viscosities of the samples that were exposed to light had more than doubled their original values of 120.7 and 125.0 (at 26C) centistokes, respectively, while those of the oil and trivernolin that were protected from light had increased a max of 27% and 4%, respectively. Also, a nitrogen atmosphere provided the most protection against loss of oxirane oxygen. In fact, the oil samples that were stored under nitrogen retained their original level of epoxy component.

As shown in Figures 1 and 2, storage of low FFA *Vernonia* oil and trivernolin for six months at 100C in a nitrogen atmosphere had little effect on their epoxy contents. Addition of a stabilizer, *tert*-butylhydroquinone (0.3%) also prevented any appreciable loss of epoxy from trivernolin. However, the viscosities of these samples increased greatly in six months to 300.4, 292.1 and 298.0 centistokes, respectively. The oil and the trivernolin that had no stabilizer added were completely polymerized, and the oil that had stabilizer added was too viscous to measure. The oxirane oxygen content of these samples decreased considerably in six months (Figs. 1 and 2).

The epoxy content of low FFA *Vernonia* oil was not affected adversely by storage at 4C for six months and had a max increase in viscosity of 21%. The epoxy content of trivernolin decreased only 2–4%, but the viscosities of the samples stored with and without stabilizer increased to 215.7 and 209.7 centistokes, respectively, while that of the sample stored under nitrogen increased to 168.5.

These results show that under certain conditions of storage *Vernonia* oil and trivernolin undergo changes in their physical nature that are not always indicated by the oxirane oxygen values. On the other hand, a decrease in oxirane oxygen content was accompanied by an increase in viscosity.

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Determination of Refining Loss in Oil of Pistacia Seeds

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Abstract

The laboratory refining loss and the neutral oil content of the crude oil of Pistacia seeds are determined by the Wesson, acetone-insoluble and chromatographic methods and the results are compared.

For a variety of samples with a different free fatty acid content, the refining loss by the chromatographic method is determined and an expression for the relationship between laboratory refining loss and free fatty acid content of Pistacia oil is proposed.

Introduction

THE REFINING EFFICIENCY of a vegetable oil is given by the ratio $\frac{N}{N + N_1}$, where N is the refinery yield of neutral triglycerides calculated as the wt percentage of the crude oil and $N + N_1$ the actual neutral oil, i.e., the actual percentage of neutral triglycerides in the crude oil, determined by analysis. To check refining efficiency, both N and $N + N_1$ are required. From these data, the amt of neutral oil which is lost (N_1) through the saponification and emulcification may be determined.

The refinery yield of neutral oil may be determined by various methods (1–3). On the other hand actual percentage of neutral triglycerides is usually determined by one of three generally recognised methods, Wesson (4–6), acetone-insoluble (7–9) and chromatographic (10–16).

Since the actual results of any of these three methods differ, attempts have been made to establish a correlation between them. Purdum and Werber (17) determined the refining loss of many samples of cotton seed and soybean oil by the Wesson and acetone-insoluble methods and found relationships between them and the cup-test (3); but though the chromatographic method is receiving increasing attention very few attempts have been described to correlate it with other methods.

This work concerns correlation of the refining loss determined by Wesson, acetone-insoluble and chromatographic method. Also the chromatographic refining loss of Pistacia seed oil is compared with its free fatty acid (FFA) content.

Since *Pistacia lentiscus L.* and *Terebinthus L.* are abundant in Greece, the oil from their seeds has multiple uses. There is no technological research reported on this oil in the literature, therefore this oil was chosen for the above determination and correlation.

Procedures

The Refining Loss

To check the refining loss, five different kinds of Greek Pistacia oils were analysed. For each one, various specimens were examined and average values for phosphatides, FFA, moisture and volatile matter, and neutral oil were determined.

1. *Acetone-Insoluble Method.* The sum of moisture and volatile matter, FFA and phosphatides give the laboratory refining loss according to this method.

TABLE I

Neutral Oil by the Acetone-Insoluble Method

Sample No.	% FFA	% Most. and vol. m.	% Phosph.	Total % ref. loss A	% Neutral oil
1	6.31	0.12	0.03	6.46	93.54
2	6.88	0.17	0.05	7.10	92.90
3	19.02	0	0.06	19.08	80.92
4	3.32	0.46	0.05	3.83	96.17
5	5.60	1.77	0.05	7.42	92.58

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TABLE II
Neutral Oil by Wesson and Chromatographic Methods

Sample No.	Specimen No.	By Wesson Method: % Refining loss W	By Wesson Method: W/A	By Chromatographic Method: % Refining loss X	By Chromatographic Method: X/A	By Chromatographic Method: X/W
1.	a	7.27		7.25		
	b	7.80		7.50		
	c	8.00		7.00		
	d	8.15				
	Avg	7.81	1.208	7.25	1.122	0.928
2.	a	8.56		8.00		
	b	8.20		7.75		
	c	8.38		7.05		
	d	9.10				
	Avg	8.56	1.205	7.60	1.070	0.888
3.	a	21.43		21.79		
	b	19.81		20.32		
	c	22.40		20.53		
	d	22.80				
	Avg	21.61	1.132	20.88	1.091	0.966
4.	a	3.99		4.56		
	b	4.20		4.32		
	c	3.80		4.02		
	d	3.97				
	Avg	3.99	1.041	4.30	1.122	1.077
5.	a	9.38		10.25		
	b	8.30		9.27		
	c	9.04		9.80		
	d	8.64				
	Avg	8.84	1.191	9.77	1.316	1.106

Though for reasons given below the original acetone-insoluble method was not followed, its name was retained in the present method as originally appearing in the literature (7–9).

Phosphatides, FFA, moisture and volatile matter were determined as follows:

a) *Phosphatides.* The determination of phosphatides is the most sensitive and time-consuming part of the method. According to Pilette and Bagot (20) the acetone-insoluble method does not give good results when the phosphatide content is small. On the other hand, Purdum and Werber (17) have proposed the colorimetric determination of phosphorus according to the quick method of Becker and Krull (21).

The same method was followed in this work. Standard solutions of $Na_2HPO_4 \cdot 12H_2O$ were measured at 700 mμ and then the oil specimens were treated according to the method and measured under the same conditions.

b) *Moisture and Volatile Matter.* The Official and Tentative Methods of AOCS (18) was applied. The amt of moisture and volatile matter in the samples examined was found to be between zero and 1.77%. The results are tabulated in Table I.

c) *Free Fatty Acids.* The percentage of FFA (19) was calculated on the assumption that their average mol wt was 278. This number was derived from the average saponification value of the fatty acids of Pistacio oil, which was found to be 202.

The sum of moisture and volatile matter FFA and phosphatides gave the laboratory refining loss (A). The refining loss substracted from 100 gave the neutral oil content shown in Table I.

TABLE III
FFA Content of Pistacia Oil and Corresponding Refining Loss Determined by the Chromatographic Method

Sample No.	% FFA	% Refining loss mean v.	Sample No.	% FFA	% Refining loss mean v.
4	3.32	4.30	6	9.62	10.30
9	4.20	5.40	11	12.02	12.82
5	5.60	9.77	7	12.56	14.00
1	6.31	7.25	12	14.98	15.05
2	6.88	7.60	8	16.07	17.05
10	8.55	9.55	3	19.02	20.88

2. *The Wesson Method.* The refining loss as modified by Jamieson (6) was followed. The crude oil dissolved in petroleum ether is neutralized with 14% alcoholic KOH solution. Neutral oil is recovered by successive washes with petroleum ether.

Four determinations were made on each sample. In Table II the refining loss (W) and the neutral oil as well as their mean values for each sample are given. Also, the ratio of the refining loss obtained by the Wesson method over the corresponding refining loss obtained by the acetone-insoluble method for each sample is given.

3. *The Chromatographic Method.* The neutral oil according ot the AOCS chromatographic method, (16) was followed.

Grade F. Alumina 80–200 mesh was treated and used as described in the method.

The same samples used for the Wesson and acetone-insoluble methods were used. Each sample was run in triplicate.

In Table II the neutral oil and the refining loss (X), their mean values for each sample and the ratio $\frac{X}{A}$ as well as the ratio $\frac{X}{W}$ are given.

Comparison of the Results

The results obtained by the Wesson and chromatograpic methods are in all cases higher than corresponding results obtained by the acetone-insoluble method, irrespective of the FFA content of the oil.

As far as the Wesson and acetone-insoluble methods are concerned the results are in qualitative argeement with the results of Purdum and Werber (17) for cotton seed and soybean oil: since the phosphatide content of Pistacia oil is low, the ratio $\frac{W}{A}$ was expected to be small but higher than unity. Indeed, mean values of the refining loss obtained by the Wesson method, correlated with the corresponding refining loss obtained by the acetone-insoluble method give in all cases a ratio $\frac{W}{A}$ higher than unity (Table II).

On the other hand, the correlation of the mean values of the refining loss obtained by the chromatographic method with the corresponding results of the acetone-insoluble method gives a ratio $\frac{X}{A}$ also higher than unity in all cases (Table II). Both the Wesson and chromatographic methods seem to give similar results. However, to correlate X with W, more data in some other kinds of oil are needed.

Correlation of the Refining Loss with the FFA Content

For the correlation of the refining loss obtained by the chromatographic method with the FFA content of

Pistacia oil, the collection of more data in a wide range of percentage in FFA was needed. To accomplish this, samples of pistacio oil examined were mixed in a manner to produce a variety of new samples covering the range of 0–20% in FFA content.

For all the new samples the FFA content and the laboratory refining loss according to the chromatographic method were determined. Three or four specimens were examined for each sample and the mean value was taken. Table III shows that this value is increased by increasing percentage of FFA.

A plot of mean values of the refining loss against percentage of FFA gives a straight line. The slope and the intercept of this line, calculated by the method of least squares, were found to be, respectively, $b = 1.015$ and $a = 0.81$. The s.d. of b and a were found to be $S_b = \pm 0.029$ and $S_a = \pm 0.30$.

It is evident that even within two standard deviations, *a* exists and therefore— as expected from the theory—a refining loss exists even when the FFA content equals to zero.

The correlation coefficient of the straight line obtained was found to be $r = 0.99$ giving a very good criterion of linearity.

Consequently, for the average relationship between refining loss determined by the chromatographic method and FFA content of Pistacia oil, the following expression may be proposed:

percentage refining loss = 0.81 + 1.015 (percentage FFA)

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The Expansion and Extraction of Rice Bran

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Abstract

Expansion of rice bran as a pretreatment for solvent extraction was studied. It was found that the expanded bran showed no rise in free fatty acid (FFA) even when stored at room temp, in open containers, for a period of three months, and a slight rise after one year storage; and that the bran was agglomerated into large particles which eliminated the "fines" and channeling problems characteristic of rice bran; and that the retention time for good extraction was on the order of 45 min; and that the percolation rate for a four ft depth of expanded bran was on the order of 35 gpm/ft^2.

Introduction

THE PROBLEMS ENCOUNTERED in the solvent extraction of rice bran are well known and widely reported and have rendered the usual type extractors, the total submergence columns and percolation units, practically useless in handling rice bran. The problems with rice bran are associated with its finely granulated nature and its tendency towards rapid conversion of the rice oil into FFA. Fines cause problems in the clarification of miscella (4,10), the condensation of the fines-ladened vapor from the desolventizers (4) and channeling within the baskets (4); they have become so troublesome as to force some operators to run their extractors far below capacity (10).

The rapid conversion of rice oil into FFA is due to the action of a lipolytic enzyme which is activated during the milling operation (7) and, to a minor extent, the action of bacteria and molds in the presence of air and moisture (6). The FFA level increases rapidly (6,7,17) reaching a level of 50–70% in only 90 days storage time (7). A variety of methods to inhibit the rise of FFA have been reported, some of them by chemical methods (7,17), and others by heat sterilization of the bran and storage under arid conditions (1,2,4,7,13).

When heat sterilzation treatment is given in the presence of a moisture level sufficient to cook the material, the additional benefit of fines agglomeration is obtained (4). This development of cooking rice bran to eliminate the fines and retard the FFA formation, which are the two most vexing problems concerning the processing of rice bran, would render rice bran as easily extracted as any other well prepared oil seed (1,2,4,12,13).

The deactivation of the lypolytic enzyme and the sterilization of the bran due to the temp of cooking, enables the treated bran to be stored for long periods of time with no significant increase in FFA. Cooking also releases the oil (4) similar to the effect of cooking upon other oleaginous materials. The fines agglomeration, which is due to the gelatinization of carbohydrates and proteins contained in the bran (2,4,12,13), helps to increase the percolation rate of the treated material as well as eliminate the problems encountered in the miscella clarifiers and meal desolventizers.

Much of the work with rice bran has been done by Southern Regional Research Laboratory, who published their results in a series of journal articles (2–4, 16).

Experimental Procedures

Rice Bran. The rice bran used for this project was obtained from the Blue Ribbon Rice Mills Inc.,