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Ludmiła *STODOLNIK*

Fish technology

ACTIVITY OF SELECTED PLANT RAW MATERIALS IN INHIBITION LIPIDS CHANGES BALTIC HERRING MINCED MEAT TISSUE DURING FROZEN STORAGE

AKTYWNOŚĆ WYBRANYCH SUROWCÓW ROŚLINNYCH W HAMOWANIU ZMIAN LIPIDÓW ROZDROBNIONEJ TKANKI MIĘŚNIOWEJ ŚLEDZI BAŁTYCKICH PRZECHOWYWANEJ W WARUNKACH ZAMRAŻALNICZYCH

Department of Fish Preservation, Agricultural University of Szczecin, Poland

Effect of pepper seeds, a mixture of rugosa-rose and dwarf quince seeds and an oxygen absorber on oxidation and hydrolysis of lipids and solubility of protein in 5 % NaCl solution minced muscle tissue of Baltic herring stored at -25°C was analysed.

INTRODUCTION

Small amounts of compounds occur in Baltic herring muscle tissue, which have antioxidizing properties such as α-tocoherol (0.105 mg/100 g) [Tarr 1962] and phospholipids regarded as sinergents antioxidizing effect of α-tocopherol [Yamaguchi and Toyomizu 1984], their participation in herring lipids varies from 8.9 to 17.7 % [Podeszewski, Stodolnik 1976]. At the same time herring muscle tissue contains active catalyst for lipids chemical oxidation such as iron ions - average amount 1.34 mg/100 g [Aleszko-Ożevskij et al. 1986], copper ions, their amount varies from 0.055 to 0.235 mg/100 g [Protasowicki 1987], and enzymatic system which initiates lipids oxidation found in microsomal fractions of muscle tissue [Slabyj and Hultin 1984].

As a result of such participation of the mentioned above compounds in herring muscle tissue is fast oxidation of unsaturated lipids which occur there during frozen storage as well. Therefore searching for effective ways of protecting this type of fish fatty acids against oxidation destruction is still a live issue. In earlier research [Stodolnik 1994] into usefulness of natural materials for inhibition lipids muscle tissue oxidation of Baltic herring stored at -25°C important antioxidative properties of a rugosa-rose and a dwarf quince were found. So it was decided to continue research into usefulness of plant raw materials in inhibition herring lipids

oxidation during frozen storage, regarding also reports about toxic properties of synthetic antioxidants, quoted in the previous report [Stodolnik 1994].

The aim of this research was to determine ability of pepper seeds and a mixture of rugosa-rose and dwarf quince seeds to inhibition lipids minced meat tissue of Baltic herring stored at -25°C in comparison to an oxygen absorber activity.

MATERIALS AND METHODS

Baltic herring sort "D", caught in the first half of March was used in the study. Fish were in V-VI maturity stade gonad according to Maier scale and in the state of post rigor mortis. The fish was gutted and filleted. The fillet was skinned and minced twice in an electricgrinder with 3 mm hole diameter strainer. From minced meat samples were prepared which have additions, dried at 40°C, mince seeds of pepper (*Capticum annuum* L.) amount 0.5 %, the mixture of the dwarf quince (*Chaenomeles speciosa*) 0.25 % and the rugosa-rose (*Rosa rugosa*) 0.25 % seeds as well as the oxygen absorber (ANGELESS) 0.5 %. Minced meat was carefully mixed and divided into samples of 50 g, which were placed in small bags of polyethylene film, forming cubes 1 cm width, samples were frozen and stored at -25°C. Control sample contains neither plant additions nor the oxygen absorber. Before chemical analysis the samples were thawing in air at 4°C.

Extraction of lipids from the herring muscles tissue was carried using a mixture of chloroform and methanol [Linko 1967]. Obtained extracts were used for the following chemical analysis:

lipid content - using weight method, after solvent distilling and drying remains at 80°C for 1 hour,

free fatty acids - thin-layer chromatography and densitometry method [Stodolnik 1994],

hydroperoxides contents in the chloroform layer of extracts, after their oxidation to malonaldehyde and reaction with TBA [Schmedes and Holmer 1989],

malonaldehyde contents in the methanol-water layer of the extracts using TBA [Schemedes and Holmer 1989],

conjugated dienes and trienes of fatty acids - spectrophotometric way using measurement of absorbance chloroform layer of extracts at wavelength 247 nm and 278 nm respectively and calculated absorption coefficient [Paquot 1979].

Protein solubility was measured using 5 % NaCl solution, pH 7.0, temperature 0°C, according to the procedure described in the report mentioned above [Stodolnik 1994]. Results od chemical analysis are arithmetic means of the three parallel determination. Significance of the difference of comparable mean value of chemical indicators was counted using Welch and Aspin's test [Czermiński et al. 1974].

RESULTS AND DISCUSSION

Analysed herring muscle tissue contented 6.35 % lipids. During frozen storage minced fish muscle tissue with the addition of the plant raw materials and the oxygen absorber slower oxidation occurred than in the control sample. (Fig. 1, Tab. 1). In the most active way

retarded accumulation of primary products of oxidation the mixture of a rugosa-rose and dwarf quince seeds, less the oxygen absorber and the least pepper seeds. An accumulation of malonaldehyde (TBARS - tiobarbituric acid-reactive substances) in the herring muscle tissue was slower to a significant degree only by influence of the mixture of the rugosa-rose and

dwarf quince (Fig. 2, Tab. 1). The accumulation of malonaldehyde was not inhibited by pepper seeds and actively accelerated by the oxygen absorber. This last one, however, considerably inhibited an increase of contents of conjugated dienes and trienes in lipids of the herring muscle tissue stored at -25°C (Fig. 3 and 4, Tab. 1). Similarity the accelerations of dienes and trienes inhibited the mixture of rugosa-rose and dwarf quince seeds as well as pepper seeds.

Table 1

"v" values calculated by Welch and Aspin's test [Czermiński et al. 1974] for mean value of chemical indicators of comparable samples

Comparable samples	Peroxides	Malon-aldehyde	Dienes	Trienes	Free Fatty Acids	Lipids	Protein solubility in 5% NaCl solution
Control sample with pepper seeds	10.97^{xx}	-2.31^{x}	3.26^{xx}	3.69^{xx}	0.90	-22.53^{xx}	4.39^{xx}
Control sample with rugosa rose and dwarf quince seeds	15.74^{xx}	37.01^{xx}	3.82^{xx}	2.80^{xx}	-3.55^{xx}	-8.63^{xx}	-7.60^{xx}
Control sample with oxygen absorber	9.88^{xx}	-53.13^{xx}	2.26^{x}	8.18^{xx}	-3.82^{xx}	-13.00^{xx}	-41.65^{xx}
With pepper and rugosa rose + dwarf quince seeds	8.00^{xx}	55.34^{xx}	4.79^{xx}	-0.91	-3.05^{xx}	3.73^{x}	-10.48^{xx}
With pepper seeds and oxygen absorber	-2.64^{x}	-74.38^{xx}	2.57^{x}	-0.10	-6.43^{xx}	-0.20	-50.66^{xx}
With rugosa rose + dwarf quince seeds and oxygen absorber	-8.19^{xx}	-126.25^{xx}	0.34	1.07	-2.24^{x}	-4.13^{xx}	-14.56^{xx}

^{x} Significant difference p=0.05, ^{xx} Significant difference p=0.01.

The oxidation ability of the mixture of seeds of the rugosa-rose and the dwarf quince was greater than each plants separately, which were used in other research in twice as high a concentration [Stodolnik 1994]. Rate of oxidation muscle tissue both not contained addition of antioxidants and contained them was slower than reported in earlier research [Stodolnik 1994].

Herring muscle tissue selected to research contained the same amount of lipids (6.35 and 6.40 %) in both cases but came from fish caught in different time of year. In this paper herring muscle tissue was analysed of fish caught in March in pre-spawning period, in the earlier fish caught in October, during preying period, in this period increased activity of fish enzymes is characteristic [Boczew and Sziszluk 1978], this activity, one can suppose, catalysed lipids oxidation, this role is described in other research [Slabyj and Hultin 1984, Wang et al. 1994]. Initially higher, before storage, contents of oxidation products in herring muscle tissue, analysed in this paper, higher than in the earlier research did not accelerate their accumulation during storage at -25°C, but on the contrary oxidation dynamic was slower than in muscle tissue of Baltic herring caught in October. Found differences in a rate of lipids oxidation herring muscle tissue may have been connected, among other things, with slower activity of enzymes catalyzing lipids oxidation of this specie of fish, which are in their pre-spawning period.

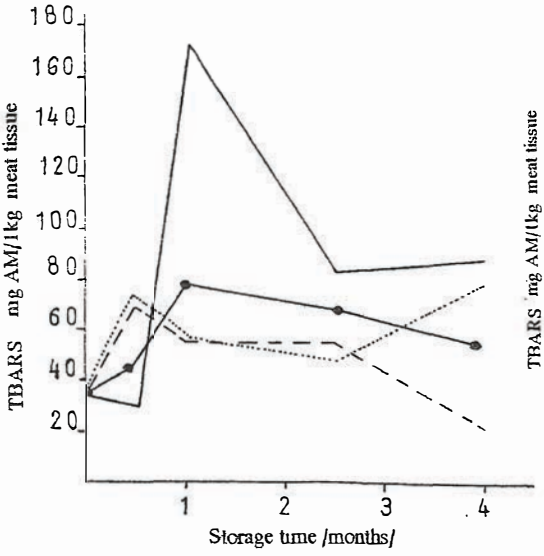

Fig.1 Effect of plant additions on lipids oxidation herring muscle tissue during frozen storage (Chloroform layer of extract)
----- control sample, with additions •-----• 0.5% pepper seeds, - - - - 0.25% rugosa rose and 0.25% dwarf quince seeds, ... 0.5% oxygen absorber

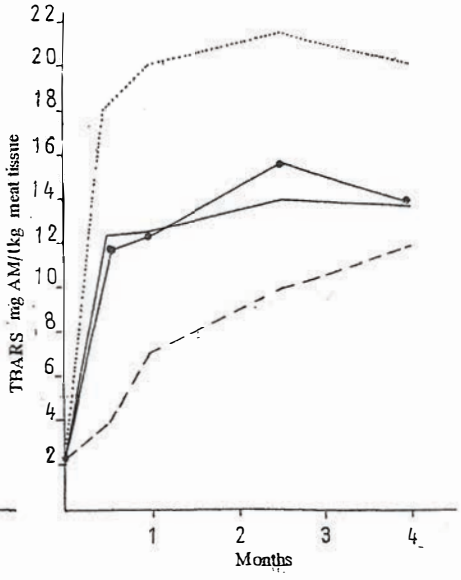

Fig. 2 Effect of plant additions on malonaldehyde amount (TBARS) in herring muscle tissue during frozen storage (methanol layer of extracts). Explanation like Fig. 1.

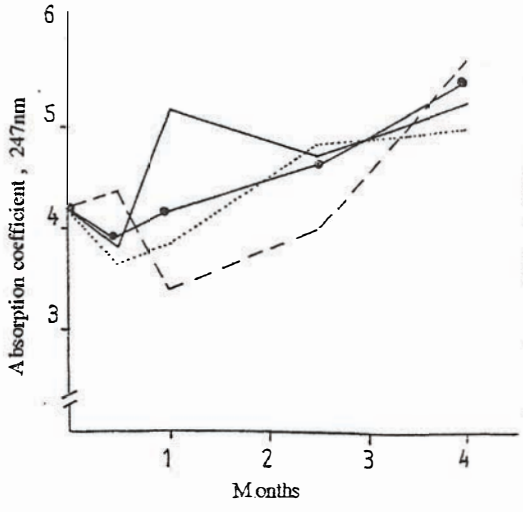

Fig. 3 Effect of plant additions on conjugated dienes of fatty acids herring muscle tissue lipids during frozen storage. Explanation like Fig. 1

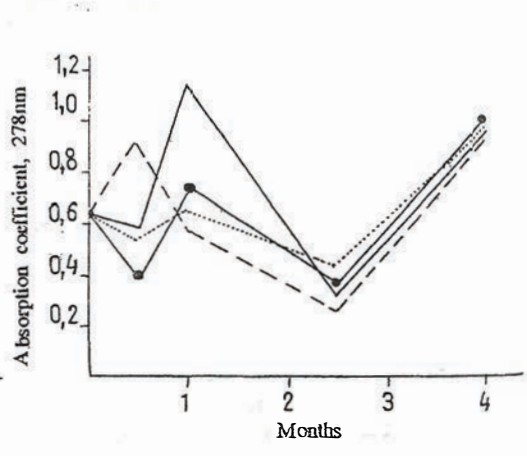

Fig. 4 Effect of plant additions on conjugated trienes of fatty acids herring muscle tissue lipids during frozen storage. Explanation like Fig. 1

Contents of free fatty acids increased significantly in muscle tissue lipids in samples contained the oxygen absorber in comparison to the other samples and contained the mixture of the rugosa-rose and the dwarf quince seeds in comparison to tissue with addition of pepper seeds and the control sample (Fig. 5, Tab. 1). Stated influence of additions on contents of free fatty acids may have been resulted by their influence on activation of lipases and phospholipases and on increased extractability muscle tissue lipids frozen storage, as well as on lipids presence in used plant raw materials, this presence in pepper seeds comes up to 30 % [Ożarowski and Jaroniewski 1989] (Fig. 6, Tab. 1). Similar changes in amount of free fatty acids in herring muscle tissue containing addition of plant antioxidants and frozen storage were found in earlier research [Stodolnik 1994]. The increase of free fatty acids converged on increase of amount of protein extracted 5 % NaCl solution, especially in muscle tissue containing oxygen absorber as well as containing the mixture of the rugosa-rose and the dwarf quince seeds (Fig. 7). Increased amount of extracted protein in herring muscle tissue stored at -25°C was recorded in earlier research under the influence of the dwarf quince seeds used in concentration 1 % [Stodolnik 1994], these manifested more active as cryoprotectants in mixture of the rugosa-rose seeds in concentration several times lower as this research found.

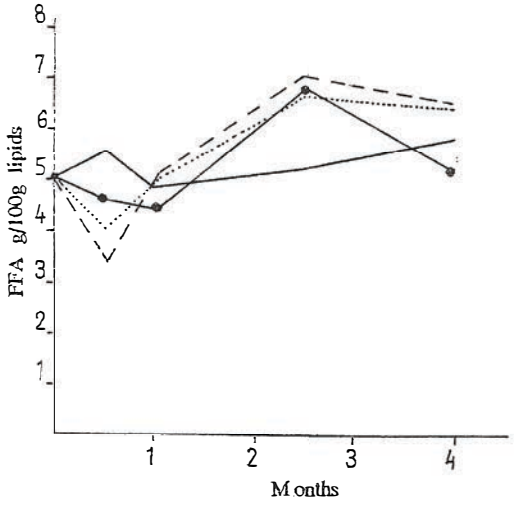

Fig. 5 Effect of plant additions on free fatty acids amount herring muscle tissue lipids during frozen storage. Explanation like Fig. 1

Oxygen absorber in the herring muscle tissue increased amount of proteins extracted 5 % NaCl solution despite high participation malonaldehyde in it, coming up to 22 mg/kg during frozen storage. The amount of malonaldehyde in this sample was almost twice as high as in the control sample (Fig. 2). Other research reported [Osman 1993] that malonaldehyde added to minced Baltic herring muscle tissue in the amount 300 mg/100 g resulted significant increase in the amount of proteins extracted 5 % NaCl solution after its frozen storage.

Earlier research [Gardner 1979] reported that malonaldehyde has ability to block amin group of proteins and with their acid group forms weak bonds. There is difficulty in explanation of mechanism of increasing proteins affinity herring muscle tissue to 5 % NaCl solution in the presence of the significant amount of malonaldehyde on the base of existing literature due to a model character of this research which refers to precisely designed experimental conditions.

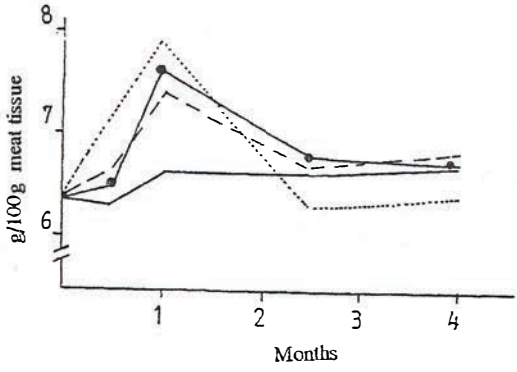

Fig. 6 Effect of plant additions on lipids extraction from herring muscle tissue during frozen storage. Explanation like Fig. 1

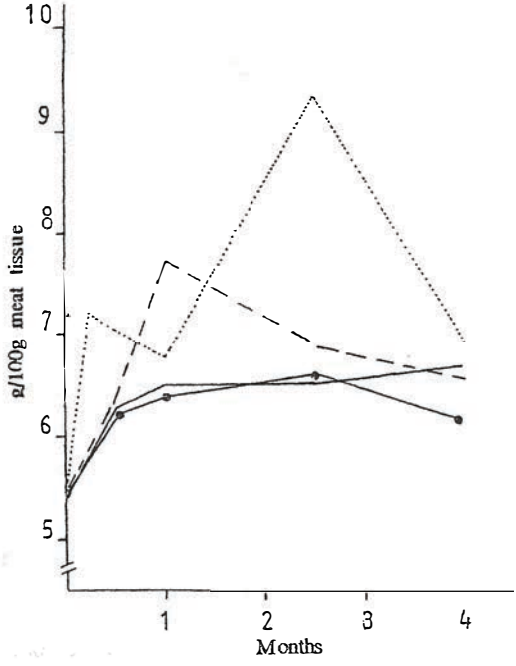

Fig. 7 Effect of plant additions on protein extraction 5% NaCl solution from herring muscle tissue during frozen storage. Explanation like Fig. 1

In natural herring muscle tissue contained 6.35 % lipids, stored at -25°C, less reactivity malonaldehyde with proteins may take place than in solution of the isolated protein fractions or/and free aminoacids. Such suggestion appears in other research which carried in model conditions [Kanner and Karel 1976], where was found that low water activity prevent malonaldehyde reaction with proteins. With regard to hydrophobic properties of lipids

components one may suppose that they inhibit reaction of malonaldehyde with functional group of proteins herring muscle tissue during storage at -25°C.

Obtained results of accumulation of products of lipids oxidation herring muscle tissue during frozen storage indicate that the use of plant raw materials and the oxygen absorber slow down oxidation but they do not affect particular stages of chinned process of oxidation in the same way. This report shows usefulness of using mixtures of plant additions, which allow inhibitations qualities complex mechanism of oxidation unsaturated fish lipids and changes in proteins solubility to be complementary to one another. As well as regarding to better effects obtained with their lower concentration in a mixture than used each addition separately in inhibition lipid oxidation and protein solubility in 5 % NaCl.

The reason of positive influence mixture of the rugosa-rose and the dwarf quince seeds on protein herring muscle tissue may be caused by contents carbohydrates in a rugosa-rose comes up to 60 % [Gumowska 1984] and in a dwarf quince seeds contents of basorin in amount up to 20 % consisting of D-galactopyranose and D-mannopyranose which intensify their individual protective qualities in relation to proteins.

Antioxidation effect of mixture rugosa-rose and dwarf quince seeds on lipids herring muscle tissue, one can suppose, it is connected with contents of bioflavonoids in them though less than in their fruit, in a rugosa-rose fruit 180 mg/100 g [Wilska-Jeszka 1988] and ascorbic acid in a rose up to 1200 mg/100 [Gumowska 1984] and even to 10 % [Ożarowski and Jaroniewski 1989] and in a dwarf quince - 65 mg/100 g [Lesińska 1988], which intensify each other antioxidative properties. The significance of flavonoids and organic acids from plant materials in inhibition lipid oxidation other research reported [Hemeda and Klein 1990, Haraguchi et al. 1992]. Antioxidative pepper seeds ability, based mainly on slowing the rate of accumulation primary product of oxidation may be connected with the presence characteristic for them steroids saponins (capsidin) with found antibiotic properties. [Ożarowski and Jaroniewski 1989].

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STRESZCZENIE

Analizowano wpływ dodatku nasion papryki (0,5 %), mieszaniny nasion dzikiej róży (0,25 %) i pigwowca (0,25 %) oraz absorbera tlenu AGELESS (0,5 %) do rozdrobnionej tkanki mięśniowej śledzi bałtyckich na utlenianie i hydrolizę lipidów oraz rozpuszczalność białek w czasie przechowywania w temperaturze -25°C.

Uzyskane wyniki wykazały, że zastosowane surowce roślinne i absorber tlenu spowalniają proces oksydacji lipidów, ale nie oddziałują jednakowo na kumulowanie hydronadtlenków, aldehydu malonowego, dienów i trienów. Ogólnie tempo procesu utleniania lipidów najaktywniej zmniejszała mieszanina nasion róży i pigwowca. Zawartość wolnych kwasów tłuszczowych zwiększała się w lipidach tkanki mięśniowej śledzi, zawierającej dodatki roślinne i absorber tlenu. Ilość białek, ekstrahowanych 5% roztworem NaCL, była największa w tkance mięśniowej ryb zawierającej absorber tlenu, a następnie mieszaninę nasion róży i pigwowca, zaś najmniejsza - w próbie kontrolnej. Z przeprowadzonych badań wynika celowość stosowania szczególnie mieszaniny analizowanych nasion, powodującej intensyfikację ich właściwości antyoksydacyjnych w tkance mięśniowej śledzi w czasie zamrażalniczego przechowywania.

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Author's address:
Prof. tit. D.Sc. Ludmiła Stodolnik
Department of Fish Preservation
Agricultural University of Szczecin
Kazimierza Królewicza 4
71-550 Szczecin
Polska (Poland)