 GC equipped with FID, on-board integrator, and a SP2380 (Supelco, Bellefonte, PA, USA) capillary column (30 m  $\times$  0.25 mm i.d., 0.20  $\mu$ m film thickness). Carrier gas was He at 1 mL/min. The oven temperature was initially held at 150 °C for 15 min, then increased to 210 °C at 2 °C/min, followed by an increase to 220 °C at 50 °C/min. The injector and detector temperatures were set at 240 and 270 °C, respectively.

#### Statistical Analysis

Phytosterol content of oils at different heating times were compared by analysis of variance using Statistical Analysis System Version 9.1 (SAS Inc., Cary, NC). The mean phytosterol contents at each time point were compared by *t* tests using the least significant difference method, where  $p < 0.05$  was deemed statistically different.

## Results and Discussion

#### Fatty Acid Composition of Oils

The FA compositions of the oils used for continuous and intermittent frying are shown in Table 1. The total amount of saturated fatty acids is similar between all of the oils except for the HOSun, which had about half the amount of saturates as the other oils. SBO, ESBO, ELLSBO, and Corn oil were all similar in their total content of polyunsaturated fatty acids (PUFA), but the SBO and ESBO both had higher amounts of 18:3, which has a relative rate of oxidation 2.4 times that of 18:2 [23]. Based on fatty acid composition alone, it would be expected that HOSun and HSBO, with their lower PUFA content, would be the least degraded upon frying, followed by ELLSBO and Corn, because of their higher PUFA. SBO and ESBO would be expected to be the most degraded, due to their higher content of PUFA including linolenic acid.

**Table 1** Fatty acid composition of oils used for fry studies

| Oil    | SFA <sup>a</sup> | PUFA <sup>b</sup> | 18:1              | 18:2 | 18:3 |
|--------|------------------|-------------------|-------------------|------|------|
| SBO    | 15.8             | 59.9              | 24.3              | 53.1 | 6.8  |
| ESBO   | 15.3             | 61.5              | 22.7              | 54.1 | 7.4  |
| ELLSBO | 15.0             | 56.9              | 28.2              | 55.4 | 1.5  |
| HSBO   | 16.9             | 19.1              | 64.0 <sup>c</sup> | 18.4 | 0.7  |
| HOSun  | 7.5              | 9.2               | 83.3              | 8.9  | 0.3  |
| Corn   | 14.3             | 58.4              | 27.3              | 57.2 | 1.2  |

Expressed as percentage of total fatty acids. Values are average of triplicate analysis. *SBO* soybean oil, *ESBO* expeller pressed soybean oil, *ELLSBO* expeller pressed low-linolenic acid soybean oil, *HSBO* hydrogenated soybean oil, *HOSun* high-oleic sunflower oil, *Corn* corn oil, *SFA* saturated FA, *PUFA* polyunsaturated FA

<sup>a</sup> Includes 14:0, 16:0, 18:0, 20:0, and 22:0

<sup>b</sup> Sum of %18:2 and %18:3

<sup>c</sup> Includes both *cis*- and *trans*-isomers of 18:1

### Phytosterol Content of Oils

The phytosterol content and composition of the oils (Table 2) are similar to values found in the literature [3, 4]. The SBO and ESBO were similar in phytosterol content, while ELLSBO and HSBO had slightly higher phytosterol content. Since phytosterols are known to vary by variety, season, and due to processing influences [3, 4], conclusions about the differences in phytosterol content cannot be made from this data. Total phytosterol content of HOSun was higher than the soybean oils, while Corn had 2–3 times higher phytosterol content than the other oils. Sitosterol was the most prominent phytosterol in all of the oils. Sitostanol was present in trace amounts in all of the oils, but it was not quantifiable except in Corn. HOSun was unique in that it had a high percentage of the less common sterols such as  $\Delta^7$ -avenasterol and  $\Delta^7$ -stigmastenol.

### Continuous Fry Study

During the 9 h of continuous potato chip frying, the percentage of TPC and PTAGs slowly, but steadily increased in all of the oils. However, TPC after 9 h were between 5.0 and 6.7% (Fig. 1), while the level of PTAGs (Fig. 2) remained below 3% in all of the oils. Both of these values are well below the recommended discard limits of 24 and 12% for total polar compounds and polymeric materials, respectively, indicating that the oils were still of fairly good quality [24]. The formation of TPC as well as PTAGs was lowest in HSBO and HOSun, likely because of their low amounts of PUFA. Corn oil after 9 h had higher TPC but lower PTAGs than ESBO and ELLSBO, but this may be because it had a higher level of TPC at 0 h. Despite their differences in 18:3 contents, the ESBO and ELLSBO had similar levels of PTAGs and TPC.

After 9 h of continuous frying the reduction in phytosterol content ranged from 4 to 6% in all of the oils except for HSBO, which had a net gain of 1.2%, compared to initial phytosterol content (Fig. 3). However, the only oil where phytosterol content was significantly ( $p < 0.05$ ) lower was Corn (5% reduction), where phytosterol content decreased linearly over time. These results are consistent with another study [17], which reported only slight changes in phytosterol content of sunflower (6% reduction), and high oleic sunflower (8% reduction) oils after 2 days of industrial frying. Factors such as absorption of oil by foods, interchange of oil between food products and the frying oil, and the replenishment of lost oil with fresh oil will all influence phytosterol content during continuous frying, which may explain why there were fluctuations over frying time, rather than continuous loss. It is difficult to definitively characterize the slight changes in phytosterol content seen in this study as indicative that phytosterols are stable to frying. However, if phytosterols were more unstable during frying, then even replenishment with fresh oil would

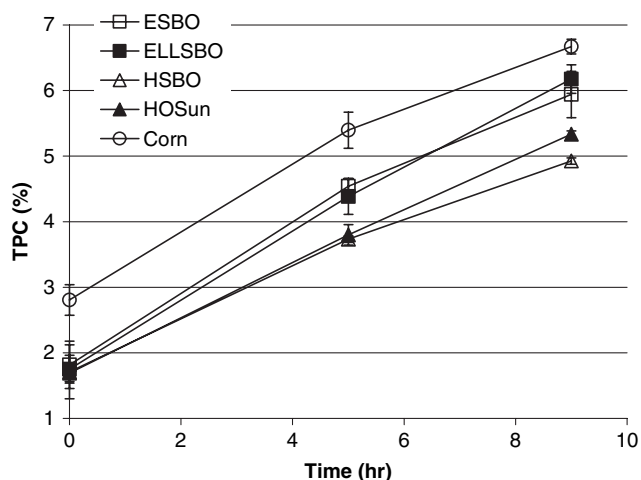
**Table 2** Phytosterol content (mg/100 g) and composition of oils used for fry studies

| Oil    | Campesterol            | Stigmasterol          | $\beta$ -sitosterol     | Sitostanol           | Avenasterol           | Others <sup>a</sup>    | Total            |
|--------|------------------------|-----------------------|-------------------------|----------------------|-----------------------|------------------------|------------------|
| SBO    | 33.5 $\pm$ 1.2 (11.9)  | 57.0 $\pm$ 1.6 (20.2) | 181.1 $\pm$ 4.1 (64.2)  | Tr. <sup>b</sup>     | 10.7 $\pm$ 3.0 (3.8)  | Tr.                    | 282 $\pm$ 8.9    |
| ESBO   | 39.8 $\pm$ 0.85 (14.9) | 61.4 $\pm$ 0.9 (22.9) | 154.6 $\pm$ 1.3 (57.7)  | Tr.                  | 12.0 $\pm$ 1.1 (4.5)  | Tr.                    | 267.8 $\pm$ 2.4  |
| ELLSBO | 52.3 $\pm$ 1.6 (15.4)  | 47.9 $\pm$ 1.3 (14.1) | 227.2 $\pm$ 5.4 (66.7)  | Tr.                  | 13.0 $\pm$ 1.3 (3.8)  | Tr.                    | 340.4 $\pm$ 9.1  |
| HSBO   | 40.8 $\pm$ 1.3 (12.3)  | 66.0 $\pm$ 1.9 (19.9) | 212.1 $\pm$ 1.9 (64.0)  | Tr.                  | 12.3 $\pm$ 3.4 (3.7)  | Tr.                    | 331.2 $\pm$ 1.8  |
| HOSun  | 11.7 $\pm$ 1.7 (3.0)   | 24.3 $\pm$ 2.1 (6.1)  | 229.5 $\pm$ 7.8 (57.8)  | Tr.                  | 15.7 $\pm$ 0.5 (4.0)  | 115.5 $\pm$ 6.4 (29.1) | 425.5 $\pm$ 13.5 |
| Corn   | 98.6 $\pm$ 3.2 (11.7)  | 64.3 $\pm$ 2.5 (7.6)  | 611.8 $\pm$ 19.9 (72.4) | 29.8 $\pm$ 1.4 (3.5) | 40.1 $\pm$ 1.3 (4.75) | 1.0 $\pm$ 0.08 (0.12)  | 844.7 $\pm$ 28.3 |

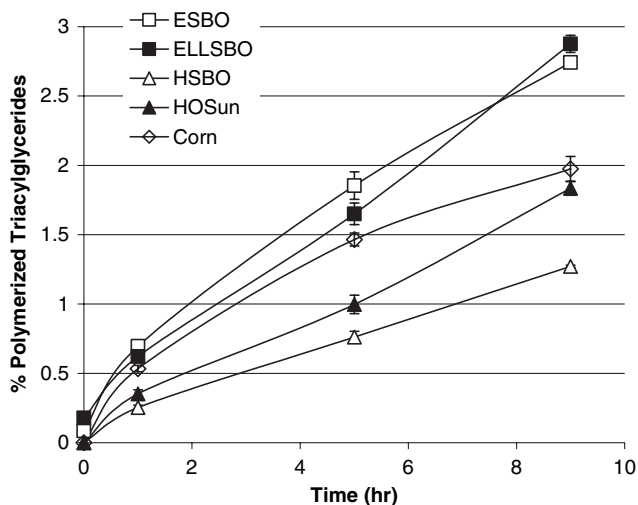
All values are the average  $\pm$  standard deviation of triplicate analysis. Figures in parentheses denote the corresponding percent composition. See Table 1 for abbreviations

<sup>a</sup> Includes  $\Delta^7$ -avenasterol and  $\Delta^7$ -stigmastenol in HOSun; in Corn, others denotes campestanol

<sup>b</sup> *Tr* trace amounts detected

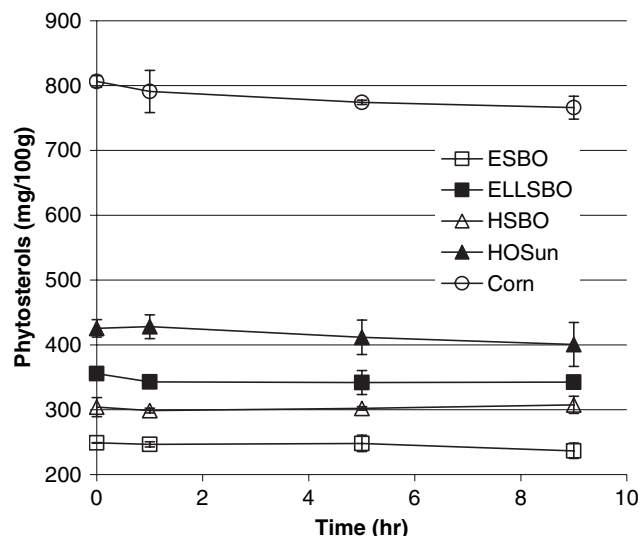


**Fig. 1** Total polar compounds (%) in oils during continuous frying of potato chips. See Table 1 for abbreviations. Error bars represent SD for duplicate analyses



**Fig. 2** Formation of triacylglyceride polymers (area %) in oils during continuous frying of potato chips. See Table 1 for abbreviations. Error bars represent SD for triplicate analysis

not be enough (due to dilution effects) to compensate for phytosterol degradation, and measured decreases would be more substantial. In a continuous fryer, oil is constantly being absorbed by the food product, filtered, and supplemented with fresh oil, such that complete turnover of oil can sometimes occur in 8–12 h. Thus, oil degradation, including the triglycerides as well as other components of vegetable oils can occur much more slowly than during intermittent, or batch frying [25]. In this study, oil from the continuous frying was still of good quality, at least as determined by measurements of TPC and PTAGs, at the end of the 9-h frying study. The quantities of oil, potatoes, and time required for the pilot-scale continuous frying



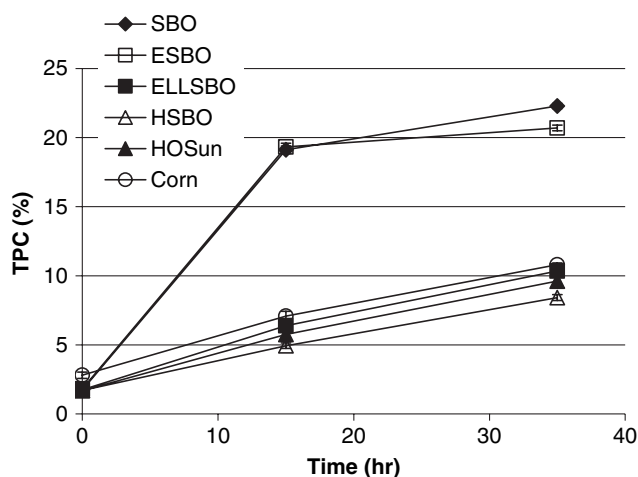
**Fig. 3** Phytosterol content of oils at different time points during the continuous frying of potato chips. See Table 1 for abbreviations. Error bars represent SD for triplicate analysis

experiments did not allow us to carry out these studies further. Therefore, it was of interest to determine the loss of phytosterols, and the extent of oil degradation, in the same oils subjected to the more harsh conditions of intermittent frying, which is more comparable to the type of frying that would occur in restaurants and in consumer homes.

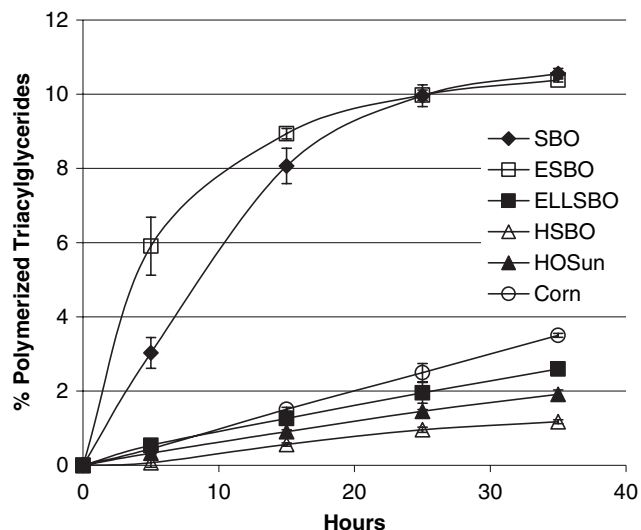
#### Intermittent Fry Study

The formation of both TPC and PTAGs in oils during intermittent frying followed similar trends (Figs. 4, 5). In ESBO and SBO, TPC and PTAGs formed at much higher rates than the other oils, and were nearing the recommended discard limits by the 35 h frying time. ESBO had slightly lower TPC (20.7%) compared to the regular SBO (22.3%) after 35 h. The higher degradation rate for these two oils is expected considering their higher 18:3 content. The rates of TPC formation in Corn, ELLSBO, HOSun, and HSBO were similar. After 35 h, HSBO had the lowest TPC (8.4%), followed by HOSun (9.6%), ELLSBO (10.3%), and Corn (10.8%). The rate of PTAGS formation was also lowest in HSBO (1.2%), followed by HOSun (1.9%), ELLSBO (2.6%), and Corn (3.5%).

Changes in phytosterol content during intermittent frying did not follow any consistent pattern in terms of either the FA composition or the extent of degradation of the oils (Fig. 6). Phytosterol content in Corn decreased steadily over frying time such that 14.8% (significant,  $p < 0.05$ ) were lost after 35 h. In HSBO, phytosterol content dropped by 9% (significant,  $p < 0.05$ ) after the first 5 h of frying, but remained fairly steady from that point on. A similar



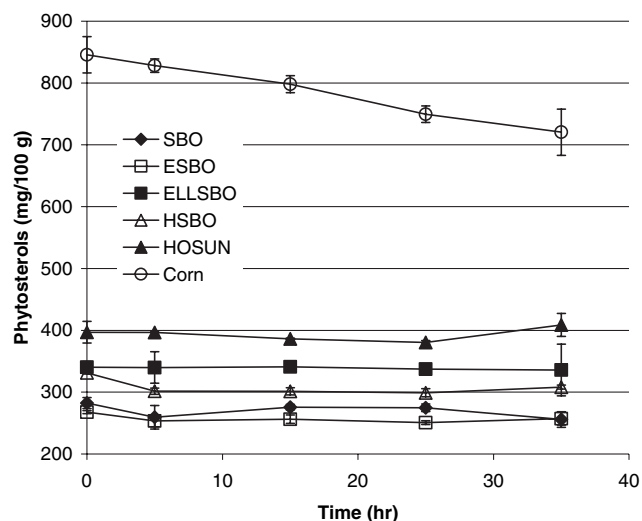
**Fig. 4** Total polar compounds (%) in oils during batch frying of tortilla chips. See Table 1 for abbreviations. *Error bars* represent SD for duplicate analyses



**Fig. 5** Formation of triacylglyceride polymers (area %) in oils during batch frying of tortilla chips. See Table 1 for abbreviations. *Error bars* represent SD for triplicate analysis

trend of an initial decrease in phytosterol contents, followed by stabilization was seen in SBO and ESBO. However, by 35 h phytosterol content in SBO dropped by 9.4% (significant,  $p < 0.05$ ), whereas in ESBO phytosterol content was only 4% lower (not significant). There was no significant decrease in phytosterol content in either HOSun or ELLSBO.

Previous heating studies have demonstrated preferential loss of phytosterols based on the degree of unsaturation of the B-ring [26], and the presence of an ethylidene group in the side chain, as with  $\Delta^5$ -avenasterol and citrostadienol [27]. In this study, the content of individual phytosterols during intermittent frying was also examined to see if there



**Fig. 6** Phytosterol content of oils at different time points during the batch frying of tortilla chips. See Table 1 for abbreviations. *Error bars* represent SD for triplicate analysis

was any preferential loss (data not shown). In Corn, campesterol, stigmasterol, sitosterol, and avenasterol were lost to similar extents (14.4, 13.9, 14.4, 13.8% loss, after 35 h, respectively) while only 10% of the sitostanol was lost. This is likely due to the higher stability of the saturated stanols compared to sterols, which have one or more double bonds. In SBO, slight preferential loss of stigmasterol (11.8%) was seen compared to campesterol and sitosterol (both around 10%), whereas there was no significant loss of avenasterol. On the other hand, in HSBO, there seemed to be a preferential loss of avenasterol (15% loss) as well as campesterol and stigmasterol (about 10% each) whereas less sitosterol (4.9%) was lost. Avenasterol was also preferentially destroyed in ESBO and ELLSBO (40 and 3.7% after 35 h, respectively), despite the fact that the total phytosterol loss in those oils was low. In HOSun, the only phytosterols lost were  $\Delta^7$ -stigmasterol and  $\Delta^7$ -avenasterol (2.8%).

When comparing a conventionally extracted soybean oil (SBO) with an expeller pressed soybean oil (ESBO), phytosterol loss in the former was more than double that in the latter, despite their similarity in phytosterol composition, fatty acid composition, and in the rates of oil degradation, as measured by TPC and PTAGS. In addition, ELLSBO had similar fatty acid composition to Corn, yet had slightly lower TPC and PTAG formation during intermittent frying, and only lost 1.35% of phytosterols. Expeller pressed oils are often found to be more stable than their hexane-extracted counterparts [30, 31]. Some have suggested that this is due to the removal of antioxidant compounds during hexane extraction, while others suggest that it may be due to antioxidant compounds produced through Maillard browning reactions that are formed at the

temperatures used during oilseed roasting and/or expeller pressing [30, 32].

In these studies, reduction of phytosterol content ranged between 4 and 6% in most oils during continuous frying, and between 1 and 15% during intermittent frying. This data combined with other studies [17–19] indicate that phytosterol loss during frying is not as extreme as seen when oils are heated without frying [26, 27]. In comparing continuous and intermittent frying, it is interesting to note that although oil degradation progressed further in all of the oils as measured by TPC and PTAGs, especially in ESBO, there was little difference between the two frying methods in phytosterol loss except for in Corn and HSBO.

Although several heating studies have demonstrated that phytosterol loss is higher in more saturated media [14, 16], suggesting that unsaturated fatty acids are oxidized preferentially to sterols, no relation between fatty acid composition and phytosterol loss was found in this study. However, most of the oils used were similar in content of saturates, except for the HOSun, which had less saturates than the other oils. Instead, the oils varied in 18:2 and 18:3, and the differences in PUFA were balanced out by 18:1 content. This suggests that in vegetable oils low in saturates, factors other than fatty acid composition of the medium play a role in phytosterol destruction during frying.

One such factor may be the concentration of natural antioxidants such as tocopherols in the oils. Soybean, corn, and sunflower oils all generally have between 500 and 1,500 mg/kg tocopherols with varying amounts of the four-tocopherol homologues [28]. While both soybean and corn oil have predominantly  $\lambda$ -tocopherol, as well as some  $\alpha$ - and  $\delta$ -tocopherols, sunflower oil has mostly  $\alpha$ -tocopherol. Tocopherols are degraded or volatilized during the frying process, but their loss often varies depending on the homologue and the composition of the oil [29]. One explanation for the stability of phytosterols in oils may be that the tocopherols were preferentially oxidized over phytosterols, and thus phytosterols were not oxidized until most or all of the tocopherols in the oils were lost. Tocopherols were analyzed as well and the data are will be presented in another report. In Corn, tocopherols degraded more slowly than in any of the other oils (data not shown), which may partly explain why phytosterols degraded more quickly. However, this trend was not seen in the other oils, so there are probably multiple factors involved in phytosterol stability. For example, the higher concentration of phytosterols in Corn as compared to the other oils may have been another factor explaining the increased rate of loss. In addition, the form of phytosterol, whether free or esterified, may also play a role in how quickly they are degraded during frying. Soupas et al. [13] demonstrated that esterified phytosterols were less stable than free

phytosterols upon heating. In corn oil, phytosterols occur in approximately equal proportions of free and esterified forms, while in soybean and sunflower oils, 30–40%, respectively, are found in the esterified form [4], but these ratios vary significantly due to growing and processing conditions [3]. Systematic studies of phytosterol concentrations and levels of esterification in relation to their stability are the subject of future studies.

**Acknowledgments** The authors would like to gratefully acknowledge Kathy A. Rennick and Linda A. Parrott for their technical expertise.

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