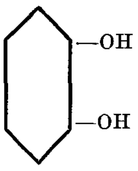
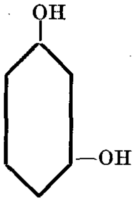
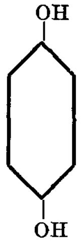
investigate the odours of ketals made from other dihydric phenols, resorcinol and hydroquinone, and also from orcinol



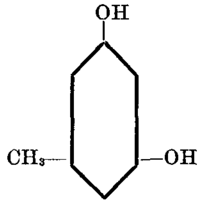
pyrocatechol



resorcinol

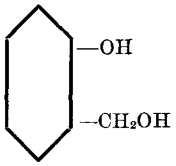


hydroquinone



orcinol

It is unlikely that the trihydric phenols such as phloroglucinol would give ketals similar in configuration and complexity to those from pyrocatechol but it would be a simple and interesting experiment to condense phloroglucinol with diisopropyl ketone and see what the odoriferous properties of the product offer. Saligenin



which is at one and the same time a phenol and an alcohol is another body which, condensed with diisopropyl ketone, might offer unusual possibilities. It would indeed seem that in the ketals, the perfumers are confronted with a field which is wide, probably fertile and almost completely unexplored.

REFERENCES

1. U. S. Patent 2,341,306 (to du Pont de Nemours & Co.).
2. British Patent 352,474, I. G. Farbenindustrie A. G. (1931).
3. British Patent 385,139, I. G. Farbenindustrie A. G. (1932).
4. *Rec. Trav. Chim. Pays. Bas.*, 1935, p. 998.
5. A. Weissenborn. U. S. Patent 2,169,984 (to Winthrop Chemical Co. Inc.) (1939).

The Flavor Problem of Soybean Oil. I. A Test of the Water Washing-Citric Acid Refining Technique

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DURING the past 12 years soybean oil production has risen from an inconspicuous place among edible and industrial oils to one of major importance and from less than 50 million pounds per year to 1,300 million pounds per year. The scarcity of other food oils during the late war was responsible for much of this expansion. However, edible soybean oil does not have the flavor stability of the oils it has replaced. It is the opinion in the edible oil industry that unless the flavor stability is substantially improved, considerable contraction in production, processing, and consumption of soybeans may result. It has been pointed out that the solution of this problem will benefit agriculture, industry, and the public (1, 2).

Studies of the relationships of phospholipids to flavor stability were initially undertaken at the Northern Regional Research Laboratory because recent investigations had indicated that phospholipids were responsible for flavor instability of dehydrated eggs (3). Additional impetus and direction were given in the reports of Warren H. Goss of this Laboratory who, on behalf of the Technical Industrial Intelligence Committee, recently conducted an investigation of the German oilseed industry (4, 5). These accounts stated that the German oil refiners consider "lecithin" responsible for flavor instability. "Lecithin" was reportedly removed by two successive water washings of freshly extracted soybean oil prior to alkali refining. Traces of lecithin which remained were thought to be inactivated by the introduction of citric acid (0.01%) during deodorization.

In the laboratory-scale experiments to be described, a crude, degummed, extracted soybean oil was given an additional water washing. This sample and the original sample were given identical refining and deodorization processing with the exception that 0.01% citric acid was added to the washed sample during deodorization. The chemical and organoleptic evaluations of the samples during storage indicate that washing, followed by the prescribed treatment with citric acid, effects a significant increase in flavor stability.

Materials and Methods

The crude soybean oil on which the refining experiments were conducted was extracted by a plant in which the equipment is identical with that used in a number of German oil mills. During production of the oil operators of the plant exercised care to avoid heating the oil excessively during any step of the process. However, there is evidence that any extracted oil which had been stripped of solvent at comparatively low temperatures would have been satisfactory for this experiment. "Lecithin" was removed according to normal degumming practice by passing the oil, containing a small amount of water, through two successive centrifuges. The water was obtained by the condensation of the direct steam used in the scrubbing section of the still. German practice includes an additional water washing between the centrifugings. The equivalent of this additional washing was carried out in our Laboratory as follows: 10% of water was sprayed into the crude oil at 65° C. with

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rapid stirring, and the emulsion was held for 3 hours at 65° C. with stirring. The emulsion was then centrifuged at 370 G. for 1 hour in a batch centrifuge, and the oil was decanted from the water and oil-water emulsion.

The alkali refining, water washing, bleaching, and deodorization processes were effected on a sample of oil "washed" as just described and upon an "unwashed" or control sample as follows: Sodium hydroxide (26.8 ml. of 12° Bé caustic per liter of oil or 0.2 gram excess per 100 grams) was added to the oil at 20° C. and the emulsion rapidly stirred for 1 hour, heated to 65° C. and held for one-half hour with slow stirring. It was then allowed to cool and settle overnight before chilling the foots and decanting the oil. Two successive water washings were effected by spraying 10% of water into the oil, which was maintained at 100° C. The water was allowed to settle out by gravity. After vacuum drying, the oil was bleached under reduced pressure with 4% of a mixture of Fuller's earth (A.O.C.S. Bleaching earth) and Darco G-60 (15-1) at a temperature of 110° C. for one-half hour. The temperature was then lowered to 70° C. and the oils were filtered. They were then deodorized for 3 hours in an all glass deodorizer at 210° C. with the passage of 0.8% of steam per hour at 1 mm. pressure. In the case of the sample which was initially water washed, citric acid (0.01%) was "flashed" into the oil at the beginning of the deodorization (Temp. 60° C., 3 mm. pressure) as a 20% aqueous solution. This sample will subsequently be referred to as "washed-citrated" and the untreated sample as "unwashed." After cooling to 70° C., water pumped nitrogen gas was admitted to the deodorizer, and the oil was drawn off directly into 8-ounce glass sample bottles. The bottles, two-thirds full, were closed with cellophane-covered cork stoppers.

Washed-citrated and unwashed samples were stored in darkness at 60° ± 1° C. Bottles were removed from storage at 0, 1, 3, 7, and 15 days. Samples were also stored at room temperature in darkness and sampled at 6, 12, 18, and 24 weeks. During the interval between removal from storage and their evaluation, samples were held at —30° C.

Organoleptic evaluation of the oils was performed following the procedure outlined in a subsequent paper (6).

Results

The effect of water washing of the crude oil and of subsequent refining operations upon nitrogen and phosphorous content and on the Lovibond color is given in Table I. Nitrogen was determined by an improved procedure which involves the splitting off and concentration of nitrogenous groups before Kjeldahl digestion (7). This procedure recovers phospholipid nitrogen quantitatively. Colorimetric phosphorous determinations were made on the same hydrolyzate as used for the nitrogen determination. The water washing step reduced the phosphorous content to less than half and the nitrogen to a value below .0001%. Both washed-citrated and unwashed oils after alkali refining, bleaching, and deodorization contained only traces of phosphorous. It is also apparent from Table I that the additional water washing results in lower Lovibond red colors in the crude, bleached, and deodorized oils.

TABLE I.

Refining of "Washed" and "Unwashed" Soybean Oils.

Stage of refining	Nitrogen	Phosphorous	Color (Lovibond)	
			Yellow	Red
	%	%		
Unwashed, crude	0.0016	0.009	70*	6.4*
Washed, crude	0.0000	0.004	70*	4.7*
Unwashed, alkali-refined, bleached	....	....	35	3.0
Washed, alkali-refined, bleached	....	....	35	2.4
Unwashed, deodorized	0.0000	<0.001	3	0.8
Washed-citrated deodorized	0.0000	<0.001	5	0.5

* One-inch oil depth.

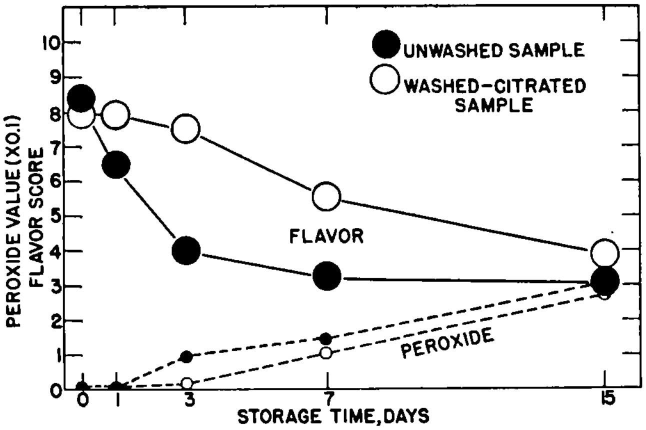

FIG. 1. Decrease in flavor score and increase in peroxide content of "washed-citrated" and "unwashed" samples stored at 60° C.

Results of the organoleptic evaluations of the two oils stored at 60° C. are given in Figure 1. The radius of the circles used is approximately the standard error. The unwashed sample is seen to undergo immediate and rapid flavor determination while the washed sample shows no significant flavor loss during 3 days' storage at 60° C. A statistically significant difference (significant at the 5% level) in flavor score occurred between the washed-citrated and unwashed samples after 1 day of storage; a highly significant difference (significant at the 1% level) occurred at the 3- and 7-day periods; and no significant difference was found at the 15-day period. The pair of samples stored for 3 days at 60° C. was also submitted to a taste panel conducted at the National Soybean Processors Association meeting on April 22, 1946. The results of that scoring by expert tasters of the industry and of research institutions were similar to those given by our panel. A highly significant difference in taste scores was found between washed-citrated and unwashed samples by both panels.

In numerous subsequent experiments washed-citrated and unwashed oils have been prepared. Washed-citrated samples have in all cases possessed higher flavor stability during storage than the unwashed samples.

The quality of flavors of the soybean oils varied as they were aged at 60° C. Flavor responses as well as numerical scores of the panel members for each sample were tabulated and the percentage of the panel designating each of the various flavors was calculated. The percentage response of the panel for five principal flavors are given for the unwashed sample in Figure 2 and for the washed-citrated sample in Figure 3. In both samples bland responses fall rapidly. Buttery responses are initially high but also decrease. Beany responses in both washed-citrated and unwashed samples reach a maximum after 1 day's storage. The painty flavor is seen to become prominent in the

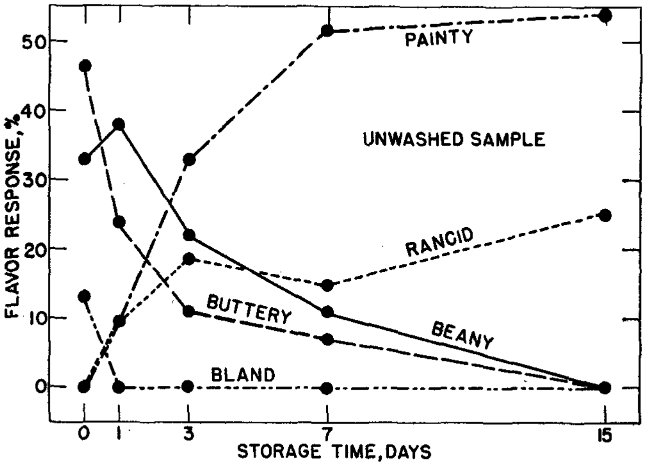

Fig. 2. Change in flavor quality of the "unwashed" sample during storage at 60° C. Other minor flavors not plotted include grassy and burned.

unwashed samples at 3 days' storage at 60° C. This objectionable flavor does not become prominent in the washed-citrated sample until after the seventh day. At 15 days, however, there is no significant difference either in flavor response or in numerical score between the two samples. It is therefore apparent that the washing-citric acid process may not remove the flavor precursors but only delay the time of their conversion to undesirable products.

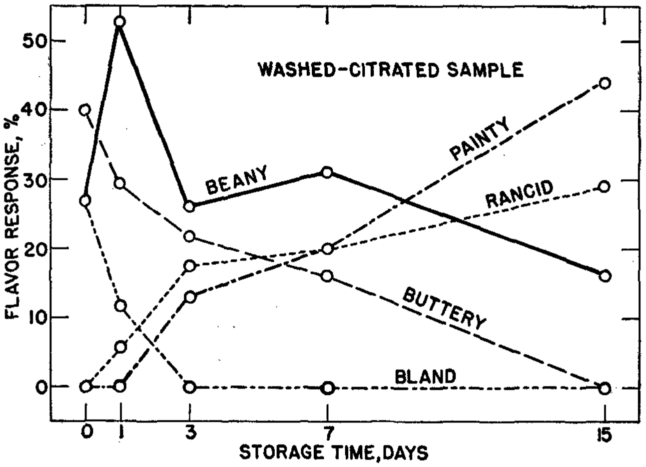

Fig. 3. Change in flavor quality of the "washed-citrated" sample during storage at 60° C.

Shown in Figures 1 and 4 are the results of various tests performed on the oils stored at 60° C. Judged by both Kreis tests (colorimetric determination with Filter 460 mg.) (8) and peroxide determinations milliequivalents oxygen per kilo) (9), the washed-citrated sample was the more stable; however, only a slight change was detected during the first day of storage of the unwashed sample although significant loss in flavor had occurred. Spectrophotometric densities (—3650Å) in both the washed-citrated and unwashed samples increased equally to a limiting value. At wavelength 4500Å (Figure 4), the increases in density were followed by decreases in both samples; however, a slight decrease began in the unwashed sample after 3 days' storage and a marked decrease in the washed-citrated sample after 7 days' storage. Since carotenoid absorption contributes to the density at 4500Å, the decrease is probably due to carotenoid destruction. Destruction, therefore, is probably more rapid in the unwashed sample which also has the higher peroxide value. Judged by these physical and chemical tests, the washed-citrated sample is more stable than the unwashed sample. These data corroborate the conclusions drawn from the less precise organoleptic data that the process of water washing and citric acid addition significantly improves the stability of soybean oil.

In addition to storage at 60° C. the two oils were stored at room temperature in darkness for 24 weeks. Results of peroxide determination and of the organoleptic evaluations are given in Figure 5. Peroxides are seen to develop more rapidly in the unwashed sample than in the more flavor-stable, washed-citrated sample. No statistically significant loss in flavor occurred in the washed-citrated sample during 12 weeks' storage, but a highly significant loss in flavor occurred in the unwashed sample during 6 weeks' storage. Since a score of 6.5, our borderline score between acceptability and nonacceptability, was reached by the unwashed sample in 3.3 weeks and by the washed-citrated sample in 15 weeks, more than a fourfold increase in storage life was effected by the water washing-citric acid treatment.

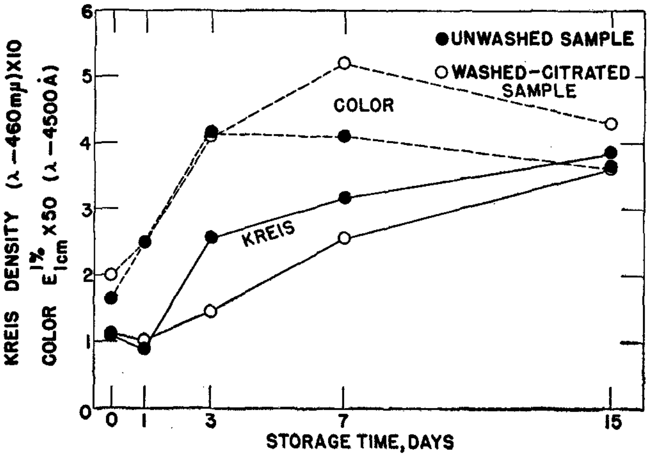

Fig. 4. Change in Kreis test and optical density (4500Å) of "washed-citrated" and "unwashed" samples stored at 60° C.

Discussion

While the water washing-citric acid process has been found to improve significantly the flavor stability of this carefully processed sample of soybean oil, it should be pointed out that high quality edible oils are a result of proper handling throughout all steps of their processing; the water washing-citric acid process cannot be expected to obliterate the ill effects of poor quality beans or of faulty refining practice. In this connection, it will be remembered that the German refiners attributed the flavor instability of soybean oil to traces of "lecithin" (4, 5, 10). The expelling process was thought to give inferior oils because the high temperature tended to "set" the "lecithin" and interfere with its removal during subsequent degumming operations (4, 5). The additional water-washing step was instituted before neutralization in order to remove thoroughly the "lecithin." Traces remaining were thought to be "inactivated" by citric acid in the deodorizer.

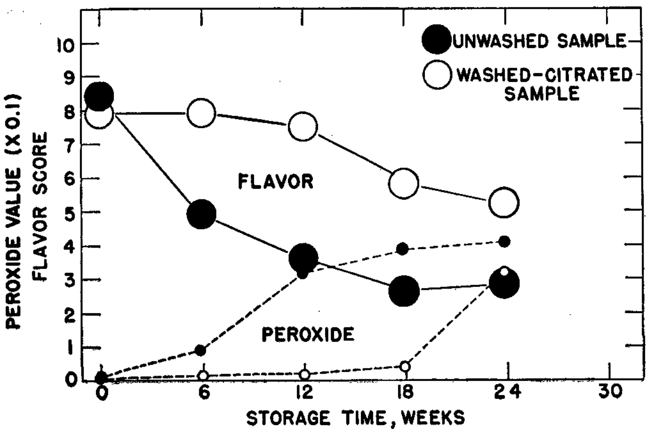

FIG. 5. Decrease in flavor score and increase in peroxide content of "washed-citrated" and "unwashed" samples stored at room temperature.

While the results presented here are compatible with the hypothesis that phospholipids are responsible for the flavor instability of soybean oil, no direct evidence of their implication has yet been obtained by us. Experiments are underway to test the "lecithin hypothesis" and other German claims. Obviously much remains to be done both in the laboratory and on a commercial scale, on shortenings as well as oils, before the practical value of this process for improving the flavor stability of soybean oil can be ascertained.

Summary

The future of the soybean oil industry depends in part upon increasing the flavor stability of edible soybean oil. A procedure, which is reported to have been used by the German soybean oil refiners for combating flavor instability, has been tested on laboratory scale and appears to have distinct merit. Oils subjected to a particularly thorough degumming operation and to the subsequent addition of a small amount of citric acid during deodorization possessed a significantly higher flavor stability than did those subjected to a conventional type of refining.

Acknowledgment

The authors wish to acknowledge the continued interest and advice of Warren H. Goss of the Engineering and Development Division in the conduct of these studies. They are indebted to the Glidden Company's Soya Products Division for the special care and precautions taken in the production of the sample of crude oil; to Jean P. Earls and C. Louise Reinbold of the Oil and Protein Division for certain analytical determinations, to Carol M. Jaeger of the Commodity and Development Division for the statistical evaluation of the organoleptic results; and to the 12 members of the panel for their conscientious cooperation.

REFERENCES

1. Alderks, O. H., Oil and Soap *22*, 232-238 (1946).
2. Robinson, H. E., and Black, H. C., Ind. Eng. Chem. *37*, 217-219 (1945).
3. Boggs, M. M., Dutton, H. J., Edwards, B. G., and Fevold, H. L., Ind. Eng. Chem. *38*, 1082 (1946).
4. Goss, W. H., Processing Oilseeds and Oils in Germany, Oil and Soap *23*, 241-244 (1946).
5. Goss, W. H., Report on Germany—Fats, Oils, and Oilseeds. Summary on Investigations, Publication No. 1270, Publication Board, U. S. Dept. of Commerce, Washington, D. C. (1946).
6. Moser, H. A., Jaeger, C. A., Cowan, J. C., and Dutton, H. J., J. Am. Oil Chemists' Soc. *24* (1947).
7. McGuire, T. A., Earle, F. R., and DuHon, H. J., Unpublished manuscript.
8. Pool, M. F., and Prater, A. N., Oil and Soap *22*, 215-216 (1945).
9. Wheeler, D. H., Oil and Soap *9*, 89-97 (1932).
10. Markley, K. S., Industry of Germany and the Occupied Countries, Fats, Oils and Oilseeds, Fiat Final Report No. 414, Publication Board, Dept. of Commerce, Washington, D. C. (1946).

Report of the Referee Examining Board 1946-47

FOR the year 1946-7 30 referee certificates were issued, including 27 renewals. The routine work of the Referee Board, but not of the Society, has been considerably decreased by transfer of responsibility for check seed and check oil samples to the Smalley Foundation Committee. The performance of the laboratories of the referee chemists on all the check samples is being followed as closely as ever by the Referee Board.

Although none of the problems of the Referee Board require action by the Society at the present time, there is one question which should perhaps be brought to the attention of the membership. At present the check samples afford the most effective means of maintaining a high standard of performance of referee laboratories. Regular use of check samples is practical only where large numbers of laboratories have intensive interest in the same test methods, such as refining tests for grading cottonseed oil.

It is relatively simple to provide check samples for referee chemists when the demand for referee certificates comes almost entirely from members who are interested also in appointment as Official Chemists of either the National Cottonseed Products Association or the National Soybean Processors Association. The problem becomes more difficult when applications are made for certificates reading on miscellaneous products by laboratories interested only in the prestige arising from the approval of our Society. There are signs of a growing interest in certificates reading on miscellaneous products, and this may lead to a situation making it very difficult for any Committee to vouch for the accuracy of a laboratory's work. If the problem becomes a serious one, the Society and not the Referee Board should decide whether or not our Referee Certificates should be limited to a relatively small list of products.

G. W. Agee
E. B. Freyer
J. P. Harris
S. O. Sorensen
A. S. Richardson, chairman