Oxidative Stability of Natural and Randomized High-Palmitic- and High-Stearic-Acid Oils from Genetically Modified Soybean Varieties[1]

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ABSTRACT: The oxidative stability of soybean oil triacylglycerols (TAG) obtained from genetically modified soybeans was determined before and after chemical randomization. Soybean oil oxidative studies were carried out under static oxygen headspace at 60°C in the dark and oxidative deterioration was monitored by peroxide value, monomeric and oligomeric oxidation products, and volatile compounds. Randomization of the soybean oil TAG improved the oxidative stability compared to the natural soybean oil TAG. Oxidative stability was improved by three factors. Factor one was the genetic modification of the fatty acid composition in which polyunsaturated acids (such as linolenic and linoleic acids) were decreased and in which monounsaturated fatty acids (such as oleic) and saturated acids (palmitic and stearic) were increased. Factor two was the TAG compositional modification with a decrease in linolenic and linoleic-containing TAG and an increase in TAG with stearic and palmitic acids in combination with oleic acid. Factor three was the TAG structure modification accomplished by an increase in saturated fatty acids and a decrease in linoleic and linolenic acids at the glycerol moiety carbon 2.

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KEY WORDS: Food formulation, high-palmitic, high-stearic, margarine, oxidative stability, randomized soybean oil, soybean oil, triacylglycerol, triacylglycerol structure, triglyceride.

Research has been directed toward the improvement, through plant genetic manipulation, of the properties of vegetable oils for uses such as frying oils, salad oils, margarines, confectionery products, and baking shortenings by altering the fatty acid (FA) composition and the triacylglycerol (TAG) composition (1–6). Also, food products can be prepared from blends by randomization of vegetable oils and by interesterification of vegetable oils such as cottonseed, peanut, soybean, corn, and canola with hydrogenated soybean or cottonseed hard stocks (7). The physical properties (solid fat index and drop melting point) of the soybean oil (SBO) for food formulation requirements (margarines) were previously found to be improved after randomization. The interesterification reaction may be chemically or enzymatically catalyzed, and the result is a slight change in TAG composition and a major change in TAG structure to produce improved food products (3–7). In addition to analysis of structured fat physical properties such as melting range, solid fat index, and crystal structure as determined by dropping point, dilatometry, pulsed nuclear magnetic resonance, differential scanning calorimetry, and X-ray analyses (7), it is important to analyze TAG composition and structure. Correlation of fat physical properties can be made with TAG composition (quantity of individual TAG in the structured fat) (7). Also, it is important to know the oxidative or storage stability of the structured fat in regard to TAG composition and structure (8–12). We report here studies on the oxidative stability of SBO high in palmitic and stearic acid, which had previously been found to be suitable margarine base stock candidates after randomization.

EXPERIMENTAL PROCEDURES

Materials. SBO were laboratory-refined, -bleached, and -deodorized oils (13). Non-TAG components were removed by solid-phase extraction chromatography before oxidation studies (10). Randomized oils were prepared in the presence of sodium methoxide as a catalyst (14).

Methods. TAG purification by solid-phase extraction and TAG composition by reversed-phase high-performance liquid chromatography (RP–HPLC) coupled with evaporative light-scattering detector (ELSD) methods were previously reported (15). FA analysis by capillary gas chromatography (GC) of the transmethylated oils, TAG structure by lipolysis-GC analysis, HPLC determination of carotenoids, and determination of colorimetric peroxide values (PV) were previously reported (10). The identity of the TAG quantitated by RP–HPLC–ELSD was determined by RP–HPLC coupled with an atmospheric pressure chemical ionization (APCI) mass spectrometer (MS) (16). TAG linoleic- and linolenic-acid-derived oxidation products were determined by RP–HPLC on a Betasil 5 μm phenyl ODS column, 15.0 × 0.46 cm, Keystone Scientific, Inc. (Bellefonte, PA), with

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methanol pumped at 0.2 mL/min as the mobile phase. The ultraviolet detector was set at 234 nm. TAG secondary oxidation products such as TAG hydroperoxy cyclic peroxides, and bis-hydroperoxides eluted at 13 to 15.5 min and TAG monohydroperoxides eluted at 16 to 19 min. The summation of the HPLC peak areas for these components gave total linoleic-plus linolenic-acid-derived oxidation products formed. Total SBO tocopherols were detected using the above RP–HPLC system with the detector set at 298 nm. The total SBO tocopherols eluted as one peak at 11.5 to 14 min. Tocopherol detection limit was 0.5 μg/g oil. TAG monomer, dimer, oligomer, diacylglycerol, monoacylglycerol, and free FA were detected by size exclusion chromatography (SEC) on four SEC columns [two 500-Å and two 100-Å pore-size columns in series (Waters, Millipore Inc., Milford, MA)]. The mobile phase was tetrahydrofuran pumped at 0.5 mL/min. The detection limit for these products was 0.1% of the total sample injected. Volatile compound analysis was conducted by purge and trap-GC–ion trap MS with purge and trap (Tenax) test tube heated at 100°C for 15 min; GC column DB 1701 (J&W Scientific, Folsom, CA, 30 m × 0.32 mm), heated from −20°C to 214°C at 3°C/min; ion trap MS operated in the EI mode with mass scan range 23 to 350 *m/z* over 0.8 s. Compound identifications were made from spectral comparisons with the National Institute of Standards and Technology NIST-92 MS library (Varian, Inc., Walnut Creek, CA), and from retention time comparisons with standard compounds.

Autoxidation of purified TAG samples was conducted at 60°C in the dark in a forced-air oven. Samples (500 mg each) were weighed into 20 mL vials flushed with oxygen. Duplicate TAG samples per variety were prepared for each oxidation time (24, 48, and 72 h). Three 15-mg samples were removed from each TAG sample per time period for PV determination by the colorimetric ferric thiocyanate method (10) in triplicate; two 50-mg samples for volatile compound headspace analysis in duplicate; and one 50-mg sample for oxidation product analysis by RP–HPLC.

Oxidative stability. Oxidative stability was determined by ΔPV, the PV change with oxidation time for each oil (duplicate samples from each SBO variety, analysis precision of ±0.0015 ΔPV units per hour) from the linear regression of the PV vs. time plot for 0 to 72 h. A control SBO was common to each oxidation experiment to verify reproducibility of oxidation conditions (10,12).

RESULTS AND DISCUSSION

Genetically modified soybeans high in palmitic acid and stearic acid were processed into refined, bleached, and deodorized oils. FA compositions of the modified oils along with the control SBO are in Table 1. As in genetically modified high-stearic-acid SBO (4), natural SBO high in palmitic acid lack sufficient solids for use in margarine or spread formulations. However, after randomization, sufficient solids were present to allow formulation into margarines, especially for oils A and C. SBO A and C had the largest amount of total saturated FA at 34.9 and 42.6% respectively (Table 1). The low linolenic (Ln) SBO E with 7% total saturated FA lacked sufficient solids for good physical properties for use in margarine formulation. TAG structure analyses (Table 2) confirmed that palmitic and stearic acid were essentially absent on carbon 2 for the natural oils. This denoted the natural oils as having the symmetrical saturated-unsaturated-saturated FA (SUS)-type TAG. However, after randomization, significant amounts of the higher-melting-point saturated-saturated-unsaturated FA (SSU)-type TAG were formed. This probably accounted for the desired elevation in the melting points and solid fat index profiles for the randomized (compared to the natural) oils.

TABLE 1
Fatty Acid (FA) Composition of High-Palmitic-Acid and High-Stearic-Acid Soybean Oils (SBO)

	Fatty acid composition (%)[a]					
	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	Total saturated FA
Control SBO	10.0	4.2	25.4	53.4	7.0	14.2
A	8.5	26.4	18.0	38.9	8.2	34.9
B	24.8	4.3	16.4	43.9	10.1	29.1
C	23.6	19.0	9.3	38.0	10.0	42.6
D	18.3	4.4	24.0	49.6	3.1	22.7
E	3.7	3.3	31.4	58.6	2.9	7.0

[a]Determined by gas chromatography of the transmethylated triacylglycerols (10). Fatty acid composition standard deviation = 0–0.5%.

The effect of FA, TAG composition, and structure on the oxidative stability of SBO containing high amounts of palmitic and stearic acids, before and after randomization, was investigated. The oil samples showed considerable FA variation (Table 1). The oxidizable FA contents ranged from low to high: Ln (2.9–10.1%), linoleic (L) (38.0–58.6%), and oleic (O) (9.3–31.4%). The saturated fatty acids, palmitic (P) and stearic (S) ranged from low to high (3.7–24.8%) and (3.3–26.4%), respectively. Palmitic and stearic FA were not oxidizable FA under our test conditions. Oils A–D were high in saturated FA (S plus P) (22.7–42.6%) compared to normal SBO (14%) and low Ln SBO E (7%). Three of these four oils (A, B, C) were high in the oxidatively unstable Ln (8–10%) and low in oxidatively stable O (38–43.9%). One SBO (D) had a good balance of monunsaturated FA O (24.0%) and polyunsaturated FA L (49.6%) and had low Ln (3.1%) with a high saturated FA (22.7%) content compared to normal SBO.

Each of the genetically modified oils was randomized for evaluation as a margarine base stock, as well as to determine the oxidative stability of the randomized oil vs. nonrandomized or natural oil. Randomization of the oils was verified by agreement of the FA composition of the total oil (Table 1) with the FA composition at glycerol carbon 2 of the oil (Table 2).

The SBO were purified of non-TAG components to permit valid comparison of oxidative stability based on the composition of the TAG. However, not all tocopherols could be removed from the oil (17) and about 4 μg of total tocopherols per gram of oil remained. However, the purified oils were verified to have no other kinds of non-TAG components by the

TABLE 2
FA Composition on Carbon-2 and [carbons 1(3)] for Nonrandomized and Randomized SBO[a]

	Fatty acid composition on carbon-2 [carbons 1(3)] (%)[b]					
	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	Total saturated FA
Nonrandomized SBO samples						
Control SBO	0.0 (15.0)	0.0 (6.3)	24.6 (25.9)	69.3 (45.4)	6.2 (7.4)	0.0 (21.3)
A	0.7 (9.0)	1.3 (29.6)	8.1 (16.9)	86.6 (34.3)	3.3 (6.6)	2.0 (38.6)
B	1.1 (38.7)	0.0 (5.9)	12.4 (14.6)	72.6 (29.4)	13.0 (8.8)	1.1 (44.6)
C	1.4 (34.4)	1.1 (25.1)	11.2 (8.4)	71.6 (20.8)	14.7 (7.1)	2.5 (59.5)
D	0.1 (28.9)	0.0 (6.3)	22.0 (23.6)	72.7 (35.9)	3.6 (2.9)	0.1 (35.2)
E	0.4 (5.6)	0.0 (5.0)	27.5 (29.0)	69.9 (56.7)	2.2 (2.6)	0.4 (10.6)
Randomized SBO samples						
A	9.0 (8.2)	26.7 (26.3)	17.2 (18.4)	38.9 (38.4)	8.2 (8.7)	35.7 (34.5)
B	27.3 (26.4)	4.1 (3.9)	13.8 (14.4)	44.1 (44.9)	10.3 (10.5)	31.4 (30.3)
C	23.6 (23.6)	18.9 (19.1)	9.9 (9.0)	38.5 (37.8)	9.2(10.4)	42.5 (42.7)
D	21.2 (19.4)	4.5 (4.2)	23.0 (23.8)	48.4 (49.3)	3.0 (3.3)	25.7 (23.6)
E	4.8 (3.5)	4.5 (2.7)	27.7 (29.0)	59.8 (62.0)	2.0 (2.8)	9.3 (7.7)

[a]Determined by regiospecific analysis (10).
[b]Standard deviation = 0–0.5%. For abbreviations see Table 1.

HPLC procedures listed in the Experimental Procedures section and were free within stated detection limits of free fatty acids, oxidation products, carotenoids, chlorophyll, and diacylglycerols. The refined, bleached, and deodorized oils, before randomization, typically contained 40–50 µg/g oil total tocopherols, 1% diacylglycerols, and 0.1% oligomers but no detectable free fatty acids or monoacylglycerols. Randomization did not affect the total tocopherol or oligomer concentration although the diacylglycerol composition increased about 5% compared to natural oils.

To investigate oxidative stability of the oil with respect to TAG FA, TAG composition, and structure before and after randomization, duplicate purified samples of each SBO variety were used to compare the experimental oxidative stability of the natural and randomized oils. Also, a predictive oxidative stability was calculated for each oil based on the unsaturated fatty acid composition (18). This calculation expresses the oxidizability of each FA with oxidatively resistant oleic acid at $0.02 \times$ oleic concentration + the oxidatively unstable linoleic acid at $1 \times$ the linoleic concentration + linolenic acid at $2 \times$ linolenic concentration (Table 3). The experimental oxidative stability data showed that for the natural high-saturated FA oils, the high-linolenic, high-linoleic and low-oleic SBO B was the least stable, and lower-linoleic SBO A was the most stable high-saturated FA SBO. However, of the five SBO samples studied, low saturated FA SBO E was more stable than high-saturated FA SBO A. Unfortunately, SBO E had low saturated FA and was not a suitable margarine formulation oil. Because of its very-low-linolenic and higher-oleic acid composition, SBO E had better stability than any of the other SBO samples studied. For the natural oils, the experimental and predicted oxidative stability order was in agreement for SBO samples B, C, and D. For these samples, the oleic, linoleic, and linolenic concentration played the major role in regard to oxidative stability (10–12). However, for oil A, which had greater experimental than predicted oxidative stability, TAG composition (Tables 4 and 5) was high for LOO or LOS and SLS, which are known to be oxidatively stable (10,12). Therefore, for natural oil A, the types of TAG were apparently more important than the total amount of L and Ln in the determination of actual oxidative stability (10–12).

Within experimental error, randomization increased the oxidative stability of SBO samples A–D as compared to the natural oils (Table 3). Oxidative stability of SBO E was essentially the same before and after randomization. However, this oil contained only 7% total saturated FA compared to 22.7–42.6% total saturated FA for SBO A–D. Thus, for SBO E the increase in TAG structure SSU was not of the magnitude of the SBO A–D after randomization. Although a small amount of non-TAG components (about 4 µg total tocopherol per gram of oil) remained, this tocopherol concentration was the same for all natural and randomized oils and no other non-TAG components were detected in the natural and randomized oil samples. Therefore, the change in oxidative stability between the natural and randomized oil was not because of changes in trace amounts of tocopherols (17) that remained in the purified oils. These changes in oxidative stability of course cannot be related to fatty acid composition (Table 1),

TABLE 3
Experimental and Predicted Oxidative Stability of High-Saturated-FA SBO Before and After Randomization[a]

	Oxidative stability		
	Experimental		Predicted
	Natural	Randomized	Natural or randomized
B	0.8342	0.4571	0.645
D	0.6980	0.6948	0.643
C	0.6851	0.6739	0.636
A	0.6545	0.6420	0.692
E	0.6527	0.6535	0.650

[a]Experiment: ΔPV is the rate of peroxide value change with storage time (meq peroxide/h). Precision is ±0.0015 meq peroxide/h. Predicted: (oxidizability) = 0.02(oleic) + 1(linoleic) + 2(linolenic) percent (10,18). Oxidative stability is defined as rate of peroxide value change with oxidation time.

TABLE 4
TAG Composition of Nonrandomized and Randomized Samples Used in Oxidative Stability Studies[a]

	TAG composition (%)										
TAG[b]	SBO control	SBO A	SBO A(R)	SBO B	SBO B(R)	SBO C	SBO C(R)	SBO D	SBO D(R)	SBO E	SBO E(R)
LnLnLn	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
LnLnL	0.8	0.0	0.0	0.0	0.0	0.5	0.5	0.9	0.7	0.3	0.3
LnLL	6.6	2.7	1.7	1.3	1.4	1.6	3.2	3.6	5.6	2.8	3.4
LnLnO	0.4	0.0	0.0	0.0	0.0	0.1	0.9	0.4	0.4	0.1	0.3
LnLnP	0.0	0.0	0.0	0.0	0.0	0.5	0.3	1.2	0.5	0.1	0.1
LLL	15.6	29.1	25.6	10.2	12.3	2.7	5.6	6.9	9.2	6.2	7.2
LnLO	5.6	2.2	1.8	1.9	1.9	0.8	1.6	3.0	3.3	1.8	2.8
LnLP	3.6	0.0	0.1	2.2	1.3	7.5	5.8	10.7	7.9	2.3	1.8
LLO	15.8	26.4	36.4	12.7	18.4	2.4	3.9	6.9	8.7	7.0	9.4
LnOO	1.1	1.2	0.3	0.7	0.5	0.0	0.0	0.5	0.3	0.2	0.3
LLP	12.4	5.7	4.4	18.6	17.7	17.7	19.2	21.1	20.6	11.6	11.1
LnOP	2.0	0.3	0.1	1.6	0.8	0.5	0.8	3.9	2.0	0.4	0.4
LnPP	0.0	0.0	0.0	0.0	0.0	0.6	0.1	2.7	0.0	0.0	0.0
LOO	8.2	13.5	16.2	7.3	7.9	1.7	1.6	1.3	4.3	2.7	3.1
LLS	2.7	3.8	3.1	2.8	2.5	8.2	10.0	4.3	2.0	13.0	15.9
LOP	9.5	3.7	3.9	15.7	16.6	6.2	6.3	9.9	11.9	5.8	5.9
PLP	1.7	0.5	0.3	9.6	6.7	14.2	9.7	15.2	12.1	2.1	1.7
OOO	3.2	5.0	2.2	2.8	0.9	0.5	0.3	0.0	0.5	1.2	0.8
LOS	3.3	3.0	2.6	2.7	2.0	3.7	4.2	0.6	1.0	12.0	12.3
POO	2.9	1.3	0.5	3.6	2.4	1.0	0.1	0.9	0.9	0.6	0.2
SLP	1.5	0.3	0.1	2.7	1.7	16.0	12.3	3.0	2.4	8.8	7.1
POP	0.6	0.3	0.1	2.2	2.6	1.5	1.3	1.9	2.8	0.3	0.2
PPP	0.1	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.0	0.2	0.2
SOO	0.9	0.9	0.5	0.9	0.9	0.3	0.5	0.1	1.4	2.2	1.5
SLS	0.3	0.0	0.1	0.0	0.2	7.0	5.3	0.5	0.2	12.0	7.3
SOP	0.4	0.0	0.0	0.0	0.8	1.6	1.8	0.5	0.6	1.6	1.6
PPS	0.1	0.0	0.0	0.0	0.4	1.0	2.5	0.3	0.7	0.8	0.7
SOS	0.1	0.0	0.0	0.0	0.1	0.7	0.7	0.0	0.1	3.4	2.2
PSS	0.1	0.0	0.0	0.0	0.1	0.3	1.3	0.0	0.0	0.2	0.5
SSS	0.1	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.0	0.1	0.2

[a]Determined by reversed-phase high-performance liquid chromatography (HPLC) with evaporative light-scattering detector (15). HPLC peak area % standard deviation was ±0.1–0.7% for triplicate analyses.
[b]Triacylglycerols (TAG) palmitic (P), stearic (S), oleic (O), linoleic (L), and linolenic (Ln) acids, (R), randomized oil.

which did not change during randomization. Some of the change in oxidative stability between natural and randomized oils may be related to change in TAG composition (Tables 4 and 5). Randomized oils actually showed a slight increase in oxidatively unstable TAG such as LnLL, LLL, LLO, and LLS and a decrease in stable TAG such as PLP and SLP (Tables 4 and 5). This might have been expected to have decreased the oxidative stability of the randomized compared to the corresponding natural oils (10,12). Randomization actually increased the oxidative stability of all these oils except for SBO E. Other factors than TAG composition must be involved in the improvement of the oxidative stability of the randomized oils. The effect on oxidative stability between natural and randomized oils may be because of the dramatic TAG structure change. The unsaturated FA concentration was greatly reduced and the saturated FA concentration was greatly increased on the glycerol moiety carbon *sn*-2. TAG structures were identified by analysis of the FA composition at the internal carbon 2 and external carbons 1(3) (Table 2) positions of the TAG glycerol moiety. Unsaturated FA content at glycerol carbon 2 for the natural SBO samples showed considerable variation: Ln (2.2–14.7%), L (69.9–86.6%), and O (8.1–27.5%). A small amount of saturated FA was found at the glycerol carbon 2 for the natural oils. For the randomized SBO samples, considerable saturated FA increase was found at glycerol carbon 2. The randomized samples showed considerable variation of saturated FA at glycerol carbon 2 with P (4.8–27.3%) and S (4.1–26.7%). After randomization, L and Ln decreased and O remained about the same concentration at glycerol carbon 2, and there was a great increase for saturated fatty acids at carbon 2 with a corresponding decrease for unsaturated FA compared to the natural oils. Thus, the TAG of the randomized oils were predominantly of an SSU FA structure, compared to SUS FA structure for the natural oils. For the external glycerol moiety carbons 1(3) of the randomized samples, Ln (2.8–10.5% variation) and L (37.8–62.0% variation) increased and O (9.0–29.0% variation) stayed about the same concentration compared to the natural oils. The opposite trend was observed for the saturated FA composition P (3.5–26.4% variation) and S (2.7–26.3% variation), which decreased at the external glycerol moiety carbons 1(3) of the randomized oils compared to the natural oils. Increase of O and reduction of L and Ln concentration on glycerol moiety carbon 2 that occurred here during ran-

TABLE 5
TAG Composition Analysis of High-Saturated-FA SBO Samples Used in Oxidative Stability Studies from Genetically Modified Soybean Varieties[a]

TAG	B	B(R)	D	D(R)	C	C(R)	A	A(R)	E	E(R)
LnLnLn	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
LnLnL	0.0	0.7	0.0	0.0	0.0	0.5	0.0	0.3	0.0	0.0
LnLL	3.6	5.6	1.3	1.4	1.6	3.2	3.0	3.4	2.7	1.7
LnLnO	0.4	0.4	0.0	0.0	0.7	0.9	0.3	0.3	0.0	0.0
LnLnS*	1.2	0.5	0.0	0.0	1.0	0.3	0.3	0.1	0.0	0.0
LLL	6.9	9.2	10.2	12.3	2.9	5.6	6.2	7.2	29.1	25.6
LnLO	3.0	3.3	1.9	1.9	1.3	1.6	2.4	2.8	2.2	1.8
LnLS*	10.7	7.9	2.2	1.3	7.1	5.8	2.9	1.8	0.0	0.1
LLO	6.9	8.7	12.7	18.4	2.7	3.9	7.0	9.4	26.4	36.4
LnOO	0.5	0.3	0.7	0.5	0.0	0.0	0.5	0.3	1.2	0.3
LOO	1.3	4.3	7.3	7.9	0.9	1.6	2.3	3.1	13.5	16.2
LLS*	25.4	22.6	21.4	20.2	23.0	29.2	24.6	27.0	9.5	7.5
LnOS*	3.9	2.0	1.6	0.8	2.0	0.8	1.0	0.4	0.3	0.1
LOS*	10.5	12.4	18.4	16.6	10.9	10.5	16.9	18.2	6.8	6.5
S*LS*	18.7	14.7	12.8	8.6	35.8	27.3	21.9	16.1	0.8	0.5
OOO	0.0	0.5	2.8	0.9	1.4	0.3	1.5	0.8	5.0	2.2
S*OO	1.0	2.3	4.2	3.3	0.6	0.6	3.4	1.7	0.2	1.0
S*S*S*	0.0	0.7	0.0	0.5	1.4	4.0	1.5	1.6	0.0	0.0
S*OS*	1.7	3.5	2.7	2.2	2.7	3.8	6.3	4.0	0.3	0.1

[a]Saturated fatty acids palmitic and stearic are considered oxidatively equivalent and are added together and listed as S* in the TAG. See Tables 2 and 4 for other abbreviations. *S = sum of all saturated acids present, i.e., SOS represents for S*, palmitic, stearic, etc.

domization has previously been determined to increase oil oxidative stability (10,12). This structure change may explain the increased oxidative stability of randomized oils compared to the natural oils. Thus, for these high-saturated-FA SBO, TAG structure difference, which is usually a minor influence on SBO oxidative stability (10,12), was apparently more important than TAG composition difference for the oxidative stability difference between the randomized and the natural oils (Table 3).

The oils were further analyzed by SEC for TAG monomeric and oligomeric oxidation products and by RP–HPLC with UV detection for TAG monohydroperoxides and secondary oxidation products. Natural oils were found to have about 3% oligomer and about 7% dimer by 72 h oxidation time. The randomized oils were found to have about 1% oligomer and 4% dimer by 72 h. Therefore, some polymer was produced during the oxidation of the oils in the dark at 60°C. There is no evidence of diacylglycerol, monoacylglycerol, or free FA formation during the oxidation. For both the randomized and nonrandomized oils, the concentration of monohydroperoxides and secondary oxidation products such as hydroperoxy cyclic and bis-hydroperoxides remained at a ratio of about 9:1 during the oxidation period.

Volatile compounds produced from the thermal decomposition of the oxidation products formed by 72 h oxidation time for the natural and randomized oils are listed in Table 6. Up to 49 volatiles were detected in these oils. The most abundant volatiles consistently greater than 2% (listed with its volatile precursor) were hexanal (L), propanal (Ln), 2-heptenal (L), pentane (L), pentanal (L), heptadienal (Ln), and nonanal (O). There were no major differences observed between the types of volatiles between natural and randomized oils; however, there were higher concentrations of L-derived volatiles pentane, pentanal, and hexanal, and less concentration of the O-derived volatile nonanal in the randomized samples as compared to the natural oils.

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TABLE 6
Volatile Composition of Thermally Decomposed TAG Oxidation Products of Oxidized SBO Samples[a]

Selected volatile (with fatty acid precursor)	Volatile composition (peak area %)									
	A	A(R)	B	B(R)	C	C(R)	D	D(R)	E	E(R)
Ethanal (Ln)	0.0	0.1	0.0	0.2	0.1	0.1	0.0	0.3	0.0	0.0
Pentane (L)	2.4	6.0	3.8	9.5	2.3	5.6	15.1	17.6	6.7	14.3
Furan	0.2	0.2	0.3	0.1	0.2	0.2	0.5	0.0	0.1	0.0
Propanal (Ln)	11.6	13.2	15.2	13.2	12.5	16.5	21.5	8.5	5.8	3.3
Butanal	0.8	0.6	0.7	0.5	1.3	0.5	2.0	1.3	0.6	0.5
2-Butanone	0.0	0.0	0.0	0.0	1.6	0.1	0.0	0.0	0.0	0.0
2-Ethylfuran	1.2	0.1	2.4	2.0	1.1	1.6	1.9	0.2	0.4	0.2
2-Butenal	1.2	1.0	1.2	0.7	0.9	1.4	0.3	0.3	0.3	0.1
1-Penten-3-one	0.5	0.9	0.9	1.5	0.5	1.2	0.2	0.1	0.3	0.1
Pentanal (L)	4.1	5.5	3.3	5.6	2.8	4.4	5.4	14.2	6.2	6.9
1-Penten-3-ol	2.9	2.1	3.0	0.2	2.7	4.2	0.6	0.6	0.9	0.4
Octane (O)	0.2	0.1	0.2	0.1	0.2	0.0	0.9	1.1	0.2	0.7
(*E,Z*)-1,4-Octadiene	0.0	0.0	0.0	0.0	0.0	0.0	2.1	0.0	0.0	0.0
(*E,Z*)-1,4-Octadiene	0.0	0.0	0.0	0.0	0.0	0.0	1.7	0.0	0.0	0.0
(*E*)-2-Pentenal (Ln)	0.9	2.4	2.4	1.5	2.0	3.1	0.5	1.1	0.6	0.6
3-Hexanone	1.2	0.0	1.1	0.0	11.0	0.0	0.9	0.0	0.0	0.0
1-Pentanol	0.7	0.7	0.5	0.7	1.5	0.5	0.1	0.2	0.8	0.5
Hexanal (L)	16.9	28.6	17.8	33.1	12.6	22.3	31.1	40.9	33.7	58.2
2-Methyl-cyclopentanone	0.3	0.1	0.2	0.1	1.2	0.1	0.0	0.1	0.2	0.1
(*E*)-2-Hexenal (Ln)	1.2	0.7	1.9	0.4	2.0	0.7	0.7	0.5	0.9	0.8
2-Heptanone	0.2	0.4	0.3	0.0	0.1	0.1	0.0	0.0	0.7	0.1
Heptanal (O)	0.8	0.7	1.2	0.9	0.9	0.6	0.6	0.9	1.5	0.9
Decane	0.0	0.0	0.1	0.1	0.0	0.0	2.9	0.0	0.0	0.0
2,4-Nonadiene (Ln)	2.7	3.7	3.4	4.0	5.4	4.9	0.0	0.3	1.8	0.4
2,4-Nonadiene (Ln)	2.1	3.5	2.6	2.5	4.3	4.9	0.0	0.3	1.2	0.3
2-Pentyl furan	2.3	15.2	3.3	0.8	1.6	1.4	5.1	0.5	2.3	0.6
(*E,E*)-2,4-Hexadienal	0.2	0.1	0.5	0.03	0.5	0.1	0.0	0.1	0.0	0.0
4-Octen-3-one	0.1	0.1	0.0	0.2	0.0	0.1	0.0	0.05	0.2	0.0
(*E*)-2-Heptenal (L)	11.1	11.7	10.3	6.7	7.6	11.1	0.8	4.4	19.0	5.6
1-Octen-3-ol	2.8	3.8	3.2	0.0	2.4	2.7	0.0	0.0	6.5	0.0
6-Methyl-5-hepten-2-one	1.1	0.0	2.3	0.0	0.5	0.0	0.0	0.0	0.1	0.0
Octanal (O)	3.8	0.3	1.5	0.3	1.4	0.2	0.2	0.1	1.1	0.2
Undecane	3.8	0.1	1.3	0.1	1.1	0.0	2.8	0.0	0.1	0.0
(*Z,E*)-2,4-Heptadienal (Ln)	2.3	2.4	2.1	1.4	3.4	3.3	0.0	0.2	0.6	0.2
(*E,E*)-2,4-Heptadienal (Ln)	2.9	3.7	4.0	3.4	3.9	4.6	0.2	0.5	1.5	0.3
Dodecane	0.0	0.0	0.0	0.0	0.0	0.1	1.4	0.0	0.0	0.0
(*E*)-2-Octenal (O)	0.5	1.2	0.6	1.2	0.4	0.7	0.0	2.7	1.0	1.9
Nonanal (O)	14.7	1.6	8.5	0.8	8.3	1.1	0.0	0.4	4.7	0.4
(*E* or *Z*)-2-Methyl-4-hexen-3-ol	0.0	0.9	0.1	3.2	0.1	0.4	0.0	1.3	0.4	1.1
(*E,E*)-3,5-Octadien-2-one	0.1	0.1	0.4	0.0	0.3	0.2	0.0	0.0	0.1	0.0
(*E*)-2-Nonenal (L)	0.0	0.0	0.1	0.1	0.0	0.1	0.0	0.1	0.1	0.0
Decanal (O)	1.0	0.2	0.6	0.0	0.7	0.0	0.0	0.0	0.3	0.0
(*Z,E*)-2,4-Nonadienal	0.0	0.1	0.1	0.1	0.2	0.2	0.0	0.1	0.0	0.0
(*E,E*)-2,4-Nonadienal	0.0	0.1	0.1	0.1	0.1	0.1	0.0	0.06	0.2	0.1
(*E*)-2-Decenal	0.0	0.1	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.1
Tetradecane	1.0	0.0	0.5	0.0	0.4	0.05	0.0	0.0	0.1	0.0
(*Z,E*)-2,4-Decadienal (L)	0.0	0.1	0.0	0.6	0.0	0.05	0.0	0.1	0.0	0.2
(*E,E*)-2,4-Decadienal (L)	0.0	0.2	0.0	2.3	0.0	0.2	0.0	0.5	0.1	0.7
(*E*)-2-Undecenal (O)	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.1

[a]See Tables 2 and 4 for abbreviations.

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