EFFECT OF PRE-TREATMENT ON THE QUALITY OF SMOKED BALTIC SPRATS

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Baltic sprats (Sprattus sprattus balticus) are a good source of protein, vitamins D₃, B₁₂, minerals, and unsaturated fats. In response to consumer demand, various types of fish products of stable quality are available all year round. Pre-treatment with brine containing acetic acid, salt (NaCl), and/or granulated CaCl₂ in various concentrations and proportions can be used to stabilise quality. The aim of the study was to evaluate the effect of various pre-treatment methods on smoked Baltic sprat sensory and technological parameters. Prior to smoking, fish was treated in a solution of additives in various proportions for 30 min. Untreated sprats were used as a control sample. The use of pre-treatment allowed reduction of the smoking losses; the combination of NaCl and acetic acid resulted in about 26% smoking loss. If no pre-treatment was applied, the drying losses after 24-hour storage were 1.6%, while using the solution of NaCl and CaCl₂ it decreased to 0.3%. Both the pre-treatment method and freezing affected fish pH. The pH of smoked fresh sprats was 6.73 and for smoked frozen sprats, it was 6.38. Sensory testing using the Just About Right (JAR) method demonstrated that the use of acetic acid made smoked fish texture firmer.

Keywords: fresh and frozen sprats, brine, smoking, texture, sensory attributes.

INTRODUCTION

Sprats are one of the most used fish in Latvian fish processing companies, because the demand is growing and the annual catch is continuously increasing, and is annually 300 000 tonnes in the Baltic sea (Usydus *et al.*, 2012). Baltic sprats are seasonal fish with no stable quality all year round, with changing chemical composition, and it has an impact on raw material quality. The quality of raw material is a main factor affecting the quality of the final product. Baltic sprats (*Sprattus sprattus balticus*) are small (10–20 cm long), easily perishable and fatty fish, which are very nutritionally valuable. They contain high levels of proteins 15–17%, water 57–73%, lipids 10–24% and ash 2–4% (Timberg *et al.*, 2011). They are a good source of vitamins (B₁₂ and D₃), minerals (iodine, selenium), and unsaturated fatty acids (omega-3 fatty acids — eicosapentaenoic acid and docosahexaenoic acid) (Merdzhanova *et al.*, 2018). Timberg *et al.* (2011) reported correlation between lipid and water content; the lipid content increases and water content decreases in autumn and typically, all producers prefer the use of sprats caught in autumn. Composition parameters vary during the season and sprats caught in autumn have the best sensory characteristics.

The main parameters that affect the final product quality are raw material quality, processing technology, storage time and temperature. pH is an indicator of fish freshness; fresh fish pH is about 7 (Abbas *et al.*, 2008), for smoked fish it is about 6.7–6.8. During storage, the pH increases because alkaline bacteria start growing and due to histidine decarboxylase synthesis. Abbas *et al.* (2008) reported that sensory attributes have a key role in quality assessment. Sensory evaluation in the fish industry allows quick identification of defects. However, to provide stable quality, there is an option to use some pre-treatment methods, like application of NaCl, CaCl₂ and acetic acid. These additives are cheap, easy to obtain and are usual additives in fish processing company.

The use of some pre-treatment methods and smoking are among the traditional and oldest methods to prevent food oxidation and natural degradation of compounds, to ensure stable quality all year. In the smoking process, lipid, protein, salt content increases along with a decrease in water content (Lerfall and Østerlie, 2011). Salt together with smoke or other additives are important factors to reduce microbiological activity. An increase of salt concentration decreases water content in fish and makes the texture firmer

(Bjørnevik *et al.*, 2018). Pre-treatment improves quality. It tenderises muscle cells of fish, because water holding capacity decreases, there are water losses and additives diffuse in muscle cells (Özden, 2005). The use of acetic acid in pre-treatment allows decreasing pH. It involves ionic strength increase, it tenderise the texture and extends the shelf life of the final product (Serdaroglu *et al.*, 2015). Frozen fish muscle texture changes during storage. The product becomes hard and dry, the water holding capacity decreases and textural properties such as juiciness decrease (Andrews, 2014). Freezing and thawing affect fish hardness, colour changes and oxidation of lipids, and promotes free amino acid formation (Timberg, 2012). Textural changes during cooking affects proteins. Myofibril (myosin and actin) starts shrink above 60 °C and muscle starts to toughen, and stromal protein hydrolyses connective tissue, weakening it. Differences in pH are responsible for changes in colour (Adebisi and Virginia, 2012).

The aim of the study was to evaluate the effect of various pre-treatment methods on smoked Baltic sprat sensory and technological parameters.

MATERIALS AND METHODS

Raw material. In the experiments two types of sprats caught in the Baltic Sea West of Gotland (FAO27. III. d. 28. 2) were used — fresh and frozen. Fresh samples were obtained from fish caught in September 2020 using an otter trawl method (OTM), fish size 1 and freshness category A. Frozen samples were obtained from fish caught in September 2019 using an OTM, and stored at -18 ± 2 °C with relative air humidity $75 \pm 5\%$; the freshness and the size category were the same as that of fresh sprat. Sprats were frozen in 10 kg blocks covered with polyethylene bag, packaged in the cardboard boxes and delivered to the company freezer for further storage.

The following ingredients were used for fish pre-treatment: acetic acid (E260) purchased from supplier company “Safrans” (Riga, Latvia), fine NaCl salt “Ekstra” (Mozirsol, Belarus), and granulated calcium chloride anhydrous CaCl_2 (E509, CaCl_2 content (97%), $110.99 \text{ g} \cdot \text{mol}^{-1}$, Lachner, Czech Republic).

Preparation of fish samples. First, the brine solutions were prepared according to the concentrations indicated in Table 1. The frozen fish before use was defrosted in a water spray defroster until the internal temperature reached 0 °C, and then the fish were soaked in brine for 30 minutes.

After pre-treatment, the fish were hot smoked in a commercial smoking chamber (Rauch Spectrum, Germany) with an automatic control system using beech wood chips. The main processing parameters were selected as follows: drying 35–38 minutes, cooking 10–12 minutes, steam 2–5 minutes, smoke 10–15 minutes, and cooling 5–10 minutes. Three batches of smoked fish were made per pre-treatment type.

Table 1. Sample abbreviations and pre-treatment methods applied

Identification of samples	Ingredients per 1 kg of brine, g		
	NaCl	CaCl_2	Acetic acid
Control	–	–	–
Na	29.13	–	–
3Na2Ca	28.64	16.71	–
2Na3Ca	16.70	28.64	–
Ace	–	–	9.90
NaAce	28.84	–	7.14
CaAce	–	28.84	7.14

Sensory evaluation. The smoked fish samples were analysed using Just-About-Right (JAR) scaling to measure the sensory attribute (colour, texture, flavour, and taste) intensity and acceptability. Each smoked fish sample was rated on a 5-point JAR non-structured scale with the following description — 1 “too little” to 5 “too much” and 3 middle “Just-About-Right” where “the right” was ideal for descriptor and endpoints (too high and too low). Eight experts (three male and four female, average age 42 years) from the fish processing company participated in the sensory evaluation of smoked fish. The evaluation was performed in two sessions, with 14 samples in two days. Fresh smoked sprat samples were evaluated on the first day, and frozen smoked sprat samples on the second day. Smoked fish samples for the sensory evaluation were served randomly and each sample was marked with random 3-digit number. Warm black tea and crackers were provided to clean the palate between samples.

Determination of smoking and drying losses. The smoking loss (SL) is one of the main technological parameters of interest to the producer. Lower smoking losses provide larger income from the final product. The smoking losses were calculated using weight before pre-treatment and weight after smoking in g:

$$SL, \% =$$

$$\frac{\text{weight before pretreatment, g} - \text{weight after smoking, g}}{\text{weight before pretreatment, g}} \times 100$$

Values below 30% are considered very good, because typically in production smoking loss ranges between 35–50%, where 50% or above is considered unacceptable.

After smoking, the fish can be used immediately or stored in cooling chambers at 2 ± 1 °C for 48 hours till further processing. Fish was stored in perforated plastic boxes. Typically, the highest drying losses (DL) are observed within first 24 hours with further changes below 0.5%. Therefore, for study purposes, fish after smoking was cooled for 24 hours before evaluation of drying loss according to the following formula.

DL, % =

$$= \frac{\text{weight before storage, g} - \text{weight after storage, g}}{\text{weight before storage, g}} \times 100$$

Determination of pH. For pH testing, 1 g of blended smoked fish sample was mixed to make a homogenous mass and 9 g of distilled water was added, stirred and tested immediately using a pH-meter JENWAY 3520 (Jenway, EU). Each sample was tested in triplicate.

Determination of colour. For testing of smoked fish colour, the sample was placed on a wooden pad and covered with polyethylene film. For colour measurements, a ColorTec-PCM (Accuracy Microsensors Inc., ASV) with software Color Tec – Color Sowf QCW for data analysis was used. Colour was measured on the surface of 5–7 smoked fish, obtaining at least ten measurements, not more than three per one fish.

Determination of texture. For texture analysis, a texture analyser TA.HD.Plus (Stable Microsystems, UK) equipped with a Warner-Bratzler blade set with a knife was used. Each fish was cut longitudinally and the bone removed, resulting in two pieces of sprat fillet. The width of each piece was measured before cutting and added as a parameter in the software. Then the fish was placed longitudinally on the slotted platform, and the blade was moved at $2 \text{ mm} \cdot \text{s}^{-1}$ for 10 mm. Each fillet was cut once to obtain cutting strength ($\text{N} \cdot \text{mm}^{-1}$), which shows the firmness of the fish. At least seven measurements were made per sample.

Statistical analyses. All results were reported as average values. Averages and standard deviations ($\pm$ SD) were calculated using MS Office Excel 2016 software. The results of sensory evaluation were analysed using Penalty analysis software XLSTAT 2020 (Addinsoft, USA). Penalty analysis was used to identify sensory quality, i.e. overall liking, based on the sensory attributes presented to experts.

RESULTS

The pre-treatment method applied affected fish weight after soaking. Fish weight loss may reach 5% during soaking, but as the diffusion of additives in fish muscle cells has been started before smoking, it can decrease smoking losses in technological process. Smoking includes also drying, cooking, adding smoke, and cooling. Smoking and drying losses are reported in Table 2.

The smoking losses without any pre-treatment were similar for fresh and frozen sprats (about 30%): 1.6% and 1.8%, respectively. Overall, lower losses for fresh fish were observed compared to frozen sprats. The use of NaCl resulted in smoking losses similar to the control sample. Using this method drying losses in the cooling chamber were about 3.4–3.5%, and using NaCl in combination with acetic acid decreased smoking losses by about 4–5%, reached the lowest value (loss of 25–26%) among the treatments. Using this combination, the drying losses were 2.10–2.20% and the

Table 2. Smoked sprat technological losses

Samples	Smoking losses, %		Drying losses, %	
	fresh (F)	frozen (FR)	fresh (F)	frozen (FR)
Control	29.57 $\pm$ 0.64	29.68 $\pm$ 0.27	1.60 $\pm$ 0.16	1.80 $\pm$ 0.06
Na	28.04 $\pm$ 0.17	30.39 $\pm$ 0.58	3.40 $\pm$ 0.34	3.50 $\pm$ 0.07
3Na2Ca	32.31 $\pm$ 0.26	30.76 $\pm$ 0.56	0.30 $\pm$ 0.03	0.40 $\pm$ 0.07
2Na3Ca	30.73 $\pm$ 0.44	31.95 $\pm$ 0.07	1.70 $\pm$ 0.17	1.70 $\pm$ 0.03
Ace	22.09 $\pm$ 0.09	33.02 $\pm$ 0.17	4.90 $\pm$ 0.56	4.80 $\pm$ 0.40
NaAce	26.05 $\pm$ 0.20	25.67 $\pm$ 1.54	2.10 $\pm$ 0.24	2.20 $\pm$ 0.10
CaAce	32.21 $\pm$ 0.02	36.09 $\pm$ 0.11	0.60 $\pm$ 0.06	0.80 $\pm$ 0.03

Means and standard deviations are presented (n = 3).

sum of losses after 24 hours was below 30%, which was the best result in our study. That means that treatment with cooking salt and acetic acid can reduce smoking losses. Acetic acid for fresh smoked sprats allowed reducing smoking losses to 22% and for frozen smoked sprats — 36%.

Smoking losses reached 32% when the combination of salt (CaCl_2) and acetic acid was used, and this treatment lowered the drying losses after 24-hour storage to 0.6–0.8%.

The pre-treatment method had an influence on smoked sprat sensory attributes (colour, texture, taste, flavour) intensity and liking. The results were similar for fresh smoked and frozen smoked sprats, except for texture (Tables 3–4). For both control samples, all analysed sensory properties were less pronounced and acceptable to the experts (Tables 3 and 4). From analyses of the obtained data, it can be concluded that the texture of the control sample was not significantly affected by the pre-treatment method; it was too soft (75% of the experts recorded too little). Based on the penalty analysis of fresh smoked and frozen smoked sprats colour, we can recommend to use combinations of NaCl and CaCl_2 (2Na3Ca and FR_2Na3Ca) and CaCl_2 and acetic acid (CaAce and FR_CaAce) to improve product colour (Tables 3 and 4). Penalty analysis results showed that for fresh smoked sprats, addition of different ingredients can influence flavour intensity and overall acceptance. However, for frozen smoked sprats, the addition of acidic acid gives a sour aroma, which gives ambiguous results — some liked it (37.5% — JAR), while some indicated it being too pronounced (25% — too much) or insufficient (37.5% — too little). Taste of samples Ace, FR Ace was too acid (75% and 63%) and the intensity needs to be reduced. The addition of different salts (NaCl and CaCl_2 combination) can improve smoked sprats taste.

For fresh fish, the pH was about 7, and after smoking it decreased to 6.38 for frozen and 6.73 for fresh smoked sprats (Table 5). The pH of fresh smoked sprats without treatment was the highest. Pre-treatment with acetic acid and CaCl_2 reduced pH to 5.74 for fresh and 5.51 for frozen fish. The pH is responsible for microbiological activity and ensures product shelf life. The combination of CaCl_2 and NaCl, irrespective of the proportion decreased pH to 5.88 and 5.94 for frozen and fresh sprats, respectively.

Table 3. Penalty values (%) of fresh smoked sprats

Sensory attribute	Parameter	Control	Na	3Na2Ca	2Na3Ca	Ace	NaAce	CaAce
Colour	Too little	62.5	37.5	12.5	0	0	0	0
	JAR	37.5	37.5	50.0	62.5	75.0	62.5	87.5
	Too much	0	25.0	37.5	37.5	25.0	37.5	12.5
	Penalties		0.133	0				
Texture	Too little	75.0	37.5	12.5	12.5	0	0	0
	JAR	25.0	62.5	75.0	50.0	37.5	87.5	62.5
	Too much	0	0	12.5	37.5	62.5	12.5	37.5
	Penalties			-0.5	0.25			
Flavour	Too little	87.5	25.0	0	0.	0	12.5	12.5
	JAR	12.5	62.5	62.5	87.5	62.5	87.5	75.0
	Too much	0	12.5	37.5	12.5	37.5	0.0	12.5
	Penalties		0					0.667
Taste	Too little	87.5	25.0	12.5	25.0	0	0	12.5
	JAR	12.5	37.5	75.0	62.5	37.5	75.0	50.0
	Too much	0	37.5	12.5	12.5	62.5	25.0	37.5
	Penalties		0.333	-0.500	0.200			0.25

Table 4. Penalty values (%) of frozen smoked sprats

Sensory attribute	Parameter	FR_Control	FR_Na	FR_3Na2Ca	FR_2Na3Ca	FR_Ace	FR_NaAce	FR_CaAce
Colour	Too little	87.5	62.5	75.0	0	37.5	12.5	12.5
	JAR	12.5	37.5	25.0	62.5	62.5	50.0	75.0
	Too much	0	0	0	37.5	0	37.5	12.5
	Penalties						0.500	-0.333
Texture	Too little	75.0	62.5	37.5	37.5	12.5	0	0
	JAR	25.0	37.5	62.5	37.5	25.0	75.0	62.5
	Too much	0	0	0	25.0	62.5	25.0	37.5
	Penalties				-0.200	0.500		
Flavour	Too little	62.5	37.5	37.5	12.5	37.5	12.5	37.5
	JAR	25.0	50.0	62.5	75.0	37.5	75.0	50.0
	Too much	12.5	12.5	0.0	12.5	25.0	12.5	12.5
	Penalties	0	-0.500		0	0.533	0.667	0
Taste	Too little	62.5	37.5	12.5	25.0	0.0	12.5	0
	JAR	25.0	25.0	75.0	75.0	25.0	50.0	87.5
	Too much	12.5	37.5	12.5	0	75.0	37.5	12.5
	Penalties	-0.167	-0.167	0.167			-0.250	

Table 5. Sprat pH after pre-treatment

Samples	Fresh (F)	Frozen (FR)
Control	6.73 ± 0.01	6.38 ± 0.03
Na	6.43 ± 0.01	6.53 ± 0.01
3Na2Ca	5.94 ± 0.03	5.88 ± 0.02
2Na3Ca	5.91 ± 0.01	5.90 ± 0.04
Ace	6.36 ± 0.03	6.28 ± 0.05
NaAce	6.22 ± 0.03	6.12 ± 0.04
CaAce	5.74 ± 0.06	5.51 ± 0.10

Means and standard deviations are presented (n = 3).

The lightness (L*) was 58.19 for samples of fresh smoked sprats without pre-treatment and 54.04 for frozen smoked

sprats (Table 6). The L* value for fresh smoked sprat decreased to 39.91–47.41 in samples treated with the combination of CaCl₂ and NaCl. This confirmed that samples of fresh smoked sprats are lighter than frozen samples. Additionally, more yellow colour was observed for frozen smoked sprats pre-treated with acetic acid (b* value 36.51) compared to fresh smoked sprats (b* value 28.48).

For all samples, using NaCl or CaCl₂ without acetic acid, lightness increased more for frozen smoked sprats than for fresh, but with acetic acid it increased more for fresh smoked sprats.

One of the most important smoked sprat quality parameters is the texture. If it is low, the texture is too soft. The texture is better if the cutting strength is higher (Fig. 1).

Table 6. Colour of smoked fish

Samples	L*		a*		b*	
	fresh	frozen	fresh	frozen	fresh	frozen
Control	58.16 ± 11.09	54.04 ± 9.31	-10.32 ± 1.99	-6.29 ± 6.91	26.81 ± 10.84	27.97 ± 12.42
Na	56.97 ± 14.61	62.11 ± 12.53	-6.09 ± 3.25	-4.82 ± 10.29	25.01 ± 13.98	21.11 ± 9.04
3Na2Ca	47.41 ± 12.78	55.78 ± 6.84	-8.19 ± 9.33	-5.04 ± 9.21	25.80 ± 15.49	20.45 ± 17.76
2Na3Ca	39.91 ± 8.27	50.69 ± 11.77	-5.82 ± 7.13	-4.86 ± 14.10	20.55 ± 14.00	26.51 ± 14.82
Ace	50.75 ± 14.73	61.15 ± 8.34	-10.76 ± 9.40	-11.55 ± 8.89	28.48 ± 14.20	36.51 ± 10.69
NaAce	54.43 ± 10.97	50.43 ± 8.93	-9.91 ± 5.06	-13.83 ± 9.77	33.43 ± 9.83	28.25 ± 10.73
CaAce	59.05 ± 11.77	58.62 ± 12.1	-10.99 ± 8.71	-8.81 ± 9.13	30.48 ± 12.01	28.00 ± 6.84

Means and standard deviations are presented (n = 10).

Fig. 1. Cutting strength required to shear fish fillet.

Significantly softer texture was observed for fresh smoked sprats compared to frozen sprats. The pre-treatment method had various effects on the texture of fresh or frozen fish. The pre-treatment of frozen sprats with NaCl caused softening of the texture, reaching similar values to fresh sprats.

DISCUSSION

The use of pre-treatment can improve the quality of smoked sprats, but there is a need to determine which methods can improve quality during the particular catching season. During the season there are changes in the quality of Baltic sprats and the composition, and there is a correlation with lipid and water content, with the highest lipid amount in autumn (Timberg *et al.*, 2011). Pre-treatment and freezing (ice crystal formation, protein denaturation, lipid oxidation etc.) (Dawson *et al.*, 2018) affect fresh or frozen sprat quality and technological changes; it can improve and give better results than using fish without pre-treatment (Babikova *et al.*, 2020). However, the used pre-treatment methods have different effect on fresh or frozen sprats for drying and smoking losses, but similar in the sensory evaluation (Möllmann *et al.*, 2004).

It is important to obtain lower technological losses in production; smoking and drying losses for frozen sprats were higher than those for fresh sprats.

If smoked fish is stored till production, the drying losses are important. For frozen sprats, drying losses were higher than for fresh sprats, but using pre-treatment methods it was possible to decrease them to 0.3–0.4%.

According to Martinez *et al.* (2012), salting induces changes in muscle proteins, which causes modification of fish texture and water holding capacity. In our study, samples 3Na2Ca and 2Na3Ca demonstrated harder texture, which is in agreement with other researchers, who reported an increased hardness of fish filets with increased brine concentration (Bjørnevik *et al.*, 2018; Ruiz-Alonso *et al.*, 2021). Acetic acid use in brine may result in protein denaturation, thus leading to increased hardness of the smoked sprats (Bjørnevik *et al.* 2018).

The sensory evaluation was performed using the JAR method (%). The results were similar for fresh and frozen sprats, and there was no effect of the storage time. However, without treatment, there was a bigger difference between fresh and frozen sprats, with JAR values between 13 and 50%. Means drops were plotted versus the percentage of expert values for fresh and frozen sprat's sensory attributes (Fig. 2). Control samples for fresh sprats (Control) and for frozen (FR_Ace) sprats treated acetic acid resulted in too low intensity for texture, colour and flavour to obtain a tasty product.

Using pre-treatment methods, the pH decreased, which affects microbiological activity and increases product shelf life (Köse, 2010). Frozen sprats and sprats processed using acids result in a harder texture compared to fresh sprats without treatment (Serdaroglu *et al.*, 2015).

CONCLUSIONS

The use of pre-treatment allowed to improve quality parameters of smoked sprats and reduce both drying and smoking losses. The sensory evaluation results showed similar results for fresh and frozen sprats. Among the sensory tests, the best result was found for fish treated with 6 g NaCl and 2 g of acetic acid. Pre-treatment method and freezing affected the smoked fish pH, which was higher (pH 6.73) for smoked fresh sprat compared to the smoked frozen sprat (pH 6.38), and using the pre-treatment with acetic acid

Fig. 2. Mean drop plot vs. % of smoked sprat sensory attributes: (a) colour; (b) texture, (c) flavour, (d) taste. Too little is marked by “-”, too much is marked by “+”. The dashed line presents 20% of samples.

and CaCl_2 the pH decreased to 5.74 for fresh and 5.51 for frozen fish.

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PIRMAPSTRĀDES IETEKME UZ KŪPINĀTU BRĒTLIŅU KVALITĀTI

Baltijas brētliņas (*Sprattus sprattus balticus*) ir labs olbaltumvielu, vitamīnu, kā arī minerālvielu un nepiesātināto taukskābju avots. Patērētāji pieprasa nemainīgas kvalitātes zivju produktus visu gadu. Lai to nodrošinātu, var lietot dažādas zivju pirmapstrādes metodes, izmantojot etiķskābi, sāli (NaCl) un/vai granulas veida CaCl₂ dažādās koncentrācijās un proporcijās. Pētījuma mērķis bija novērtēt dažādu pirmapstrādes metožu ietekmi uz kūpinātu Baltijas brētliņu sensorajiem un tehnoloģiskajiem rādītājiem. Pirms kūpināšanas zivis tika izturētas šķīdumā ar piedevām dažādās proporcijās 30 minūtes. Paraugs bez pirmapstrādes tika izmantots kā kontroles paraugs. Izmantojot brētliņu pirmapstrādi, iespējams samazināt kūpināšanas zudumus. Ja pirmapstrādes šķīdums satur NaCl un etiķskābi, iespējams samazināt kūpināšanas zudumus par 26%. Nožuvums uzglabāšanas kamerā paraugiem bez pirmapstrādes bija 1,6%, bet, izmantojot pirmapstrādi ar NaCl un CaCl₂, tas samazinājās līdz 0,3%. Pirmapstrāde un arī saldēšana ietekmē zivju pH. Kūpinātu brētliņu pH – 6,73, bet saldētu un tad kūpinātu brētliņu pH – 6,38. Sensorā novērtēšana, izmantojot JAR (*Just-About-Right*) metodi, parādīja, ka to kūpināto brētliņu struktūra, kuras apstrādātas, izmantojot etiķskābi, ir stingrāka.