Physical and Chemical Properties of Alumina Bleached Cottonseed Oil[1]

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Abstract

No detectable amount of polymerization or triene conjugation occurred on bleaching refined cottonseed oil with either activated alumina or with sulfurous acid-treated alumina, although insignificant amounts of diene conjugation and *trans*-isomerization occurred. AOM stability, tocopherol content, and fatty acid composition, as determined by gas-liquid chromatography (GLC), were comparable with values obtained with oil bleached with natural earth. Hydrogenation of the oils proceeded normally. Taste panel evaluations of the deodorized oils revealed their flavor stability to be equal to that of the same oil bleached with AOCS official earth.

Introduction

FINELY-GROUND activated alumina is superior to conventional Fuller's earths for the removal of problem pigments from refined off-colored cottonseed oils (6,11,12). In admixture with small amounts of activated charcoal, to remove green pigments, activated alumina is also an efficient bleaching agent for normal cottonseed oils (11). More recently, sulfurous acid-treated aluminas were reported (12) to be active in removing both the red and green cottonseed oil pigments, even in the absence of activated charcoal. Moreover, oils bleached with sulfurous acid-treated alumina were found to contain no detectable traces of sulfur and gave a negative response to the Halphen test. Seed oils of plants belonging to the order Malvales give a positive Halphen test. It is presumed that the Halphen test is specific for substances containing a cyclopropene ring.

Determinations of chemical and physical properties, hydrogenation behavior and the organoleptic flavor stability of alumina-bleached and deodorized cottonseed oils are reported in this communication.

Procedures

The refined cottonseed oils were fresh samples from the vacuum dryer of a commercial refinery, and were stored under refrigeration.

All bleaching experiments with activated alumina and with sulfurous acid-treated alumina were carried out under reduced pressure (0.5–1.0 mm Hg) at 225C; 4 g of adsorbent, prepared as described previously (12) were used per 100 g of oil. Reference oils were obtained by bleaching with 4% of AOCS official natural earth (1) under atmospheric pressure at 120C for 30 min. The bleached oils were filtered and steam-deodorized in glass equipment (2) at 220–225C for 2 hr.

Oil colors were measured by both the color index proposed by Pons, Kuck, and Frampton (10) and the AOCS Lovibond method (1).

Appropriate methods of the AOCS (1) were used in determining chlorophyll-like pigments, unsaponifiable materials, peroxide value, AOM stability, iodine value, diene and triene conjugation, and isolated *trans* isomers calculated as trielaidin. Total tocopherols were determined by the method of Stern and Baxter (13). The Halphen test was carried out following the procedure proposed by Deutschmann and Klaus (3).

Viscosity measurements were made at 40 ± 0.02C using Ostwald-type Viscosimeters, and the data are reported as kinematic viscosity in centistokes.

Laboratory scale hydrogenations were conducted in glass equipment, as described by Feuge and Cousins (4), at 170C using 0.2% of a supported nickel catalyst of commercial origin, and which was prepared by reduction of electrolytically precipitated nickel hydroxide.

Glycerides were converted to methyl esters by potassium methylate catalyzed transesterification as described by Luddy et al. (7), and the methyl esters were subjected to analyses by GLC. A 6-ft by ¼-in. column packed with 80–100 mesh Chromosorb-P coated with diethylene glycol succinate polyester (10% by wt of the solid phase) was used for the GLC analysis. A Beckman GC-2 instrument equipped with a thermal conductivity detector and inlet temp of 300C was used for all analyses. The column temp was maintained at 190C and helium at 30 lb pressure was used to develop the chromatograms. Component fatty acids of the mixed esters were calculated from relative areas under appropriate peaks.

Freshly bleached and deodorized oils were packaged under both nitrogen and air and shipped to a commercial cottonseed oil processor for evaluation of color and flavor stability.

Experimental Results and Discussion

Effect of Bleaching Time. Samples of a commercially refined cottonseed oil, 300 g each, were bleached with 12 g of activated alumina where the time of heating at 225C ranged 5–60 min. A 50-g sample was taken from each bleached oil for analysis, the remainder of the oil was deodorized, and this in turn was also subjected to analysis. Comparable experiments were carried out with AOCS official natural earth as the bleaching agent to simulate conventional practice. The data show in Table I.

It may be noted that the oils bleached with activated alumina have lower color indices than the corresponding oils bleached with natural earth. The same is true for the deodorized oils.

It is suggested, on the basis of the data for tocopherols, that these constituents are only slightly affected by alumina bleaching. In addition, the AOM stability (9–11 hr) of the deodorized oils, which were subjected to alumina bleaching at 225C up to about 30 min, is comparable to that observed for the control earth-bleached oil. It may be noted that in each case reported, deodorization of the oils improved the AOM stability.

The conditions used in bleaching with activated alumina induced very little isomerization of the component fatty acids, as indicated by the low levels of diene and triene conjugation, and *trans* isomers in the bleached and deodorized oils.

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TABLE I

Influence of Bleaching Time on Properties of Alumina Bleached Cottonseed Oil

Adsorbent used	Bleach time in min	Oil properties								
		Color index	Viscosity [a]	Iodine value	Total tocopherols	Peroxide value	AOM stability	Conjugation		Isolated *trans* isomers
								Diene	Triene	
					%	me/kg	hr	%	%	%
None [b]	0	172.2	34.48	108.6	0.056	4.9	9.7	0.53	......	2.68
Bleached oils										
Natural earth [c]	30	38.0	....	108.4	....	2.1	9.4	0.0	0.17	2.76
Alumina [d]	5	36.2	....	108.6	....	2.0	9.3	0.46	0.0	2.98
Alumina	15	27.4	....	108.9	....	0.9	7.9	0.54	0.0	3.19
Alumina	30	21.6	....	108.5	....	0.8	7.8	0.56	0.0	3.10
Alumina	60	21.0	....	108.6	....	1.0	7.8	0.76	0.0	2.97
Deodorized oils										
Natural earth	30	36.6	34.60	108.5	0.057	0.9	12.4	0.0	0.17	2.74
Alumina	5	22.4	34.65	108.4	0.056	0.8	9.4	0.50	0.0	2.91
Alumina	15	21.6	34.68	108.7	0.043	0.8	10.9	0.54	0.0	2.98
Alumina	30	21.0	34.42	108.5	0.046	0.8	9.1	0.65	0.0	3.42
Alumina	60	20.0	35.10	108.4	0.043	0.8	8.1	0.68	0.0	3.53

[a] In centistokes, 40C.
[b] Refined oil.
[c] Atmospheric bleach, 120C.
[d] Vacuum bleach, 225C.

Iodine values (I.V.) of the oils bleached with activated alumina for 5–60 min are the same as that of the refined oil. Viscosity data indicate strongly that no measurable polymerization occurred on bleaching with activated alumina for 5–30 min at 225C.

Properties of Normal and Acid Alumina Bleached Oils

Chemical Properties. Three kg portions of a commercially refined oil were each bleached with 120 g of activated and with sulfurous acid-treated alumina for 45 min at 225C under reduced pressure. The oil bleached with sulfurous acid-treated alumina was washed with an excess of 30% aqueous sodium carbonate to remove acidic material produced by the treatment. The oil was then washed with water to remove any residual carbonate. As a control, 3 kg of the same oil was bleached with AOCS official natural earth for 30 min at 120C. Each of the bleached oils was steam-deodorized for 2 hr at 225C.

The data in Table II indicate no significant differences between oil bleached with either natural earth, activated alumina, or sulfurous acid-treated alumina, and they are in agreement with the observations recorded in Table I. Of particular interest here is the fact that sulfurous acid-treated alumina had no adverse effect on fatty acid isomerization, as judged from diene and triene conjugation and *trans* isomer formation. Values for unsaponifiable fraction, I.V. and viscosity of the oils are comparable with the control earth-bleached oil and support the suggestion that little, if any, polymerization can be attributed to the acid-modified alumina.

To confirm the conclusion that there was no measurable polymerization, samples of the refined, earth bleached, and acid alumina-bleached oils were saponified by use of AOCS method Ca6b-53. The soaps were washed with ether to remove unsaponifiable material. The fatty acids were recovered and analyzed for dimeric and polymeric fatty acids by the silicic acid partition chromatographic method proposed by Frankel, et al. (5). The data, plotted in Figure 1, indicate in each case only single monomeric fatty acid peaks in the elution volume range of 50–125 ml. Moreover, based on the average equivalent weight of the fatty acids added to the columns, it was apparent that monomeric fractions recovered accounted for quantitative recovery of the acids in the original sample. With this chromatographic technique, dimeric fatty acids are eluted in the elution volume range of 200–300 ml, while higher polymers are eluted beyond 400 ml. There was no evidence for the presence of either dimeric or polymeric fatty acids in the oils examined.

TABLE II

Chemical Properties of Refined Cottonseed Oil Before and After Bleaching

Oil property	Refined oil R-111	Bleached and deodorized oils		
		Natural earth OM-11	Activated alumina OM-12	H_2SO_3-treated alumina OM-13
Color index	161.0	10.8	5.6	10.5
Chlorophyll, ppm	0.70	None	0.058	0.079
Halphen test	Positive	Positive	Positive	Negative
Unsaponifiable, %	0.39	0.44	0.52	0.48
Iodine value, Wijs	110.0	110.6	110.6	110.7
Viscosity (40C),[a]	33.08	33.89	34.13	33.80
Diene conjugation, %	0.0	0.38	0.44	0.59
Triene conjugation, %	0.0	0.02	0.01	0.02
Trans isomers as trielaidin, %	3.2	3.7	3.8	4.3
Fatty acid composition [b]				
Myristic—(C 14) %	0.9	1.0	1.0	0.9
Palmitic—(C 16) %	25.6	26.9	26.4	26.9
Palmitoleic—(C 16=) %	0.8	0.7	0.9	0.8
Stearic—(C 18) %	2.0	1.5	1.4	1.7
Oleic—(C 18=) %	18.1	18.0	17.6	17.3
Linoleic (C 18==) %	52.6	51.7	52.7	52.3

[a] In centistokes.
[b] By gas liquid chromatography.

Fatty acid composition of the oils, as determined by GLC, are also recorded in Table II. The data indicate a normal fatty acid pattern for all of the bleached

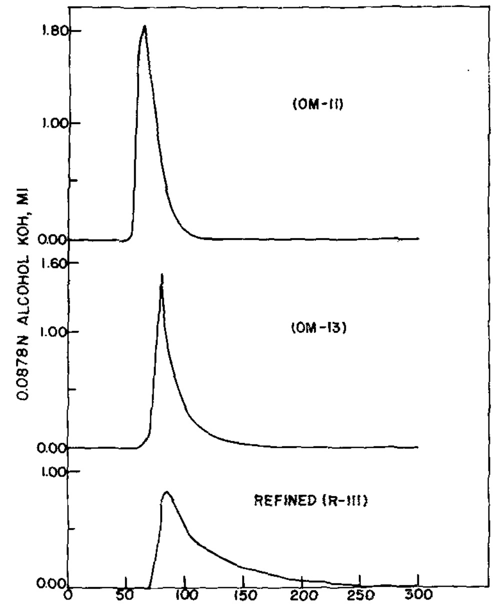

FIG. 1. Partition chromatographic analysis of cottonseed oil fatty acids for dimeric and polymeric products. R-111—Refined oil; OM-13—Oil bleached with sulfurous acid alumina; OM-11—Oil bleached with natural bleaching earth.

TABLE IV

Flavor and Color Stability of Bleached and Deodorized Cottonseed oils

Oil property	Storage time-days at 140F	Stored in air			Stored under nitrogen		
		Natural earth OM-11	Activated alumina OM-12	H_2SO_3-treated alumina OM-13	Natural earth OM-11	Activated alumina OM-12	H_2SO_3-treated alumina OM-13
Peroxide value, me/kg	0	0.9	3.9	0.7	0.9	3.9	0.7
Lovibond color, Y:R	0	10:2.3	4:0.4	11:1.2	10:2.3	4:0.4	11:1.2
Flavor	0	7.8	7.4	7.6	7.8	7.4	7.6
Fatty acids, %	0	0.02	0.02	0.04	0.02	0.02	0.04
Lovibond color, Y:R	3	15:2.7	5:0.5	15:1.5	10:2.0	4:0.4	11:1.2
Flavor	3	7.5	7.0	7.5	7.0	6.5	6.5
Fatty acids, %	3	0.03	0.03	0.04	0.02	0.03	0.04
Lovibond color, Y:R	7	17:2.4	5:0.5	16:1.6	10:1.8	4:0.4	15:1.5
Flavor	7	5.5	4.0	5.0	7.0	6.0	6.5
Fatty acids, %	7	0.03	0.03	0.04	0.02	0.03	0.04

oils. This is further emphasized by tracings of the gas chromatograms in Figure 2.

Hydrogenation. Although oils bleached with sulfurous acid-treated alumina have been found to be free of sulfur (12), laboratory hydrogenation experiments were conducted to determine if hydrogenation proceeds normally with these oils. The data in Figure 3 indicate that the rate of hydrogenation is fairly constant for oils bleached with both activated and sulfurous acid-treated alumina. Apparently, catalyst poisons are not present in the oils.

The I.V. and *trans* isomer content of the oils bleached with either activated or sulfurous acid-treated alumina as shown by the data in Table III, are comparable with the values for the control earth-bleached oil.

Each of the hydrogenated oils was converted to methyl esters and analyed GLC. The oils show no significant differences in fatty acid composition, and the conclusion is that hydrogenation of the oils bleached with activated alumina and sulfurous acid-treated alumina is normal.

Color and Flavor Stability. AOM stability of vegetable oils has frequently been reported to be an unreliable index of their organoleptic stability (8,9). Flavor stabilities of earth, activated alumina, and sulfurous acid-treated alumina bleached, and deodorized oils were determined by a commercial oil processor. Oil samples were stored at 140F under a nitrogen atmosphere and under air. The results, recorded in Table IV indciate that the color and flavor stability of the oils bleached with the alumina preparations compare favorably with the earth-bleached control oil. After 7 days at 140F, the flavor score of all oils was essentially the same. On the scale used where 10 represents an ideal oil, the values are about normal for cottonseed oils. No significant color reversion occurred for alumina bleached oils stored either under air or nitrogen.

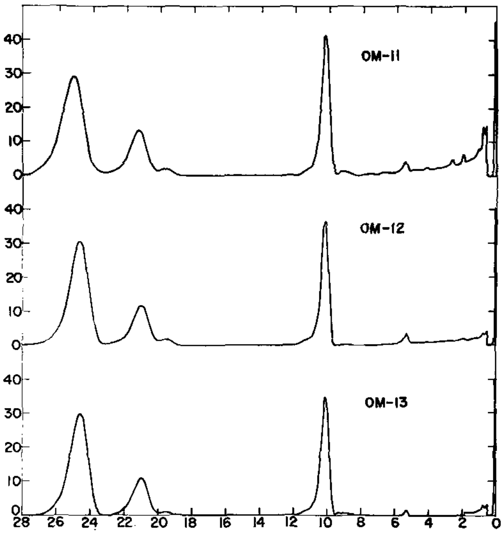

FIG. 2. Gas-Liquid Chromatograms—methyl esters of bleached cottonseed oils. OM-11—Natural earth; OM-12—Activated alumina; OM-13—Sulfurous acid-treated alumina.

TABLE III

Hydrogenation of Bleached Cottonseed Oils

Property of Hydrogenated oil	Type of bleached oil		
	Natural earth	Activated alumina	H_2SO_3-treated alumina
Color index	13.8	10.0	13.7
Hydrogen uptake/25 g. cc	680.0	595.0	680.0
Hydrogenation rate, cc/min	38.2	32.0	29.6
Iodine value, Wijs	80.4	82.9	79.4
Trans isomers, as trielaidin, %	26.0	20.6	24.5
Fatty acid composition			
Myristic %	1.2	1.2	1.0
Palmitic %	25.5	26.8	25.8
Palmitoleic %	1.0	0.8	0.8
Stearic %	2.1	1.8	2.0
Oleic %	51.7	49.0	51.9
Linoleic %	18.5	20.3	18.5

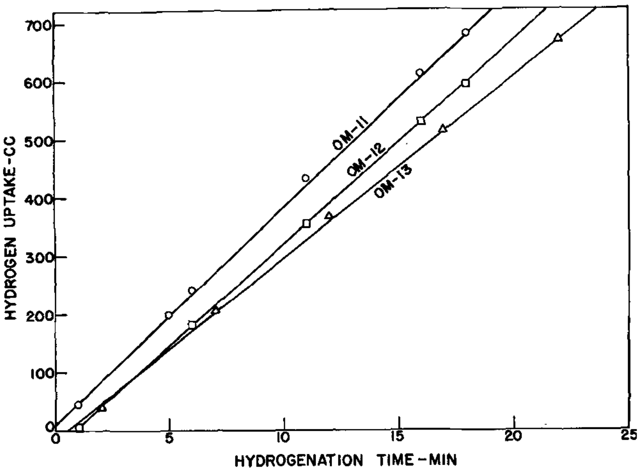

FIG. 3. Hydrogenation of bleached cottonseed oils. OM-11—Oil bleached with natural earth; OM-12—Oil bleached with normal activated alumina; OM-13—Oil bleached with sulfurous acid-treated alumina.

Consideration of the results from chemical analysis of these oils, the hydrogenation data, and the flavor stability allows the conclusion that bleaching of cottonseed oil with either activated or sulfurous acid-treated aluminas has no adverse effect on the quality of the oil. This observation, and the opportunity to produce Halphen negative cottonseed oils, may be an important consideration in the commercial use of alumina in bleaching cottonseed oils.

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The Reaction of Phosphorus Trichloride with Fatty Acids

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Abstract

An investigation of the reaction of phosphorus trichloride with fatty acids has provided a reliable guide to choice of reaction conditions. Excesses of 25–100% phosphorus trichloride are required for high conversions; the shorter the chain length of the acid, the larger the excess of reagent required.

We consider the reaction path to be satisfactorily established and have shown several hypotheses made to account for the formation of hydrogen chloride as a by-product, to be unnecessary.

Two alternative mechanisms for the reaction are proposed and discussed.

Introduction

RECENT WORK in these laboratories has utilised fatty acid chlorides as intermediates, and a clean, rapid and economical method of preparation was sought. Acid chlorides may be readily prepared by a variety of reagents and Bauer (1) has made a cost comparison favouring phosphorus trichloride as the most economical reagent. A survey of the literature, however, revealed a wide variation in recommended usage (1–6). Sonntag (2) has remarked that no satisfactory account of the reaction of phosphorus trichloride with carboxylic acids is available, and that work is required to establish the contributions of the various reactions postulated. The generally accepted (2,7,8) stoichiometry of the reaction is given by equation I, with production of an upper layer of

$$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3 \qquad [I]$$

acid chloride containing phosphorus chlorides, and a lower layer of impure phosphorus acid. We refer to this impure phosphorous acid as "phosphorous acid," to distinguish it from pure crystalline phosphorous acid. All phosphorus trichloride/carboxylic acid reactions evolve hydrogen chloride, and it is the failure of equation I to account for this by-product which has led to the confused and hesitant explanations in the current textbooks (2,7–9).

Experimental

Raw Materials. The fatty acids used were acetic (99.6% May and Baker laboratory chemicals), octanoic (98% B.D.H. laboratory reagent grade), oleic (95–100% B.D.H. laboratory reagent grade), and tallow (mw 266). Phosphorus trichloride was from Albright and Wilson, Ltd.

Infrared Spectra. IR curves were obtained in CCl_4 solution on a Perkin-Elmer "Infracord" spectrophotometer.

General Method of Reaction. A convenient sample size (100–200 g) of liquid or molten fatty acid was treated with phosphorus trichloride over a set period with or without agitation, and allowed to separate into two layers. The syrupy lower layer, essentially (3) phosphorous acid, was run off leaving a water-white layer of acid chloride, containing unreacted fatty acid and chlorides of phosphorus. All runs were carried out under anhydrous conditions, and hydrogen chloride evolved during the reaction was flushed out at the end of the reaction period with dry nitrogen. Yields were estimated from the weight of product, its analysis for free fatty acid (IR carbonyl stretching intensity using calibration curves), and phosphorus chlorides content (volumetric analysis for phosphorus). Hydrogen chloride was estimated by back titration after absorption in a caustic trap, in front of which was a solid CO_2/methanol trap to retain volatile acid chlorides.

Discussion

An examination of the reaction variables: agitation, time, temp and excess of phosphorus trichloride, adopting the stoichiometry of equation I, and confining ourselves to acetic, caprylic, and tallow acids, afforded results in Table I. The following conclusions were made on the basis of these experimental results:

1) Little reliance could be placed upon the analyses of acetyl chloride, which partly hydrolysed during the combined operational and analytical procedures (Table I, runs 24–29).
2) Reaction rate for all three acids was rapid, a period of 2 hr ensured reaction completeness and clean separation of layers. (Table I, 17,18,20).
3) Evolution of hydrogen chloride was temp-dependent (Table I, 3 and 12; 5,7, and 11; 21,22 and 23).
4) Yield of acid chloride was independent of temp over the range 70–160F, although operation at 180F or above caused drastic reductions in yield (Table I, 2,4,8 and 13).
5) The effect of agitation was insignificant compared with that of the excess of phosphorus trichloride. (Table I, 1 and 2; 6 and 7).

In later experiments, conditions were fixed at 2 hr reaction time, no agitation, and minimum temp at which the fatty acid was liquid, leaving the excess