Molecular-Weight Distributions of Degradation Products in Selected Frying Oils[1]

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ABSTRACT: Polar isolates of frying oils used for frying French fries, potato chips, or French fries/tortilla chips were analyzed for nonvolatile components by high-performance size-exclusion chromatography (HPSEC) with viscometric (VIS)/refractometric (RI) detection. The degradation products were separated on three mixed-bed polystyrene/divinylbenzene columns with tetrahydrofuran as eluent. Dual VIS/RI detection of the column effluent enabled simultaneous determination of analyte molecular weights (MW) and concentrations. MW of individual components were calculated from viscosity data with the use of a universal calibration technique. HPSEC of polar samples obtained from different oilseed lines yielded triglyceride-derived products in which the corresponding nonvolatile components had variable MW and compositions. Elevated levels of high-MW components were correlated with the extent of frying oil degradation to serve as indicators for frying oil stability. MW/concentration profiles of degradation products varied notably with frying times. The distribution patterns of degradation products were markedly affected by other frying conditions and oil varieties and therefore served as fingerprint properties of specific oils. High-oleic sunflower oil (HOSUN) (used for frying French fries) appeared to be more stable than cottonseed oil: at 30 h, the concentrations of the highest MW components were 0.63 vs. 0.89 mg/100 mg oil. HOSUN (used for frying French fries/tortilla chips) tended to be more stable than sunflower oil (SUN), as the most abundant (at 30 h, 3.99 vs. 4.34 mg/100 mg oil) species were components 4 (MW = 1385) and 3 (MW = 2055) for HOSUN and SUN, respectively. High-oleic soybean oil (HOSBO) was notably more stable than soybean oil: at 40 h, the concentrations of the highest MW (2980 vs. 6315) components were 0.21 vs. 4.51 mg/100 mg oil.

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KEY WORDS: Frying oil, high-performance size exclusion chromatography, molecular-weight distribution, nonvolatile component, oil stability, viscometric detection.

Frying oils are stabilized by modifying the fatty acid compositions through plant breeding genetic modifications or partial hydrogenation to withstand the effects of oxidation, polymerization, and hydrolysis. Partial hydrogenation increases saturated fatty acids and *trans* fatty acids and decreases polyunsaturated fatty acids to produce more stable oil. Fatty acid targets for breeding usually include increasing oleic acid and decreasing linolenic and linoleic acids. Over the last 15 yr, various oilseeds with fatty acid compositions modified by plant breeding genetic modifications have been developed, including high-oleic sunflower, high-oleic canola, low-linolenic soy, low-linolenic canola, and mid-oleic sunflower. Oils with lower linolenic acid and/or higher oleic acid than commodity oil have shown improved frying stability compared to the unmodified oils (1–9).

Characterization of nonvolatile components in frying oils is essential for the evaluation of the quality and oxidative stability of the oils. Fried foods are important food commodities consumed by the general population. Food frying can lead to enhancement in flavor depending on the quality and stability of the oils used. Because of the use of high temperature, frying processes are usually accompanied by thermolysis, hydrolysis, oxidative degradation, and polymerization (10,11). Chromatographic analysis of nonvolatile polar products provides information on the extent of frying oil deterioration.

Degradation products of frying oils are conventionally analyzed by high-performance size-exclusion chromatography (HPSEC) with concentration detectors such as an evaporative light scattering detector or a refractive index detector (12–16). In the existing methods, molecular weights (MW) of nonvolatile components are determined by calibration with known MW and retention volumes of standards. However, the conventional methods for MW detection are inadequate to provide absolute MW information on polymeric species of the oils. Application of a dual HPSEC–viscometric (VIS)/refractometric (RI) detection method for the analysis of nonvolatile components of frying oils has not been described. In this paper, we report the first HPSEC–dual VIS/RI detection technique for the analysis of frying oils. MW/concentration distribution data for nonvolatile components separated on high-efficiency polymer columns are presented.

EXPERIMENTAL PROCEDURES

Materials. Refined, bleached, and deodorized (RBD) cottonseed oil (CSO), RBD high-oleic sunflower oil (HOSUN), RBD mid-oleic sunflower oil (MOSUN), RBD sunflower oil (SUN), RBD soybean oil (SBO), RBD high-oleic soybean oil (HOSBO), and RBD low-linolenic soybean oil (LLSBO) were obtained from commercial oil processors. All oils contained citric acid as the only additive. Various blends of oils

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were made with CSO and HOSUN (2:1 and 1:2 ratios) and with HOSBO and LLSBO (1:1, 3:1, and 9:1 ratios) to obtain oils with a range of linoleic and oleic acid contents.

Eight polystyrene MW standards (200–65,000) were obtained from American Polymer Standards (Mentor, OH). Oleic acid, monoolein, diolein, and triolein were obtained from Sigma Chemical Co. (St. Louis, MO). Solvents for column chromatography and HPSEC were high-performance liquid chromatography-grade high-quality products of Fisher Chemicals (Fair Lawn, NJ).

Methods. Fatty acid compositions of the initial oils were determined by capillary gas chromatography (GC) with a Varian (Palo Alto, CA) model 3400 chromatograph equipped with an SP-2380 column (30 m, 0.25 mm i.d., 0.20 µm film thickness; Supelco, Bellefonte, PA). Column temperature was held at 170°C for 10 min and temperature-programmed to 220°C at 3°C/min. Other GC conditions were: injector, 240°C; detector, 280°C.

Amounts of polar compounds were analyzed in duplicate by the AOCS column chromatography method (17). The method was slightly modified in the following manner: Aliquots (1 g) of fried oil samples in duplicate were chromatographed on silica gel (25 g) and eluted with petroleum ether/diethyl ether (87:13) for the removal of nonpolar fractions followed by chloroform/methanol (1:1) for the isolation of polar fractions. Chromatographic fractions were monitored by silica gel thin-layer chromatography (0.025 × 20 × 20 cm) with hexane/diethyl ether/acetic acid (80:20:1, vol/vol/vol) as the developing solvent and iodine as the visualizing agent. Whereas elution with diethyl ether as described in the AOCS procedure led to insufficient recovery (90–95.3%) of the polar materials, replacement of diethyl ether with chloroform/methanol (1:1) produced the polar fractions in quantitative yield (99.5–100%).

Oils were used to prepare a variety of fried foods as follows. Set 1: HOSUN; 10, 20, 30, and 40 h of frying at 190°C; French fried potatoes. Set 2: CSO, HOSUN, and 1:2 and 2:1 blends; 30 h of frying at 190°C; French fried potatoes. Set 3: SUN, MOSUN, and HOSUN; 10, 20, and 30 h of frying at 190°C; French fried potatoes and tortilla chips. Set 4: SBO, HOSBO, LLSBO, and 9:1, 3:1, and 1:1 blends of HOSBO and LLSBO; 10, 20, 30, and 40 h of frying at 190°C; French fried potatoes and tortilla chips. Set 5: CSO, HOSUN, and 1:2 and 2:1 blends; 9 and 18 h of frying at 190°C; potato chips.

Potato chips were prepared according to Warner *et al.* (18), and oils for analyses were collected before frying and after 9 and 18 h of intermittent frying at 190°C. French fried potatoes were prepared according to Warner *et al.* (18) with intermittent frying at 190°C and a total heating/frying time of 30 h. Oil samples were collected before frying and after 30 h of frying. Two of the sets of oils were used to fry tortilla chips and French fried potatoes alternately. Fresh white corn tortilla chips were purchased locally and fried intermittently at 190°C with total heating/frying time of 40 h. Frying conditions (e.g., the size of fryer and the amount of makeup oil) often were varied to meet specific requirements for different sets of experiments. For example, it was necessary to use a small fryer when only limited amounts of oils were available for frying. Furthermore, different sets of samples of the same oils used in different experiments were not identical because of differences in sample lots, aging, and sources.

HPSEC with dual VIS/RI (19). HPSEC separations of nonvolatile components were carried out with a Thermo Separation Products (San Jose, CA) model P4000 liquid chromatograph interfaced with a Viscotek (Houston, TX) differential Wheatstone bridge viscometer and a Waters (Milford, MA) model 410 refractometer connected in parallel. The detectors were coupled to three Polymer Laboratory (Amherst, MA) high-efficiency mixed-bed (100–1000-Å pore sizes) PLGEL Mixed-E columns (3 µm, 300 × 7.5 mm i.d.) connected in tandem. In exploratory experiments with whole oil samples, two Waters µStyragel 500 Å (7 mm × 30 cm) columns were used. Analytical samples in tetrahydrofuran (THF) (10–70 mg/mL) were injected onto the columns through a Thermo Separation Products model AS3000 autosampler and eluted with THF at a flow rate of 0.8 mL/min. The THF mobile phase was recirculated through the HPSEC system and replenished with fresh THF after 150–200 injections.

Using a universal calculation software (20) for alignment of VIS/RI signals with a narrow polystyrene standard, a MW calibration plot (log [η × MW] vs. elution volume, where η is intrinsic viscosity obtained from the viscometer signal output) was constructed. MW and concentrations of nonvolatile components were determined by manipulation of the universal calibration data for the MW and concentration of each analyte peak computed automatically with the Viscotek data processing software (20). The percent composition data for the nonvolatile components were converted to the concentration values (mg/100 mg oil) based on the whole oils assayed.

Statistical analysis. Standard deviations of duplicate analyses were computed and are reported in the tables as relative standard deviations (RSD).

RESULTS AND DISCUSSION

MW determinations of macromolecular polymers having MW much higher than those of frying oil polymers can be achieved by HPSEC with right-angle laser light scattering detection. At the outset of this work, attempted HPSEC analyses of frying oils with a right-angle laser light scattering detector (which is not an evaporative light scattering detector) failed to yield satisfactory results, owing to the low optical constant and relatively low MW of the frying oils. However, subsequent experiments with dual VIS/RI detectors interfaced to the HPSEC system produced good results. Polar frying oil components are traditionally characterized by calibration with standard plots of logarithmic MW vs. HPSEC retention times. Concentration detectors used for these purposes yield erroneous information on MW. Furthermore, the customary designation of the nonvolatile components as the monomer, dimer, trimer, tetramer, and high polymer of triglyceride derivatives may be an oversimplification and technically ambiguous. The com-

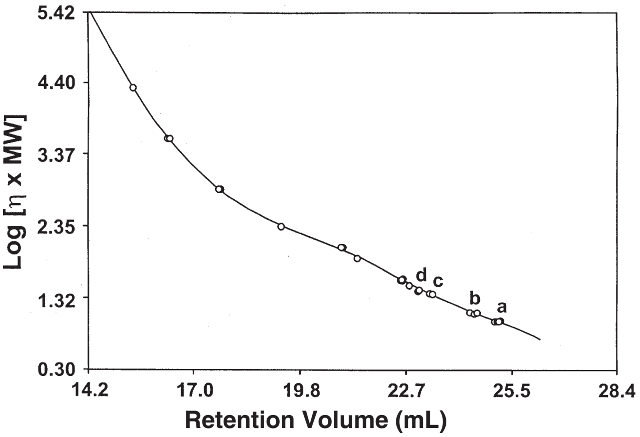

FIG. 1. Universal calibration plot of log [η × MW] vs. retention volume, where η is intrinsic viscosity and MW represents molecular weight. Open circles for oleic acid, monoolein, diolein, and triolein are labeled as a, b, c, and d, respectively. Others are for the eight polystyrene standards.

plex analyte species in frying oils should be much better represented by their absolute MW determined by a universal calibration method utilizing plots of log [η × MW] vs. elution volume (Fig. 1).

Table 1 shows the fatty acid compositions of the oils used in this study. The percentages of oleic acid (18:1) in the high-oleic varieties HOSBO and HOSUN were 84 and 78%, respectively. The amounts of the 18:1 species in the blended oils ranged from 42.9–79.6%. Linoleic acid (18:2) was present in SUN at the highest percentage (72.6%) among the oils evaluated and was found at lowest abundance (1.6%) in HOSBO. Generally, most oils had very low levels (0.0–2.9%) of linolenic acid (18:3); a slightly higher content (5.9%) was found in SBO. Except for CSO and CSO/HOSUN (2:1), which contained relatively high levels of palmitic acid (16:0), fatty acid analyses of the remainder of the oils revealed the presence of small amounts (2.2–9.7%) of saturated acids [16:0 and stearic acid (18:0)].

TABLE 1
Fatty Acid Composition of the Oils (%)[a]

Variety[b]	16:0	18:0	18:1	18:2	18:3
CSO	24.3	2.20	16.5	54.9	0.10
CSO/HOSUN (2:1)	16.2	3.00	42.9	35.7	0.10
CSO/HOSUN (1:2)	7.90	3.80	67.5	18.7	0.10
HOSUN	3.90	4.10	78.0	12.1	0.10
SUN	5.80	3.10	18.4	72.6	0.00
MOSUN	4.80	2.90	59.5	32.7	0.00
SBO	9.70	3.50	26.2	53.1	5.90
HOSBO	6.30	3.70	84.0	1.60	2.40
LLSBO	8.50	4.90	38.9	44.8	2.70
HOSBO/LLSBO (9:1)	5.70	3.80	79.6	5.80	2.60
HOSBO/LLSBO (3:1)	6.80	5.00	72.7	12.4	2.50
HOSBO/LLSBO (1:1)	7.50	4.00	60.9	23.0	2.90

[a] The composition is based on area percentage.
[b] CSO, cottonseed oil; HOSUN, high-oleic sunflower oil; SUN, sunflower oil; MOSUN, mid-oleic sunflower oil; SBO, soybean oil; HOSBO, high-oleic soybean oil; LLSBO, low-linolenic soybean oil.

In the initial phase of this work, whole aged used HOSUN and CSO oil samples [different sets from those used subsequently (Tables 3–5 and 7)] were analyzed by HPSEC–VIS/RI with Waters μStyragel columns (Table 2), which were later found not as efficient as Polymer Laboratory PLGEL Mixed-E columns (12) (used to obtain the data presented in Tables 3–5 and 7). Four major components were separated. Components i and iv were mixtures of respective low- and high-MW species not resolved with these columns. The high percentage of component i in both oils (70–77%) was due to the presence of nonpolar triglycerides (TG) admixed with polar TG in the whole oil samples. The MW of the corresponding components were variable. The results exemplify the practical applicability of the HPSEC–VIS/RI method for whole oil assays.

As demonstrated by the data summarized in Tables 2–7, MW and concentrations of the separated components were functions of frying time and oil type. Increased frying times resulted in definite changes in MW/concentrations of the corresponding components. Without exception, the highest MW component, 1, was absent in all unused zero-time oils. In view of the complexity of food frying processes mimicking industrial frying operations, degradation products would be formed as complex mixtures principally derived from a diversity of TG in oils. The data in the tables show no evidence of the formation of well-defined nonvolatile components in the forms of distinct increments of TG monomer (dimers, trimers, tetramers, etc.). Generally, no systematic trends of variations in individual component MW with frying times were observed. It must be pointed out that different sets of analyses with oil samples of the same type belonging to different sets/batches, differing in their history or sources, can lead to nonidentical results, because deep frying involves many experimental variables. As the MW of the six components shown in Tables 2–7 are a function of intrinsic viscosity η (obtained from the viscometer signal output) and elution volume and is determined by an MW calibration plot of log [η × MW] vs. elution volume (Fig. 1), HPSEC–VIS/RI chro-

TABLE 2
Molecular-Weight (MW) Distribution and Composition (%) of Whole Aged Oils (30 h)[a]

Sample[b]	Component i	ii	iii	iv
HOSUN				
MW distribution	1355	3369	5271	6700
Composition (%)	77	11	5	7
CSO				
MW distribution	1000	1623	2257	2315
Composition (%)	70	16	7	7
RSD[c] range (MW)	5.0–6.6	3.7–9.0	4.0–7.9	6.3–9.8
RSD range (%)	6.5–8.8	5.9–8.9	8.0–9.3	8.7–10

[a] Analyzed by high-performance size-exclusion chromatography with viscometric/refractometric detection (HPSEC–VIS/RI).
[b] See Table 1 for abbreviations.
[c] RSD, relative standard deviation.

TABLE 3
Amounts and MW and Concentration Distributions of Degradation Products (Components 1–6) in HOSUN Oil Used for French Fried Potatoes[a]

Time (h)	Polar compounds (%)	MW distribution 1	2	3	4	5	6	Concentration distribution[b] 1	2	3	4	5	6
0	1.49	ND[c]	3405	2095	1415	1245	ND	ND	1.57	4.03	14.4	1.96	ND
10	20.2	6755	5620	4455	1720	1530	780	1.10	3.25	9.23	9.18	2.30	0.43
20	31.3	6655	5700	3990	2555	1590	ND	2.14	3.76	6.37	11.0	1.30	ND
30	38.4	7530	4325	2315	1660	1580	ND	2.98	4.22	6.57	10.6	1.14	ND
40	45.3	7650	5080	3290	1640	1530	ND	2.98	4.22	6.57	10.6	1.14	ND
RSD[b] range	1.1–1.3	6.6–7.9	6.0–8.0	9.1–9.8	7.7–10	8.5–9.5	9.0–10	3.8–7.1	6.0–9.1	5.9–8.9	7.7–9.9	6.3–8.7	3.3–4.0

[a] Analyzed by HPSEC–VIS/RI.
[b] Concentration in units of mg/100 mg oil.
[c] ND, none detected. For other abbreviations, see Tables 1 and 2.

matograms of individual oil samples show each peak MW of the six components with a different retention volume. It is also obvious that the viscosity factor η of polymeric components varies with frying time. Accordingly, the components given in these tables have different peak MW because they eluted with different retention volumes.

Table 3 shows that MW and concentrations of the major components of HOSUN used for French fries varied significantly with changes in frying time. Changes in the MW/concentrations of the corresponding components with intermediate frying times (10–30 h) were rather erratic, presumably owing to fluctuation in frying conditions simulating industrial frying procedures. However, an increase in frying time from 0 to 10, 20, 30, or 40 h invariably promoted formation of higher MW components with high MW distribution. The MW/concentrations of the first three early-eluting components, 1, 2, and 3, at 40 h were greater than those of the corresponding components at 0 h. The data in Table 3 also show that the highest MW component (component 1) was absent in the zero-time oil but formed as soon as frying commenced. Prolonged frying tended to lower the concentrations of components 4 and 5 (Fig. 2).

Table 4 compares HPSEC analyses of HOSUN and CSO oils used for French fries. Both oils exhibited similar MW/concentration distribution patterns to those shown in Table 3. All HOSUN components at 30 h had notably higher MW than the corresponding CSO components despite close similarity in their zero-time MW distributions. However, at 30 h, lower amounts of high-MW components 1, 2, and 3 (Fig. 3) were found in HOSUN as compared to those in CSO (component 1, 0.63 vs. 0.89 mg/100 mg oil; component 2, 1.13 vs. 1.65 mg/100 mg oil; component 3, 2.22 vs. 5.02 mg/100 mg oil). The results suggested that, in comparison with CSO, HOSUN appeared to be more stable but seemed to polymerize to a greater extent to yield higher MW species. The oxidative stability of oils seemed to follow the order HOSUN > blends > CSO. Tables 3 and 4 show two sets of data for HOSUN used for French fries, both of which include data for the zero-time oil and for a frying time of 30 h. The differences in the numbers for the two sets of samples are due

TABLE 4
Amounts and MW and Concentration Distributions of Degradation Products (Components 1–6) in HOSUN/CSO Oils Used for French Fried Potatoes[a]

Oil	Time (h)	Polar compounds (%)	MW distribution 1	2	3	4	5	6	Concentration distribution[b] 1	2	3	4	5	6
HOSUN	0	2.32	ND[c]	2050	1565	1155	985	630	ND	0.11	0.63	1.17	5.54	1.09
	30	37.4	5190	4435	3525	1575	ND	ND	0.63	1.13	2.22	4.02	ND	ND
HOSUN/ CSO (2:1)	0	2.97	ND	2400	2045	1365	1160	815	ND	0.16	0.75	1.58	4.09	0.59
	30	37.4	4585	3770	2955	1370	1215	460	0.57	1.04	2.05	3.54	0.3.3	0.08
HOSUN/ CSO (1:2)	0	4.76	ND	1975	1560	1285	1035	435	ND	0.18	0.60	1.50	2.76	0.24
	30	39.6	4755	3460	2245	1500	960	ND	0.68	1.30	4.14	1.48	0.35	ND
CSO	0	5.78	ND	2005	1730	1170	1045	585	ND	0.24	0.81	1.81	3.20	0.24
	30	42.5	2270	2030	1755	895	670	ND	0.89	1.65	5.02	1.85	0.42	ND
RSD[b] range		1.1–1.2	6.9–9.9	7.8–8.6	9.3–9.9	7.9–9.9	8.8–9.7	9.5–9.9	4.8–7.9	6.6–9.0	7.5–9.8	6.3–8.6	7.0–8.8	5.6–6.1

[a] Analyzed by HPSEC–VIS/RI. For abbreviations, see Tables 1–3.
[b] Concentration in units of mg/100 mg oil.

TABLE 5
Amounts and MW and Concentration Distributions of Degradation Products (Components 1–6) in SUN Varieties Used for French Fried Potatoes/Tortilla Chips[a]

Oil	Time (h)	Polar compounds (%)	MW distribution						Concentration distribution[b]					
			1	2	3	4	5	6	1	2	3	4	5	6
SUN	0	2.24	ND	2720	1300	1203	980	ND	ND	0.63	1.33	3.70	0.88	ND
	10	9.91	4390	3650	2665	1580	1190	ND	0.09	0.36	2.82	1.39	0.45	ND
	20	27.0	3390	2800	2040	1110	957	ND	0.28	0.73	3.20	1.12	0.23	ND
	30	38.6	3450	2785	2055	1165	1010	ND	0.79	1.48	4.34	1.34	0.22	ND
HOSUN	0	2.68	ND	2220	1890	1310	1133	767	ND	0.07	0.40	1.09	3.43	0.76
	10	15.6	3475	3055	2255	1380	980	ND	0.31	0.83	2.16	4.60	0.66	ND
	20	31.5	3460	2860	2160	1330	885	ND	0.38	0.77	1.71	3.19	0.28	ND
	30	38.8	3665	2870	2210	1385	985	ND	0.70	1.22	2.28	3.99	0.33	ND
MOSUN	0	2.84	ND	2375	2095	1405	1155	810	ND	0.07	0.44	1.34	4.20	1.07
	10	14.6	4045	3290	1475	1275	1040	ND	0.25	0.60	2.83	1.46	0.45	ND
	20	33.2	3565	2915	1375	1265	950	ND	0.59	1.08	3.70	1.55	0.33	ND
	30	39.8	3533	2777	2163	1340	953	ND	1.42	2.44	4.04	0.37	ND	ND
RSD[b] range		1.1–1.2	6.3–9.0	7.5–8.9	9.6–10	7.8–9.8	8.1–9.5	9.9–10	4.5–7.9	5.0–6.9	3.9–8.6	6.9–9.9	5.0–8.8	3.3–4.9

[a] Analyzed by HPSEC–VIS/RI. For abbreviations, see Tables 1–3.
[b] Concentration in units of mg/100 mg oil.

to the use of nonidentical HOSUN oils originating from different sample batches and stored for different lengths of time and are also partly due to variations in frying conditions such as fryer size and makeup oil. Therefore, it is not possible to correlate data from different sets of experiments.

Table 5 shows data for SUN oil varieties used for French fries/tortilla chips. Although no appreciable variations in MW distributions were observed among SUN, HOSUN, and MOSUN oils, clear differences in concentration distributions were demonstrated for these oils. At 30 h, concentrations of the two early-eluting components, 1 and 2, of MOSUN were markedly higher than those of SUN and HOSUN. At zero time, both HOSUN and MOSUN had highest levels of component 5, whereas SUN had component 4 as the most abundant species (Table 5). Concentration distributions at frying times of 10 and 20 h showed no definitive trends for the three

TABLE 6
Amounts and MW and Concentration Distributions of Degradation Products (Components 1–6) in SBO Varieties Used for French Fried Potatoes/Tortilla Chips[a]

Oil	Time (h)	Polar compounds (%)	MW distribution						Concentration distribution[b]					
			1	2	3	4	5	6	1	2	3	4	5	6
SBO	0	2.45	ND	3965	3465	2450	1740	1190	ND	0.17	0.90	4.20	7.07	1.69
	20	29.5	2475	2220	1900	990	925	ND	1.79	4.02	15.3	5.44	0.84	0.30
	40	46.1	6315	4960	2390	2310	1615	ND	4.51	6.65	15.9	4.39	0.57	ND
HOSBO	0	1.03	ND	1860	1285	1110	1010	660	ND	0.13	0.52	1.59	0.30	0.27
	20	9.60	3230	3030	2235	1325	915	ND	0.17	0.46	1.50	3.80	0.69	ND
	40	15.9	2980	2820	2140	1285	910	ND	0.21	0.49	1.32	2.87	0.38	ND
HOSBO/ LLSBO (9:1)	0	1.26	ND	4475	3320	1790	1430	1015	ND	ND	0.30	0.99	2.36	0.3
	20	14.0	2925	2305	1520	945	ND	ND	0.40	1.31	3.01	0.6.1	ND	ND
	40	22.9	3870	3185	2490	1150	975	ND	0.32	0.70	1.57	3.03	0.24	ND
HOSBO/ LLSBO (3:1)	0	1.44	ND	3535	1890	1280	785	ND	ND	0.20	0.78	1.46	2.92	ND
	20	6.41	4060	2650	1145	880	ND	ND	0.17	0.78	1.94	0.42	ND	ND
	40	12.7	3330	2985	2300	1265	955	ND	0.15	0.41	2.71	1.35	0.42	ND
HOSBO/ LLSBO (1:1)	0	1.61	ND	2915	1975	1005	805	ND	ND	0.27	0.96	2.64	0.94	ND
	20	6.74	4190	2030	1680	860	ND	ND	0.17	1.60	1.64	0.95	ND	ND
	40	10.4	3770	2180	1500	1130	ND	ND	0.32	2.46	1.24	0.51	ND	ND
LLSBO	0	1.89	ND	2260	1460	1270	1090	685	ND	0.47	1.30	3.51	0.77	0.34
RSD[b] range		1.2–1.3	6.9–8.9	7.9–8.9	9.1–10	7.7–10	8.9–9.8	9.2–10	3.7–7.0	5.5–8.9	6.2–9.5	7.0–8.7	5.0–7.3	3.3–4.5

[a] Analyzed by HPSEC–VIS/RI. For abbreviations, see Tables 1–3.
[b] Concentration in units of mg/100 mg oil.

TABLE 7
Amounts and MW and Concentration Distributions of Degradation Products (Components 1–6) in HOSUN/CSO Oils Used for Potatoes Chips[a]

Oil	Time (h)	Polar compounds (%)	MW distribution						Concentration distribution[b]					
			1	2	3	4	5	6	1	2	3	4	5	6
HOSUN	0	2.32	ND[c]	2050	1565	1155	985	630	ND	ND	0.63	1.17	5.54	1.08
	9	4.53	3785	2925	1605	1240	1110	770	ND	0.13	0.7.2	1.06	2.52	0.3
	18	7.19	3565	3250	1700	1245	930	ND	0.20	0.81	0.89	2.68	0.33	ND
HOSUN/ CSO (2:1)	0	2.97	ND	2400	2045	1365	1160	815	ND	ND	0.75	1.58	4.09	0.59
	9	6.52	6200	2630	2110	1840	845	ND	0.28	1.94	2.40	4.57	0.62	ND
	18	8.42	4935	2390	1800	1495	1000	ND	0.31	3.91	3.00	1.55	0.40	ND
HOSUN/ CSO (1:2)	0	4.76	ND	1975	1560	1285	1035	435	ND	0.18	0.60	1.50	2.76	0.24
	9	6.63	3525	2295	1970	1095	ND	ND	1.20	1.53	3.67	0.47	ND	ND
	18	9.02	4230	2185	1440	1145	ND	ND	0.23	2.80	1.37	0.64	ND	ND
CSO	0	5.78	ND	2005	1730	1170	1045	585	ND	0.24	0.81	1.81	3.20	0.24
	9	7.75	4140	3285	2010	1240	795	ND	0.25	1.30	2.50	3.99	0.19	ND
	18	10.3	3850	2280	1620	1385	920	ND	0.23	2.82	1.37	0.64	0.13	ND
RSD[b] range		1.1–1.2	6.5–7.9	7.0–9.0	9.2–9.8	7.9–9.0	8.4–9.9	9.2–10	3.9–6.0	5.8–9.7	6.2–9.9	5.9–9.8	7.1–9.9	3.7–5.9

[a] Analyzed by HPSEC–VIS/RI. For abbreviations, see Tables 1 and 2.
[b] Concentration in units of mg/100 mg oil.
[c] ND, none detected.

oils. In the absence of information on relative antioxidant levels in the zero-time oils, it is unclear why MOSUN degraded to the highest extent among the oils in the SUN series.

Table 6 shows data for SBO varieties used for French fries/tortilla chips (Figs. 1 and 2). At zero time, MW distributions of SBO differed from those of modified varieties HOSBO, and LLSBO. The latter two oils bear close resemblance in MW distribution patterns regardless of their dissimilar concentration profiles. Blending these oils resulted in redistribution of MW and concentrations. As compared to other oils in the series, SBO had higher MW for the corresponding components, indicative of a higher degree of polymerization presumably stemming from the higher level of 18:3 species (Table 1). At 40 h, large differences in MW distributions of SBO (MW ranging from 1615 to 6315) and HOSBO (MW ranging from 910 to 2980) were observed. Similarly, concentrations of corresponding components of SBO were significantly higher than those of corresponding components of HOSBO (e.g., 4.51 vs. 0.21 mg/100 mg oil for component 1; 6.65 vs. 0.49 mg/100 mg oil for component 2). The observations illustrated that HOSBO was much more stable than SBO. At 40 h, formation of component 2 (2.46 mg/100 mg oil) from the blended oil HOSBO/LLSBO (1:1) was substantially greater than that from HOSBO (0.49 mg/100 mg oil). Thus, the frying oil stability was found to increase in the following order: SBO < LLSBO < HOSBO.

Table 7 shows data for HOSUN and CSO used for potato

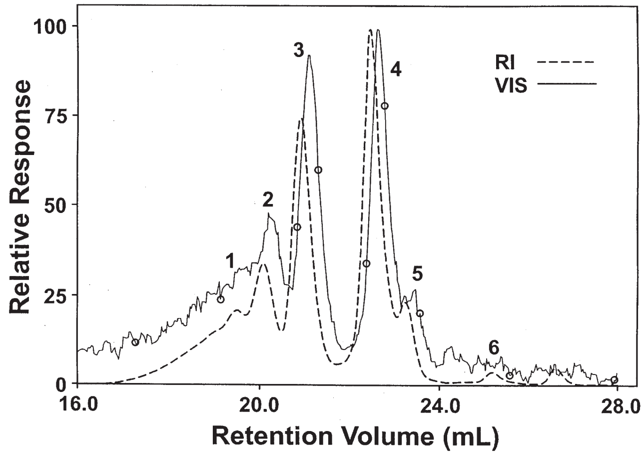

FIG. 2. Chromatograms obtained by high-performance size-exclusion chromatography with dual viscometric (VIS)/refractometric (RI) detection for high-oleic sunflower oil (HOSUN) at a frying time of 30 h.

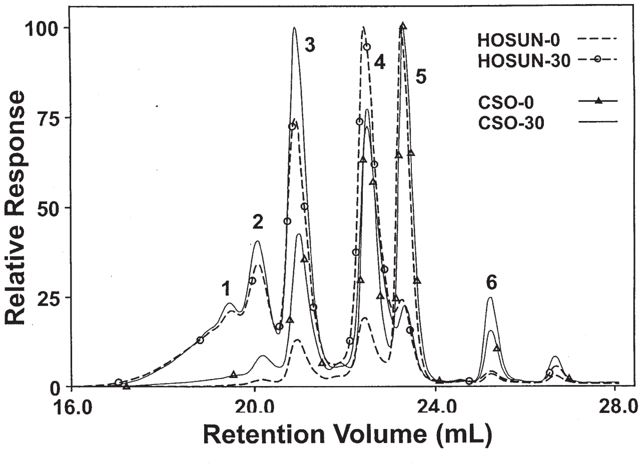

FIG. 3. Comparison of RI chromatograms of HOSUN and cottonseed oil (CSO) at frying times of 0 and 30 h. See Figure 2 for abbrevations.

chips. MW distributions of the two oils were alike, but the MW profiles of the blended oils were slightly different from those of individual oils. Thus, at 18 h, the two blended oils HOSUN/CSO (2:1) and HOSUN/CSO(1:2) showed the presence of high-MW polymeric component 1 with MW values higher than those of the corresponding component in the parent oils. Inspection of the data in this table indicated that changes in component concentrations of HOSUN with increasing frying times (0–8 h) were smaller than those of CSO and blended oils. The amount of the high-MW polymeric component 2 of CSO increased from 0.24 mg/100 mg oil at zero time to 2.82 mg/100 mg oil at a frying time of 18 h, whereas the corresponding component of HOSUN increased from zero to 0.81 mg/100 mg oil. From the concentration/ MW distribution data (Table 7), it is clearly demonstrated that the frying stability of oils increased in the order blends < CSO < HOSUN.

In conclusion, MW and concentration distributions of nonvolatile components in frying oils can be simultaneously determined by HPSEC with VIS/RI detection. HPSEC–right-angle light scattering detection techniques (which are not the same as evaporative light scattering detection systems) are not suitable for the analysis of fried oils owing to the low MW of the frying oil degradation products. The combined use of a viscometer and a universal calibration software can provide valuable information on MW distributions and extent of polymerization. MW of nonvolatile components of frying oils cannot be accurately determined by the conventional calibration method of plotting logarithmic MW against retention volumes. The new method presented in this study allows differentiation of MW distributions and degradation patterns of various frying oils, including modified varieties. Frying oil stability and degradation profiles can be assessed by numerical presentation of MW/concentration distributions of frying oil components in various samples.

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