

# CHANGES IN SESAMOL, SESAMOLIN AND SESAMIN CONTENT OF SESAME OIL IN THE COURSE OF ITS EXTRACTION AND REFINING PROCESSES

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The unsaponifiable matter of sesame oil contains sesamol, sesamolin and sesamin as its characteristic components. Sesamol, 3,4-methylenedioxyphenol of the formula  $\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\text{OH}$ , is known as an effective antioxidant for oils, while sesamolin and sesamin are recognized as synergists for pyrethrins. Beroza<sup>1)</sup> found the synergistic potency of sesamolin to be about five times as high as that of sesamin. Sesamolin,  $\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\text{OC}_{13}\text{H}_{13}\text{O}_4$ , is readily hydrolyzed with mineral acid to give sesamol and samin,  $\text{C}_{13}\text{H}_{14}\text{O}_5$ . Sesamin,  $\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\text{C}_{13}\text{H}_{13}\text{O}_4$ , is similar to sesamolin in its structure, but it does not undergo acid-hydrolysis. The color reaction for sesame oil, using furfural and hydrochloric acid, known as the Baudouin or Villavechia test is attributed to free sesamol which is primarily present or formed by hydrolysis of sesamolin in sesame oil. The sesamol, sesamolin and sesamin content of sesame oil and its changes in the course of oil refining treatments have been studied by several authors. Beroza and Kinman<sup>2)</sup> reported the effect of strain, growing location, ageing and frost damage of sesame seeds on the sesamol, sesamolin and sesamin content of oil. Honig<sup>3)</sup> found the bleaching of sesame oil with acid treated bleaching earth to result an increase of its sesamol content. Budowski and co-workers<sup>4)</sup> found that neutral bleaching earth and activated carbon, as well as acid treated earth, tend to liberate sesamol from sesamolin but the total of the free and bound sesamol in sesame oil is reduced by the bleaching process, and also that sesamol is almost entirely removed from the oil by the deodorization process. They<sup>5)</sup> also concluded that an exceedingly high stability of hydrogenated sesame oil is attributable to the formation of free sesamol in the course of hydrogenation. Mathur and Tilara<sup>6)</sup> showed that the intensity of color developed in the Baudouin test for bleached sesame oil is much affected by the kinds of bleaching earth and activated carbon used in the bleaching process.

In order to know the effect of extraction and refining processes commonly used in our country upon the sesamol, sesamolin and sesamin content of sesame oil, and also to examine whether the oil bearing products such as oil foots, soap stock and spent bleaching earth obtainable in the refining processes may be utilized as sources for the recovery of sesamol, sesamolin and sesamin, the authors were supplied with oil samples and oil bearing products described below by the courtesy of a major oil mill producing sesame oil, and analyzed these oil samples and the oils extracted from these oil bearing products for their sesamol, sesamolin and sesamin content.

### Determination of Sesamol, Sesamolin and Sesamin

A spectrophotometric method for the determination of sesamol, sesamolin and sesamin in sesame oil was reported by Suarez *et al.*<sup>7)</sup> Later, Beroza<sup>8)</sup> found that the determination of sesamin by this method is often inaccurate due to the presence of some optically interfering substances in oil. In such cases, it was found better to separate previously a concentrate of sesamin from the oil by chromatography and then determine sesamin in this concentrate by the spectrophotometric method. For the determination of sesamol and sesamolin, Beroza also recommended to run a parallel measurement with a sample of known content of sesamol and sesamolin for the standardization of the absorption data for the sample under examination, since the absorption data for the color developed with pure specimen of sesamol and sesamolin often show a considerable variance due to some uncontrollable factors. In our study, sesamol, sesamolin and sesamin were determined by the convenient method substantially same as described by Suarez *et al.*; —the oil sample is dissolved in chloroform-isooctane (1 : 4), and free sesamol is extracted from the chloroform-isooctane solution, using a potassium hydroxide solution in methanol-water (1 : 4) (methanol-water is used in our experiments while ethanol-water was used by Suarez *et al.*). Furfural and sulfuric acid are added to the methanol-water solution containing free sesamol to develop red color, and the absorption at 518 m $\mu$  is measured. The sesamol content is calculated from the absorption data. A portion of the chloroform-isooctane solution freed from free sesamol is used for the determination of sesamolin or bound sesamol by hydrolyzing sesamolin to give free sesamol in the presence of sulfuric acid and furfural and then measuring the absorption at 518 m $\mu$ . Another portion of the chloroform-isooctane solution is used for the determination of sesamin by measuring absorption at 288, 255 and 320 m $\mu$ . The wavelengths, 288 m $\mu$  (287–288 m $\mu$ ) and 255 m $\mu$ , correspond to the absorption maximum and minimum, respectively. The wavelength 320 m $\mu$  stands at the same distance above the wavelength, 287–288 m $\mu$ , as the wavelength 255 m $\mu$  is below the latter. The wavelengths of maximum and minimum absorptions are in some cases sifted from 288 m $\mu$  and 255 m $\mu$ , respectively. In such cases, the wavelengths of observed maximum and minimum absorptions and a wavelength standing at the same distance above the wavelength of maximum absorption as the wavelength of minimum absorption is below the latter, are used in place of 288, 255 and 320 m $\mu$ , respectively.

### Preparation of Oil Samples

Samples of crude and refined oils, foots, gums, soap stock, spent adsorbent, expression cake and extraction meal were supplied by the courtesy of a major oil mill producing sesame oil in August, 1956. These were produced by the processing treatments shown in Tables 1 A-1 C. Yields of the materials given in Tables 1 A-1 C denote the approximate data informed from the oil mill. The oil content of samples, excepting oil samples, was determined in the following way. The oil in cake and meal was determined by extraction with ether in a Soxhlet extractor. Oil foots and gums were shaken with a relatively large quantity of ether, the mixture was filtered, and the oil was obtained from the ether solution by distilling off ether. The soap stock was diluted with ethanol-water (1 : 4), and the neutral oil was extracted from the diluted soap stock by extraction with ether. Hence, the oil con-

tent of soap stock given in Table 1 B does not include the content of fatty acids in the form of soap. The adsorbent used for bleaching oil consisted of a mixture of acid-activated earth and activated carbon. The spent adsorbent was first extracted for 2-3 hr. with ether using a Soxhlet extractor to give the oil (A). Since the residue in the extractor appeared still to retain a considerable amount of oil, it was taken out from the extractor and then refluxed with a relatively large amount of ether for about 1 hr. On removing ether from the ether solution, the oil (B) was obtained.

### Results and Discussion

The oil samples and the oils extracted from the oil bearing products on the occasion of the determination of their oil content were analyzed for sesamol, sesamol and sesamin. The results are shown in Table 2.

Comparing crude oil and oil from expeller cake in Table 2, the former has a smaller sesamol and sesamin content and a larger sesamol content than the latter in the case of pressing with previous roasting (Table 1 A), whereas the former has a larger sesamol content and a smaller sesamol and sesamin content than the latter in the case of pressing without previous roasting (Table 1 B). Oil from oil foots has a smaller content of sesamol, sesamol and sesamin than crude oil in the case of pressing with previous roasting, while it has a larger sesamol and sesamin content in the case of pressing without previous roasting. However, it requires a further study to know whether such variances in the distribution of sesamol, sesamol and sesamin among crude oil, oil from expeller cake and oil from oil foots are caused solely by different pressing treatments, i.e. with or without previous roasting of seeds.

As is seen from Tables 1 B and 2, hexane-extraction of the expeller cake gives an extraction meal. A further extraction of this meal with ether gives 1.6% of an oil which has a sesamol and sesamin content of more than twice as large as that of the oil from expeller cake. Hence, sesamol and sesamin appear to be more or less difficultly extractable with hexane.

Effects of various refining processes upon sesamol, sesamol and sesamin are also seen from the data given in Table 2. Oils from gums and soap stock have

TABLE 1 A. Processing Treatments Followed  
in Preparation of the Samples

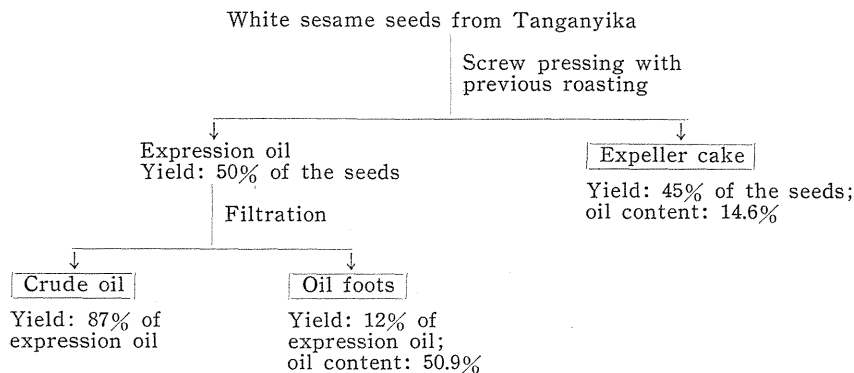


TABLE 1 B. Processing Treatments Followed in Preparation of the Samples

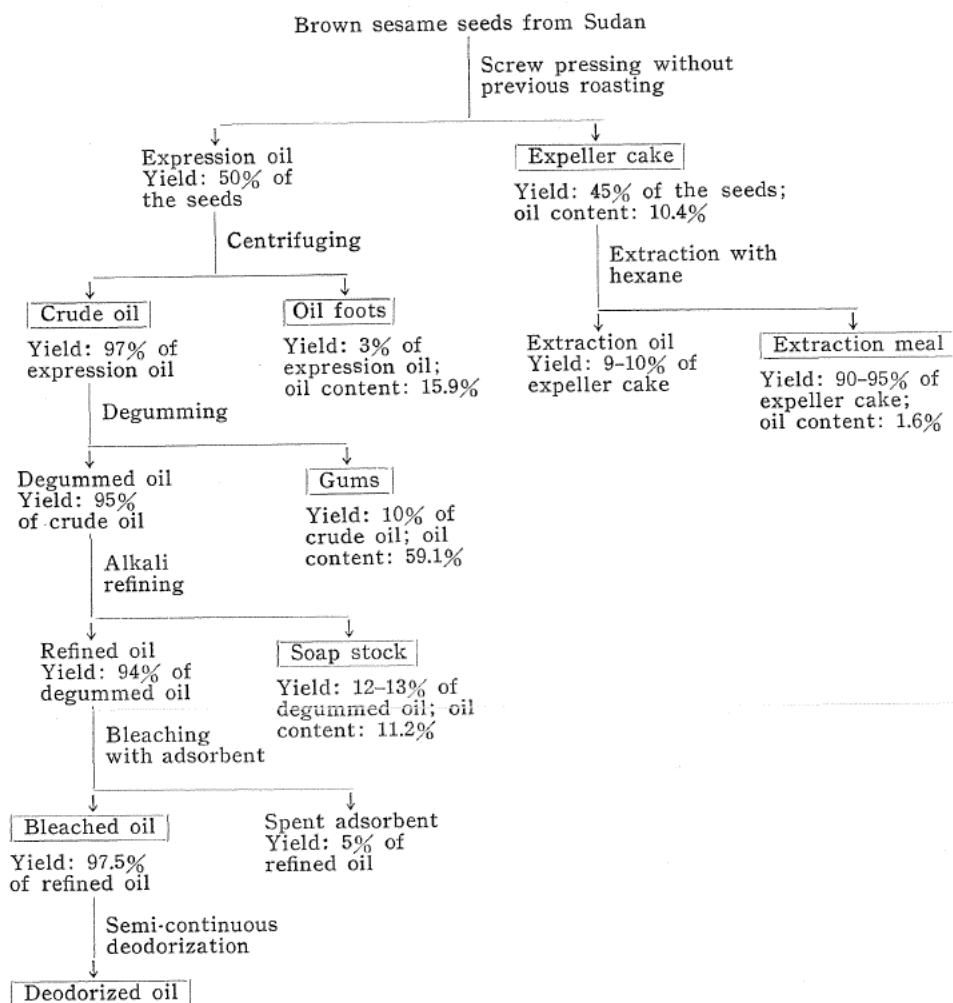


TABLE 1 C. Processing Treatments Followed in Preparation of the Samples

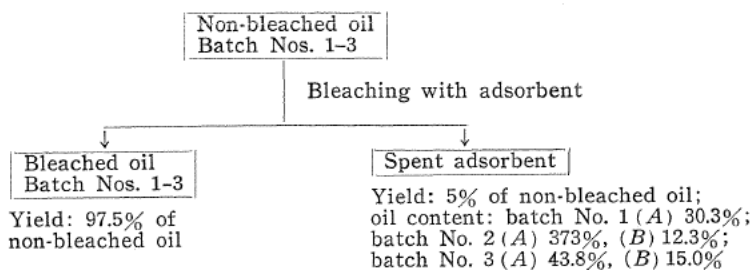


TABLE 2. Sesamol, Sesamolin and Sesamin in Samples

Sample	Sesamol (%)	Sesamolin (%)	Total sesamol (%)	Sesamin (%)
In Table 1 A				
Crude oil	0.005	0.271	0.106	0.805
Oil from oil foots	—	0.194	0.072	0.727
Oil from expeller cake	0.021	0.205	0.098	1.146
In Table 1 B				
Crude oil	0.007	0.137	0.058	0.434
Oil from oil foots	—	0.340	0.127	0.898
Oil from expeller cake	—	0.196	0.073	0.561*
Oil from extraction meal	—	0.513	0.191	1.294**
Oil from gums	0.002	0.216	0.083	0.849
Oil from soap stock	0.006	0.542	0.208	1.972
Bleached oil	0.006	0.011	0.010	0.284
Deodorized oil	—	—	—	0.270
In Table 1 C				
Batch No. 1 non-bleached oil	0.003	0.282	0.108	0.987
" bleached oil	0.023	0.009	0.026	0.751
" oil (A) from spent adsorbent	0.019	0.005	0.021	1.698
Batch No. 2 non-bleached oil	0.003	0.244	0.094	0.954
" bleached oil	0.049	—	0.049	0.834
" oil (A) from spent adsorbent	0.038	0.006	0.040	1.652
" oil (B) from spent adsorbent	0.038	0.012	0.042	4.231
Batch No. 3 non-bleached oil	—	0.269	0.100	1.049**
" bleached oil	0.015	—	0.015	0.778
" oil (A) from spent adsorbent	0.036	—	0.036	1.812
" oil (B) from spent adsorbent	0.061	—	0.061	3.423

Notes: Total sesamol is free sesamol plus bound sesamol in the form of sesamolin. In the columns of sesamol (%), sesamolin (%) and total sesamol (%), the blanks indicate a very minor percentage, smaller than 0.002%. Sesamin (%) was calculated from the absorption data at 288, 255 and 320  $m\mu$  with the exception of three samples, for which the wavelength of minimum absorption shifted from 255  $m\mu$  to 262  $m\mu$  or 259  $m\mu$ . \* Calculated from the absorption data at 288, 262 and 313  $m\mu$ . \*\* Calculated from the absorption data at 288, 259 and 316  $m\mu$ .

a larger sesamolin and sesamin content than the crude oil. Especially, the oil from soap stock has a remarkably large sesamolin and sesamin content. Hence, the refined oil obtained by degumming and alkali-refining should have a smaller sesamolin and sesamin content than the crude oil. The bleached oil obtained by treating the alkali-refined oil with adsorbent contains 0.006% of sesamol, 0.011% of sesamolin and 0.284% of sesamin. The sesamin content of oil is not reduced to a marked degree during the deodorization process, but the sesamol and sesamolin which are contained in a minor amount in the bleached oil are still more decreased during the deodorization process. Thus the degumming, alkali-refining, bleaching and deodorization processes bring out a decrease in the sesamolin and sesamin content of treated oil. Calculating the loss of sesamolin and sesamin caused by each processing treatment from the data in Table 2 and the yield of materials given in Table 1 B, it appears that the bleaching process causes the largest loss of sesamolin and sesamin. The free sesamol content of bleached oils and oils from spent adsorbents is larger than 0.003% level of non-bleached oils, whereas the sesamolin content of bleached oils and oils from spent adsorbents is smaller than that of non-bleached oils, 0.244–0.282%. The total sesamol (free and bound sesamols) content

is larger for non-bleached oils than for bleached oils and oils from spent adsorbents. It is thus seen that although sesamol is partly converted to sesamin during the bleaching process, the total sesamol is reduced by about 50-80% during the bleaching process. Comparing the sesamin content of non-bleached oils, bleached oils and oils from spent adsorbents, bleached oils have a little smaller content of sesamin, and oils from spent adsorbents have the largest content of sesamin. Sesamin also appears to be destroyed to an extent of about 10-20% during the bleaching process. Sesamin is fairly strongly adsorbed on adsorbents. When the oil retained by adsorbents is fractionally extracted by extracting more than half of the oil with ether in a Soxhlet extractor and then refluxing the residue with ether to effect a thorough extraction of oil, the oil obtained by the latter extraction is found to have a very large content of sesamin. Based on these results, an oil fraction rich in sesamin may be recovered from spent adsorbents by fractional extraction.

### Summary

With the object of tracing sesamol, sesamolins and sesamin in the course of the extraction and refining processes of sesame oil, samples of crude and refined oils and oils extracted from expeller cake, hexane extraction meal, oil foots, gums, soap stock and spent adsorbent (mixture of acid treated earth and activated carbon) were analyzed for sesamol, sesamolins and sesamin. Sesamolins and sesamin in oil decrease more and more by degumming, alkali-refining, bleaching and deodorization processes. The deodorized oil eventually obtained contains, even if it does, sesamol and sesamolins in an amount of less than 0.002%. The bleaching process affects most markedly sesamol, sesamolins and sesamin. Although free sesamol is formed from sesamolins to some extent during the bleaching process, sesamolins are destroyed to a marked extent during the bleaching process. Since sesamin is rather strongly adsorbed on adsorbent, the spent adsorbent may be advantageously utilized for the recovery of an oil fraction rich in sesamin by fractional extraction.

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