While it should be possible to apply a correction for sesamolin, the colorimetric method presents a number of other disadvantages. The most serious of these are a) the development of gas bubbles in the mixture at the time the color is measured, b) rapid fading of the color, and c) handling the hazardous reagent prepared with 30% hydrogen peroxide and 72% perchloric acid. The centrifugation of this mixture, which is part of the method, is a hazardous operation. For these and other reasons it is believed that the present method constitutes an improvement over the colorimetric method both with respect to simplicity, accuracy, and lack of hazards.

Summary

A new method for the determination of sesamin in sesame oils is described. It is based on the measurement of the ultraviolet absorption of sesame oil following the removal of sesamol by treatment with alkali and correction for the absorption resulting from the presence of sesamolin. The advantages of the new method over the previously described colorimetric method are discussed. The accuracy of the method is attested by a comparison of the determined values with those for known added amounts of sesamin in cottonseed and sesame oils. When applied to four crude oils, the content of sesamin was found to range from 0.50 to 0.96%.

Ultraviolet absorption spectra curves are reported for sesamin, sesamolin, sesamol, and sesame oil.

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Sesame Oil. VII. Optical Rotation and the Minor Components of Sesame Oil

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THE unsaponifiable matter of sesame oil is known to contain sesamin, sesamolin, and phytosterols, each of which is optically active and therefore assumed to be responsible for the observed optical rotation of this oil. It seemed of interest to compare the observed optical rotation of the four crude sesame oils described in the preceding publication (1) of this series with the optical rotation calculated from the known amounts of sesamin, sesamolin, and sterols in these oils. The sesamin content of these oils is given in Table I together with the sesamolin content of the same oils calculated from the values for bound sesamol given in a previous paper (2) of this series.

The content of free sterols for each oil was determined by the method of Klostermann and Opitz (3) as follows: A solution of the oil in a mixture of ethyl ether and petroleum naphtha was treated with an alcoholic solution of digitonin, and the precipitated sterol digitonides determined gravimetrically. Total sterols were similarly determined using the fatty acids obtained after saponification of the oil and acidification of the soaps. The bound sterols were calculated by difference.

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TABLE I

Minor Constituents and Optical Rotation of Crude Sesame Oils

Sesame oil	Sesamin, %	Sesamolin, %	Sterols			Optical Rotation[a]	
			Free, %	Bound, %	Total, %	Found[b]	Calculated
SO-1	0.496	0.386	0.201	0.154	0.355	0.93	0.97
SO-2	0.709	0.356	0.215	0.161	0.376	0.95	1.04
SO-3	0.690	0.362	0.199	0.192	0.391	1.02	1.04
SO-4	0.963	0.431	0.239	0.300	0.539	1.44	1.30

[a] Angle of rotation, α_D^{25} in a 1 dm. cell. [b] See Reference 6.

The specific rotations in chloroform solution of sesamin, sesamolin, and phytosterols of sesame oil have been reported by several authors. The following reported values which were used for the present calculation are: sesamin +68.6 (4), sesamolin +218 (4), and phytosterol −34.4 (5). These values may not be strictly comparable since they were obtained under conditions which may not have been identical, but they can be used to calculate the rotations of the crude sesame oils whose compositions with respect to these constituents have been determined. The following equation was used:

$$\alpha = \frac{\text{Specific gravity} \times (68.6\ C_1 + 218\ C_2 - 34.4\ C_3)}{100}$$

where α is the calculated optical rotation of the oils in a 1 dm. cell, and C_1, C_2, and C_3 are the percentage concentrations of sesamin, sesamolin, and phytosterol, respectively, of the oils. The specific gravity of the oils was given in a previous publication (6) of this series.

The results of this calculation are given in column 8 of Table I and the observed optical rotations are given in column 7 of the same table. The agreement between the previously reported and the calculated rotations are quite satisfactory despite the diverse source of the values for the specific optical rotations used and the fact that the calculated rotations are based on measurements made in chloroform solutions. The observed values were determined on the oils in the absence of solvent.

Since the amount of unsaponifiable matter of these oils has been reported elsewhere (6), the contribution of sesamin, sesamolin, and total sterols to the unsaponifiable matter can be calculated. When this was done, it was found that the sum of these components accounts for from 75 to 85% of the total unsaponifiable matter of the four crude sesame oils.

Summary

The optical rotations of four crude sesame oils were calculated on the basis of their known contents of sesamin, sesamolin, and phytosterols and the reported optical activities for each of these components. The calculated optical rotations were compared with those observed for the oils in the absence of solvent and were found to agree remarkably well.

Sesamin, sesamolin, and phytosterol have been shown to be responsible for the observed optical rotations of several sesame oils and to account for 75 to 85% of the total unsaponifiable matter of these oils.

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Isolation of Natural Arachidonic Acid as Its Methyl Ester[1]

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IN a recent publication (1) this laboratory reported the isolation of pure natural linoleic and linolenic acids as their methyl esters by adsorption fractionation on silicic acid. Tobacco seed oil and linseed oil, respectively, were the sources of these acids. The natural acid esters differed significantly from corresponding debromination acid esters in the intensity of ultra-violet absorption at their maxima under the conditions of the alkali-isomerization spectrophotometric method of analysis. In view of these findings, revised constants were suggested for this method when it is used for analyzing natural oils. Since many animal fats, particularly glandular fats, contain significant amounts of arachidonic acid in addition to linoleic and linolenic acids, it is important to extend this investigation to the isolation of natural arachidonic acid and study of the ultra-violet absorption characteristics of its alkali-isomerized product.

The presence of eicosatetraenoic acid in liver lipids was first shown in 1909 by Hartley (2) by identification of bromination and oxidation products. Lewkowitsch (3) suggested the name arachidonic acid for this compound. Later work has established the presence of this acid in phospholipids of liver, brain, and egg yolk. In fact, it has since been shown that small amounts are present in almost every animal tissue and glandular fat. A review of the literature is given by Ralston (4).

Brown and associates (5, 6) prepared arachidonic acid by bromination-debromination techniques and also reported its preparation in 90-95% purity by fractional crystallization and distillation (7, 8). Recently White and Brown (9) announced the preparation of methyl arachidonate from beef suprarenals by adsorption fractionation on alumina. They also reported evidence for the presence of a C_{20} acid having five double bonds. Their complete description of this work however has not been published. No information was given in the report regarding the ultra-violet absorption characteristics of their preparations after isomerization with alkali. Such information would appear essential for establishing homogeneity of the acids.

In the present paper the authors describe the preparation of pure methyl arachidonate in which the principal fractionation was accomplished by chromatographic absorption treatment on silicic acid columns. Some initial concentration of arachidonic acid was achieved by low-temperature crystallization, and the final purification was accomplished by fractional distillation in vacuo.

Experimental and Results

Since the work of Brown and co-workers indicated that beef suprarenals or adrenal glands are a satisfactory source of arachidonic acid, these glands were used as a starting material in the present work.

Preliminary Adsorption Fractionation Experiments. Our preliminary experiments on fractionation of methyl esters of beef suprarenals on silicic

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