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professional paper

Effect of Olive Fruits Storage in Sea Water on Oil Quality

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Summary

Lengthy and/or unsuitable storage of olive fruits can significantly decrease the quality of virgin olive oil. Dipping in sea water is a traditional and still very frequent method of preserving olives in Croatia. Changes in standard olive oil quality indicators during storage of olive fruits (cultivar »Bjelica«) have been studied in comparison with storing in brine (4 % solution of natrium chloride), drinking water and in wooden boxes in the open air. The samples of oil were obtained by processing olives in the pilot plant composed of a hammer crusher and a press with steel nets. During the 30 days of storage in aqueous media, there was a slight increase in the content of free fatty acids, while in the samples stored in the open air, the increase was significantly higher. The peroxide values and absorbance coefficient at 232 nm were decreasing during storage in aqueous media while absorbance coefficient at 270 nm remained constant. With dipping olives in brine and sea water the desired fragrant characteristics of oil disappeared after 10 days, while in samples exposed to the air they were noticeable even after 30 days of storage. For oils obtained from olives kept in brine and sea water undesired taste and smell of brine were characteristic. Overall quality index decreased in all of the studied methods of storage and no significant differences have been observed between them. The most evident difference between storage methods was exerted trought the fraction of total chlorophylls. In aqueous media it increased by about 8 times, while in the open air it decreased by about 1.5 times in regard to reference sample. The results lead to the conclusion that storing olives in aqueous media does not change significantly basic physicochemical quality indicators but reduces oil quality primarily due to undesired changes of sensory characteristics.

Key words: olive fruits storage, sea water, virgin olive oil, quality

Introduction

Virgin olive oil is one of the rare oils in human nutrition, which is used crude. In its production only mechanical and physical methods are used, which, in controlled heating conditions of processing, cause minimal changes in oil composition. It is, thus, understandable that the quality of the product is largely dependent on the quality of olive fruits at the time of processing *(1,2)*. Olives of good quality mean fresh, healthy, technologically ripe and undamaged fruits. Therefore, the top quality of oil is in fact the final result of correct and timely application of technological methods in the olive growth as well as of fast and well coordinated techniques in harvesting and processing.

In Croatia, olives are grown in a relatively narrow coastal area along the Adriatic sea and on the islands. Approximately 2500 t of olive oil are produced a year, *i.e.* about 0.6 kg per inhabitant *(3)*, making 0.12 % of world production *(4)*. In spite of such small production there are problems like lack of manual labour for harvesting, and remote and insufficient capacity of oil mills.

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In such circumstances storing olives is almost unavoidable, decreasing the quality of fruits at the time of processing.

A great number of different methods of olive fruits storage that have been studied confirm the importance of the problem. Storage in wooden boxes or on nets in the open air is considered a classical way *(5,6)*. Cantarelli *(7)* and Petruccioli *et al.* *(8)* studied possibilities of keeping olives by dipping them in water solutions of salt, acids and alkali. From these methods the authors picked out dipping olives in sea water and HCl and NaCl solutions as the most suitable because of low content of free fatty acids, constant peroxide values and the pleasant flavour of the obtained oil even after 90 days of olive storage. Modified atmosphere with different volume ratios of CO_2 and O_2 in combination with low temperatures has recently attracted special interest *(9–12)*. The results of these studies show that cooling in the air at 5 °C and RH 90–96 % lasting from 45 to 60 days, does not cause any disorders in normal metabolic functions of the fruits and slows down significantly the development of moulds. Lower temperatures, increased CO_2 and decreased O_2 concentrations cause physiological disorders in fruits and thus do not improve the quality of oil.

Despite advantages of controlled conditions of olive storage, traditional dipping in sea water is still very frequent in Croatia. This practice is so deeply rooted that producers do the same even when there is no particular need for fruit storage until the time of processing. These facts motivated us to study the changes in standard indicators of oil quality developed in this specific method of olive storage.

Table 1. Methods of Bjelica olive fruits storage before pilot plant processing

No.	Sample	Methods of storage
1	Reference	Fruits were processed 24 hours after harvesting.
2 3 4	Air-10 Air-20 Air-30	Fruits were placed in wooden boxes in a 5 cm layer, exposed to air and daily turned in a dry and cool room for 10, 20 and 30 days;
5 6 7	Sea-10 Sea-20 Sea-30	Fruits were put in 5 L jars with a wide neck and then filled up to the top with sea water. The samples were kept in a cool room for 10 20 and 30 days.
8 9 10	Sea-10a Sea-20a Sea-30a	Fruits were put in 5 L jars with a wide neck and then filled up to the top with sea water. The water was changed every fifth day and samples were kept in a cool room for 10, 20 and 30 days.
11 12 13	Brine-10 Brine-20 Brine-30	Fruits were put in 5 L jars with a wide neck and then filled up to the top with 4% NaCl solution. The samples were kept in a cool room for 10, 20 and 30 days.
14 15 16	Water-10 Water-20 Water-30	Fruits were put in 5 L jars with a wide neck and then filled up to the top with drinking water. The samples were kept in a cool room for 10, 20 and 30 days.
17 18 19	Water-10a Water-20a Water-30a	Fruits were put in 5 L jars with a wide neck and then filled up to the top with drinking water. The water was changed every fifth day and samples were kept in a cool room for 10, 20 and 30 days.

Material and Methods

Healthy olives of Bjelica cultivar grown in the Pula area (Croatia) were handpicked in mid-November. From the total amount of picked fruits, samples of 3 kg were selected, which underwent methods of storage shown in Table 1.

Fruits were processed by pilot plant composed of a hammer crusher, a mixer and a press with steel nets. After crushing, the obtained olive paste was malaxed for 25 minutes at 30 °C, then pressed at maximum pressure of $3.04 \cdot 10^7$ Pa. The oil was recovered from liquid phase by centrifugation at 4000 r.p.m. for 10 minutes. After filtration, oil samples were stored at 0 °C until the analysis was made.

The content of free fatty acids, peroxide value and standard absorbance values at 232 and 270 nm were determined according to the standard methods of the European Union *(13)*.

Total chlorophylls were determined according to the official A.O.C.S. method *(14)*, which requires measuring absorbances directly in oil at 630, 670 and 710 nm with carbon tetrachloride as a blank test. If necessary oil samples were diluted with carbon tetrachloride in mass ratios 1:3 or 1:4. Measuring was done on the spectrophotometer Cary 50 (Varian).

A panel of 9 trained assessors carried out evaluation of sensory characteristics according to the official method of the European Union *(13)*. The oil samples (15 mL each) were presented in covered blue glasses at (28 ± 2) °C. The cover was removed and the sample was smelt and tasted by each panelist. The sensory characteristics were judged using a special profile sheet.

Overall quality index (O.Q.I.) was calculated according to the equation:

$$\text{O.Q.I.} = 2.55 + 0.91\ \text{S.E.} - 0.71\ \text{FFA} - 7.35\ K_{270} - 0.066\ \text{PV},$$

where S.E. is an overall grading of sensory quality evaluation, FFA is a fraction of free fatty acids expressed as mass fraction of oleic acid, K_{270} is a standard absorbance value at 270 nm and PV is a peroxide value (mass concentration). The International Council for Olive Oil proposed this equation with the aim of collecting different analytical indicators of oil quality into an unique indicator, which value ranges from 0 (the worst quality) to 10 (the best quality) *(15)*.

Results and Discussion

In this study the quality of virgin olive oil was determined by customary physicochemical indicators and evaluation of sensory characteristics (panel test). The amount of total chlorophylls and the overall quality index were determined as additional information about the quality. The results of these determinations are shown in Tables 2 and 3, and Figs. 1 and 2.

Table 2. Standard quality parameters of Bjelica olive oil samples obtained from fruits stored under different conditions

No.	Sample	FFA w(oleic a.)/%	Peroxide value (PV) γ(O)/mmol kg^{-1}	K_{232}	K_{270}	Sensory evaluation score
1	Reference	0.14	1.95	1.488	0.103	7.0
2	Air-10	0.22	1.03	1.219	0.103	6.0
3	Air-20	0.54	1.13	1.336	0.105	5.5
4	Air-30	1.29	1.54	1.302	0.079	6.0
5	Sea-10	0.22	0.84	1.498	0.106	6.0
6	Sea-20	0.24	0.71	1.307	0.110	5.3
7	Sea-30	0.36	0.63	1.225	0.106	5.5
8	Sea-10a	0.19	0.80	1.408	0.093	5.8
9	Sea-20a	0.23	0.65	1.506	0.107	5.0
10	Sea-30a	0.30	0.55	1.282	0.101	5.2
11	Brine-10	0.20	0.67	1.259	0.100	5.5
12	Brine-20	0.28	0.71	1.395	0.116	5.0
13	Brine-30	0.27	0.50	1.274	0.106	5.3
14	Water-10	0.25	0.88	1.326	0.104	5.8
15	Water-20	0.26	0.98	1.311	0.105	5.3
16	Water-30	0.27	0.63	1.188	0.098	5.5
17	Water-10a	0.22	0.96	1.339	0.094	5.9
18	Water-20a	0.27	0.89	1.180	0.107	5.5
19	Water-30a	0.30	0.59	1.176	0.091	6.0

a = change of water every fifth day

Table 3. Sensory analysis of Bjelica olive oil samples obtained from fruits stored under different conditions

Sample	Positive characteristics						Negative characteristics				
	Odour				Taste		Odour and taste				
	Fruity	Apple	Other ripe fruit	Green	Bitterness	Piquancy	Vinous	Moldy	Rancid	Vegetable water	Brine
Reference	3	1	-	2	2	2.5	-	-	-	-	-
Air-10	1	-	1	1	2	2	-	-	-	1	-
Air-20	-	-	-	-	0	2	-	-	1	2	-
Air-30	2	-	-	1	1	2.5	-	-	-	2	-
Sea-10	-	-	-	-	2	2	1	-	-	1	1
Sea-20	-	-	-	-	3	2	-	1	-	2	2
Sea-30	-	-	-	-	2	2	-	-	-	-	2
Sea-10a	-	-	-	1	3	2	-	-	-	-	2
Sea-20a	-	-	-	-	3	2	-	1	-	-	2
Sea-30a	-	-	-	-	3.5	2	-	-	-	-	2
Brine-10	-	-	-	-	4	2	-	-	-	-	2
Brine-20	-	-	-	-	3.5	2	-	-	-	-	2
Brine-30	-	-	-	-	3	2	-	-	-	-	2
Water-10	-	-	-	-	2	2	-	-	-	1	-
Water-20	-	-	-	-	2	2	-	-	-	2	-
Water-30	-	-	-	-	1.5	2	-	-	-	1.5	-
Water-10a	-	-	-	-	1	2	-	-	-	1	-
Water-20a	-	-	-	-	2	2	-	-	-	2	-
Water-30a	1	-	-	1	2	2	-	-	-	1.5	-

Intensity of perception: 1 scarce, 2 mild, 3 medium, 4 strong, 5 extreme

Sample 1 was obtained by processing healthy and undamaged olive fruits of Bjelica variety 24 hours after harvesting. Low fraction of free fatty acids, low peroxide value and high score of sensory evaluation in sample 1 confirm that the quality of olives at the time of processing was good. This sample served as a reference in the study of subseqvent changes in oil quality during storage of fruits. Brine and drinking water were chosen as a storage medium with the aim of checking the effect of natrium chloride in brine as well as natrium chloride and other dissolved salts (KCl, $MgCl_2$, $MgSO_4$, $CaCl_2$) in sea water on possible changes in oil quality during storage. The period of 30 days was chosen as the usual time in traditional olive storage in sea water.

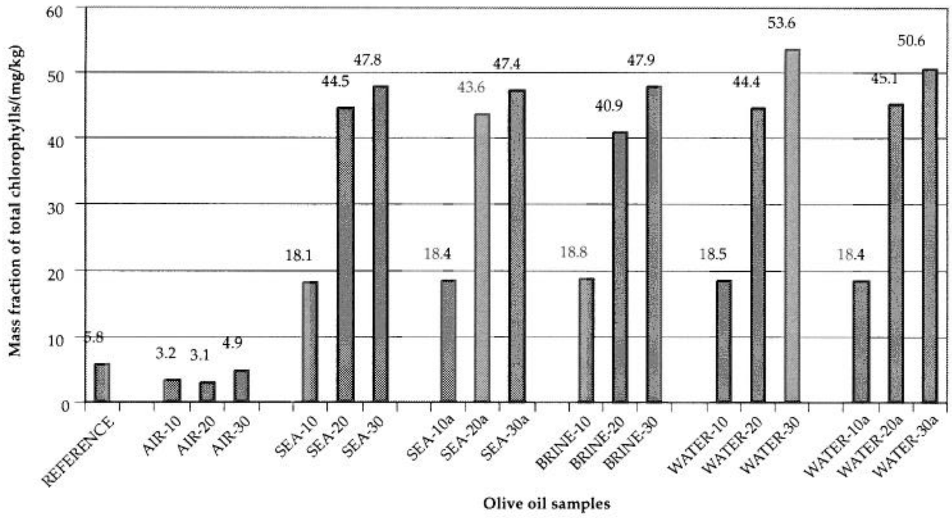

Fig. 1. Content of total chlorophylls in Bjelica olive oil samples obtained from fruits stored under different conditions

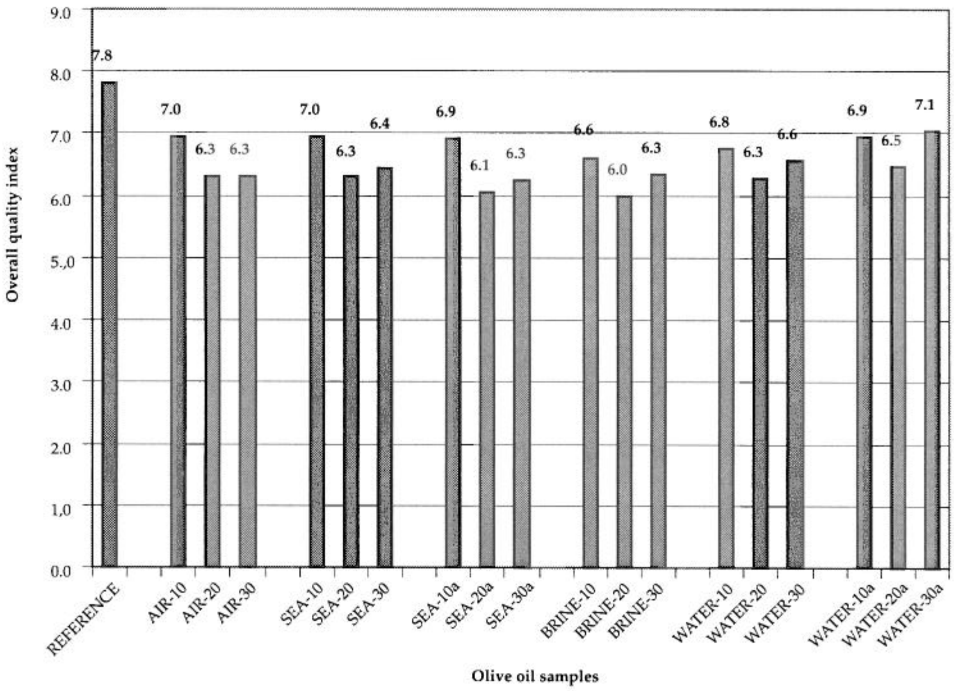

Fig. 2. Overall quality index of Bjelica olive oil samples obtained from fruits stored under different conditions

Fruit storage in wooden boxes in the open air resulted in a decrease of overall quality index after 10 days (Fig. 2). The reason was primarily poorer sensory evaluation because of less expressed »fruity« odour and the appearance of defect »vegetable water«. After 20 and 30 days of such storage, the fraction of free fatty acids increased significantly, while the defect »vegetable water« passed from scarce to mild intensity. In the storage conditions in our trial (thin layer of fruits and daily turning) heating of the mass of fruits, caused by their metabolic activity, did not occur. Likewise, there was no visible development of moulds or yeasts quoted in literature as the main causes of undesired taste and smell *(5,11,16)*. The decrease in quality in this case can be attributed to the effect of pectolytic enzymes and the loss of water by diffusion through fruit membrane *(17)* damaging the cell structure of the pulp and making oil drops accessible to endogenous lipase and lipoxygenase.

On the contrary, only a slight increase in the fraction of free fatty acids, about 0.15 %, and a slight decrease in peroxide value were observed during storage of fruits in sea water (samples 5 trought 10). Since the fruits preserved the tightness while staying in water, only slightly losing the firmness, we suppose that the water medium in which the olives were kept did not allow the decrease in turgor in the pulp cells. In this way the cell structure remained undamaged and oil drops inaccessible to hydrolytic enzymes. On the other side, the water in which the olives were dipped significantly decreased oxygen accessibility. This stopped further production of peroxides. Their slight decrease during storage is explained by transformation into secondary products of oxidation. In support of this is also the gradual fall in K_{232} values (indicating existence of primary products of oxidation), although the values of K_{270} (indicative of secondary oxidation products) mostly did not change.

In the samples kept in brine (11 trought 13) and in drinking water (14 trought 19) we observed almost identical changes of basic physicochemical indicators of oil quality. Only the peroxide values in samples from drinking water after 10 and 20 days of storage were slightly higher than in samples from sea water. These results lead to the conclusion that, when the points in question are basic physicochemical parameters, the conservation effect is primarily do to water and not to salts dissolved in it.

As far as storage in the open air is concerned, after 10 days of storage in aqueous media, sensory evaluation score was lower than 6.5, which is the limit for the »extra« quality according to the EEC regulations *(13)*. The fruity smell almost completely disappeared in all the samples kept in aqueous media, and scarcely to mildly expressed defects »brine« and »vegetable water« appeared. As for taste properties, it is interesting that throughout the period of storage the piquancy mostly remained unchanged in all the samples, including those stored in the air, while bitterness increased in samples from sea water and brine. These observations do not agree with the pleasant flavoury and sweet properties of oil quoted for this method of storing by Petruccioli *et al.* *(8)*. These disparities can be attributed to differences in methods applied in evaluating sensory characteristics of oil samples.

Significant changes were observed in the mass fraction of total chlorophylls in oil, ranging from 3.1 to 53.6 mg/kg (Fig. 1). Although they are not included among standard quality parameters in international regulations *(13,18)*, chlorophylls are important for their active role in oxidative processes during oil conservation *(19)*. Oils obtained from olives stored in the open air had the lowest chlorophyll values. This can be explained by the formation of primary products of oil oxidation (increase of peroxide value) and activation of lipoxygenase accompanied by chlorophyll degradation into colourless products *(11,20)*.

When considering the oils obtained from olives kept in aqueous media, the amounts of total chlorophylls tripled after 10 days, with regard to the reference sample. After 20 days of storage these values increased approximately 7.5 times and after 30 days 8.5 times in comparison with the reference sample.

Such changes can be explained by slowing down of the chlorophyll transformation into colourless products by dipping fruits into water. Mínguez-Mosquera *et al.* *(21)* established that in olives preserved in 12 % NaCl solution no changes in fraction of total chlorophylls occurred, but only transformations into their corresponding green to grey-brown derivates, caused by catalytic activity of chlorophyllase. We also suppose that water medium affects the permeability of the cell walls in fruits, making chlorophyll more accessible to oil drops in processing olives.

Conclusions

Negative changes in basic physicochemical indicators of oil quality are by far less expressed when olives are stored in aqueous media than when stored in wooden boxes exposed to air. However, keeping olives in aqueous media results in faster and almost complete disappearance of desirable odour properties of olive oil, which is not the case for storage in the open air. Characteristic undesirable properties of oil produced from olives stored in sea water and brine are the taste and smell of brine. However, among the studied methods of olive storage no significant differences have been observed with regard to overall quality index, which, besides the basic physicochemical parameters, includes the score of sensory evaluation. The most evident difference between olive oils obtained after storage of fruits in the open air and in the aqueous media is in the fraction of total chlorophylls.

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Utjecaj čuvanja maslinovog ploda u morskoj vodi na kakvoću ulja

Sažetak

Dugotrajno i/ili neprikladno skladištenje plodova masline bitno može umanjiti kakvoću djevičanskog maslinovog ulja. Uranjanje maslina u morsku vodu tradicionalan je i još uvijek često primjenjivan način čuvanja plodova u Hrvatskoj. Promjene standardnih pokazatelja kakvoće ulja tijekom takva načina skladištenja maslina sorte Bjelica uspoređivane su s razultatima dobivenim čuvanjem maslina u salamuri (4 %-tna otopina natrijeva klorida), pitkoj vodi, te na zraku u drvenim sanducima. Uzorci ulja dobiveni su preradbom plodova u pilotnom postrojenju, koje se sastoji od mlina čekićara i preše sa čeličnim mrežama. Tijekom 30 dana čuvanja u vodenim medijima, u svim je uzorcima blago porastao maseni udjel slobodnih masnih kiselina, dok je u uzorcima čuvanim na zraku taj porast bio kudikamo veći. Vrijednosti peroksidnog broja i koeficijenta apsorbancije pri 232 nm opadale su tijekom čuvanja u vodenim medijima, dok je koeficijent apsorbancije pri 270 nm ostao konstantan. Uranjanjem maslina u salamuru i morsku vodu poželjna mirisna svojstva ulja nestala su već nakon 10 dana, a u uzorcima izloženim zraku bila su zamjetljiva i nakon 30 dana. Ulja dobivena od maslina čuvanih u salamuri i morskoj vodi imala su karakterističan nepoželjan okus i miris po salamuri. U svim postupcima čuvanja snizio se ukupni indeks kakvoće i među njima nisu uočene bitne razlike. Uspoređujući načine čuvanja, najočitija razlika uočena je u udjelu ukupnih klorofila. U vodenim je medijima porasla za otprilike 8 puta, dok se na zraku smanjila 1,5 put u usporedbi s referentnim uzorkom. Rezultati upućuju na zaključak da se čuvanjem maslina u vodenim medijima bitno ne mijenjaju osnovni fizikalno-kemijski pokazatelji kakvoće ulja, osim što se smanjuje njegova kakvoća zbog nepoželjnih promjena senzorskih svojstava.