

CRYSTALLINE DEPOSIT FROM SESAME OIL

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Sesame oil has usually a solidifying point in the range of -3°C to -6°C and a cloud point below 0°C .¹⁾ In this country, it is generally used for edible purposes without previous winterization. However, it deposits not seldom small amounts of solid in the course of storage in the cold season. In such cases, it is sometimes filtered before its shipment from oil mill. According to Ubbelohde,²⁾ sesame oil is winterized in most cases, but substances actually removed by winterization are composed not of solid glycerides but of some unknown non-lipid compounds, and it is preferable to remove such compounds causing turbidity in oil by filtration after standing oil in a cold place for about one week.

Two samples of filter residue obtained from sesame oil which became turbid in the course of storage in the cold season have been submitted to the authors for examination. In this paper, the results of our examination are recorded.

Sample No. 1. In an oil mill in Tokai District, a lot of sesame oil produced from Iraquian seed by the expeller method was stored in the winter season for a long time, and then filtered. Sample No. 1 was prepared from the filter residue by a further filtration at about 100°C for the removal of mechanical impurities. It was a liquid at ordinary temperature, and had acid value 2.0, saponification value 190.0 and iodine value 108.1. Since the iodine value of Sample No. 1 falls within the range of the iodine values for ordinary samples of sesame oil, 103-116,³⁾ it is seen that the saturated components of the original sesame oil are not much concentrated in Sample No. 1. It scarcely deposited any solid even after standing at 5° - 0°C for two days, though it formed crystalline solid after a long storage at a still lower temperature (see below).

Sample No. 1 (465 g) was dissolved in 2 liters of acetone, the solution was cooled at -5°C , and the solid material (A) was filtered with suction, yielding 11 g of crystalline solid melting at about 30°C . On standing a solution of this crystalline solid in acetone over a night at ordinary temperature, a small amount (less than 0.1 g) of solid material (B) separated. This was removed by filtration, the filtrate was cooled down, and the crystalline solid separated was repeatedly recrystallized from acetone and ethanol-ether. The melting point was steadily raised until the final crystalline material (C, 5 g) showed M.P. 36.5° - 38°C .

The solid material (B) had M.P. 59° - 60.5°C . Although a close examination on this material could not be performed, it was free from sterol, and appeared to contain wax esters similar to the high melting fraction obtained from Sample No. 2 described later in this paper.

The crystalline material (C) had S.V. 187.3 and I.V. 28.3 from which it was found to consist of glyceride having one oleic acid group and two saturated acid

groups (calculated for oleo-distearin, S.V. 189.2 and I.V. 28.5). Its melting point lies close to that of 1-oleo-distearin, 38.5° C.⁴ But the fatty acid mixture obtained from this material had M.P. 62.5°-63° C after recrystallization from acetone and M.P. 65°-66.5° C and N.V. 192.4 after further recrystallizations from ethanol. Both neutralization value and melting point were almost unaltered after the removal of last traces of unsaponifiable matter followed by a further recrystallization from acetone; M.P. 65°-66° C and N.V. 191.0. The neutralization value indicates that the saturated acid mixture obtained above contains arachidic acid (calculated, N.V. 179.5) besides stearic acid (calculated, N.V. 197.2). Accordingly, the crystalline material (C) is not a pure oleo-distearin; it is contaminated with some oleo-disaturated glycerides containing arachidic acid group.

The material contained in the mother liquors of the recrystallizations, which were carried out for the preparation of the crystalline material (C) from the solid material (A), was recovered and dissolved in acetone, and the solution was cooled at about -10° C. The crystalline substance (3.5 g) separated had M.P. 31°-32° C after recrystallization from acetone. The melting point was only slightly raised even after several recrystallizations from acetone and ethanol-ether. The final product (D) showed M.P. 33° C, S.V. 193.3 and I.V. 28.3. On fractionally recrystallizing the fatty acid mixture of this product from ethanol, there was obtained a fraction of M.P. 61.5°-63° C and N.V. 190.9 which was considered to be a mixture of stearic and arachidic acids. Accordingly the product (D), like the crystalline material (C), is not a single glyceride but a mixture of oleo-disaturated glycerides. Since the product (D) had a lower melting point and a higher saponification value than the crystalline material (C), the presence of palmitic acid among the saturated acid components was suspected, but it could not be demonstrated in these experiments.

The material contained in the acetone filtrate of the solid material (A) was recovered and allowed to stand at 0°--5° C for 20 days. It became a semi solid mass. It was rapidly filtered through a dry filter paper with suction in order to remove a portion of liquid substance. The material rich in solid substance on the filter paper was fractionally crystallized from acetone. The highest melting fraction (E, 5 g) showed M.P. 36.5°-37° C, S.V. 189.3 and I.V. 27.6 and was considered to have the same composition as the crystalline material (C). A lower melting fraction (F, 11 g) had M.P. 27°-28° C, S.V. 191.8 and I.V. 51.2. The iodine value is considerably higher than the value calculated for oleo-distearin. On brominating the fatty acid mixture of this fraction, there was obtained tetrabromostearic acid of M.P. 114° C which indicated the presence of linoleic acid group in the fraction (F).

Sample No. 2. This sample is a filter residue obtained by filtration of refined and bleached expeller sesame oil in the winter season. The oil was produced in another oil mill in Tokai District from sesame seed, probably of southern product, imported through Hongkong. At ordinary temperature, Sample No. 2 consisted largely of a liquid with a lesser amount of white crystalline solid.

Sample No. 2 (200 g) was dissolved in 600 cc of acetone, the solution was cooled with ice, and 8 g of crystalline solid was obtained. The acetone filtrate was cooled at -10° C, but no crystalline solid separated, while an oily substance separated from the solution. The crystalline solid melted mostly at about 50° C

and became clear at about 70° C. Recrystallization of this material from ether gave 2 g of crystalline substance (G) of M.P. 75°-78° C and S.V. 126.5. This was saponified and separated into fatty acid components and unsaponifiable components (35%). The fatty acid components showed M.P. 70°-72.5° C and N.V. 171.1 after recrystallization from acetone, and M.P. 77°-77.5° C after a further recrystallization. Hence, the fatty acid components were found to contain more or less higher members than arachidic acid (calculated, N.V. 179.5). The unsaponifiable components showed M.P. 72°-74° C and acetyl V. 146.8, and contained more or less higher members than docosanol (calculated, acetyl V. 152.2). Thus the substance (G) was found to contain predominantly wax esters. Concentration of the mother liquor of the substance (G) followed by cooling gave a product of M.P. 56.5°-57° C and S.V. 173.8, but there was not obtained such a low melting crystalline solid as obtained from Sample No. 1.

As is seen from the results described above, Samples No. 1 and No. 2 differ markedly in their solid constituents; the solid constituents of Sample No. 1 consist mainly of solid glycerides and contain no appreciable amount of wax esters, while the solid constituents of Sample No. 2 contain a large proportion of wax esters. Although it is not inconceivable that this difference is attributable to the difference in the solid constituents of the original sesame oils from which Samples No. 1 and No. 2 were obtained, it may be possible that the difference in the solid constituents of Samples No. 1 and No. 2 would manifest itself even if the solid constituents of the original sesame oils were equally composed of solid glycerides with a relatively small proportion of wax esters, since the solid glycerides of sesame oil crystallize out only when the oil is stored in the cold season for a long period, while the wax esters of sesame oil crystallize out much easily in the cold season. Thus it is reasonably postulated that Sample No. 1 obtained by standing the sesame oil in a cold place for a long period contains a relatively large amount of solid glycerides while Sample No. 2 contains only wax esters as its main solid constituents.

Summary

The solid constituents of two samples of filter residue obtained by the filtration of sesame oil in the cold season were examined. The solid constituents were found to contain glycerides and wax esters. The glycerides consisted mainly of oleo-disaturated glycerides in which oleo-distearin together with glycerides having arachidic acid group were found. Also the presence of a small amount of solid glycerides having linoleic acid group was indicated. The wax esters were found to contain higher homologue of arachidic acid among the component fatty acids and higher homologue of docosanol among the component fatty alcohols.

References

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