Molecular Distillation of a Hydrogenated Cottonseed Oil and Certain Characteristics of the Distilled Fractions

W. S. SINGLETON and A. E. BAILEY
Southern Regional Research Laboratory[1]
New Orleans, Louisiana

Introduction

In the course of a general investigation of the stability of vegetable oils, the authors have had occasion to make a complete molecular distillation of a hydrogenated cottonseed oil, and have examined the distilled fractions with respect to their fatty acid composition and antioxygenic properties. There appears to be no reports in the literature of any previous examination of hydrogenated cottonseed oil conducted in this manner, and the only comparable distillation of unhydrogenated oil, by Riemenschneider, Swift, and Sando (9), was carried out at a time when relatively little was known concerning the molecularly distillable constituents of vegetable oils.

Distillation of the Oil

Commercially refined cottonseed oil having an iodine value of 108 was hydrogenated to an iodine value of 68.5, and steam deodorized at 400° F. for 30 minutes. A charge of 2,770 grams of the deodorized oil was then molecularly distilled into different fractions, employing the same still and the same method of operation as described previously in connection with the molecular distillation of peanut oil (1). The operational data pertaining to the distillation are recorded in Table 1.

TABLE 1

Molecular Distillation of Hydrogenated Cottonseed Oil: Operational Data.

Fraction number	Temp. of distillation, °C.	Wt. of fraction, gms.	Portion of total charge in fraction, percent	Portion of total charge, cumulative percent
D-1	100*	0.00	0.0	0.0
2	120	1.35	0.049	0.049
3	140	4.21	0.152	0.201
4	160	9.03	0.326	0.527
5	180	12.98	0.469	0.996
6	200	44.9	1.62	2.61
7	215	90.1	3.25	5.86
8	225	156.8	5.66	11.52
9	240	258.1	9.32	20.84
10	240	265.1	9.57	30.41
11	240	545.0	19.68	50.09
12	240	540.5	19.50	69.59
13	240	551.2	19.90	89.49
14	.....	291.1	10.51	100.00
(residue)				

*No distillate could be collected at this temperature, although a small amount of distilled material collected on the condensing surfaces.

Analysis of the Fractions

Determinations of iodine values, thiocyanogen values, and saponification values were made according to official methods of the A.O.C.S. on the larger distilled fractions, as well as on the original oil and the residue.

Each fraction was assayed for tocopherol content (calculated as α-tocopherol) by both the Parker-McFarlane modification of the Emmerie-Engel method (6), and the Quackenbush modification of the Furter-Meyer method (7).

The Mehlenbacher modification (5) of the Swift method, wherein the test sample of oil is aerated at 110° C., was used for determining the stability of the original oil, the larger distilled fractions, and certain mixtures of the smaller distilled fractions with various substrates. The analytical data are contained in Table 2.

Comparative Degrees of Fractionation of Cottonseed and Peanut Oils

It is of interest to compare the glyceride fractionation obtained in this distillation with comparable molecular distillations made previously by the present authors and others (1) on hydrogenated and unhydrogenated peanut oils. The comparative data on the three oils are to be found in Table 3. Only fractions 8 to 14 inclusive, comprising approximately 90 percent of each oil, are included in the tabulation, inasmuch as yields of the lower fractions were variable, and the pertinent data are obscured by the distillation of much unsaponifiable material.

More or less comparable molecular distillations of unhydrogenated cottonseed oil and unhydrogenated soybean oil have been carried out respectively by Riemenschneider, Swift, and Sando (9), and Detwiler, Bull, and Wheeler (2). The data of these investigators, together with the above-mentioned data on peanut oils, provide material for the complete comparison of the various oils which is presented in Table 4.

The data of Table 4 appear to be entirely consistent with the known fatty acid compositions of cottonseed, peanut, and soybean oil, which are on a percentage basis approximately as follows:

		Cottonseed (4)	Peanut (3)	Soybean (4)
Saturated acids	C_{16} and below	24.8	8.3	10.1
	C_{18}	1.1	3.1	2.4
	C_{20} and above	1.3	6.6	0.9
Unsaturated acids	Almost all C_{18}	72.8	82.0	86.6

As pointed out by Detwiler, Bull, and Wheeler (2), the relatively high degree to which cottonseed oil fractionates with respect to unsaturation may be attributed to the large amount of lower molecular weight saturated acids in this oil. The slight tendency toward fractionation observed in the case of peanut oil is undoubtedly due to the circumstance that this oil contains saturated acids lower and higher in molecular weight than the unsaturated acids, in approximately equal proportions. Soybean oil is intermediate between cottonseed and peanut oils in its tendency to fractionate, as is to be expected

[1] This is one of four regional research laboratories operated by the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

Table 2.

Analysis of Molecularly Distilled Fractions of Hydrogenated Cottonseed Oil.

Fraction number	Chromogenic substances, calculated as α-tocopherol, percent		Stability, hrs. to rancid odor at 110° C.	Peroxide value* at rancid odor end-point	Iodine value	Thiocyanogen value	Saponification value
	Emmerie-Engel	Furter-Meyer					
2	7.67	8.5	.....	.....	.....	.....	.....
3	8.21	12.2	.....	.....	.....	.....	.....
4	13.00	12.6	.....	.....	.....	.....	.....
5	3.89	3.8	.....	.....	.....	.....	.....
6	0.20	0.25	54	120	53.2	49.9	186.4
7	0.010	0.05	16.0	56	59.4	53.9	192.0
8	nil	0.02	10.0	28	61.9	54.6	195.7
9	nil	0.02	8.5	25	63.7	56.6	196.3
10	nil	0.015	7.0	19	64.9	57.8	196.1
11	nil	0.010	6.8	22	65.2	58.1	195.9
12	nil	0.007	4.5	21	69.6	62.3	195.0
13	nil	0.006	2.3	23	73.4	66.0	193.7
14 (residue)	nil	0.10	3.5	13	76.8	69.1	191.5
Original oil	0.085	0.090	11.7	47	68.5	62.2	194.0

* Milliequivalents per kilogram of sample.

from its composition. The data of Rawlings (8) on the large scale molecular distillation of soybean oil are less complete than the above-mentioned laboratory data, but are in qualitative agreement with the latter. The results obtained by the same author in the molecular distillation of corn oil would indicate that this oil probably fractionates similarly to soybean oil.

The fact that the linoleic acid content scarcely varies in the hydrogenated cottonseed oil samples is evidence of the random distribution of hydrogen to glycerides with fatty acids of different chain lengths.

Antioxygenic Properties of the Distilled Fractions

The antioxidants of hydrogenated cottonseed oil appear to distill similarly to those of peaunt oils. There is a marked concentration of tocopherols and related substances in the fractions distilling at 120° to 180° C., and the large fractions distilling thereafter are progressively lower in these substances and lower in stability. There is evidently some concentration of antioxidants in the residue. The marked separation of glycerides according to degree of unsaturation makes any comparison of stabilities in the distilled fractions somewhat uncertain. However, even when allowance is made for their low unsaturation, the high stabilities of Fractions 6 and 7 appear somewhat remarkable.

In order to evaluate the first distilled fractions with respect to their antioxygenic characteristics, a number of stability tests were made in which these fractions were added to lard and to a distillate (D-12) low in antioxidants. For comparison, the same substrates were also tested after the addition of various amounts of pure α- and γ-tocopherols. Results of the stability tests are shown in Table 5. In each case, the amount of distillate (antioxidant concentrate) added was calculated in terms of percentage of tocopherols, on the basis of its Emmerie-Engel assay.

The chief point of interest in the stability data is the relatively low antioxygenic activity of the first distilled fractions, D-2 and D-3. D-2 appears to be only a very weak antioxidant, and D-3 is considerably less potent that D-4 or D-5. Obviously, the substances responding to the Emmerie-Engel and Furter-Meyer tests in these distillates are either lacking in antioxygenic power, or are prevented from being fully effective by the presence of unrecognized substances

TABLE 3

Fractionation of Glycerides by Molecular Distillation; Comparison of Hydrogenated Cottonseed Oil With Hydrogenated and Unhydrogenated Peanut Oils.

	Fraction number	Iodine value	Thiocyanogen value	Composition of fatty acids in fraction, percentage*		
				Saturated	Oleic	Linoleic
Hydrogenated cottonseed oil	Original oil	68.5	62.2	27.7	64.9	7.4
Hydrogenated cottonseed oil	8	61.9	54.6	36.7	54.6	8.7
Hydrogenated cottonseed oil	9	63.7	56.6	34.4	57.2	8.4
Hydrogenated cottonseed oil	10	64.9	57.8	33.0	58.6	8.4
Hydrogenated cottonseed oil	11	65.2	58.1	32.6	59.0	8.4
Hydrogenated cottonseed oil	12	69.6	62.3	27.7	63.7	8.6
Hydrogenated cottonseed oil	13	73.4	66.0	23.4	67.9	8.7
Hydrogenated cottonseed oil	14 (residue)	76.8	69.1	19.8	71.1	9.1
Hydrogenated peanut oil	Original oil	68.0	66.3	22.6	75.8	1.6
Hydrogenated peanut oil	8	66.3	64.1	25.2	72.6	2.2
Hydrogenated peanut oil	9	68.2	67.0	21.7	77.3	1.0
Hydrogenated peanut oil	10	68.7	67.3	21.4	77.4	1.2
Hydrogenated peanut oil	11	69.4	68.1	20.4	78.5	1.1
Hydrogenated peanut oil	12	70.4	69.1	19.2	79.7	1.1
Hydrogenated peanut oil	13	69.7	68.9	19.4	80.1	0.5
Hydrogenated peanut oil	14 (residue)	61.6	60.5	29.3	69.8	0.9
Unhydrogenated peanut oil	Original oil	92.8	72.8	16.8	58.8	24.4
Unhydrogenated peanut oil	8	92.0	70.9	19.2	55.1	25.7
Unhydrogenated peanut oil	9	92.5	71.4	18.6	55.7	25.7
Unhydrogenated peanut oil	10	93.0	71.9	18.0	56.3	25.7
Unhydrogenated peanut oil	11	93.8	72.9	16.8	57.7	25.5
Unhydrogenated peanut oil	12	94.8	74.2	15.3	59.6	25.1
Unhydrogenated peanut oil	13	94.5	73.9	15.6	59.3	25.1
Unhydrogenated peanut oil	14 (residue)	95.1	65.0	27.0	36.0	37.0

*Calculated from iodine (I.V.) and thiocyanogen (T.V.) values, by the following formulas:

% Oleic = (2.530) T.V. — (1.350) I.V.
% Linoleic = (1.248) I.V. — (1.256) T.V.
% Saturated = 100% — (% Oleic + % Linoleic).

TABLE 4

Comparative Degrees of Fractionation Obtained in the Molecular Distillation of Cottonseed, Peanut and Soybean Oils.

		Iodine value	Composition of fatty acids, percentage			
			Saturated	Oleic	Linoleic	Linolenic
Unhydrogenated cottonseed oil (Riemenschneider, *et al.*)	Original oil	108.3	28.0	18.9	53.1	....
	First distillate	100.0	32.5	19.5	48.0	....
	Last distillate	120.9	18.8	22.7	58.5	....
	Residue	118.9	22.4	18.0	59.6	....
Hydrogenated cottonseed oil (present investigation)	Original oil	68.5	27.7	64.9	7.4	....
		61.9	36.7	54.6	8.7	....
		73.4	23.4	67.9	8.7	....
	[illegible]	76.8	19.8	71.1	9.1	....
Unhydrogenated peanut oil (Bailey, *et al.*)	Original oil	92.8	16.8	58.8	24.4	....
	First distillate	92.0	19.2	55.1	25.7	....
	Last distillate	94.5	15.6	59.3	25.1	....
	Residue	95.1	27.0	36.0	37.0	....
Hydrogenated peanut oil (Bailey, *et al.*)	Original oil	68.0	22.6	75.8	1.6	....
	First distillate	66.3	25.2	72.6	2.2	....
	Last distillate	69.7	19.4	80.1	0.5	....
	Residue	61.6	29.3	69.8	0.9	....
Unhydrogenated soybean oil (Detwiler, *et al.*)	Original oil	137.8	13.8	24.3	55.9	5.4
	First distillate	132.9	17.2	20.0	58.8	3.1
	Last distillate	143.7	9.1	23.4	67.0	0.5
	Residue	142.9	10.3	25.0	60.3	4.1

capable of inhibiting or counteracting their influence. The latter possibility seems much the more probable, although further work will be required to fully decide the question.

On the basis of the Emmerie-Engel assay, the tocopherols in the potent distillates, D-4 and D-5, are more effective antioxidants than pure α-tocopherol, but less effective than γ-tocopherol.

Summary

1. A hydrogenated cottonseed oil has been molecularly distilled, and the distilled fractions examined.

2. Fractionation of a molecularly distilled oil occurs, as is to be expected, on the basis of variations in molecular weight of the glycerides. The composition of cottonseed oil is such that there is a considerable separation of the glycerides according to their degree of unsaturation. The composition of peanut oil is such that similar separation can only be slight. Soybean oil is in this respect intermediate between cottonseed oil and peanut oil.

3. Molecular distillation of hydrogenated cottonseed oil causes a segregation of tocopherols and related compounds similar to that observed in peanut oil. However, the fractions first distilled from the oil are relatively weak in antioxygenic properties. It appears probable that their lack of effectiveness is due to the presence of unknown substances capable of inhibiting or counteracting the action of tocopherols. However, the presence of substances other than tocopherols, which respond to or interfere with the Emmerie-Engel test is not to be excluded. The tocopherols in the potent fractions are more effective than α-tocopherol, but less effective than γ-tocopherol.

Acknowledgment

The authors wish to acknowledge with thanks and appreciation the assistance of Maizie Caravella and B. Ashby Smith in determining the iodine, thiocyanogen, and saponification values in this work, and of Carroll Hoffpauir in making the tocopherol assays.

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TABLE 5

Antioxygenic Activity of Molecularly Distilled Fractions of Hydrogenated Cottonseed Oil in Comparison With Pure Tocopherols.

Substrate used	Antioxidant added	Stability* of substrate containing indicated percentage of tocopherols (according to Emmerie-Engel assay)				
		0%	0.0312%	0.0625%	0.125%	0.25%
Molecularly distilled fraction D-12	D-2	4.4	4.1	.....	.....	.....
Molecularly distilled fraction D-12	D-3	4.4	8.7	7.0	7.2	7.5
Molecularly distilled fraction D-12	D-4	4.4	13.6	12.0	12.3	11.5
Molecularly distilled fraction D-12	D-5	4.4	14.1	13.6	14.8	16.5
Molecularly distilled fraction D-12	γ-tocopherol	4.4	13.6	14.3	17.3	24.7
Lard	D-2	1.9	4.0	.....	.....	.....
Lard	D-3	1.9	6.2	.....	.....	.....
Lard	D-4	1.9	11.0	.....	.....	.....
Lard	D-5	1.9	9.7	.....	.....	.....
Lard	α tocopherol	1.9	8.5	.....	.....	.....
Lard	γ-tocopherol	1.9	14.0	.....	.....	.....
Lard	50-50 mix of α and γ	1.9	13.5	.....	.....	.....

* Stability in terms of hours to rancid odor at 110° C.