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FOOD TECHNOLOGY

Natural antioxidants in the stability of ray liver oil

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ABSTRACT: *The effect of the addition of natural antioxidants on oxidative stability of ray (**Rhinoptera bonasus**) liver oil was evaluated. Different concentrations of rosemary extract, α-tocopherol, and caffeic acid (w/w) were added to the oil. Afterwards, concentration of each antioxidant that gave the highest stability was used in an accelerated stability test (Schaal method). The protective effect was established by the retention in the oil of fatty acids eicosapentaenoic (EPA) and docosahexaenoic (DHA), and concentration of volatile compounds. The best concentrations were: 2.5% of rosemary extract, 0.5% of α-tocopherol, and 0.06% of caffeic acid. Rosemary extract showed to be the product with the greatest ability to retard oxidation, followed by α-tocopherol, and caffeic acid. A high correlation between the peroxide value and the concentration of the 2-decenal, 1-penten-3-ol, and 2-octenal, was reported, suggesting that this can be used to assess the development of oxidative rancidity in the ray liver oil.*
Key words: *ray liver oil, natural antioxidants, EPA, DHA, volatile compounds.*

Antioxidantes naturais na estabilidade do óleo de fígado de gaviões-do-mar

RESUMO: *Objetivo desta pesquisa foi avaliar o efeito da adição de antioxidantes naturais sobre a estabilidade à oxidação do óleo de fígado de gavião-do-mar (**Rhinoptera bonasus**). Primeiro, determinou-se a concentração de antioxidante que maior proteção proporcionava ao produto. Foram adicionadas diferentes quantidades de extrato de rosmaninho, α- tocoferol e ácido cafeico (w/w) ao óleo, sendo sujeito a aquecimento. O efeito protetor foi estabelecido a partir do nível de retenção de ácidos gordos poli-insaturados eicosapentaenoico (EPA) e docosahexaenoico (DHA) nas amostras. Posteriormente, a concentração que deu melhor resultado para cada antioxidante foi utilizada num estudo de armazenamento acelerado (Método de Schaal), com a finalidade de estabelecer a durabilidade do produto. Paralelamente, foi analisada a concentração de compostos voláteis relacionados com a oxidação de óleos de peixe. Observaram-se diferenças significativas entre a quantidade de EPA e DHA remanente, para as concentrações de antioxidantes adicionados, correspondendo os melhores resultados a: 2,5% extrato de rosmaninho, 0,5% α-tocoferol e 0,06% ácido cafeico. Por outra parte, o desenvolvimento da prova de Schaal mostrou o extrato de rosmaninho, como o produto com a maior capacidade de retardar a oxidação, seguido por α-tocoferol, ácido cafeico. Foi encontrada correlação entre o valor de peróxido e a concentração de compostos voláteis, 2-decenal, 1-penten-3-ol e 2-octenal, o que sugere que estes possam ser empregues, para determinar a evolução do ranço oxidativo, no óleo de fígado de gavião-do-mar (**Rhinoptera bonasus**).*
Palavras-chave: óleo de fígado de *gavião-do-mar, antioxidantes naturais, EPA, DHA, compostos voláteis.*

INTRODUCTION

Nowadays, a great interest for fish oil consumption has been raised due to its fatty acid composition, being the main source of ω-3 polyunsaturated fatty acids (PUFA´s), such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA). EPA and DHA recognized for its health benefits and pharmacological qualities (MOON & SHIBAMOTO, 2009).

In Mexico, ray fishery represents an important activity with a production of 9,360 metric tonnes in 2013 (CONAPESCA, 2013); unfortunately, only its meat is commonly used, discarding the rest, such as its liver. It has been shown that ray liver constitutes a rich source of ω-3 fatty acids, with EPA + DHA contents similar to cod oil and other marine species (NAVARRO-GARCIA et al., 2010). Thus, ray (***Rhinoptera bonasus***) liver oil could be used as an alternative source for ω-3 PUFA´s; however, due to the high degree of instauration of these oils, special care has to be taken in order to avoid lipid oxidation and rancidity, which can affect its shelf life (IGLESIAS & MEDINA, 2008). In order to avoid this problem, antioxidants have been commonly used as an indispensable tool to improve the oil shelf life (BARTEE,

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et al., 2007). Synthetic antioxidants have been commonly used; however, their use has been restricted due to its possible toxic effects. Nowadays, efforts have been conducted to substitute their use for natural antioxidants such as phenolic compounds (DE LEONARDIS & MACCIOLA, 2003; SIRIWARDHANA et al., 2004; MORENO-ÁLVAREZ et al., 2007). Although studies have used different natural antioxidants to prevent or retard the oil oxidation from different sources, no study has been conducted on the use of them in ray liver oil.

Hence, the objective of the present study was to study the effect of natural antioxidants on the oxidative stability of ray (***Rhinoptera bonasus***) liver oil, as well as assessing the possibility of using volatile compounds as a parameter for evaluate oxidative status.

MATERIALS AND METHODS

Sampling and oil extraction

Ray specimens of ***Rhinoptera bonasus*** were captured in the Gulf of México near Ceyba playa shore in Campeche, Mexico. Dissected livers were placed on polyethylene bags and frozen at -20°C for their transportation to the Aquaculture Nutrition Laboratory at the Department of Scientific and Technological Research of the University of Sonora (DICTUS). The oil was extracted by the procedure described by KANG et al. (1998).

Chemical characterization of ray liver oil

The fatty acid profile was determined through gas chromatography (Ce 1i-07 AOCS, 2009), tocopherols were conducted through high-resolution liquid chromatography (Ce 8-89, AOCS, 2009) and peroxide value determined (Cd 8b-90 AOCS, 2009).

Evaluation of the ray liver oil stability

The stability of ray (***Rhinoptera bonasus***) liver oil with rosemary extract (RM), tocopherol (TOC), and caffeic acid (CA) was evaluated by two different oxidation accelerated tests using tert-butylhydroquinone (TBHQ) as control (0.02%). Antioxidants were obtained from Dresen Química, S.A. de C.V. México, except CA, which was obtained from Sigma (St. Louis, MO).

Heating oxidation accelerated test. The heating accelerated test was conducted according to (BHALE et al., 2007) with a slight modification. Briefly, antioxidant solutions were prepared (% w/w) as follows: 0.02, 1, 2.5, 5% for RM; 0.02, 0.3, 0.5, 0.8% for TOC; 0.02, 0.03, 0.06, 0.1% for CA. The concentration of TOC present in the oil was taken into account and was added the rest to reach the desired concentration. Oxidation degree was evaluated as follows:

EPA or DHA in oil (after heating)/EPA or DHA in oil (before heating)] × 100.

Schaal´s method

Solutions of 2.5% RM, 0.5% TOC, 0.06% CA, and 0.02 TBHQ were mixed with 26 g of oil. The vials were set on a stove at 60±2°C for 35 days, monitoring the oxidation process, in term of PV and volatile compounds produced, at 0, 7, 14, 21, 28, and 35 days.

Evaluation of volatile compounds

Volatile compounds were evaluated by the solid-phase microextraction technique/gas chromatography (SPME/GC) (RICHARDS et al., 2005). The volatile were analyzed using a 15m×0.25mm i.d. CP-SIL 8 CB capillary column (Varian, Walnut Creek, CA, USA). Individual components were identified by comparing retention times with standards: 3-hexenal, hexanal, 2-hexenal, heptanal, 2,4-hexadienal, 2-heptenal, 1-octen-3-ol, 2-penthylfurane, 2,4-heptadienal, 2-octenal, octanal, nonanal, decanal, ethylvinylketone, 2-decenal, 2,4-decadienal, and 1-penten-3-ol (Supelco-Sigma, Aldrich Química, México). Calibration curves of each compound were used for the quantification.

Statistical analysis

Descriptive statistics (mean ± standard deviation) were calculated in triplicate. An analysis of variance was carried out in order to determine the mean differences in the oil stability due to the use of natural antioxidants. Significant differences among the means were tested using Tukey´s test ($P<0.05$). Besides, a liner regression analysis was conducted between the peroxide values and the volatile compounds concentration. A Statistical Package for the Social Sciences (SPSS17) for Windows was used.

RESULTS AND DISCUSSION

Fatty acid content

The fatty acid profile showed that unsaturated fatty acids constituted the major fraction (62.7%) in the oil, with EPA, C22:5 w-3, and DHA contents of 3.8±0.64, 6.0±0.30 and 19.8±1.44%, respectively. This value was higher than the one reported by NAVARRO-GARCIA et al. (2004) for ***Gymnura marmota*** and ***Dasyatis brevis*** with EPA + DHA content of 18 and 16%, respectively. MENDEZ et al. (1996) reported for cod liver oil, 16.1% of these PUFA´s, oil considered as an excellent source of ω-3 fatty acids. Therefore, ***Rhinoptera bonasus*** liver oil can be used as an alternative source for this type of PUFA´s.

Tocopherol content

In the ***R. bonasus*** liver oil it was only detected the isomer α-tocopherol (16.7mg 100 g^{-1}). Result agrees with PARAZO et al. (1998), who reported a high selectivity of α-isomers in fish liver oil. NAVARRO-GARCIA et al. (2004) reported α-tocopherol contents in different ray species from 1.6 to 64.9mg $100g^{-1}$.

Evaluation of the oil stability by the heating oxidation accelerated test

Table 1 shows the effect of antioxidant concentration on the stability of EPA and DHA in ***R. bonasus*** liver oil. After heating the samples, TBHQ showed a good antioxidant protection for EPA and DHA. However, the best antioxidant protection observed for these PUFA´s was shown by 2.5% rosemary extract, showing 100% of retention for EPA and DHA. In a study by BHALE et al. (2007), the use of 2.5% rosemary extract (as in the present study) presented the highest EPA and DHA retentions (60% for both fatty acids) in menhaden oil.

Caffeic acid showed its best protection at a concentration of 0.06%, with 87% and 79% retention of EPA and DHA, respectively (Table 1). This result agrees with DE LEONARDIS & MACCIOLA (2003), who reported that the best oxidation stability for cod liver oil was reached at the same concentration (0.06% caffeic acid) as in the present study, indicating that this compound possess maximum antioxidant properties on highly unsaturated fish oil at that concentration.

With respect to the use of α-tocopherol as antioxidant, 0.5% was the concentration that showed the best EPA and DHA stability, both approximately with 85% PUFA´s retention (Table 1). HUANG & FRANKEL (1997) reported 0.01% of α-tocopherol as the optimum for antioxidant activity on corn oil. FRANKE, (1996) reported that α-tocopherol activity depends of the evaluated system. Thus, the ***R. bonasus*** oil system, being highly unsaturated, required more tocopherol concentration.

Curiously, the highest concentrations of each antioxidant showed destabilizing conditions, reducing their antioxidant effectiveness. This is

Table 1 - Effect of antioxidant concentration on EPA and DHA retention in ray (***Rhinoptera bonasus***) liver oil treated by a heating oxidation accelerated test.

TREATMENT (% w/w)	EPA (%)	Retention (%)	DHA (%)	Retention (%)
----------THBQ----------				
No antioxidant	2.3 ± 0.2^{a}	61.4	10.7 ± 0.1^{a}	53.9
0.02	3.7 ± 0.3^{b}	97.3	16.4 ± 0.7^{b}	82.9
Raw, fresh oil	3.8 ± 0.6^{b}		19.8 ± 1.5^{c}	
----------CAFFEIC ACID----------				
No antioxidant	2.3 ± 0.2^{a}	61.4	10.7 ± 0.1^{a}	53.9
0.02	2.7 ± 0.1^{ab}	71.0	14.8 ± 0.6^{b}	74.5
0.03	2.8 ± 0.4^{ab}	75.0	14.1 ± 0.9^{b}	71.2
0.06	3.3 ± 0.2^{bc}	86.6	15.7 ± 0.3^{b}	79.0
0.10	3.1 ± 0.0^{abc}	82.2	15.6 ± 0.3^{b}	78.6
Raw, fresh oil	3.8 ± 0.6^{c}		19.8 ± 1.5^{c}	
----------TOCOPHEROL----------				
No antioxidant	2.3 ± 0.2^{a}	61.4	10.7 ± 0.1^{a}	53.9
0.02	2.0 ± 0.2^{a}	52.8	10.6 ± 1.0^{a}	53.5
0.30	2.6 ± 0.2^{ab}	68.4	13.7 ± 0.9^{b}	69.4
0.50	3.2 ± 0.1^{bc}	85.1	17.0 ± 0.4^{c}	85.7
0.80	2.8 ± 0.2^{ab}	74.2	13.3 ± 0.8^{b}	67.0
Raw, fresh oil	3.8 ± 0.6^{c}		19.8 ± 1.5^{d}	
----------ROSEMARY EXTRACT----------				
No antioxidant	2.3 ± 0.2^{a}	61.4	10.7 ± 0.1^{a}	53.9
0.02	2.4 ± 0.2^{ab}	63.0	12.4 ± 0.6^{a}	62.5
1.00	3.1 ± 0.0^{bc}	84.0	17.7 ± 0.1^{b}	89.5
2.50	3.8 ± 0.2^{c}	100.0	19.9 ± 0.7^{c}	100.0
5.00	3.4 ± 0.2^{c}	90.5	18.9 ± 0.4^{bc}	95.2
Raw, fresh oil	3.8 ± 0.6^{c}		19.8 ± 1.5^{c}	

Data are the mean ± SD (n = 3). Different superscripts in the same column indicate significant differences (P<0.05).

probably due to the complex compound composition, which can act as prooxidants.

Evaluation of oil stability by the Schaal´s accelerated test

Peroxide value

Raw, fresh ***R. bonasus*** liver oil showed an initial peroxide value of 2.1±0.3mEq Kg^{-1}. HUSS (1988) established 7mEq Kg^{-1} as the maximum limit to accept fish oil. YIN & SATHIVEL (2010), reported a value of 5.70mEqO_2 Kg^{-1} for menhaden oil, which is more than twice the value reported for the specie in this study. This result is probably due to the protector effect of the natural antioxidant (α-tocopherol) reported in the ***R. bonasus*** liver oil.

All antioxidants evaluated showed good antioxidant activity for up to 14 days ($P>0.05$), except the rosemary extract (2.5%), which reached ($P\leq0.05$) 21 day (Figure 1). Equivalence between peroxide value (from Schaal´s test) and time at room temperature has been established (SIRIWARDHANA et al., 2004), where 24h at 60°C corresponds to one month storage at room temperature. Thus, the shelf life of ray oil would be as follows: when using no antioxidant less than 14 months, TBHQ (0.02%), CA (0.06%), and TOC (0.5%) a bit more than 14 months, and finally, RM (2.5%) for more than 21 months.

Volatile compounds

From 16 volatile compounds evaluated only 9 (hexanal, 2-heptenal, 2-pentylfuran, octaldehyde, 2-octenal, decanal, 2-decenal, 2,4-decadienal, and 1-penten-3-ol) were detected in all treatments for the 35 days of the study, and the 6 main are shown in table 2. In most cases, volatiles production was inhibited by the use of antioxidants, especially for 1-penten-3-ol and 2-heptenal. Volatile compound detected in the highest concentration was 1-penten-3-ol (Table 2), which value increased almost 35 times at day 28 (TBHQ, no antioxidant). KULAS et al. (2002) reported similar results in menhaden oil stored for 20 weeks and fish oil added with tocopherol, respectively. In contrast, use of antioxidants effectively inhibited the formation of this compound in the oil studied (Table 2). This compound is formed by the action of the 15-lipoxygenese on EPA (20:5 n-3) (IGLESIAS & MEDINA, 2008). Volatile compounds such as 1-penten-3-ol, and 2,4-heptadienal have been identified in fish oil (HSIEH et al., 1989) and associated in the oxidation process, as contributors of off-flavors.

Correlation analysis between peroxide value and volatile compounds concentration showed a high correlation only for 2-decenal, 1-penten-3-ol, and 2-octenal (Table 3). Thus, these compounds can be used as potential markers to evaluate the oxidation of the ray liver oil.

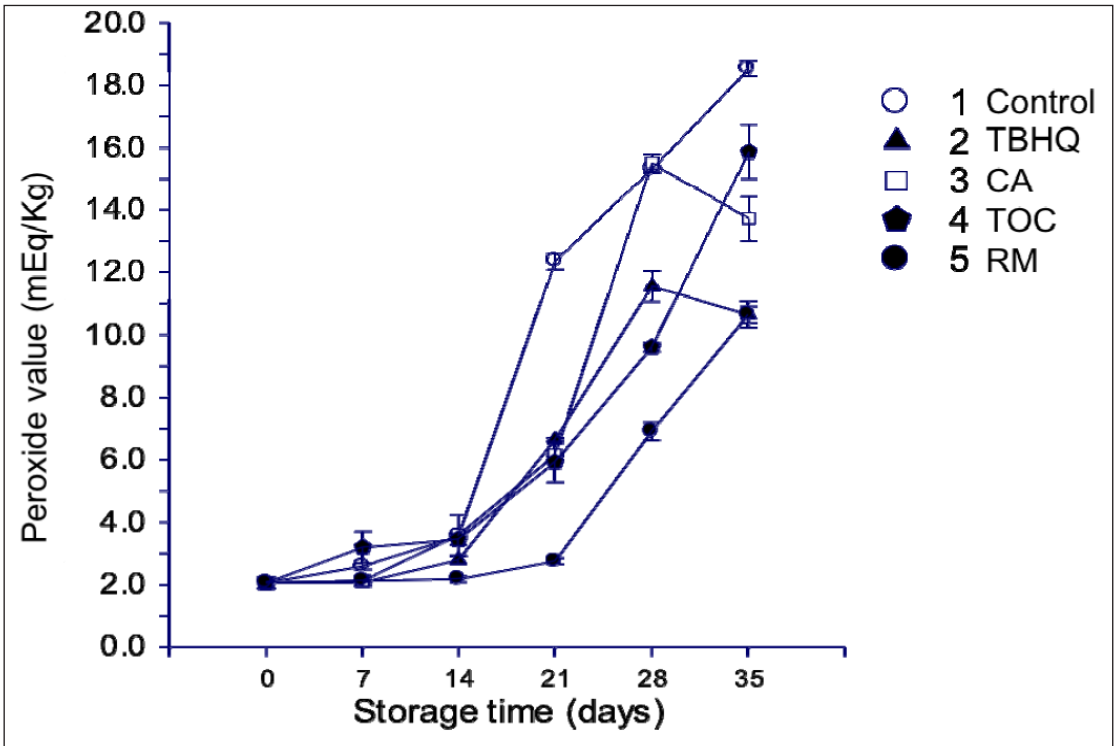

Figure 1 - Effect of different antioxidants on the peroxide value (mEq kg^{-1}) in ray (***Rhinoptera bonasus***) liver oil by Schaal´s accelerated test (60°C).

Table 2 - Main volatile compounds (mg x 10^{-2}) reported in ***Rhinoptera bonasus*** ray liver oil during the Schaal´s accelerated test (60°C).

Compound	Treatment	Days of storage at 60°C					
		0	7	14	21	28	35
2-heptenal	N.A.	0.8 ± 0.5	3.2 ± 0.5	6.1 ± 0.5	13.1 ± 0.4	12.7 ± 0.6	8.8 ±5.0
	TBHQ	0.8 ± 0.5	1.7 ± 0.0	1.6 ± 0.2	3.2 ± 1.0	5.2 ± 0.2	5.6 ±0.3
	CA	0.8 ± 0.5	0.9 ± 0.0	1.7 ± 0.0	2.3 ± 0.0	5.2 ± 0.2	6.1 ± 0.0
	RM	0.8 ± 0.5	1.6 ± 0.0	0.9 ± 0.0	6.0 ± 0.1	10.2 ± 0.2	12.0 ± 0.3
	TOC	0.8 ± 0.5	6.9 ± 0.1	1.8 ± 0.2	5.7 ± 0.3	8.7 ± 0.3	10.6 ± 0.0
2,4-heptadienal	N.A.	n.d.	1.0 ± 0.7	0.9 ± 0.0	2.3 ± 0.0	2.5 ± 0.2	2.0 ± 0.0
	TBHQ	n.d.	6.7 ± 0.0	2.1 ± 0.3	2.6 ± 0.3	3.7 ± 0.2	2.0 ± 0.0
	CA	n.d.	0.5 ± 0.0	2.3 ± 0.1	2.8 ± 0.1	4.1 ± 0.1	2.9 ± 0.1
	RM	n.d.	n.d.	n.d.	2.1 ± 0.1	2.6 ± 0.0	1.5 ± 0.0
	TOC	n.d.	1.0 ± 0.0	3.5 ± 0.2	3.7 ± 0.3	2.7 ± 0.0	1.9 ± 0.4
2-octenal	N.A.	0.7 ± 0.1	3.2 ± 0.5	4.4 ± 0.3	14.4 ± 0.3	16.7 ± 0.2	11.1 ±.6.1
	TBHQ	0.7 ± 0.1	5.5 ± 0.3	2.9 ± 0.0	7.5 ± 1.0	12.9 ± 0.0	15.3 ± 0.0
	CA	0.7 ± 0.1	3.2 ± 0.1	3.9 ± 0.1	8.1 ±0.3	14.7 ± 0.2	17.2 ± 0.2
	RM	0.7 ± 0.1	1.3 ± 0.1	0.5 ± 0.0	2.0 ± 0.0	8.0 ± 0.3	14.5 ± 0.4
	TOC	0.7 ± 0.1	7.3 ± 0.0	2.5 ± 0.0	6.1 ± 0.1	12.0 ± 0.2	14,7 ± 0.1
1-octenal	N.A.	n.d.	1.1 ± 1.3	0.32 ± 0.0	4.3 ± 0.0	4.6 ± 0.0	2.6 ± 1.4
	TBHQ	n.d.	0.9 ± 0.1	1.4 ± 0.1	2.5 ± 0.2	3.8 ± 0.0	3.0 ± 0.0
	CA	n.d.	0.5 ± 0.0	1.6 ± 0.1	2.6 ± 0.1	3.5 ± 0.0	3.3 ± 0.1
	RM	n.d.	n.d.	n.d.	0.8 ± 0.2	1.5 ± 0.1	1.5 ± 0.0
	TOC	n.d.	1.8 ± 0.2	1.4 ± 0.0	2.2 ± 0.0	3.3 ± 0.0	2.8 ± 0.0
2-decenal	N.A.	0.3 ±0.0	0.8 ± 0.1	1.0 ± 0.1	2.9 ± 0.0	3.7 ± 0.0	2.5 ± 1.2
	TBHQ	0.3 ±0.0	1.1 ± 0.0	1.6 ± 0.0	2.1 ± 0.4	2.9 ± 0.0	4.2 ± 0.1
	CA	0.3 ±0.0	0.6 ± 0.0	0.8 ± 1.2	1.9 ± 0.1	|3.4 ± 0.1	5.3 ± 0.1
	RM	0.3 ±0.0	0.4 ± 0.0	0.8 ± 0.0	2.3 ± 0.2	2.7 ± 0.1	4.0 ± 0.1
	TOC	0.3 ±0.0	3.1 ± 0.0	3.8 ± 0.0	5.3 ± 0.1	7.7 ± 0.2	9.8 ± 0.4
1-penten-3-ol	N.A.	9.4 ± 1.1	1.0 ± 0.0	148.7 ± 2.7	326.0 ± 8.4	288.6 ± 5.6	83.7 ± 52.1
	TBHQ	9.4 ± 1.1	18.2 ±1.5	17.9 ± 0.3	19.0 ± 6.2	27.9 ± 0.0	84.9 ± 1.6
	CA	9.4 ± 1.1	12.0 ± 0.7	14.8 ±0.2	13.9 ± 6.8	42.2 ± 2.4	102.2 ± 1.1
	RM	9.4 ± 1.1	7.2 ± 0.4	9.3 ± 0.0	18.0 ± 0.7	39.8 ± 10.3	98.4 ± 2.9
	TOC	9.4 ± 1.1	18.7 ± 0.1	21.7 ± 0.0	34.4 ± 0.9	47.2 ± 0.0	56.3 ± 3.8

n = 3; n.d.= not detected; N.A. no antioxidant.

Table 3 - Significant linear relationships between peroxide value and concentration of volatile compounds.

Volatile compound	Antioxidant used			
	TBHQ (0.02%)	CA (0.06%)	TOC (0.5%)	RM (2.5%)
1-penten-3-ol	y = 17.73x + 1.44	y = 13.97x + 2.14	y = 27.83x - 2.01	y = 14.43x + 2.30
	R^2 = 0.88	R^2 = 0.93	R^2 = 0.91	R^2 = 0.95
2-decenal	y = 367.28x -0.81	y = 267.98x + 1.16	y = 145.04x - 0.56	y = 337.33x +0.79
	R^2 = 0.93	R^2 = 0.99	R^2 = 0.89	R^2 = 0.92
2-octenal	y = 87.47x + 0.15	y = 75.27x + 0.68	y = 88.73x + 0.27	y = 91.19x + 2.58
	R^2 = 0.89	R^2 = 0.92	R^2 = 0.83	R^2 = 0.97

TBHQ = tert-butylhydroquinone; CA= Caffeic acid; RM= Rosemary extract; TOC= tocopherol. $\alpha = 0.05$.

CONCLUSION

Addition of natural antioxidants (rosemary extract, tocopherol, and caffeic acid) to ray (***Rhinoptera bonasus***) liver oil significantly protected to eicosapentaenocic and docosahexaenoic acids from the oxidative deterioration at the conditions evaluated. The best results were in decreasing order: rosemary extract>tocopherol>caffeic acid. Volatile compound determination by SPME showed that measuring of 2-decenal, 1-penten-3-ol, and 2-octenal can be used as an alternative technique to monitor the oxidative process in this type of oil.

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REFERENCES

AOCS (AMERICAN OIL CHEMISTS' SOCIETY). **Official methods and recommended practices**. 6.ed. Urbana, IL: AOCS, 2009. 1200 p.

BARTEE, S. et al. Effects of antioxidants on the oxidative stability of oils containing arachidonic, docosapentaenoic and docosahexaenoic acids. **Journal of the American Oil Chemists' Society**, v.84, n.4, p.363-368, 2007. ISSN 0003-021X. Available from: <http://dx.doi.org/10.1007/s11746-007-1046-4>. Accessed: Jul. 12, 2015.

BHALE, S.D. et al. Oregano and rosemary extracts inhibit oxidation of long-chain n-3 fatty acids in menhaden oil. **Journal of Food Science**, v.72, n.9, p.C504-C508, 2007. ISSN 0022-1147. Available from: <http://onlinelibrary.wiley.com/doi/10.1111/j.1750-3841.2007.00569.x/full>. Accessed: Jul. 15, 2015.

CONAPESCA. **Anuario Estadístico de Acuacultura y Pesca**. Mazatlán, México: Comisión Nacional de Acuacultura y Pesca, 2013. 299 p.

DE LEONARDIS, A.; MACCIOLA, V. Effectiveness of caffeic acid as an anti-oxidant for cod liver oil. **International Journal of Food Science and Technology**, v.38, n.4, p.475-480, 2003. ISSN 0950-5423. Available from: <http://onlinelibrary.wiley.com/doi/10.1046/j.1365-2621.2003.00707.x/full>. Accessed: Jul. 25, 2015.

FRANKEL, E.N. Antioxidants in lipid foods and their impact on food quality. **Food Chemistry**, v.57, n.1, p.51-55, 1996. ISSN 0308-8146. Availablre from: <http://www.sciencedirect.com/science/article/pii/0308814696000672>. Accessed: Aug. 5, 2015.

HSIEH, T.C.Y. et al. Characterization of volatile components of menhaden fish (brevoortia-tyrannus) oil. **Journal of the American Oil Chemists Society**, v.66, n.1, p.114-117, 1989. ISSN 0003-021X. Available from: <http://link.springer.com/article/10.1007/BF02661797>. Accessed: Aug. 8, 2015.

HUANG, S.W.; FRANKEL, E.N. Antioxidant activity of tea catechins in different lipid systems. **Journal of Agricultural and Food Chemistry**, v.45, n.8, p.3033-3038, 997. ISSN 0021-8561. Available from: <http://pubs.acs.org/doi/abs/10.1021/jf9609744>. Accessed: Aug. 10, 2015.

HUSS, H.H. **Fresh fish quality and quality changes**. Roma, Italia: FAO, 1998. 147 p.

IGLESIAS, J.; MEDINA, I. Solid-phase microextraction method for the determination of volatile compounds associated to oxidation of fish muscle. **Journal of Chromatography A**, v.1192, n.1, p.9-16, 2008. ISSN 0021-9673. Available from: <http://www.sciencedirect.com/science/article/pii/S0021967308004998>. Accessed: Aug. 10, 2015.

KANG, S.J. et al. Similarities in the lipid class profiles of oils from Atlantic and Pacific dogfish livers. **Journal of the American Oil Chemists Society**, v.75, n.11, p.1667-1672, 1998. ISSN 0003-021X. Available from: <http://link.springer.com/article/10.1007/s11746-998-0109-5>. Accessed: Aug. 15,2015.

KULAS, E. et al. Effect of α-, γ-, and δ-tocopherol on the distribution of volatile secondary oxidation products in fish oil. **European Journal of Lipid Science and Technology**, v.104, n.8, p.520-529, 2002. ISSN 1438-7697. Available from: <http://onlinelibrary.wiley.com/doi/10.1002/1438-9312(200208)104:8%3C520::AID-EJLT520%3E3.0.CO;2-H/full>. Accessed: Aug. 20, 2015.

MENDEZ, E. et al. Lipid content and fatty acid composition of fillets of six fishes from the Rio de la Plata. **Journal of Food Composition and Analysis**, v.9, n.2, p.163-170, 1996. ISSN 0889-1575. Available from: <http://www.sciencedirect.com/science/article/pii/S088915759690023X>. Accessed: Aug. 20, 2015.

MOON, J.-K.; SHIBAMOTO, T. Antioxidant assays for plant and food components. **Journal of Agricultural and Food Chemistry**, v.57, n.5, p.1655-1666, 2009. ISSN 0021-8561. Available from: <http://pubs.acs.org/doi/abs/10.1021/jf803537k>. Accessed: Aug. 20, 2015.

MORENO-ÁLVAREZ, M.J. et al. Estabilidad del aceite de soja acondicionados con extractos organicos de grapefruit (***Citrus paradisis*** Macf). **Revista de la Facultad de Agronomía**, v.24, n.4, p.709-724, 2007. ISSN 0378-7818. Available from: <http://revfacagronluz.org.ve/PDF/octubre_diciembre2007/morenoalvarez.pdf>. Accessed: Aug. 20, 2015.

NAVARRO-GARCIA, G. et al. Characterization of the lipid composition and natural antioxidants in the liver oil of ***Dasyatis brevis*** and ***Gymnura marmorata*** rays. **Food Chemistry**, v.87, n.1, p.89-96, 2004. ISSN 0308-8146. Available from: <http://www.sciencedirect.com/science/article/pii/S0308814603005727>. Accessed: Aug. 21, 2015.

NAVARRO-GARCIA, G. et al. Storage stability of liver oil from two ray (***Rhinoptera bonasus*** and ***Aetobatus narinari***) species from the Gulf of Mexico. **Food Chemistry**, v.119, n.4, p.1578-1583, 2010. ISSN 0308-8146. Available from: <http://www.sciencedirect.com/science/article/pii/S0308814609011054>. Accessed: Aug. 21, 2015.

PARAZO, M.P.M. et al. Distribution of alpha- and gamma-tocopherols in Atlantic salmon (***Salmo salar***) tissues. **Lipids**, v.33, n.7, p.697-704, 1998. ISSN 0024-4201. Available from: <http://link.springer.com/article/10.1007/s11745-998-0259-x>. Accessed: Aug. 21, 2015.

RICHARDS, A. et al. Evaluation of oxidative stability of canola oils by headspace analysis. **Journal of the American Oil Chemists' Society**, v.82, n.12, p.869-874, 2005. ISSN 0003-021X. Available from: <http://link.springer.com/article/10.1007/s11746-005-1157-3>. Accessed: Sept. 2, 2015

SIRIWARDHANA, N. et al. Lipid peroxidation inhibitory effects of Hizikia fusiformis methanolic extract on fish oil and linoleic acid. **Food Science and Technology International**, v.10, n.2, p.65-72, 2004. ISSN 1082-0132. Available from: <http://fst.sagepub.com/content/10/2/65.short>. Accessed: Sept. 2, 2015.

YIN, H.; SATHIVEL, S. Physical properties and oxidation rates of unrefined menhaden oil (***Brevoortia patronus***). **Journal of Food Science**, v.75, n.3, p.E163-E168, 2010. ISSN 0022-1147. Available from: <http://onlinelibrary.wiley.com/doi/10.1111/j.1750-3841.2010.01532.x/full>. Accessed: Sept. 6, 2015.