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THE ROLE OF THE ACIDITY OF LEMON JUICE AS A BUTTER DEOXIDANT

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In the previous work [1] it was shown that lemon juice, added to cream before churning in amounts from 0.5 to 5%, acts as an efficient deoxidant. Identical results were obtained for both freshly squeezed juice from the lemon and from that preserved in tins. The antioxidative effect of the citric fruit juice is ascribed partly to the ascorbic acid but, in the most part, to various flavonoids present in the juice in the form of highly methyxylated flavonols [2]. The strongly antioxidative effect of multihydroxyflavons as compounds capable, according to Uti [3], of fulfilling the role of free radical acceprots is also known.

We do not recommend a larger addition of lemon juice (exceeding 1%) to cream both for economic reasons and due to the fact that the increased acidity of butter can by itself reduce its oxidative life. In the present experiments we, therefore used smaller amounts of juice (only 0,2 to 1%) and we also examined the antioxidative role of the previously neutralized lemon juice.

For this, we produced on a laboratory scale 4 batches of butter with different loses of the original lemon juice, and another 4 batches with juice neutralized by means of $NaHCO_3$ down to about pH 6. For each batch, a separate dose of cream (containing 32 to 38% fot) pasteurized in an industrial plant, was used. The cream was cooled in the laboratory for a sufficiently long time and then the starter was added up to a content of 3%. The cream was batched into 5 doses of about 2 litres and each churned separately with the following additives:

1) pure cream as a control sample,
2) cream without juice added, but with an addition of 10 mg $CuSO_4 \cdot 5\,H_2O$/litre (2-nd control sample)
3) cream with 0.2% of lemon juice and 10 mg $CuSO_4 \cdot 5\,H_2O$/litre
4) cream with 0.5% of lemon juice and 10 mg $CuSO_4 \cdot 5\,H_2O$/litre
5) cream with 1% of lemon juice and 10 mg $CuSO_4$

For every batch of butter produced the titrated acidity (in Soxhlet-Henkel degrees), reduced vitamin C (i. e. ascorbic acid) and the general acidity (using our own methods [4]) were determined for the cream and butter-milk. Butter was rinsed and kneaded under laboratory conditions, with no salt added. Butter portions of about 0.5 kg wrapped in pergamin paper were stored for 6 weeks at 8 — 10°C. Periodical analyses were carried out after 0, 2, 4 and 6 weeks. Water content, dry fatless mass content, plasma acidity, fat acidity (by the Loftus-Hills-Thiel's method modified by Pietrzyk [5]) and oxidation of fat treated with thiobarbituric acid were determined for the butter. The taste and flavour of the butter were also determined and recorded.

At an early stage it appeared that:

a) lemon juice added to cream in an amount not exceeding 1% of cream by volume resulted in an insignificant increase in vitamin C content and titrated acidity as compared with the original values;

b) as a result of lemon juice neutralization with NaOH and Na_2CO_3, $NaHCO_3$ or $CaCO_3$, almost all the vitamin C (also present under the form of dehydroascorbic acid) was lost;

c) churning results in a marked drop in vitamin C content in buttermilk (down to about 50%, considering different fat contents in cream and buttermilk).

Table 1 is an illustration of these results for two random experimental batches.

Table 1

Titrated acidities and vitamin C content in cream immediately before churning, and in buttermilk (ilustrative values: 7th and 8th series of experiments)

Series Kind of lemon juice	Additives to cream		Accidity		Vitamin C in mg/100 g			
					Cream		Buttermilk	
	Lemon juice	$CuSO_4 \cdot 5H_2O$ mg/l	cream	buttermilk	Total	Red.	Total	Red.
VII Non-neutralized	0	0	10.8	12.5	1.47	1.26	1.27	1.08
	0	10	10.8	12.4	1.47	1.24	1.24	1.04
	0.2%	10	12.0	13.0	1.49	1.27	1.29	1.09
	0.5%	10	13.4	14.5	1.56	1.36	1.36	1.13
	1.0%	10	15.4	17.4	1.76	1.50	1.54	1.27
VIII Neutralized juice	0	0	10.2	10.4	1.47	1.24	1.29	1.10
	0	10	10.2	10.4	1.45	1.21	1.29	1.09
	0.2%	10	10.2	10.5	1.47	1.24	1.31	1.11
	0.5%	10	10.4	10.6	1.47	1.25	1.29	1.10
	1.0%	10	10.4	10.6	1.45	1.23	1.29	1.10

Results of the actual examination of butter are illustrated in the collective diagrams in Figs. 1—5. For reasons of brevity, mean values for 4 consecutive series of experiments have been given in the tables; it should be emphasized that the results for the individual series of tests were regular and unambiguous.

Fig. 1 shows that the larger the dose of juice, the stronger was the antioxidative action of the non-neutralized lemon juice, and that for

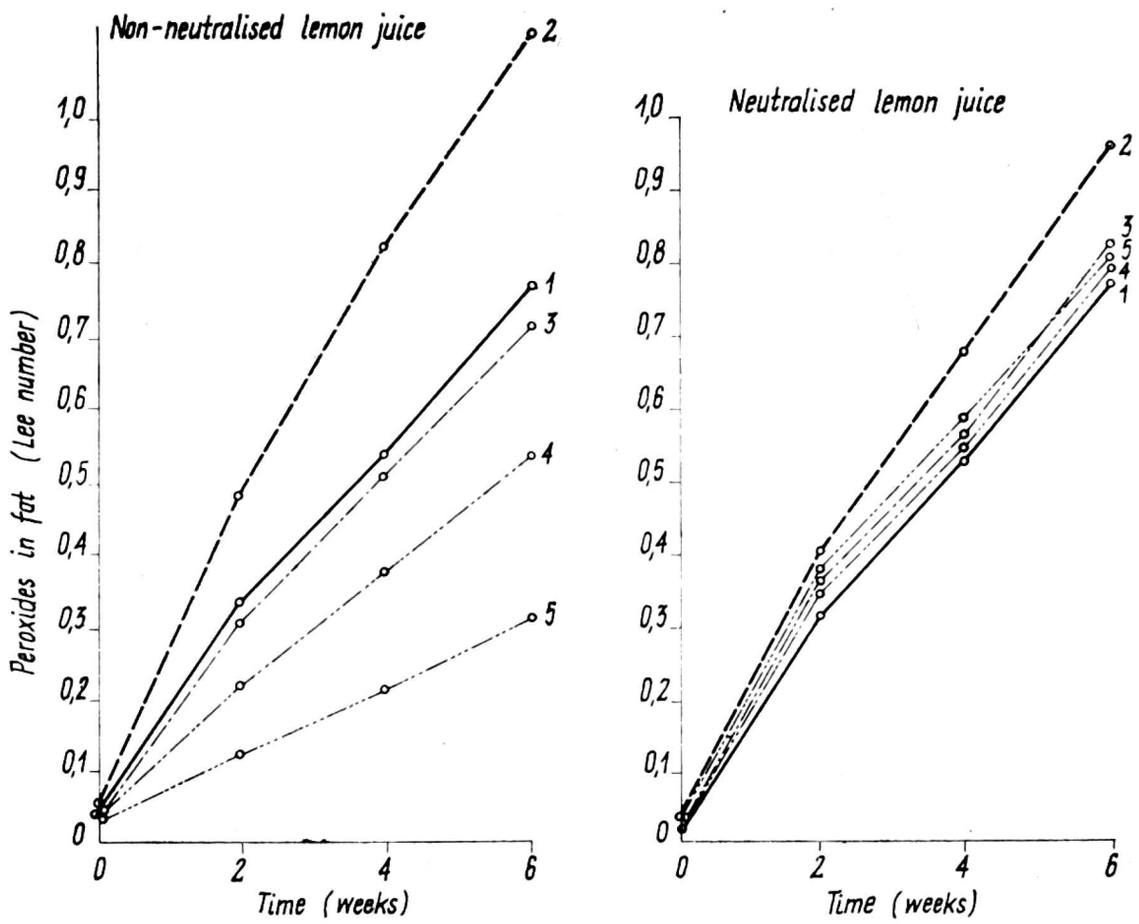

Fig. 1. Increments in the peroxide content (as a Lee number) in the fat of butter stored for 6 weeks at 8—10°C, with various doses of non-neutralised or neutralised lemon juice added: 1 — cream without lemon juice and copper; 2 — cream without lemon juice, but with 10 mg $CuSO_4 \cdot 5\,H_2O$/litre added; 3 — cream with 0.2% of lemon juice plus 10 mg $CuSO_4 \cdot 5\,H_2O$/litre; 4 — cream with 0.5% of lemon juice plus copper added as above; 5 — cream with 1% of lemon juice and copper as above

a 1% dose of juice the final peroxide content in fat was 3—4 times lower than in the respective control sample (butter without juice, but with $CuSO_4$). Moreover, experiments with neutralized juice confirm that this juice has a very weak antioxidative action. This has been confirmed in an analogous way by the results obtained from determining the degree of oxidation and of butter fat in the test, using thiobarbi-

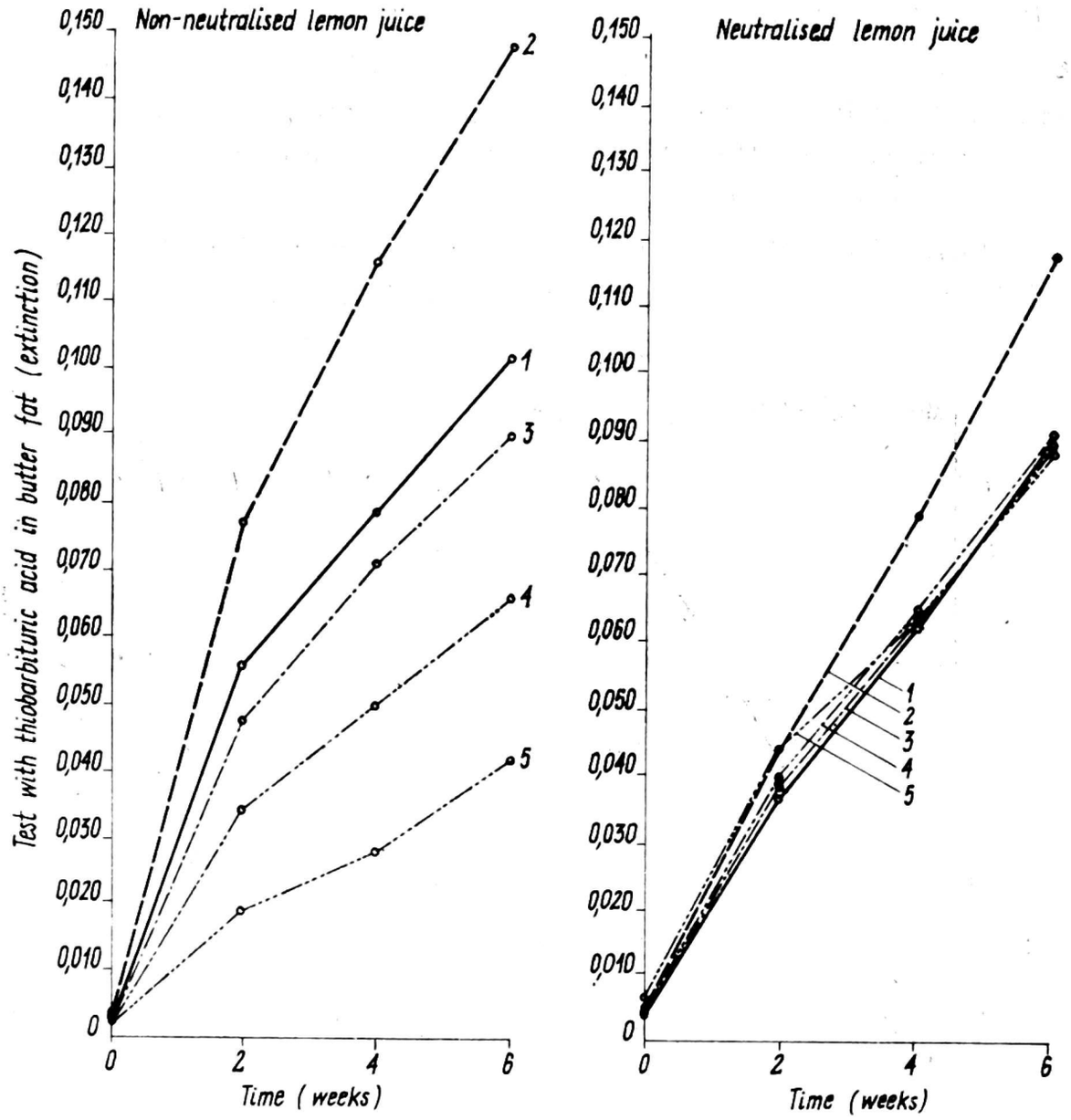

Fig. 2. The rate of butter fat oxidation in a sample with thiobarbituric acid during a 6-week storage period at 8—10°C with various doses of lemon juice added to the cream

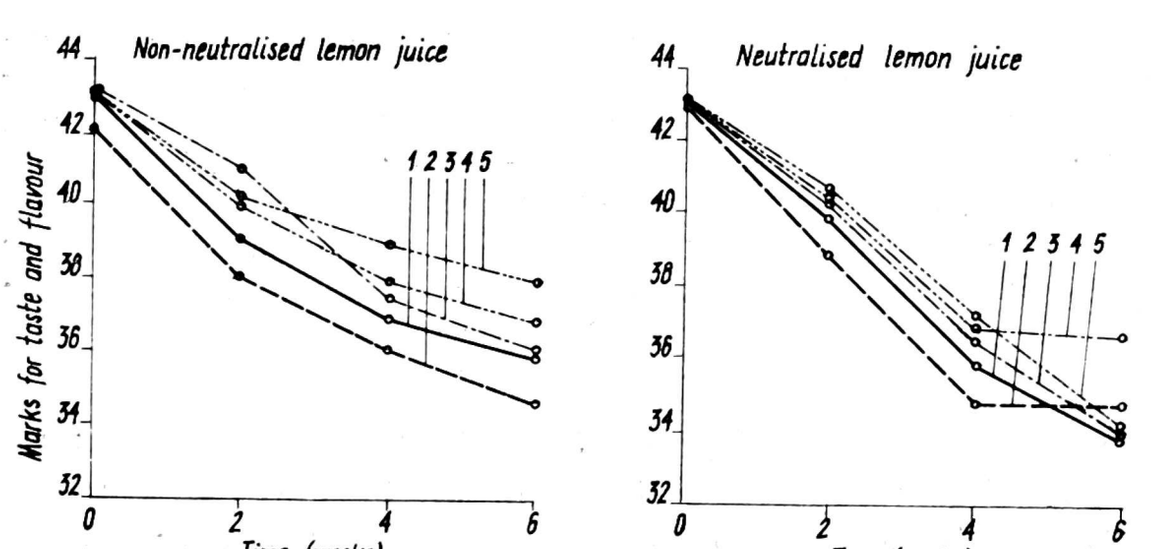

Fig. 3. Changes in the number of points obtained for the taste and flavour of the butter samples, with various doses of lemon juice added, during the 6-week storage period at 8—10°C

turic acid (Fig. 2) which, according to Patton and Kurtz [7] is supposed to react mainly on B -ketoaldehydes.—

From Fig. 3 we may conclude that generally speaking the application of lemon juice (the neutralized juice to a lesser extent) adds to the taste and flavour of butter; these are more easy to establish in the final stage of butter sample storage.

Fig. 4 shows that the increase of butter fat was uniform and similar in all the butter samples; however acidity increase with time was somewhat higher for samples with lemon juice, this being consistent, in

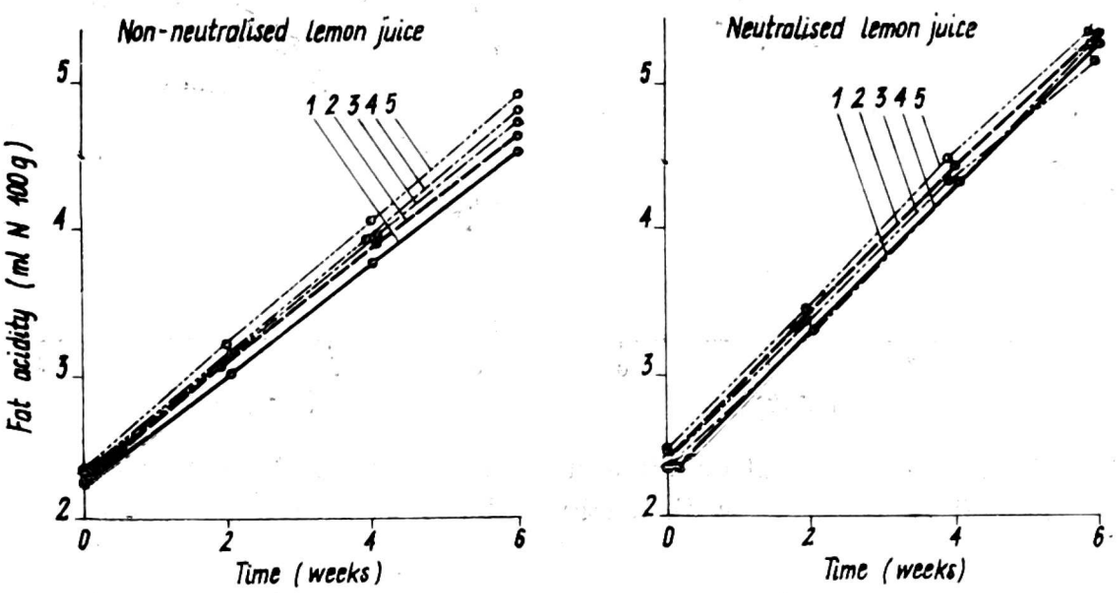

Fig. 4. Changes in butter fat acidity during the 6-week storage period at 8—10°C, with various doses of lemon juice added to the cream

general, with views regarding the antithetic character of the hydrolytic and oxidative processes of butter rancidation.

Finally, Fig. 5 shows the increments of acidity in the so-called water phase of butter, or its „plasma". Taking into account differences in cream acidity caused by the addition of lemon juice, we can state that the rate of increase is almost identical for all batches of the butter produced. It can also be assumed that the citric acid in the juice could have stimulated the development of milk acid bacteria (heterofermentative) to a certain extent. The relatively large increase in plasma acidity can also be regarded as evidence that butter samples obtained under laboratory conditions were not kneaded sufficiently well; the weak dispersion of the water phase could facilitate its acidification.

Summarizing the results, one must consider whether the almost complete absence of antioxidative action on the part of neutralized lemon juice should be ascribed chiefly to the lack of vitamin C. Taking into consideration the fact that even a 1% addition of juice increased the

content of ascorbic acid in cream by only 20—30%, and that usually the normal content of this acid is neglected when considering the oxidative life of butter, one is tempted to assume that the process of neutralization and the accompanying mixing or precipitation of lemon juice results in the simultaneous oxidation of the synergetically acting flavo-

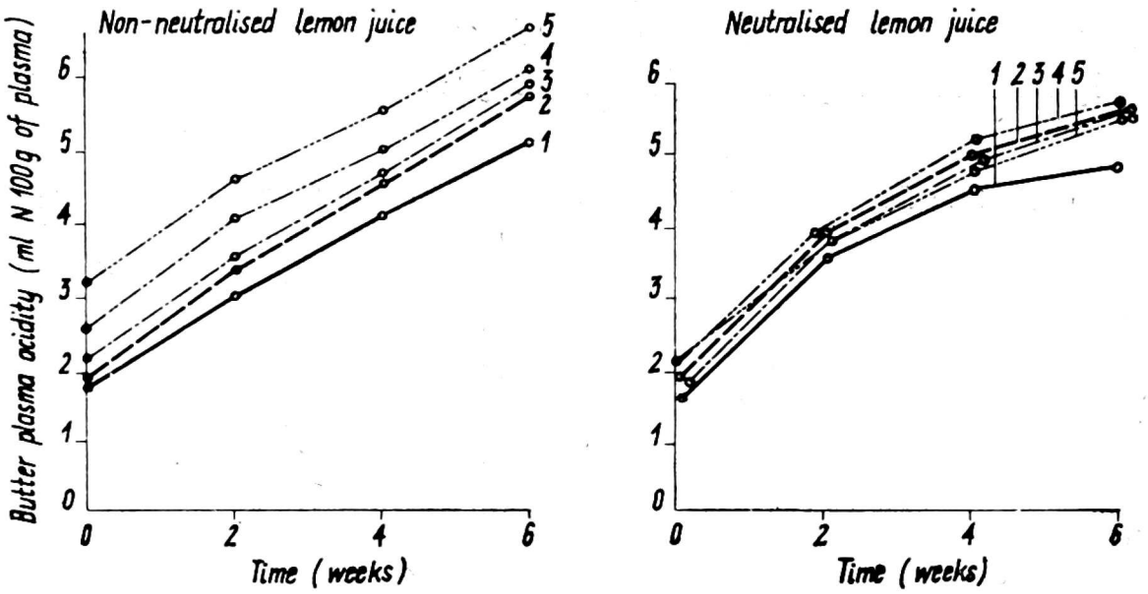

Fig. 5. Changes in butter plasma acidity during the 6-week storage period at 8—10°C, with various doses of lemon juice added

noids. Since we so far know only a little about the oxidation of polyphenols in a weak alcalic medium and since opinions as to the oxidation of flavonols and hydroxyflavons in an alcalic medium in the open air are divided, in this particular case we should restrict ourselves to the final remark that the neutralized lemon juice does not satisfactorily fulfill its antioxidative role in butter.

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Streszczenie

ROLA KWASOWOŚCI SOKU CYTRYNOWEGO JAKO PRZECIWUTLENIACZA DO MASŁA

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W kilku seriach laboratoryjnych prób z wyrobem masła z dodatkiem do śmietany soku z cytryn w dawkach 0,2 do 1% potwierdzono za pomocą paru testów chemicznych, że sok taki dobrze spełnia swe działanie antyoksydatywne w maśle i że jednak użycie soku z cytryn zobojętnionego (z pomocą $NaHCO_3$ do pH ok. 6) nie daje już prawie wcale efektu antyoksydatywnego w maśle. Stwierdzono także, że już po neutralizacji soku zanika w nim prawie w całości kwas askorbinowy (i dehydroaskorbinowy). Próby te nie dowodzą, że istotnym antyoksydatywnym czynnikiem w soku cytrynowym jest witamina C.

Résumé

LE RÔLE DE L'ACIDITÉ DU JUS DE CITRON COMME ANTIOXYDANT DANS LE BEURRE

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On a effectué 4 séries d'expériences de laboratoire qui consistaient en une fabrication de beurres avec différentes quantités de jus de citron (0, 0,2%, 0,5% et 1% ajoutés à la crème juste avant le barattage. Dans chaque série on employait, parallèlement, un jus de citron naturel ou un jus neutralisé.

On a confirmé nos résultats antérieurs (Pijanowski et Jasiewski, 1961) quant à l'action antioxygène, très distincte, du jus de citron non neutralisé et, en outre, on a démontré que le jus neutralisé devient dépourvu de son action antioxydative. Quoique le jus neutralisé ne contenait que des traces d'acide ascorbique ou déhydroascorbique, cet abaissement drastique de la capacité antioxydative du jus neutralisé peut être liée à l'oxydation des substances flavonoïdes du citron.

Les altérations d'échantillons de beurres stockés pendant 6 semaines à 8—10°C ont été illustrées par les indices Lea de peroxydes (fig. 1), par l'épreuve à l'acide thiobarbiturique (fig. 2), par les cotations pour goût et odeur (fig. 3), par les acidités de la matière grasse (fig. 4) et les acidités du sérum de beurre (fig. 5). Les 4 séries d'expériences ont donné des résultats à peu près identiques.

Summary

THE ROLE OF THE ACIDITY OF LEMON JUICE AS A BUTTER DEOXIDANT

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4 series of laboratory experiments, involving the manufacture of butter from cream to which various quantities of lemon juice (0%, 0.2%, 0.5% and 1%) had been added just before churning, were effected. In each series original lemon juice and a neutralized one were used in parallel.

Our former results (Pijanowski and Jasiewski, 1961) regarding the very distinctive antioxydant activity of the nonneutralized lemon juice were borne out, and it was also shown that neutralized juice becomes devoid of its antioxydative activity. Though neutralized juice contained only some traces of ascorbic or dehydroascorbic acids, this drastic lowering of the antioxydant capacity of neutralized quice may be related to the oxydation of the flavonoid substances of the lemon.

The spilage process of butter samples stored over a week at 8—10°C has been illustrated by the „Lea" peroxyde indexes (Fig. 1), by the thiobarbituric acid test (Fig. 2) by marks attributed for flavour and odour (Fig. 3), by fat acidities (Fig. 4), and the acidities of butter serum (Fig 5). The four series of experiments gave almost identical results.

Zusammenfassung

ZITRONENSAFT ALS ANTIOXYDANT IN DER BUTTER

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Vier Versuchsreihen sind im Laboratorium durchgeführt worden. Dabei wurde Butter, mit verschiedenen Zusätzen des Zitronensaftes (0,0, 0,2, 0,5 und 1,0%) zur Sahne unmittelbar vor dem Butterungsprozess, hergestellt. Eine jede Reihe umfasste einen Parallelversuch mit natürlichem und neutralisiertem Zitronensaft.

Die früheren Ergebnisse (Pijanowski und Jasiewicz, 1961) hinsichtlich der sehr deutlichen antioxydativen Wirkung des nicht neutralisierten Zitronensaftes wurden bestätigt. Es konnte bewiesen werden, dass der neutralisierte Saft diese antioxydative Wirkung verliert. Obwohl der letztere nur Spuren der Askorbin- oder der Dehydro-Askorbinsäure enthielt, so kann diese drastische Senkung der antioxydativen Wirkung im Zusammenhang mit der Oxydation der Flavonstoffe des Zitronensaftes erklärt werden.

Auf die Veränderungen der während 6 Wochen bei 8—10°C gelagerten Buttermuster wurde nach der Peroxydzahl (Abb. 1), nach dem Thiobarbitursäuren-

nachweis (Abb. 2), nach der Beurteilung des Geschmacks und des Geruchs (Abb. 3), nach dem Säauregehalt der Fette (Abb. 4) und nach dem Säuregehalt der Molke (Abb. 5) hingewiesen. Die vier durchgeführten Versuchsreihen ergaben ungefähr indentische Ergebnisse.

Резюме

РОЛЬ КИСЛОТНОСТИ ЛИМОННОГО СОКА, ПРИМЕНЯЕМОГО В КАЧЕСТВЕ АНТИОКСИДАНТА ДЛЯ МАСЛА

Э. ПИАНОВСКИ, Б. ШУЛЯКОВСКА, С. ЗМАРЛИЦКИ (ВАРШАВА)

Проведено несколько серий лабораторных испытаний, заключающихся в получении масла из сметаны с добавкой от 0,2 до 1% лимонного сока. Несколько химических анализов показало, что этот сок хорошо защищает масло от окисления, однако применение нейтрализованного сока (при помощи $NaHCO_3$ pH доводили до 6) почти не дает антиоксидантного эффекта в масле. Установлено также, что после нейтрализации сока почти полностью исчезает аскорбиновая (и дегидроаскорбиновая) кислота. Эти опыты не доказывают, что существенным антиоксительным агентом является витамин С.