# Cyclopropenoid Fatty Acid Content and Fatty Acid Composition of Crude Cottonseed Oils from Successive Solvent Extractions[1]

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## Abstract

The fatty acid composition and properties of six fractions of oil successively extracted from cottonseed meats has been investigated. The cyclopropenoid fatty acid concn increased regularly from 0.30–1.06%, a 3.5-fold increase. This suggests that the cyclopropenoid constituents of the oil in the seed are less accessible to the solvent. The linoleic acid concn decreased from 56.3–53.1% accounting for a slight reduction in iodine value (I.V.). The first two fractions had a markedly lower phosphatide content than the remaining fractions.

## Introduction

THE FIRST FRACTION of oil obtained in the hexane extraction of raw cottonseed meats has been reported to give a much weaker Halphen-test response than the oil obtained by subsequent exhaustive extraction (1). This implies that the cyclopropenoid constituents of the oil in the seed are less accessible to the solvent and suggested a systematic quantitative investigation. The availability of a precise and accurate analytical method for cyclopropenoid fatty acids in cottonseed oil (2) has now made it possible to make such a study and determine whether any correlation exists between cyclopropenoid fatty acid content and the fatty acid distribution in the successive fractions of oil extracted.

## Experimental

About one kg of prime cottonseed which had been dehulled in a Bauer mill and from which most of the hulls had been removed were placed in an oversized Soxhlet. The Soxhlet was filled with petroleum ether (bp 30–60C) to a level sufficient to cover the meats. The meats were steeped for 15 min at room temp and the solvent siphoned off. The meats were steeped for an additional 45 min with fresh solvent and the solvent-oil solution again collected. The Soxhlet was then wrapped with an electrical heating tape so that the solvent could be maintained at a temp near the boiling point. The meats were steeped ten more times at this temp using fresh solvent each time. The solvent was removed from each extract under a stream of nitrogen at reduced pressure. Smaller successive extracts were combined when necessary so as to give 30–50 g of oil in each of six major fractions. A sample of the "whole oil" was obtained by conventional exhaustive Soxhlet extraction of another batch of the same meats. By successive extractions, the meats yielded 24.3% of oil with a residual oil content of 0.77% in the meal as compared to a 23.9% yield of oil and a residual oil content of 0.84% by the conventional Soxhlet extraction.

The percentage of cyclopropenoid fatty acids (2), the Wijs (I.V.), and the percentage of phosphatides (3) for the whole oil and each of the six fractions were determined. Cyclopropenoid fatty acid determinations calculated as malvalic acid were made by the HBr titration method.

Methyl esters were prepared from the oil by methanolysis catalyzed by sodium methoxide. Fatty acid compositions were then determined with a Beckman model GC-2A gas chromatograph equipped with a thermal conductivity detector using a six-ft, 0.25-in. copper column packed with 20% diethylene glycol succinate (DEGS) on 80–100 mesh Gas Chrom A. The column temp was 190C with the flash chamber temp set at 300C and a helium flow rate of approx 75 ml/min. Quantitative estimations of the various components were based upon the areas beneath the chromatographic peaks determined by triangulation. The response of the thermal conductivity detector was calibrated by means of a GLC standard mixture of highly purified methyl esters obtained from the Hormel Institute. The methyl malvalate concn determined by HBr titration was subtracted from the methyl linoleate concn determined by GLC since on a DEGS column methyl malvalate is masked by the methyl linoleate peak.

## Results and Discussion

The results are presented in Table I. The malvalic acid concn increased regularly from 0.30% in the first fraction to 1.06% in the final fraction, a 3.5-fold increase. There was a regular decrease in the concn of linoleic acid. Otherwise, there was no regular change in the fatty acid composition. The final fraction, however, did have a slightly higher oleic and stearic acid content than the first fraction, which is in general agreement with the findings of Arnold and Choudhury (4) for cottonseed, and Bull and Hopper (5) for soybean extracts. The first two fractions had markedly lower phosphatide contents and slightly higher I.V. than the remaining fractions. The I.V. calculated from the GLC data are in good agreement with those obtained by the Wijs method considering the fact that the experimental determinations were made on the crude oils. The analyses for the whole oil are likewise in good agreement with those calculated from the weighted averages of the individual fractions as shown in parenthesis in Table I.

The results confirm previous finding that there is a markedly higher concn of cyclopropenoid fatty acids in the last fractions of oil extracted from cottonseed. This is of particular significance in the light of the difficulties involved in the isolation and characterization of the cyclopropenoid constituents of cottonseed oil because of the large amt of starting material neces-

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TABLE I

Analyses of Lipid Extracts

| Fraction No. | % Oil of total | % Phosphatides Px25 | I.V. (Wijs) | I.V. (GLC) | Fatty acid composition, % | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Myristic | Palmitic | Palmitoleic | Stearic | Oleic | Linoleic | Malvalic[a] |
| 1 | 24.5 | 0.16 | 109.0 | 112.3 | 1.1 | 23.6 | 1.1 | 2.0 | 15.6 | 56.3 | 0.30 |
| 2 | 14.0 | 0.05 | 110.0 | 111.5 | 1.8 | 23.0 | 1.1 | 2.3 | 15.9 | 55.6 | 0.37 |
| 3 | 13.9 | 0.52 | 107.8 | 109.0 | 1.8 | 24.8 | 1.0 | 2.1 | 15.7 | 54.2 | 0.54 |
| 4 | 14.7 | 0.45 | 107.5 | 109.3 | 1.8 | 24.8 | 1.2 | 1.9 | 15.1 | 54.5 | 0.82 |
| 5 | 18.2 | 0.50 | 107.7 | 109.0 | 1.2 | 24.2 | 0.4 | 2.6 | 16.8 | 53.9 | 0.97 |
| 6 | 14.7 | 0.59 | 107.2 | 108.9 | 0.9 | 23.4 | 0.9 | 3.1 | 17.6 | 53.1 | 1.06 |
| Whole oil[b] | | 0.41<br>(0.36) | 109.0<br>(108.3) | 111.1<br>(110.2) | 1.2<br>(1.3) | 23.3<br>(23.9) | 1.0<br>(0.9) | 2.3<br>(2.3) | 16.5<br>(16.2) | 55.0<br>(54.7) | 0.64<br>(0.66) |

[a] Determined by HBr titration.

[b] Values in parenthesis are weighted averages calculated from the individual fractions.

sary. The results also have morphological significance in that they indicate that the cyclopropenoid constituents are concd in specific areas of the seed which are not readily accessible to solvent.

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I.V. and malvalic acid determinations by J. A. Harris; phosphorus analyses by P. F. Pittman.

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# The Effect of Temperature upon Foam Fractionation

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## Abstract

An experimental investigation is presented of the effect of temp on the foam fractionation of the ethylhexadecyldimethylammonium bromide-water system. Two feed concn, two foam heights, and a temp range of 14–54C are included. For each fixed set of values of feed concn and of foam height, the greater and lesser coefficients of fractionation are both increasing functions of temp. The effect of a variation in temp on the greater coefficient is more pronounced for more dilute feed solutions, and at greater foam heights. The effect of a temp change on the lesser coefficient is more pronounced for more concd feed solutions and is not related to foam height. At any fixed temp, an increase in feed concn at constant foam height generally decreases the greater coefficient and decreases the lesser coefficient. An increase in foam height at constant feed concn increases both coefficients. The greater and lesser coefficients may be related to temp by power equations with 5% accuracy. The above results may be explained qualitatively on the basis of the response of foam stability and drainage to temp.

## Introduction

FOAM FRACTIONATION has been utilized by chemists, biochemists and engineers for the separation of organic and inorganic materials from dilute aqueous solutions. Applications of the process include the separation of enzymes, the transfer of organic solutes which by themselves have little foaming ability, the removal of radioactive metal ions from waste streams and the treatment of secondary sewage effluents for the separation of non-biodegradable organics. Several extensive reviews of the process have appeared in the literature (1,11,12). Recently, a number of studies have been made on the operating and system variables affecting the process. Grieves et al. have determined the influence of foam height and foam column diam (7), the influence of surfactant, feed concn, air rate and feed rate (5,6,8), the effect of liquid solution height (7,8) and the effect of feed position (5,8) upon the continuous foam fractionation of anionic and cationic surfactants. Other studies of this nature have been conducted by Kevorkian (9), by Kishimoto (10) and by Brunner and Lemlich (2).

The information available on the influence of temp on the process is very limited. Grieves and Wood (8) studied variations with temp of the continuous foam fractionation of ethylhexadecyldimethylammonium bromide solutions, but their temp range was limited to 24–38C. Kishimoto (10) reported the effect of temp upon the batch foaming of sodium lauryl sulfate solutions, but his temp range was limited to 10–22C. Bikerman (1) has reviewed a number of investigations concerned with the relation between foam stability and temp; however, none of these studies were concerned with foam fractionation. The overall objective of this investigation is the establishment of the influence of temp upon the greater and lesser coefficients of fractionation for the ethylhexadecyldimethylammonium bromide-water (EHDA-Br) system. Two feed concn, two foam heights and a broad range of temp are included in the experiments.

## Experimental

All of the experiments were conducted in a 10-cm diam, 105 cm high, cylindrical column, made of lucite. High-purity nitrogen was saturated with water, metered with a calibrated rotameter, and passed through twin, 50 $\mu$, fritted-glass diffusers. In each experiment, 2000 ml of the feed solution of EHDA-Br in distilled water were placed in the column. Nitrogen bubbles were dispersed through the solution for a period of 15 min with continuous foam removal at a port located at a selected height above the feed solution level. Feed concn of 87.5 mg/liter ($2.31 \times 10^{-4}$ M) and 125 mg/liter ($3.30 \times 10^{-4}$ M) were employed, with a nitrogen rate of 4950 ml/min (at Standard Temperature and Pressure) used with the 87.5 mg/liter solutions and of 3700 ml/min (STP) used with the 125 mg/liter solutions. Foam was removed at heights of 15.2 cm and of 77.8 cm above the average bulk solution level during the experiments. The temp of the solution and of the foam at the point of foam removal were measured to the nearest 0.5C throughout each run, and an average operating temp was computed. At the termination of each experiment the residual solution volume was measured and the concn of EHDA-Br