The Effect of Processing Conditions Upon the Nutritional Quality of Vegetable Oils[1]

M. D. WILDING, E. E. RICE, and K. F. MATTIL, Research Laboratories, Swift & Co., Chicago, Illinois

Abstract

On the basis of the chemical, physical, and biological criteria used, all of which have been shown to be sensitive indicators of heat damage to oils, it must be concluded that the overall nutritional quality of an oil is not adversely affected by alkali refining, adsorptive decolorizing, or deodorization; that higher temperatures of deodorization (238C) produce oils nutritionally equivalent to those deodorized at lower temperatures (160C); and that the normal processes used in manufacturing edible oils improve the resistance of these oils to heat damage.

Introduction

THIS INVESTIGATION was undertaken to determine the effect of normal processing conditions, and especially temperatures of deodorization, upon the nutritional quality of vegetable oils. There has been a considerable amount of material published relating to the nutritional effects of over-heated fats (1), but none that we are aware of has evaluated the effects of the normal processing conditions of refining, adsorptive decolorizing (bleaching), and deodorizing.

Experimental Procedures

The vegetable oils used in this study were the two most widely used in the U. S., soybean oil and cottonseed oil. Both crude oils were obtained from commercial mills, the former being produced by hexane extraction and the latter by the expeller process. All subsequent processing of the oils was carried out in laboratory scale equipment, using conditions simulating normal plant procedures.

The crude soybean oil (initial F.F.A. = 0.8%) was alkali refined by the open kettle method, using 3.3% of an 8% NaOH solution at a maximum temp of 57C. After the addition of 0.5% of a 38% sodium silicate solution, the foots were permitted to settle and the refined oil was removed by decantation. The bulk of the refined oil was bleached by a simulated open kettle atmospheric procedure, by far the most drastic method employed in industry. The oil was dried by slow agitation in an open vessel at 105C, treated with 1% acid-activated bleaching clay, and then filtered through paper on a Buchner funnel. A portion of each of the crude, the refined, and the refined-bleached oils was withheld for subsequent experimental work.

The crude cottonseed oil (initial F.F.A. = 1.44%) was alkali refined using 2% of a 9.5% NaOH solution at a maximum temp of 57C, and the decanted oil was washed with 5% water at 82C. It was then dried at 105C and bleached, using 2% acid-activated clay. Because the color at this point was still unsatisfactory, the oil was re-refined using 2.5% of an 18.8% NaOH solution at 57C, and then bleached at 105C with another 2% acid-activated clay. Again, a portion of each of the crude, the once-refined, and the re-refined and rebleached oils was set aside for subsequent experimental work.

The refined-bleached oils were divided into three portions for deodorization with water vapor at maximum temps of 160C, 204C, and 238C, respectively, for 4.5 hr at 1–2 mm absolute pressure in all-glass equipment. Upon cooling to 90C the oils were treated with 0.005% of citric acid in an ethanol solution. Deodorization was discontinued when the oils had cooled to about 50C.

A portion of each oil taken at each stage in the processing was heated without agitation in an open vessel for 120 hr at 178C, a condition which has been shown to cause severe heat damage to oils (1). All samples of the heated and nonheated oils were then subjected to the following chemical, physical, and biological testing.

The refractive indices were determined at 60C, using a Carl Zeiss refractometer fitted with a butyro scale. Viscosities were measured at 22C on a Brookfield Viscometer. The fatty acid composition was determined using methyl esters on a Barber-Colman Model 10 gas chromatograph. The column used was 6.5 ft of Pyrex glass packed with 60–100 mesh Chromosorb W coated with 20% succinic acid—diethylene glycol polyester. The amount of non-adduct forming material (NAF) in each sample was measured by a modification of the method of Firestone et al. (2). By this method free, straight chain, unmodified fatty acids which form insoluble addition compounds with urea in ethanol are separated from oxidized or polymerized fatty materials in that they do not form urea adducts. The sample analyzed was large enough to provide NAF fractions which could be evaluated biologically.

A modification of the restricted-feeding test of Rice et al. (3), using weanling mice rather than weanling

[1] Presented at the 6th Congress of the International Society for Fat Research, London, 1962.

TABLE I

Physical and Chemical Analyses of Heated and Non-heated Soybean Oil

	Free Fatty Acids (%)	Refractive Index (Butyro 60C)	Viscosity (Centipoises)	Fatty Acid Composition (G.L.C.)				
				Palmitate	Stearate	Oleate	Linoleate	Linolenate
Non-heated Oils								
Crude	0.8	50.0	47	11.4	4.3	28.4	49.7	6.2
Refined	0.05	50.1	48	11.9	3.7	27.6	50.4	6.4
Refined and Bleached	0.06	51.0	48	11.5	6.0	27.0	49.7	5.8
Ref., Bl., and Deodorized, 160C	0.05	51.1	48	12.5	4.2	28.2	49.3	5.8
Ref., Bl., and Deodorized, 204C	0.05	51.0	48	.....	.....	.....	.....	.....
Ref., Bl., and Deodorized, 238C	0.05	51.0	48	11.6	4.1	28.9	50.4	5.0
Heated Oils								
Crude	1.16	59.7	412	15.8	6.4	35.3	39.9	2.5
Refined	0.55	58.2	291	16.9	6.6	35.5	38.6	2.4
Refined and Bleached	0.80	61.0	444	17.0	6.3	35.8	37.3	3.6
Ref., Bl., and Deodorized, 160C	0.28	55.0	91	13.3	4.5	30.7	46.3	5.3
Ref., Bl., and Deodorized, 204C	0.22	54.2	80	12.6	4.5	30.7	47.2	5.1
Ref., Bl., and Deodorized, 238C	0.23	54.3	83	12.5	5.5	30.9	45.0	6.2

TABLE II

Physical and Chemical Analyses of Heated and Non-heated Cottonseed Oils

	Refractive Index (Butyro 60C)	Viscosity (Centipoises)	Fatty Acid Composition (G.L.C.)					
			Myristate	Palmitate	Palmitoleate	Stearate	Oleate	Linoleate
Non-heated Oils								
Crude	47.4	52	1.0	26.1	0.7	2.7	17.8	51.7
Refined	47.3	54	1.1	25.2	0.8	2.1	15.8	55.1
Refined and Bleached	47.5	50	0.9	24.8	0.9	2.1	15.9	55.4
Ref., Bl., and Deodorized, 160C	47.4	51	0.9	27.0	0.7	2.2	15.6	53.7
Ref., Bl., and Deodorized, 204C	47.3	51	0.9	25.9	0.6	2.2	15.8	54.6
Ref., Bl., and Deodorized, 238C	47.4	51	0.9	25.9	0.8	2.3	15.9	54.3
Heated Oils								
Crude	51.7	644	1.1	31.3	0.8	2.7	17.4	46.7
Refined	51.4	105	1.1	29.7	1.0	2.4	16.7	49.1
Refined and Bleached	50.7	92	1.0	29.4	0.9	2.4	16.8	49.5
Ref., Bl., and Deodorized, 160C	50.6	88	1.1	29.8	0.7	2.3	16.7	49.4
Ref., Bl., and Deodorized, 204C	50.7	88	1.0	28.4	0.7	2.2	16.9	50.8
Ref., Bl., and Deodorized, 238C	50.7	88	1.0	29.4	0.7	2.5	16.7	49.6

rats, was used for the biological testing. It has been demonstrated repeatedly (1) that one of the first biological effects apparent in a heat damaged fat is that there is an increase in liver size relative to body weight. This effect has been found to occur rapidly and be nearly at a maximum after only three days' feeding in weanling mice (4) as well as in weanling rats (3). The oil samples were fed at the rate of 400 mgm per mouse per day, while the NAF's were fed as 40 mgm per day in 360 mgm of of cottonseed salad oil. Each diet was fed to two mice for three days.

TABLE III

Effect of Heating Soybean and Cottonseed Oils on the Yield of NAF Fractions

	Soybean Oils		Cottonseed Oils	
	Non-heated (% NAF)	Heated (% NAF)	Non-heated (% NAF)	Heated (% NAF)
Crude	3.5	30.2	3.0	17.9
Refined	3.1	28.1	2.8	14.1
Refined and Bleached	2.7	31.1	3.2	13.2
Ref., Bl., and Deodorized, 160C	3.0	14.3	3.4	12.1
Ref., Bl., and Deodorized, 204C	3.0	12.7	3.0	12.0
Ref., Bl., and Deodorized, 238C	2.9	12.7	3.4	11.8

Results and Discussion

The physical and chemical analyses of the heated and non-heated soybean oils are summarized in Table I and those for the cottonseed oils in Table II. As expected, there are no significant differences in the unheated oils resulting from the various processing steps nor from the several conditions of deodorization.

In the heated oils, however, some rather substantial effects are apparent. It is quite evident that the fully processed oils are more stable to heat than are the crude or the partially processed. It has been observed in our laboratory in the past that one of the most sensitive indicators of heat damage in an oil is its viscosity. The nutritional value of an oil does not begin to diminish until after the viscosity starts to increase. It is interesting to note that on the basis of viscosity of the heated oils, the major improvement occurred after refining in the cottonseed oil and after deodorization in soybean oil. We have no immediate explanation for this observation.

It is of further interest to note that in the heated oils the effects as measured by increase in viscosity were also evident as increases in free fatty acid, refractive index, and apparent saturated and mono-unsaturated acids, with a concurrent decrease in apparent poly-unsaturated acids. All these are effects which have previously been observed and may be used as indices of heat damage.

It is particularly noteworthy that in all cases the deodorized oils were superior to non-deodorized oils, and that there are no indications whatever that the higher temperatures of deodorization produced oils inferior to those from lower temperature deodorization.

Nearly all of the research workers who have produced damage in their oil samples by overheating have shown that the active substances are concentrated in a fraction not adducted by urea. The amounts of non-adductible material in the various oils in this work are shown in Table III. Again, there are no significant effects apparent in the amounts of NAF obtained from the unheated oils that would indicate any adverse effects due to processing or to higher temperatures of deodorization. The amounts of NAF in the heated oils follow a pattern similar to the other chemical and physical indices. The least amount of NAF was found in the deodorized oils; no real differences resulted as a consequence of variations in deodorization temperatures.

Table IV summarizes the data obtained when the heated and non-heated oils were fed to mice for three days at the rate of 400 mgm per mouse per day. The weight gains in this short time are so small that individual numbers may have no real meaning, but as a group it is evident that there were poorer gains with the heated fats than with the non-heated. Previous experience (4) has indicated, however, that under the experimental conditions used the data for liver weight as a proportion of total body weight may be subjected to valid statistical analysis, which has been done. The only significant differences were those between the heated and non-heated oils in each category. The differences between the variously treated oils were not statistically significant at the 95% probability level. Consequently, even by this highly sensitive test, there is no evidence of nutritional damage resulting from higher temperatures of

TABLE IV

Effect of Heated and Unheated Oils on Three Day Gain and Liver Size of Mice

	Soybean Oils				Cottonseed Oils			
	Three day gain (grams)		Liver (% of body wt)		Three day gain (grams)		Liver (% of body wt)	
	Non-heated	Heated	Non-heated	Heated	Non-heated	Heated	Non-heated	Heated
Crude	1.9	1.2	5.9	9.9	2.3	1.6	6.7	8.6
Refined	2.0	1.8	6.4	10.0	2.2	1.8	6.0	8.3
Refined and Bleached	11.6	0.9	6.1	9.6	2.6	1.3	5.5	7.6
Ref., Bl., and Deodorized, 160C	2.6	1.4	6.9	9.2	2.4	1.6	6.2	7.6
Ref., Bl., and Deodorized, 204C	2.4	1.7	6.5	8.2	2.0	1.8	6.4	7.1
Ref., Bl., and Deodorized, 238C	3.0	2.0	5.6	8.4	2.4	1.2	5.5	7.5

TABLE V

Effect of NAF's from Heated and Unheated Oils on Three Day Gains and Liver Size of Mice

	Soybean Oils				Cottonseed Oils			
	Three day gain (grams)		Liver, % of body wt		Three day gain (grams)		Liver, % of body wt	
	Non-heated	Heated	Non-heated	Heated	Non-Heated	Heated	Non-heated	Heated
Crude	1.3	1.7	5.9	7.6	2.4	2.8	6.5	8.3
Refined	1.3	2.1	5.9	8.2	2.0	2.6	6.9	8.2
Refined and Bleached	1.3	1.3	6.2	8.0	2.6	2.7	7.3	7.8
Ref., Bl., and Deodorized, 160C	1.6	1.8	6.2	8.3	2.9	2.7	7.1	8.2
Ref., Bl., and Deodorized, 204C	1.3	2.4	7.1	8.0	1.8	2.8	6.4	8.7
Ref., Bl., and Deodorized, 238C	1.2	1.7	6.6	8.1	1.7	2.6	6.9	8.1

deodorization.

Table V summarizes the data obtained when the NAF'S separated from the heated and non-heated oils were fed to mice at the level of 40 mgm in 360 mgm of cottonseed salad oil per mouse per day. It should be pointed out that these 40 mgm amounts represent different quantities of starting because the oils in the heated and unheated series contain varying amounts of NAF. Again the only significant differences in liver weight were those due to heating the oils. The NAF's within either the unheated or the heated series of oils were not significantly different; but the heated series did differ from the unheated. Contrary to the observation made when the oils were fed, the weight gains at the end of three days were on the whole better for the NAF's from heated oils than from unheated.

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[Received June 19, 1962—Accepted November 5, 1962]

The Analysis of Alkyl Aryl Sulfonates by Micro Desulfonation and Gas Chromatography

E. A. SETZKORN and A. B. CAREL, Research and Development Department, Continental Oil Co., Ponca City, Oklahoma

Abstract

The structural analysis of micro quantities of alkyl aryl sulfonates by presently known chemical and spectroscopic techniques has been an exceedingly difficult task. The formidable nature of such analyses is due largely to the essential nonvolatility of the sulfonates, a fact which precludes the application of gas-liquid chromatography and mass spectrometric techniques.

The present paper describes an approach wherein gas chromatography is made applicable to analysis of micro quantities of sulfonates. The key to the approach is a microchemical desulfonation procedure. This process yields the parent hydrocarbon, which is volatile and hence amenable to analysis by gas-liquid chromatography and mass spectrometry.

Introduction

THE STRUCTURAL ANALYSIS of micro quantities of alkyl aryl sulfonates by presently known chemical and spectroscopic techniques has been a very difficult task. The difficulty in analyzing these materials rests on two major factors: (1) the essential nonvolatility of the sulfonates, which effectively precludes the application of such powerful techniques as gas chromatography and mass spectrometry, and (2) the great chemical complexity of the commercial alkyl aryl sulfonates, which consist of at least scores and perhaps hundreds of different molecular species.

An analytical method was required to support studies which were under way in our laboratories involving reactions of alkyl aryl sulfonates in the 10–40 ppm level. Some of the analytical requirements were as follows: (1) The method must be essentially quantitative and also yield qualitative information on structural changes of the sulfonate. (2) The method must apply to a variety of sulfonates of known structure and to commercial alkyl aryl sulfonates as well. (3) The method must be capable of dealing with one-liter samples containing from 10–40 ppm of sulfonate in the presence of a large excess of a complex reaction milieu including a variety of inorganic and organic compounds blended in an aqueous nutrient medium designed to promote growth of microorganisms.

Since an isolation procedure was essential, several schemes were developed to fractionally isolate certain components for special purposes; however for general

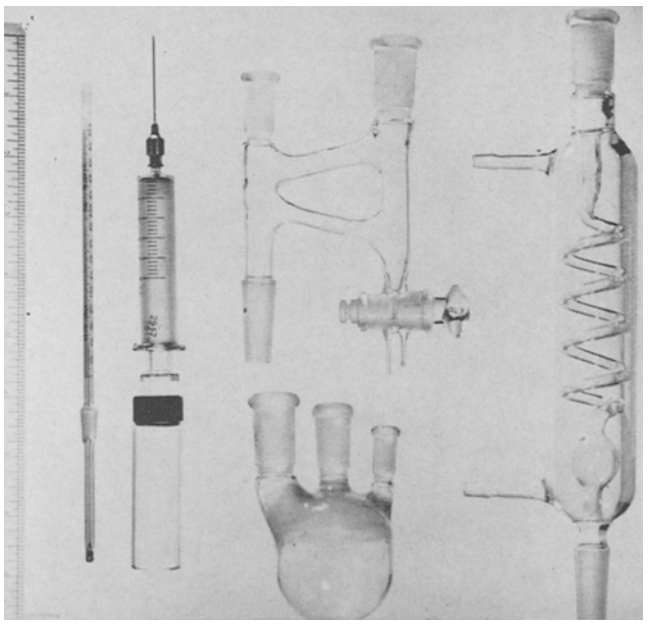

FIG. 1. Desulfonation apparatus.

Presented in part at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1960.