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STUDIES ON BUFFALO MILK FAT OXIDATION

1.—The Induction Period as Measured by Peroxide Value and TBA test, and its Relation to Iodine Value, Total Carbonyls, and Conjugated Fatty Acids.

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The induction period of butteroil and samn varies between the individual samples as well as between the products, and with the type of the test used. The average induction period determined by the TBA test is 10 days in butter oil and samn, while it is 14 days for butteroil, and 12 days for samn, as measured by the peroxide value.

The TBA test is the preferable method for the early detection of milk-fat, oxidation since it is more sensitive than the peroxide value.

The iodine value or the total carbonyls concentration in butteroil and samn have no effect on the length of the induction period. On the other hand, there is an opposite relation between the induction period and the concetration of conjugated dienes.

Milkfat is a major factor in the keeping quality of milk and milk products. Its autoxidation with oxygen results in flavour deterioration and consequently creates serious problems in storage and shelf-life. Fat impariement depends on its source as well as on its susceptibility to autoxidation.

Due to the catalytic nature of this reaction, its mechanism involves initiation, propagation and termination stages. The initiation, known as induction period is an important major stage in determining the stability of the fat towards autoxidation, and the prolonging of its shelf-life. Informations about this stage in buffalo milkfat is drastically lacking, therefore, the object of this study is to determine the induction period in butteroil and samn of buffalo milkfat.

Experimental and Methods of Analysis

Fresh buffalo milk samples were obtained from the herd of the Faculty of Agriculture, Ain-Shams University. The cream was separated, washed with hot distilled water, reseparated and then churned to butter. A portion of the butter was melted at 55°C, washed several times with hot distilled water, and the butteroil layer was separated and filtered. Another portion of the butter was converted to samn by the boiling-off-method. Both the butteroil and samn were left to stand in a loosely covered flakes, where they were exposed to a maximum amount of diffused sunlight and air.

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The peroxide value (P.V.), conjugated fatty acids (conj. F.A.), were determined according to the AOCS method (1957), while the thiobarbeturic acid test (TBA) by the method of Patton. & Kurtz (1951), the iodine value (I.V.) by the British Pharmaceopaeia method (1963), and the total carbonyls content by the method of Berry & Mckerrigan (1958), on freshly prepared butteroil and samn samples. The determinaion of P.V., T.B.A., and I.V. were continued periodically every other day during the induction period. The termination of the induction period was characterized by a sharp and sudden rise in the P.V., and TBA values.

Results and Discussion

The freshly prepared butteroil and samn were free from peroxides as indicated by the peroxide and TBA tests. This finding agreed with those reported formerly by Nelson and Dahle (1940), who found that freshly isolated milk fat usually had a peroxide value of zero inspite of a strong oxidized flavor.

A sharp rise in either one of the values was considered the termination of the induction period. Therefore, the length of this period varied between the samples and with the type of the test used, as shown in table 1.

TABLE 1.—THE LENGTH OF THE INDUCTION PERIOD, AND THE I.V. CONJ. DIENES AND T.C. OF BUTTEROIL AND SAMN SAMPLES

No. of Sample	Length of Induction period per days		I.V.	Conj. dienes %	T.C. %
	measured by T.B.A. values	Measured by P.V.			
Butteroil	7	12	32.42	1.8354	1.6040
1	12	12	28.31	1.4070	5.3880
2					
3	18	10	28.71	0.4704	23.5425
4	18	18	26.81	0.5944	97.3056
5	14	10	28.33	1.1161	40.3893
6	14	14	34.62	0.6383	80.7376
Samn					
1	10	12	31.98	1.9068	11.8424
2	12	12	31.04	1.6296	4.3373
3	18	18	28.29	0.5334	28.6199
4	12	12	28.67	1.0381	82.4040
5	18	18	34.51	0.6265	361.342

In butteroil samples, the longest induction period was 18 days as measured by the P.V. or T.B.A. test. The shortest, however, was 10 days as indicated by the P.V., and 7 days as shown by T.B.A. test. In case of samn samples, the length of the induction period coincided in both tests in all samples ranging from 12 to 18 days except in one sample as shown in table 1.

Both values in butteroil and samn samples increased during the induction period. Comparing the trend of increase in both products, Figs. 1 & 2 showed that they were similar when the T.B.A. test was used. In case of P.V. the increase was similar during the first 7 days in both products.

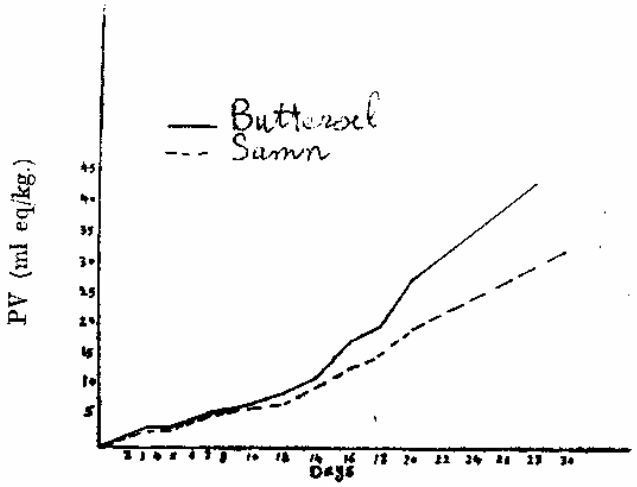

FIG. 1.—Increase in P.V. During Induction Period of Autoxidation of Buffalo Butteroil and Samn

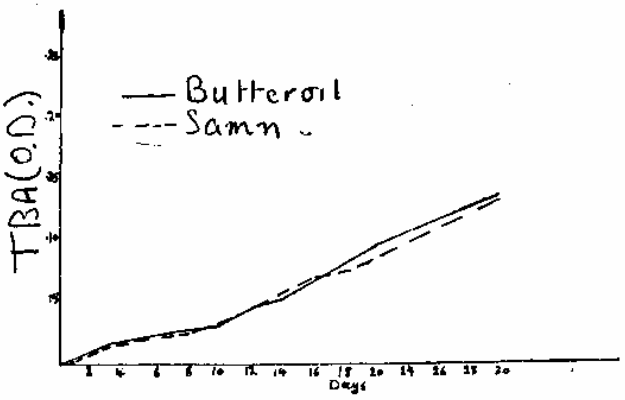

FIG. 2.—Increase in TBA Values During Induction Period of Autoxidation of Buffalo Butteroil and Samn

The induction period of autoxidation of butteroil as measured by P.V. was 14 days which was longer than in samn ; being 12 days. This was probably due to the effect of heat on the fat during samn processing, since it would hasten the rate of oxidation and accordingly would shorten the induction period as explained by Ewbank & Gould (1943). The induction period however, as measured by T.B.A. test was the same with an average of 10 days in both products, since it measures the secondary products of oxidation.

The rate of increase in T.B.A. values was comparatively smoother than in P.V., as shown in Figs. 3 & 4. Furthermore, the T.B.A. values indicated the end of the induction period earlier than the peroxide measurements. Accordingly the T.B.A. test would be the recommended test for the early detection of buffalo milkfat oxidation, due to its higher sensitivity. Supporting this conclusion, Dunkley (1951), Dunkly & Jannings (1951) and Patton and Curtz (1951) reported that the T.B.A. test was a particular sensitive test for detecting cow milkfat oxidation.

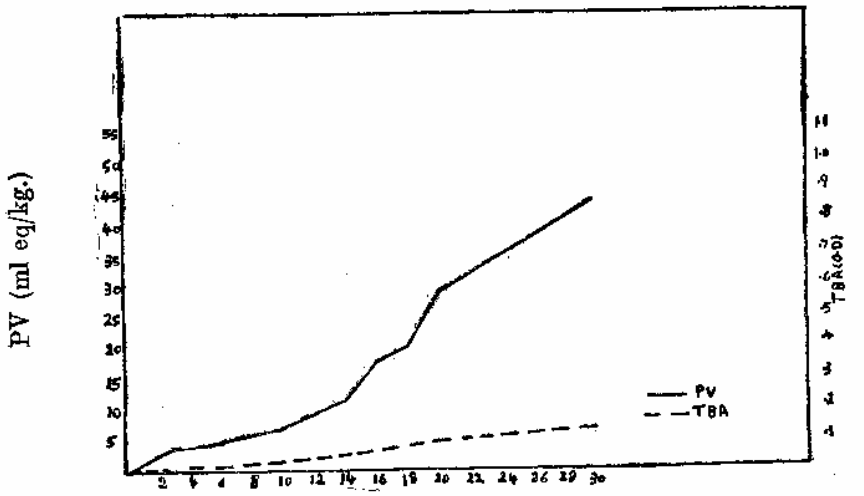

FIG. 3—Increase in P. V. and TBA Values During Induction Period of Autoxidation of Buffalo Butteroil

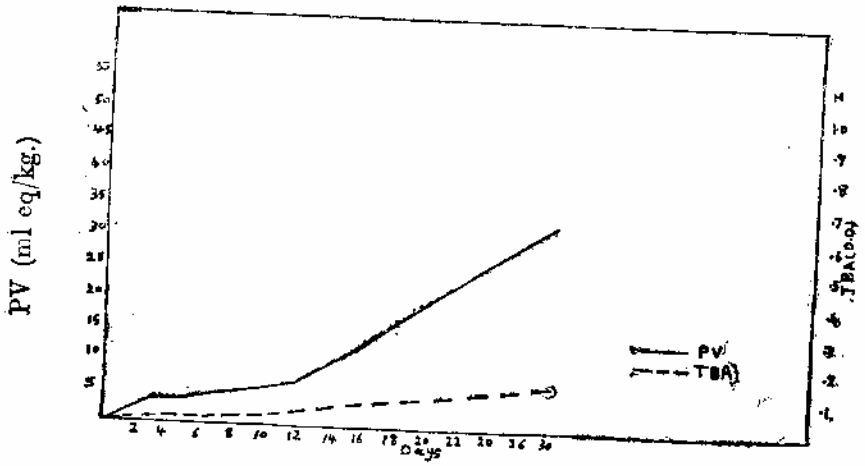

FIG. 4—Increase in P.V. and TBA Values During Induction Period of Autoxidation of Auffalo Samn

Studying the relation between some of the fat contents and constituents and the length of the induction period, it was clear that no correlation existed between the I.V. and the induction period in both butteroil and samn ; table 1. The samples with the longest induction period of 18 days did not give the lowest I.V. Also, the sample of the shortest periods did not give the highest I.V. In agreement with these findings, Lea (1938), suggested that the I.V. was not the limiting factor in determining the stability of Pig fat. Also, Corbett & Tracy (1943), and Overman, *et al.* (1939), found that there was no correlation between the stability of milkfat towards developing oxidized flavour and the I.V. contrary to that Mattson, *et al.* (1951) and Glimm, *et al.* (1952) pointed out that the induction period was shorter when the concentration of Lenoleic and polyounsaturated fatty acids were high. Moreover, Kartha (1957), found that the unsaturated glycerides of the fat were responsible for determining the end of the induction period.

There was an opposite relation between the length of the induction period and the initial concentration of the conj. dienes F.A. ; table 1. The T.B.A. values showed clearer relation than the peroxide test, either in butteroil or samn samples. In case of the P.V. this relation existed only in samn samples.

Freshly prepared buffalo milkfat contained small concentrations of saturated carbonyl compounds ; 42.5789 and 32.7776m mole/kg. in butteroil and samn respectively. Parks, *et al.* (1961), Schogt *et al.* (1961) and Winter *et al.* (1963), had identified straight and branched chain aldehydes, but they also indicated the presence of a small amounts of unsaturated aldehydes in fresh butteroil. However, the initial concentration of the carbonyl compounds in buffalo milkfat, did not affect the length of the induction period in the individual samples in either butteroil or samn, table 1.

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دراسة على اكسدة دهن اللبن الجاموسى
١ ـ فترة التحضين مقدرة بواسطة اختبارات البيروكسيد وحامض الثيوباربتيوريك وعلاقتهـا بالرقم اليودى والمكونات الكربونيلية والأحماض الدهنية الغير مشبعة ثنائية الرابطة الزوجية المتبادلة

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الملخص

تختلف طول فترة التحضين فى كل مرة من دهن الزبد المسيل والسمن باختلاف الناتج المصنع وكذلك باختلاف العينات فى الناتج الواحد وذلك بالنسبة لنوع الاختبار المستعمل فى قياسها . وكان متوسط طول فترة التحضين عند استعمال اختبار حمض الفيوباربيتوريك ١٠ أيام فى كل من دهن الزبد المسيل والسمن . بينما كانت ١٤ يوما فى حالة دهن الزبد المسيل ، ١٢ يوما فى السمن عند استعمال اختبار البيروكسيد . ويمكن اعتبار اختبار حامض الثيوباربيتوريك الاختبار المفضل فى قياس المراحل الأولى من الأكسدة فى دهن اللبن الجاموسى نظرا لأنه اكثر دقة وحساسية من اختبار البروكسيد . ليس لكل من الرقم اليودى « تركيز المركبات الكرميونيلية أى تأثير على طول فترة التحضين فى كل من دهن الزبد المسيل أو السمن المحضرة حديثا . بينما كانت هناك علاقة عكسية بين تركيز الأحماض الدهنية الغير مشبعة ثنائية الرابطة الزوجية المتبادلة وطول فترة التحضين .