Swift *et al.* (6), working with autoxidized cottonseed oil, isolated $\Delta^{2:4}$-decadienal, $\Delta^{2}$-octenal and n-hexanal. According to Swift's postulation, linoleic acid is the precursor being decomposed through the formation of the isomer hydroperoxides. However, the formation of $\Delta^{2}$-octenal and n-hexanal has not as yet been observed in this laboratory.

## Summary

Two compounds possibly contributing to the reverted flavor in soybean oil have been isolated from the condensate obtained from the deodorization of soybean oils.

From physical and chemical data compiled, including absorption and hydrogenation studies, the structure of the 2,4-dinitrophenylhydrazones have been shown to correspond closely with the 2-4-dinitrophenylhydrazones of $\Delta^{2:4}$-decadienal and acetaldehyde.

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# Sesame Oil. V. The Stability of Sesame Oil[1]

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ONE of the significant properties of sesame oil which has been most often noted or remarked upon in recent years is its marked stability towards oxidative rancidity, after hydrogenation. Grettie (1) was granted a patent in 1933 covering the addition of small amounts of *undeodorized,* hydrogenated sesame oil to lard and other fats for purposes of stabilizing the latter fats. In 1937 Grettie (2) showed that the oily material separated from the deodorizer distillate from hydrogenated sesame oil was effective as an antioxidant in lard and other fats.

In the course of an investigation of different oils of pharmaceutical importance Fiero (3,4) found that hydrogenated sesame oil was the most stable of the hydrogenated vegetable oils which he examined. This author (5) also found that hydrogenated sesame oil imparted stability to lard when added in relatively large amounts, but the unsaponifiable fraction from this oil did not exhibit any appreciable antioxidant activity. This result was quite unexpected because, as pointed out by Fiero, the composition of sesame oil did not seem to be essentially different from that of other vegetable oils having similar physical constants.

The marked stability of hydrogenated sesame oil (500 to 900 hours, A.O.M.) was also noted in the first two reports of this series (6,7). The cause of the marked stability of hydrogenated sesame oil has not heretofore been known although Olcott and Mattill (8) suggested that the presence of sesamol might be responsible for this stability. In another report (9) of the present series sesamol has been shown to exert a pronounced antioxidant activity in lard and various vegetable oil substrates. A method for the determination of free and bound sesamol has been described in a fourth report (10) in this series.

In the present report the results of an investigation of the stability of sesame oil are presented with special reference to the role of sesamol in this respect.

## Experimental

Properties of the crude, alkali-refined, bleached, hydrogenated, and deodorized sesame oils investigated were described in a previous report (7). Stabilities were determined by the active oxygen method at a temperature of 97.7°C. Free and bound sesamol was determined according to a method (10) previously described.

TABLE I

Relation of Stability of Sesame Oils to Their Contents of Free, Bound, and Total Sesamol

| Oil | Stability, A.O.M., hours;[a] | Sesamol,% | | |
|---|---|---|---|---|
| | | Free | Bound | Total |
| SO-1 | | | | |
| Crude | 33 | 0.001 | 0.144 | 0.145 |
| Alkali-refined | 15 | 0.000 | 0.143 | 0.143 |
| Bleached, official earth[b] | 32 | 0..019 | 0.069 | 0.088 |
| Bleached, "B.C. clay"[c] | 19 | 0.014 | 0.117 | 0.131 |
| Bleached, acid clay[d] | 39 | 0.075 | 0.002 | 0.077 |
| Bleached, neutral clay[e] | 43 | 0.093 | 0.004 | 0.097 |
| Bleached, carbon[f] | 17.5 | 0.011 | 0.079 | 0.090 |
| Deodorized, (B.C. bleached) | 11.0 | 0.001 | 0.119 | 0.120 |
| SO-2 | | | | |
| Crude | 19 | 0.003 | 0.133 | 0.136 |
| Alkali-refined | 9.5 | 0.001 | 0.139 | 0.140 |
| Bleached, official earth[b] | 14.5 | 0.005 | 0.079 | 0.084 |
| Bleached, "B.C. clay"[c] | 18 | 0.011 | 0.117 | 0.128 |
| Bleached, neutral clay[e] | 56 | 0.089 | 0.015 | 0.104 |
| Deodorized, (B.C. bleached) | 8.5 | 0.001 | 0.099 | 0.100 |
| SO-3 | | | | |
| Crude | 20 | 0.001 | 0.135 | 0.136 |
| Alkali-refined | 9.0 | 0.001 | 0.134 | 0.135 |
| Bleached, official earth[b] | 17 | 0.009 | 0.080 | 0.089 |
| Bleached, "B.C. clay"[c] | 11.0 | 0.006 | 0.124 | 0.130 |
| Deodorized, (B.C. bleached) | 10.7 | 0.001 | 0.001 | 0.002 |
| SO-4 | | | | |
| Crude | 4.5 | 0.001 | 0.161 | 0.162 |
| Alkali-refined | 6.9 | 0.001 | 0.164 | 0.165 |
| Bleached, official earth[b] | 17 | 0.018 | 0.110 | 0.128 |
| Bleached, "B.C. clay"[c] | 13.8 | 0.011 | 0.151 | 0.162 |
| Deodorized, (B.C. bleached) | 9.3 | 0.001 | 0.007 | 0.008 |

[a] Time required to attain a peroxide value of 100 m.e./kg.
[b] 5.5% AOCS earth.
[c] 2% clay.
[d] 3% acid type clay.
[e] 3% neutral type clay.
[f] 3% activated carbon.

Stabilities of four crude, alkali-refined bleached, and deodorized sesame oils, together with their contents of free, bound, and total sesamol, are shown in Table I. From the data in Table I it may be seen

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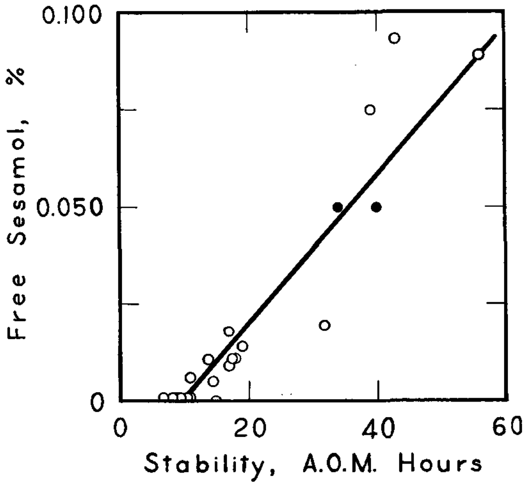

FIG. 1. Correlation between stability and free sesamol content for various refined, bleached, and deodorized sesame oils. Solid circles represent samples with added synthetic sesamol.

that the crude oils vary widely with respect to stability. After alkali-refining, however, the differences in stability between the four oils become smaller. In three of the oils a marked decrease in stability during alkali-refining is noted. The total sesamol content of the oils is not significantly affected by refining. Free sesamol occurs only in very small amounts in the crude and alkali-refined oils. It does not seem to play any appreciable role in the marked stability of three of the crude oils.

Bleaching the alkali-refined oils increases their stability to an extent depending on the type of bleaching earth used. Although the total sesamol content is reduced by bleaching to a variable extent, some of the bound sesamol passes into the free state, and the increase in stability during bleaching parallels the increase in the content of free sesamol. Of particular interest are the results obtained with the two bleaching clays denoted as "acid" and "neutral," respectively, which convert nearly all the sesamol into the free form, with a simultaneous marked increase in stability. In one case the oil bleached with neutral clay had a stability of 56 hours, A.O.M.

Deodorization removes practically all the free sesamol, and surprisingly, in some samples, bound sesamol is also removed. With the disappearance of free sesamol during deodorization the stability of the oils decreases to comparatively low values.

In Figure 1 the contents of free sesamol of the processed oils listed in Table I are plotted against the corresponding stabilities. The stabilities of two sesame oils to which synthetic sesamol had been added are also shown in this figure. Despite the diversity of the oils and the differences in the processing treatments a correlation is observed between the stability and the content of free sesamol of these oils.

The stabilities and the contents of free, bound, and total sesamol of the bleached oils, hydrogenated to shortening consistency (I.V. about 69), are given in Table II.

The data presented in Table II indicate that the content of free sesamol of these oils is high, but only insignificant amounts of bound sesamol are present. Here again it is evident that deodorization removes the free sesamol, simultaneously reducing the stability of the oils. The stability of the deodorized samples however is still considerably greater than that of other vegetable oils hydrogenated to shortening consistency.

Because of the apparent increase of free sesamol in the hydrogenated fat the contents of free, bound, and total sesamol were determined on samples withdrawn at intervals during progressive hydrogenation of two of the sesame oils. The results are shown in Figures 2 and 3. It may be seen from these figures that during hydrogenation bound sesamol is converted into free sesamol, which is accompanied by a slight decrease in the content of total sesamol. The rate of formation of free sesamol apparently differs in the two oils investigated.

In view of the fact that it has been shown that synthetic sesamol is a moderately efficient antioxidant for lard (9) the presence of free sesamol in hydrogenated sesame oil may explain the antioxidant properties of this oil when added to lard in relatively small amounts. This is borne out by the data in Table III in which the stabilities of blends of lard and hydrogenated sesame oil are shown, together with the free sesamol content of the blended fats calculated from the known free sesamol content of the hydrogenated sesame oil. Table III also includes data for lard to which synthetic sesamol was added in concentrations equivalent to those of some of the lard-oil blends.

In accordance with observations made by Grettie (1) the addition of even small amounts of hydrogenated, undeodorized sesame oil to lard produces a considerable increase in stability. Furthermore the effect produced by the addition of the hydrogenated oil is very nearly equal to that produced by the addition of an equivalent amount of synthetic sesamol. The slightly greater activity of the hydrogenated oil as compared with synthetic sesamol is probably accounted for by small amounts of antioxidants other than sesamol which are present in sesame oil, or by the presence of phosphatides which act synergistically with sesamol. It is unlikely that the substitution of 5 or 10% of the glycerides of lard by those of the hydrogenated oil would result in any appreciable change in stability.

TABLE II

Relation of Stability of Hydrogenated Sesame Oils to Their Contents of Free, Bound, and Total Sesamol

| Hydrogenated oil | Stability, A.O.M., hours[a] | Sesamol,% | | |
|---|---|---|---|---|
| | | Free | Bound | Total |
| SO-1 | | | | |
| Undeodorized | 570 | 0.097 | 0.001 | 0.098 |
| Deodorized | 380 | 0.001 | 0.000 | 0.001 |
| SO-2 | | | | |
| Undeodorized | 720 | 0.103 | 0.001 | 0.104 |
| Deodorized | 491 | ........ | ........ | 0.002 |
| SO-3 | | | | |
| Undeodorized | 560 | 0.091 | 0.001 | 0.092 |
| Deodorized | 440 | ........ | ........ | 0.003 |
| SO-4 | | | | |
| Undeodorized | 840 | 0.124 | 0.002 | 0.126 |
| Deodorized | 544 | ........ | ........ | 0.004 |

[a] Time required to attain a peroxide value of 100 m.e./kg.

It is difficult to detect the presence in sesame oil of antioxidants other than sesamol, particularly the tocopherols, because sesamol was found to give a strong Emmeric-Engel test for tocopherols. On a weight basis the color intensity of one part of sesamol was found to be equivalent to about 5 parts of pure α-tocopherol, when tested by the Emmerie-Engel method as modified by Stern and Baxter (11). On a molecular basis this ratio is approximately one mole of sesamol to two moles of α-tocopherol. Consequently a positive test given by a sesame oil does not necessarily indicate the presence of a tocopherol.

Tocopherols have been reported by Keller and Karrer (12) to be present in sesame oil in a concentration of 0.005% measured potentiometrically with gold chloride. However it is doubtful whether this method is sufficiently specific to distinguish between sesamol and tocopherols. Furter and Meyer (13) in their original report on the colorimetric determination of tocopherols by nitric acid oxidation failed to detect any tocopherol in sesame oil, and they actually used sesame oil as a substrate for the standardization of their test.

It was found that synthetic sesamol does not produce any red color under the conditions described by Furter and Meyer. Furthermore none of the different sesame oils investigated responded to the Furter-Meyer test. Consequently it seems improbable that sesame oil contains any appreciable amounts of tocopherols.

Phosphatides were determined in the four crude and alkali-refined sesame oils by multiplying the phosphorus content by the factor 24.0. This factor is based on the phosphorus content of cephalin, which has been shown by Rewald (14) to comprise the greater portion of the phosphatides in sesame seed. The phosphorus and calculated content of cephalin for the four crude and alkali-refined sesame oils are shown in Table IV. It is apparent from the data in Table IV that the phosphatide content of sesame oil is relatively small, and it does not seem that it plays an important role in the stability of this oil.

## Discussion

The experimental data reported here indicate that free sesamol is primarily responsible for the stability of sesame oil. Conditions which tend to convert bound sesamol into free sesamol increase the stability of the oil. Processing conditions which lead to an increase in the content of free sesamol are: a) bleaching, and b) hydrogenation. That "acid" bleaching earths can lead to the formation of free sesamol had been shown by Honig (15) as early as in 1925. He brought forth evidence that the efficiency of a bleaching agent with respect to free sesamol formation was dependent on its *p*H, acid earths being more effective than neutral or alkaline earths. Honig compared the action of these bleaching earths to that of mineral acids which split free sesamol from its bound form, sesamolin. Honig's conclusions were based only on qualitative evidence as he did not have available a method for measuring the concentration of free or bound sesamol in the oil. The present experimental work indicates that the "splitting power" of bleaching agents is not merely a function of their *p*H values. One neutral clay was found to produce more free sesamol than an acid clay under the same conditions. An activated carbon was found to exert marked splitting action. It is possible that the presence of moisture is of particular importance, especially when the sesamolin is adsorbed on the bleaching agent. Other factors such as the temperature and length of time of bleaching may have some influence on the amount of free sesamol produced.

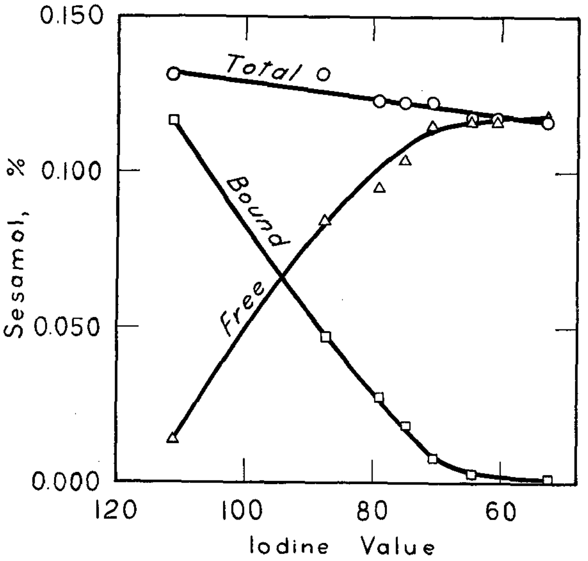

Fig. 2. Content of free, bound, and total sesamol *vs.* iodine value for progressively hydrogenated sesame oil, SO-1.

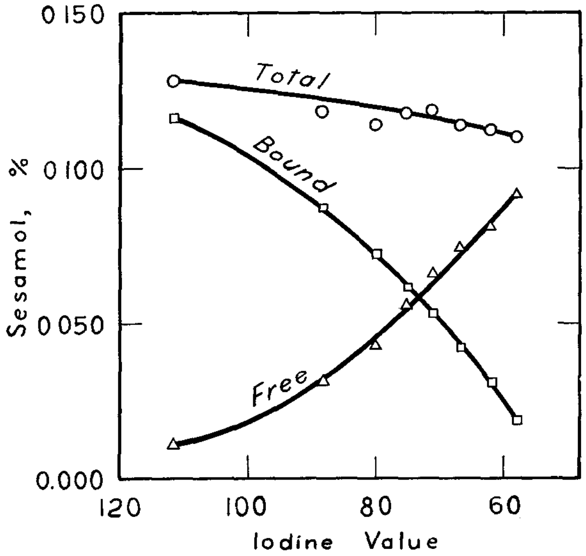

Fig. 3. Content of free, bound, and total sesamol *vs.* iodine value for progressively hydrogenated sesame oil, SO-2.

Besides bleaching, hydrogenation is highly effective in converting bound into free sesamol. In this case the formation of free sesamol is even more difficult to explain because moisture is removed from the reaction mixture prior to hydrogenation and a hydrolytic reaction cannot occur. Hydrogenolysis of the sesamolin molecule appears as the only reasonable alternative. The formation of free sesamol cannot be explained before more information is available concerning the structure of sesamolin.

Deodorization removes free sesamol which is to be expected in view of its low molecular weight (138). Synthetic sesamol boils at about 105-110°C. under a pressure of 3 mm. of mercury, and it is relatively volatile at lower temperatures; consequently it is rapidly removed from the oil under deodorizing conditions (200°C., 1 mm. Hg.). Olcott and Mattill (8) suggested that sesamol might be present in the deodorizer distillate from hydrogenated sesame oil, and this has been confirmed by the authors who found that the steam distillate from the deodorizer gave a very strong test for this substance. For some rea-

TABLE III

Stability of Blends of Lard and Hydrogenated Sesame Oil [a]

| Hydrogenated oil in mixture, % | Sesamol added, % | Sesamol in mixture, % | A.O.M. stability, hours [b] |
|---|---|---|---|
| 0 | None | 0 | 5.1 |
| 5 | None | 0.0055 | 30 |
| 10 | None | 0.011 | 48 |
| 20 | None | 0.022 | 70 |
| 30 | None | 0.033 | 84 |
| 40 | None | 0.044 | 109 |
| 60 | None | 0.066 | 160 |
| 100 | None | 0.110 | 890 |
| 0 | 0 | 0 | 5.1 |
| 0 | 0.0055 | 0.0055 | 27 |
| 0 | 0.011 | 0.011 | 42 |

[a] SO-1, I.V. 52.6, free sesamol content 0.110%.

[b] Time necessary to attain a peroxide value of 20 m.e./kg.

son as yet unknown, bound sesamol was also removed during deodorization of two of the oils.

The hydrogenated oils were found to be very stable even after deodorization, which observation is not explained by the very small amounts of free sesamol remaining in the deodorized oils. In this connection it is of interest to note that the hydrolysis of sesamolin yields, besides sesamol, a compound melting at 103°C. and having the formula $C_{13}H_{14}O_5$. The properties of this compound, called "samin" by Adriani (16), are not known. With the liberation of sesamol from sesamolin during hydrogenation a compound related to samin may be expected to form.

The experimental data reported here leave little doubt that some substance other than sesamol is active in contributing to the marked stability of hydrogenated sesame oil. Sesamol however seems to be mainly responsible for the antioxidant activity of hydrogenated sesame oil, when added to lard in small amounts. This antioxidant power is lost when the oil is deodorized as sesamol has been shown to be removed by this treatment. This observation explains the provision made by Grettie (1) that only incompletely deodorized oils can be used as an antioxidant.

The lack of antioxidant activity of the unsaponifiable fraction of hydrogenated sesame oil reported by Fiero (5) is easily explained by the fact that sesamol is soluble in alkali and therefore passes into the aqueous soap phase and is not recovered in the unsaponifiable fraction.

## Summary

The stability and the contents of free, bound, and total sesamol were determined for four crude, alkali-refined, bleached, and deodorized sesame oils. In the case of the alkali-refined, bleached, and deodorized oils, a correlation was found to exist between the stability and the free sesamol content. Bleaching increased both the stability and the content of free sesamol. In the case of one oil bleached with "neutral" clay a stability as high as 56 hours was observed. Deodorization of the bleached oils removed the free sesamol and decreased the stabilities to about 10 hours, A.O.M.

The bleached oils, after hydrogenation to shortening consistency, had stabilities ranging from 560 to 840 hours and contents of free sesamol of about 0.1%. Deodorization removed the free sesamol, which was accompanied by a reduction in stability to 380-540 hours.

Hydrogenation was found to produce a progressive liberation of sesamol and a corresponding decrease in bound sesamol while the content of total sesamol decreased only slightly. When shortening consistency was reached during hydrogenation, practically all the sesamol was present in a free form.

All of the oils gave the Emmerie-Engel test for tocopherols but not the Furter-Meyer test. Since synthetic sesamol behaves similarly, the positive result with the first of these tests is probably attributable to the presence of sesamol in these oils and not to tocopherols.

The role of sesamol in the stability of sesame oil is discussed. There is evidence that sesamol is not the only factor responsible for the high stability of the hydrogenated oil.

TABLE IV

Content of Phosphorus and Calculated Content of Cephalin in Four Sesame Oils

| Type of sesame oil | Phosphorus % | Cephalin, (P×24.0) % |
|---|---|---|
| SO-1 crude | 0.0027 | 0.065 |
| SO-2 crude | 0.0044 | 0.106 |
| SO-3 crude | 0.0055 | 0.132 |
| SO-4 crude | 0.0014 | 0.034 |
| SO-1 alkali-refined | 0.0009 | 0.022 |
| SO-2 alkali-refined | 0.0009 | 0.022 |
| SO-3 alkali-refined | 0.0013 | 0.031 |
| SO-4 alkali-refined | 0.0014 | 0.034 |

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