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A COMPARATIVE INVESTIGATION OF HYDROLYTIC AND OXIDATIVE CHANGES IN LARD, INDUCED BY SHORTWAVE IRRADIATION AND HEATING

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Lard is a product with a comparatively low hydrolytic and oxidative stability. This is due to the low content of natural antioxidants in it(Chipanel,1945); to the content of linoleic acid(Pokorny,1963),and also to the evidance of substances with pro-oxidative effect in it,according to recent studies(Popov and Janishlieva,1976).

It is known that oxidation and hydrolysis processes in lipids run simultaneously and are mutually inductive(Popov,Janishlieva,1976). For that reason the quality control in lard is done by looking for the hydrolysis and oxidation processes in it at one and the same time. Methods for the determination of peroxide value by titration are widely used for oxidative changes. Hydrolytic processes are characterized by the method of acid value,determined by titration of FFA_s with potassium hydroxide.

Recently the analysis of food fats and the identification of oxidative products in them are performed more oftem by column,thin lyer and gas chromatography and also by spectrophotometry. Using those methods, one can get rapid and compleate information about the composition of fatty acids and on the degree of oxidation having only minimum amonts of fat. The relatiomship of fatty acids composition and oxidative stability of different fats is given in the regression equation of Stankova et al(1983) Using that method ,there is a possibility to estimate the oxidative stability of any fat if its fatty acid composition is determined by gas chromatography.

The UV spectra of unsaturated lipids are used for the estimation of their oxidation and for following the oxidative process. The concentration of peroxides in lipid systems is in a linear relationship with the increased concentration of conjugated systems which are stable structures Popov,Janishlieva(1976);Par,Swoboda(1976).

The aim of this study was to characterize the oxidative and hydrolytic processes in lard, followed by standard and modern spectrophotometric and gas chromatographic methods,

MATERIAL AND METHODS

The object of investigations was lard received in two manners:1) Melted in laboratory conditions in water bath at 60°C;2) Rendered in industrial conditions at temperatures within 88-95°C. Both kinds of fats were heated at 50°C or irradiated with UV rays in the presence of oxygen.

Hydrolytic processes were followed by the standard method and titration of total free fatty acids with 0,1n KOH.Parallelly with this analysis, the FFA_s from lard were arrested on a small Celite 545 column,impregnated with a saturated solution of Na_3PO_4 and identified quantitatively by GLC, according to the procedure of Schwartz,Gadjeva (at press).

Oxidative processes were followed by the standard procedure for the determination of peroxide value. Peroxide concentration was judged by the amount of 0,01n $Na_2S_2O_3$ necessary for binding the iodine freed by peroxides. At the same tome, total carbonyl compounds in lard were determined spectrophotometrically as the absorbance of their 2,4-DNPH- derivatives at 340 nm,According to Schwartz's method(1963).

RESULTATS AND DISCUSSION

The hydrolytic processes, developed in the lard treated in two ways were followed by the titrimetric and the column- chromatographphic methods. The results are given in Table 1. The quantity of FFA in lard,rendered under industrial conditions is higher, compared to those determined in lard melted in laboratory conditions. That is observed in the very beginning and also during the treatment, and can be explained with the very severe industrial conditions - permanent wet rendering at a temperature of 88 -95°C. UV irradiation of lard results in a more intensive hydrolysis,we get a larger amount of FFA than in the lard melted at 50°C. The ultimate acid value for food fats is 0,8% oleic acid, upon UV irradiation, this value gets higher already within one hour, although that in the laboratory melted lard it remains below that number during the same period. In both methods of treatment, a stepwise increase in FFA- content is noticed till the fifth hour, for the industrially rendered lard, and till the 24 hour -for the laboratory melted one. By the column -GLC method ,we obtain higher values for FFA. Although the differences in FFA content under the conditions of the experimen are not large, it is necessary to run a much greater number of analyses in addition to prove their statistical significance, and also to ensure the exact conditions of FFA isolation. The ratoi between USFFA and SFFA is given on the

basis of the GLC analyses. Generally, that ratio shows the tendency to decrease to a greater degree upon UV treatment for both types of processed lard.

Table 1:
Changes in FFA content of lard after UV treatment and heating, determined by standard and column-GLC methods

Hours of treatment	Lard obtained under laboratory conditions. Acid value as FFA as weight % per a % oleic acid 100g lard						Lard rendered under industrial conditions. Acid value as FFA as weight % per a % oleic acid 100g lard					
	50°C	UV	50°C	USFFA SFFA	UV	USFFA SFFA	50°C	UV	50°C	USFFA SFFA	50°C	USFFA SFFA
0	0,27	0,27	0,25	1,45	0,25	1,40	0,45	0,45	0,48	1,36	0,48	1,36
1	0,50	2,38	0,65	1,36	2,32	1,34	0,55	3,86	0,67	1,30	3,95	1,28
3	0,54	4,56	0,82	1,26	4,74	1,30	4,98	8,40	5,15	1,28	9,21	1,20
5	1,97	5,90	2,18	1,22	6,12	1,22	4,75	8,95	5,10	1,20	9,46	1,10
24	2,25	0,39	2,28	1,20	0,96	1,14	0,91	1,20	1,02	1,08	1,44	1,08
48	0,56	0,46	0,60	1,16	0,40	1,08	0,59	0,52	0,68	1,04	0,49	1,00

The oxidation of lard,monitored by peroxide value and the quantity of total carbonyl compounds, is shown in Table 2. The low values of both in the beginning increase gradually. The ultimate value for the concentration of peroxides- 3 miliequi-valent O_2/kg is reached on the first hour for both in industrially rendered lard. Comparatively high quantities of carbonyl compounds corespond to those values. Peroxide value below 3MEQ O_2/kg was found in laboratory melted lard, heated at 50°G till 48h, to which coresponds the lowest quantity of carbonyl compounds,

A sharp increase in the concentration of oxidized products is observed at 24 and 48 houres of treatment with UV- rays in the lard, obtained by two manners and also in industrial lard heated at 50°C. A fast decrease of FFA content and of the USFFA/SFFA ratio coresponds to those changes.It is obvious that oxidized products are due to the participation of FFA and particularly of the USFFA in the oxidation process under the influence of atmospheric oxygen. Hydrolytic and oxidative processes are more intensive on one hand in the lard obtained under industrial conditions, or the other hand in the one irradiated with UV-rays. It is a well known fact that short wafe light,especially-UV rays break down the natural antioxidants in fat,such as vitamines, primarily vitamine B_6.

So ,the more intensive processes of hydrolysis provoke a more intensive oxidation of fat

Table 2
Oxidized products from lard after UV shortwave treatment and heating, determined by standard and spectrophotometric methods

Hours of treatment	Lard obtained under laboratory conditions. Peroxide value meO_2/kg		Total carbonyls in M 2,4 DNPH/g lipid		Lard rendered under industrial conditions. Peroxide value me O_2/kg		Total carbonyls in M 2,4 DNPH/g lipid	
	50°C	UV	50°C	UV	50°C	UV	50°C	UV
0	0,90	0,98	3,09	3,00	1,34	1,34	4,46	4,46
1	0.39	0,35	6,48	6,66	3,51	4,91	8,80	9,25
3	0,40	2,34	6,48	6,66	3,12	6,84	10,70	11,34
5	2,18	5,92	6,66	11,57	2,34	13,26	14,60	16,07
24	2,49	19,56	7,36	14,81	8,60	26,40	23,14	28,24
48	2,73	29,84	8,15	16,05	19,48	40,15	24,07	30,09

On the basis of thiese investigations and the data obtained, we can conclude that the new column/GLC and spectrophotometric methods applied, show the same trend as classical ones when following hydrolytic and oxidative changes in lard. The new column GLC method for the determination of the FFA content is rapid, sensitive and gives the full information about the changes in individual fatty acids during the period of investigation. The spectrophotometric method for determining the total carbonyl compounds applied simultaneously with the classical titrimetric one for peroxide value gives the opportunity to get more compleate characteristics of oxidative processes and products in fat.

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