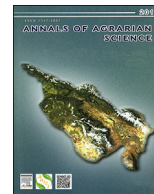




Contents lists available at ScienceDirect

Annals of Agrarian Science

journal homepage: <http://www.journals.elsevier.com/annals-of-agrarian-science>

Nuts as raw material for confectionary industry

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ARTICLE INFO

Article history:

Received 22 September 2016

Accepted 14 December 2016

Available online xxx

Keywords:

Nuts

Storage

Walnuts

Lipid oxidation

Peroxide value

Thiobarbituric value

Conjugated dienes

Fatty acid composition

Volatile compounds

ABSTRACT

The aim of this paper was to explore chemical and sensory stability of walnuts during their storage. We determined fatty acids composition, as well as chemical indicators of lipid oxidative stability (peroxide and thiobarbituric values and conjugated dienes) during accelerated storage of walnuts. Besides this, a thorough descriptive analysis was performed. The accelerated storage of walnuts was shown to cause the significant changes in sensory characteristics of walnuts, as well as the significant increase of peroxide and thiobarbituric values and contents of conjugated dienes.

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1. Introduction

Walnut is one of the most popular nut species in the world. It is characterized by high nutritional value and very positive influence on the human organism. Walnuts are used not only as an individual foodstuff, but also as the part of different food products [1,2].

Nuts are very often used in confectionery industry. However, oxidative processes in the nut fats sharply reduce the shelf life of confectionery products [3,4]. Stabilization of oxidative processes in the nuts by means of some safe and natural stabilizers such as dihydroquercetin may increase the shelf life of confectionery products with nuts [5].

Walnuts are the unique natural source both of basic nutrients and a complex of minor biologically active compounds. They contain high quantity of complete proteins and fats, that causes their high energetic value. Walnuts contain vitamins A, E and B group, as well as unique complex of micro- and macroelements [6–8].

Walnuts contain up to 60% of fat rich in mono- and poly-unsaturated fatty acids that causes their rapid rancidity. The products of lipid oxidation have a carcinogenic and mutagenic

effect on people, that's why oxidative processes in fats attract so great attention in assessing the quality of nuts [9].

The aim of this study was to explore oxidative processes that occur in fats during storage of walnuts.

2. Objectives and methods

For investigation walnuts harvested in 2015 were purchased at Moscow retail markets. To study the oxidative damage of these walnuts they were stored in thermostate at 30°C in the package from the manufacturer. The measurement of main parameters of oxidation were performed every week for 5 weeks.

To estimate the degree of oxidation of walnuts fats the walnut oil was produced by cold pressing [10]. For this purpose we measured peroxide value that shows the content of primary oxidation products (peroxides and hydroperoxides), thiobarbituric value that shows the content of secondary oxidation products, i.e. malondialdehyde, the content of conjugated dienes, volatile aromatic substances and fatty acid composition.

Peroxide value (PV) was evaluated following the GOST R 51487-99 «Plant oils and animal fats. Method of estimation of peroxide value» [11]. It consisted in the reaction in darkness of a mixture of oil and chloroform-acetic acid 2:3 (v/v) with saturated potassium iodide solution. The iodine formed was titrated with 0.1 N sodium thiosulphate until the yellow colour almost disappeared. Then after

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Peer review under responsibility of Journal Annals of Agrarian Science.

adding starch indicator titration was continued until the blue colour just disappeared. Peroxide value (meq kg^{-1}) was calculated according to the formula: $\text{PV} = \text{volume of sodium thiosulphate} \times 0.1 \text{ N} \times 1000/\text{mass of oil}$.

Thiobarbituric value (TV) [12,13] was evaluated according following methods: 5 ml oil was added to 5 ml of thiobarbituric acid solution and heated in a water bath for 40 min for pink colour development. Then the tube with mixture was first cooled for 1 h. The absorbance was measured at 532 nm using spectrophotometer. Thiobarbituric value were calculated from a standard curve of malondialdehyde and expressed as mg of malondialdehyde per kg sample.

Conjugated dienes (CD). Weighed oil samples were dissolved in 6 ml of *n*-hexane. The conjugated diene absorbance was measured at 232 nm in a spectrophotometer. The results were reported as the sample extinction coefficient E (1%, 1 cm).

Fatty acid composition were evaluated following the GOST 30418-96 «Plant oils. Method of estimation of fatty acid composition» [14]. The fatty acid methyl esters of total lipids were analyzed on gas-liquid chromatograph (Kristalljuks 4000 M) equipped with a flame ionization detector. An HP FFAP capillary column (50 m \times 0.2 mm \times 0.3 nm) was used. Column temperature was programmed from 200 to 230 °C. The carrier was nitrogen. The separated fatty acid methyl esters were identified by comparing their retention times with those of authentic samples.

Volatile compounds were determined by extraction of chopped walnuts with diethyl ether. The extract obtained was chromatographed in Chromatograph Shimadzu GC 2010 with mass detector GCMS-QP 2010 on column MDN-1 (hard-connected methyl silicone 30 m \times 0.25 mm) in temperature gradient regime at following operating parameters: injector temperature 2000°C, interface temperature 2100°C, detector temperature 2000°C. The carrier gas was helium.

Sensory analysis was performed by group of tested tasters. All the parameters were determined in threefold repetition. The results of investigation were statistically processed [15].

3. Results and analysis

Assessment of walnuts smell was performed by profile method. We used such descriptors of smell: “oily”, “fruity”, “nutty”, “sweet”, “woody” and “rancid”. The intensity of the smell was assessed according to the 10-points scale. Results obtained are presented at Fig. 1.

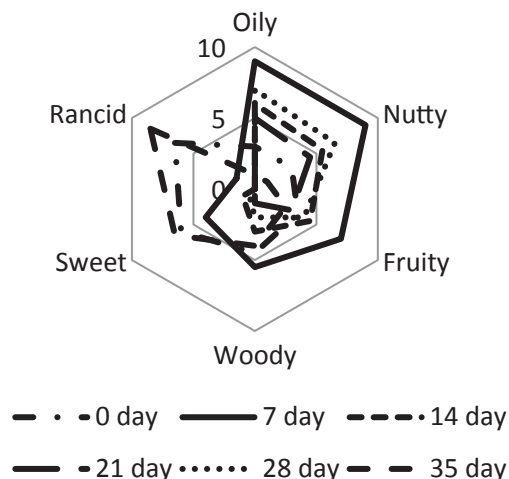


Fig. 1. Dynamics of walnuts smell intensity during accelerated storage.

During accelerated storage of walnuts the intensity of “oily” and “rancid” smells increased significantly while the intensity of “fruity” and “nutty” smells decreased.

The dynamics of peroxide value, thiobarbituric value and conjugated dienes contents during accelerated storage of walnuts is presented at Fig. 2. It is clear that all the values increased during storage.

The PVs of walnut samples were from 2.5 (day 0) to 21.0 (day 35). The TV of walnut samples during storage varied from 0.01 (day 0) to 0.4 (day 35). The CD values of walnut samples during storage varied from 0.5 (day 0) to 6.0 (day 35). Sharp increase in all the values was observed after 14 days of storage, that was connected with intensification of oxidative processes.

The correlation among peroxide value, thiobarbituric value and conjugated dienes content was calculated (Fig. 3). In general, it could be stated, that there was good positive correlation among all three parameters with coefficient more than 0.9. Maximal value of this coefficient was observed among peroxide value and conjugated dienes content.

Results of determination of volatile substances are presented in Table 1.

The data obtained show that the smell of fresh walnuts is caused by the following main substances: butyl-*s*-triazole, isobutyl-oxyethyl-butyrate, decane, dodecane, tridecane, propanoic acid, tetradecane, phthalic acid, *n*-hexadecanoic acid and di-*n*-octyl phthalate. Oxidative damage of walnuts was accompanied by

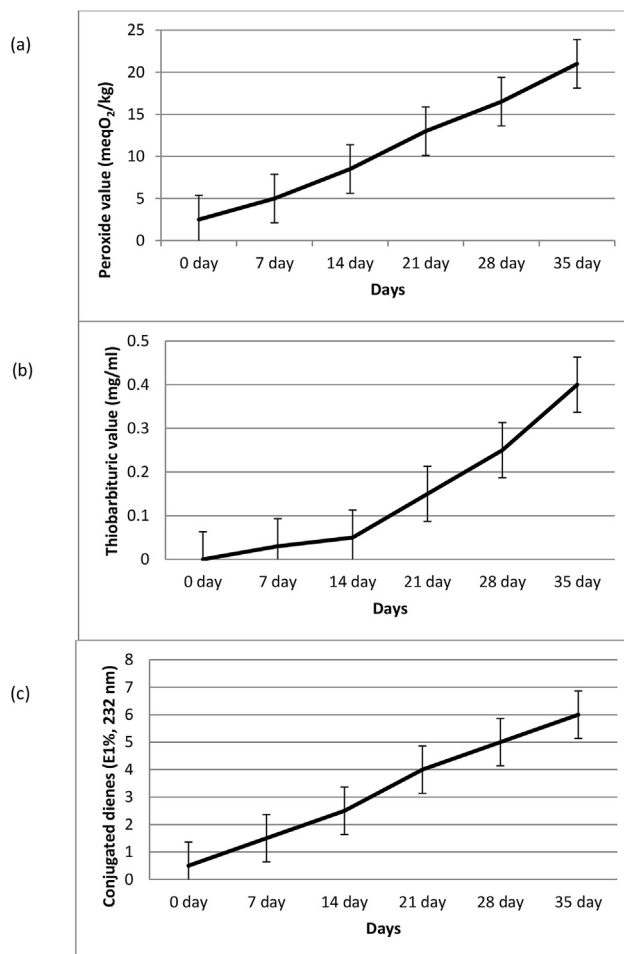


Fig. 2. (a) Peroxide value, (b) thiobarbituric value and (c) conjugated dienes contents in walnuts during storage.

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