TABLE V
Comparison of Total Gossypol Values for Cottonseed Oils and Soapstocks by Two Methods

Type of sample	Total gossypol pigments	
	p-Anisidine method [b]	Proposed method
	%	%
Crude oils		
Hydraulic-pressed	0.087	0.089
Screw-pressed	0.198	0.204
Prepress-solvent	0.314	0.311
Pure gossypol in refined and bleached oil	0.095	0.094
Acidulated soapstocks		
Blended—centrifugal-refined [a]	0.033	0.030
Hydraulic—batch-refined	0.083	0.080
Prepress—centrifugal-refined	0.421	0.451
Blended—centrifugal-refined [a]	0.495	0.532
Hydraulic—centrifugal-refined	0.788	0.794
Screw-press—centrifugal-refined	1.56	1.58

[a] Blend of hydraulic-, screw-press, and prepress-solvent oils.
[b] Improved p-anisidine method (11).

conducted over a period of several months; single analyses were performed in each instance. The average value was 0.958%, and the standard deviation ±0.0084. The coefficient of variation was 0.88% and compares favorably with the maximum precision attainable in conventional photometric analysis, generally considered to be about 0.5 to 1.0% of the amount present (2).

Summary

A method is proposed for the determination of total gossypol in cottonseed meals, crude oils, and soapstocks based on a rapid extraction of gossypol by neutralized 3-amino-1-propanol in dimethylformamide to form a stable complex, followed by colorimetric analysis of an aliquot of the extract by means of an aniline reaction. A determination can be completed in about 2 hrs. and with minor modification in 1 hr. compared to about 7 hrs. for current methods. Results obtained by the proposed procedure on meals, oils, and soapstocks are in essential agreement with those found by use of other accepted methods. Desirable features, such as stability of reagents and extracts and a high degree of reproducibility, suggest that the procedure will satisfy the requirements for a rapid and simplified method for the analysis of all cottonseed products for total gossypol.

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Pilot-Plant Preparation of Edible Safflower Oil

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PRODUCTION of safflower seed in the United States States reached a record high in 1956 when, according to recent estimates, about 100,000 acres of safflower were planted. Increasing interest in this oilseed and its potential for adaptation in portions of the Western Great Plains and Pacific Coast States as a replacement for wheat has revived efforts to find broader fields of use for the oil.

Currently much of the safflower oil produced in this country is used by the coatings industry, principally in the manufacture of non-yellowing alkyd resin and drying oils. In recent months at least two pharmaceutical preparations containing safflower oil have appeared on the market and also some food manufacturers apparently are becoming interested in the oil. In some sections of the world safflower oil reportedly is used primarily for food purposes (1, 3). There is conflicting evidence regarding its oxidative and flavor stabilities since some investigators have found the oil to be poor in these respects (5, 6). In the tests reported here however safflower oil was found to possess extremely good edible characteristics, and its oxidative stability was considerably improved when the oil was treated with a metal scavenger and an antioxidant. Whether the differences in findings between previous reports and this report result from seed variental factors, from variations in processing treatments, or from differences in methods of evaluation is not known.

The safflower oil used in the present tests was obtained from a commercial processor in two lots, one in early 1956 and the second about eight months later. Both lots were alkali-refined to a low free fatty acid content by the processor and were characterized as "nonbreak" oils. Several 100-pound batches from each lot were bleached in pilot-plant equipment with 1% of Super Filtrol[2] at 105°–110°C.(221°–230°F.) for 15 min. and filtered. The bleached oils were deodorized 4 hrs. at 218°C.(425°F.) and at 4–6 mm. of mercury absolute pressure, with about 3% of stripping steam per hour. The oils were removed from the deodorizer at 48°C.(120°F.) and stored at —18° C.(0°F.) in glass bottles. The deodorized oils were evaluated for flavor stability, using taste-panel techniques developed at this laboratory (4). Oxidative stability (A.O.M.) was evaluated for each sample by determining peroxide development after an 8-hour oxidation in the Swift stability apparatus (2).

Results

Characteristics of the two lots of safflower oil used to prepare edible oil for evaluation are given in Table I. Although the fatty acid composition of both lots

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[2] The mention in this article of commercial products or equipment or the names of their manufacturers does not constitute *endorsement* by the U. S. Department of Agriculture of such firms or products.

TABLE I
Characteristics of Safflower Oil

Characteristic	Lot 1	Lot 2
Iodine value (Wijs)	143.2	144.0
% F.F.A., nonbreak oil	0.23	0.03
Color, nonbreak oil [a]	.....	8.8
Color bleached oil (avg.)	.....	4.0
Color, deodorized oil (avg.)	.....	3.3
Composition of fatty acids: [b]		
% Saturated acids	6.5	.....
% Oleic acid	21.0	.....
% Linoleic acid	72.2	.....
% Linolenic acid	0.3	.....

[a] Colors determined by A.O.C.S. Tentative Photometric Method.
[b] Linoleic and linolenic acids determined by A.O.C.S. Tentative Method for polyunsaturated acids.

was not determined, the small difference in iodine values indicates that the composition of both lots may have been very similar. It is evident that the nonbreak oil responds well to bleaching with activated earth; however the bleaching which occurred during deodorization is believed to be less than is usually observed with soybean oil.

Oxidative stability data and taste-panel evaluation of storage tests at 60°C. for three batches of deodorized safflower oil prepared successively from Lot 1 nonbreak oil are summarized in Table II.

Despite minor variations in the vacuum attained during successive deodorizations there was no significant difference between the flavor scores of the 0-time samples or between the scores of the stored samples. On the scoring sheets used by the taste panel, a numerical score of "8" corresponds to an adjectival score of "good" and a score of "6" to "fair." Therefore all of the 0-time samples were rated "good" on the average, and all stored samples were rated "fair." Since a sample scoring "6" or above is considered acceptable for use, all the oils were still acceptable after the 4-day storage treatment. Predominant flavors for the fresh samples, described as "weak buttery" or "weak beany," were not unlike those usually assigned to freshly deodorized soybean oil of good quality. The flavors of the stored samples indicate a tendency toward the development of rancidity rather than the painty flavors often observed with oils containing appreciable quantities of linolenic acid. However further evidence, particularly at longer storage times, would be needed before definite conclusions could be reached with regard to the qualitative nature of the flavors which develop.

The improvement in oxidative stability of successive batches of oil is evidently caused by a "carry-over" effect of the citric acid from one batch to a succeeding batch. This occurred even though the deodorizer was cleaned with refluxing acetone between batches to minimize carry-over effects of added stabilizers between successive batches. Judging from previous studies conducted in the pilot plant with other vegetable oils in the same equipment under comparable conditions, the oxidative stability of safflower oil, according to the A.O.M. peroxide values is somewhat lower than that of other oils, which may be caused in part by the higher content of polyunsaturated acids in safflower oils.

The results given in Table III with oil from Lot 2 show good agreement with data in Table II. The flavor scores and typical flavors are similar for both lots of oil except that, for reasons unknown, more "weak grassy" responses were noted with the second lot. Despite the lack of a statistically significant difference between the flavor scores of the stored samples there appears to be a slight correlation between flavor stability and oxidative stability under A.O.M. conditions. Further data not shown in Table III were obtained from taste-panel evaluations of samples stored 5, 7, and 9 days. These results show no significant differences in flavor scores between the four samples after any of the storage periods. Predominant flavors of samples stored 9 days were described as rancid. Of particular interest is the greater reduction in 8-hour, A.O.M. peroxide value resulting from the addition of 0.01% propyl gallate and 0.01% citric acid in comparison with the reduction obtained with citric acid alone.

Although the oxidative and flavor stabilities of most fats and oils are improved by the addition of citric acid, to inactivate traces of metallic contaminants, antioxidants such as propyl gallate are generally effective only where a deficiency of natural antioxidants occurs, as in animal fats. Whether or not this finding indicates that safflower oil is deficient in natural antioxidants, it does give evidence that safflower oil having very good high temperature oxidative stability characteristics results from the use of a metal inactivator and an antioxidant.

TABLE II
Flavor Evaluation and Oxidative Stability of Deodorized Safflower Oil from Lot 1

Batch number	Flavor scores [a]		Predominant flavors		Peroxide value after 8-hour oxidation, A.O.M. conditions
	0-time	After storage [b]	0-time	After-storage	
1	8.3 (0.24) [c]	6.0 (6.3)	Bland Weak buttery	Weak to mod. buttery Weak rancid	39.6
2	8.0 (0.42)	6.3 (6.3)	Bland Weak buttery Weak grassy	Weak beany Weak buttery Weak rancid	29.5
3	8.3 (0.49)	6.0 (3.2)	Weak buttery Weak beany	Weak buttery Weak beany Mod. rancid	26.7

Note: 0.01% citric acid added to each batch during cooling of deodorized oil.
[a] No significant difference between 0-time flavor scores or stored flavor scores.
[b] Storage conditions: 4 days in 60° oven in stoppered, glass bottles two-thirds full.
[c] Figures in parentheses denote peroxide values.

TABLE III
Flavor Evaluation and Oxidative Stability of Deodorized Safflower Oil from Lot 2

Batch number	Flavor scores [a]		Predominant flavors		Peroxide value after 8-hour oxidation, A.O.M. conditions,
	0-time	After storage	0-time	After storage	
1	8.1 (0.35)	6.1 (2.8)	Weak buttery Weak beany	Weak to mod. buttery Weak to mod. rancid Weak beany	52.8
2 [b]	8.4 (0.35)	6.6 (4.9)	Weak buttery Weak beany	Weak to mod. buttery Weak beany Weak grassy Weak rancid	41.7
3 [c]	7.9 (0.25)	6.6 (2.5)	Weak buttery Weak beany	Weak beany Weak grassy Mod. buttery Weak to mod. rancid	29.4
4 [d]	7.8 (0.24)	6.8 (2.5)	Weak buttery Weak beany Weak grassy	Weak to mod. buttery Weak beany Weak grassy	11.8

[a] No significant difference between 0-time flavor scores or stored flavor scores.
[b] Before deodorization 0.01% citric acid added.
[c] During cooling of deodorized oil 0.01% citric acid added.
[d] During cooling of deodorized oil 0.01% citric acid and 0.01% propyl gallate added.

Summary

Tests conducted on a pilot-plant scale with two lots of commercial, alkali-refined safflower oil demonstrate that no difficulty is experienced in producing a salad oil of good, initial quality with good flavor stability when stored at 60°C. in the dark. Although results indicate safflower oil is suitable for a salad oil, they should not be construed as indicating its stability as a cooking oil since tests of this type were not conducted.

The addition of citric acid improved the oxidative stability of the oil, and citric acid plus propyl gallate gave even further improvement. No significant increase in flavor stability resulted from these additives.

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The Preparation and Infrared Spectra of Morpholides of Ricinoleic Acid and Some of Its Derivatives

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PREPARATION of the morpholides of ricinoleic acid and some of its derivatives was undertaken as part of a research program on the chemistry of castor oil. Ricinoleic acid, 12-hydroxyoleic acid, comprises about 90% of commercial castor oil. Morpholides have generally been prepared by the reaction of morpholine with acid chlorides, acids, or acid anhydrides (1–6). There appear to be only two references in the literature to the preparation of morpholides by the action of morpholine on esters and none on the reaction of morpholine with esters of long-chain fatty acids. Ratchford and Fisher (7) in a study of the preparation of N-substituted lactamides by ammonolysis of methyl lactate report a yield of 83% of the morpholide without giving experimental details. Utermohlen (8) in a patent on a process for acylating amines reported that refluxing isopropenyl acetate with morpholine in the presence of sulfuric acid as a catalyst produced N-acetylmorpholine.

Because the ammonolysis of esters is a well-recognized reaction, the preparation of the morpholides of ricinoleic acid and some of its closely related derivatives by reaction of morpholine with the methyl esters was investigated. It was found that although the reaction is rather slow, the morpholides could be obtained in substantially quantitative yield simply by refluxing the methyl esters with an excess of morpholine and condensing the evolved methanol in a Dean-Stark trap. Since the distillation temperature of methanol (65°C.) is quite different from that of morpholine (129°C.), efficient fractionation is not required and relatively little of the excess morpholine distills over with the methanol. The progress of the reaction could be followed roughly by observing the rise in refluxing temperature and more accurately by titrating the unreacted morpholine, using mixed methyl red and methylene blue indicator (9). The morpholide of stearic acid, which does not seem to have been reported previously, was prepared for purposes of comparison.

The infrared spectra of the morpholides showed characteristic absorption bands which can be used for diagnostic purposes and for analysis. A strong band at 5.78 microns is characteristic of the esters. An equally strong band at about 6.10 microns present in all the morpholides, completely separated from the 5.78 micron band and absent from the spectrum of morpholine, characterizes the morpholides.

The morpholides, but not morpholine, also exhibit a band of moderate intensity at about 10.3 microns. Hence the morpholides represent another class of compounds in which *trans* unsaturation cannot be detected by use of this band (10).

Experimental

Materials. Methyl ricinoleate was prepared from the oil by the method of Swern and Jordan (11). The methyl ricinoleate used typically had the following characteristics: N_D^{20} 1.4629; d_{25}^{25} 0.9233; $[\alpha]_D + 5.004$, all in good agreement with the reported values. The hydroxyl content was 5.43% (theory 5.45%).

Methyl ricinelaidate was prepared from methyl ricinoleate by elaidinization with sulfur according to the method of Rankov and Iochev (12). Repeated crystallization from Skelly F[2] gave a product of constant melting point, 27.5–28.0°C.

Since the preparation of the morpholides was, in general, quite similar, only the preparation of 4-ricinoleoylmorpholine will be described.

To a one-liter flask provided with a short Vigreaux column, reflux condenser, Dean-Stark trap and thermometers to measure the temperature of the liquid and vapor were added 312 g. of methyl ricinoleate (1 mole) and 174 g. of morpholine (2 moles). The reaction mixture was heated at gentle reflux for about 36 hrs., during which time the reaction temperature gradually rose from 145 to 180°C. and approximately one mole of methanol was evolved. The vapor temperature at the Dean-Stark trap was generally well below 75°C. The course of the reaction could be conveniently followed by titrating one-milliliter aliquots for unreacted morpholine from time to time. When the reaction was completed, the excess morpholine was removed under reduced pressure and the reaction product was dis-

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[2] Mention of names of firms or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.