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Lipid Composition, Natural Antioxidants and Physicochemical Characteristics in Liver Oil from Rajiforms from the Gulf of Mexico

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Abstract Lipid composition by class, fatty acids, natural antioxidants (carotenes, tocopherols) and physicochemical characteristics of liver oil from three commercial rays, *Rhinoptera bonasus* (Chucha), *Aetobatus narinari* (Pinta) and *Dasyatis americana* (Bala) from the Gulf of Mexico were analyzed. Liver oil yield for *R. bonasus*, *A. narinari* and *D. americana* were of 43.04, 41.2 and 38.2% (wet weight), respectively. Triacylglycerols were the most abundant lipid by class in *R. bonasus* (68.9%), *A. narinari* (85.9%) and *D. americana* (81.6%), while sterols esters, sterols, di- and monoacylglycerides, polar lipids and wax esters were found in minor proportions. Species showed similar carotenes concentration, 8.7, 12.8 and 8.0 μg/g for *R. bonasus*, *A. narinari* and *D. americana*, respectively. α-tocopherol concentration was higher ($p < 0.05$) for *A. narinari* (46.7 mg/100 g) than for *R. bonasus* (21.0 mg/100 g) and *D. americana* (13.7 mg/100 g). Omega-3 polyunsaturated fatty acids in *R. bonasus* were high with docosahexaenoic acid (12.1%) in a higher proportion than eicosapentaenoic acid (7%).

Keywords Food and feed science · Nutrition and health

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Introduction

Elasmobranch fish possess an atypical lipid metabolism among vertebrates. They lack true adipose tissue with the majority of lipid storage and metabolism occurring in the lobes of the liver [1, 2]. Studies by Navarro-García et al. [3, 4] on ray species from the Gulf of California showed that liver weight on these species ranged from 5 to 11% of the fish body weight, and that up to 50% of the liver weight was lipid.

Fish liver oil is the major source of n-3 polyunsaturated fatty acids (PUFAs), specifically eicosapentaenoic (EPA, 20:5n-3) and docosahexaenoic acids (DHA, C22:6n-3), compounds that are important for therapeutic uses in human health [5]. Their cardiovascular disease prevention and mortality risk reduction has been well documented [6]. DHA, the most abundant ω-3 fatty acid in mammalian brain, is claimed to be important for brain development and function [7]. EPA is a precursor of DHA. Simopoulos et al. [8] suggested a supplementary diet consumption of 300 mg/day of DHA for pregnant women in order to attain proper brain and retina formation of the fetus.

The rajiform fishery in Campeche, a state located in the southeast part of the Mexican Republic, captures 45% (1,342 tonnes) of the total rays harvested in the Gulf of Mexico and Caribbean region [9]. Fishermen only used its muscle and discard the liver, which might be an important source of oil rich in EPA and DHA (16–18% of total fatty acids) as demonstrated by Navarro-García et al. [3, 4] for

rays from the Gulf of California. In order to have an integral utilization of this resource and due to the lack of information about this oil composition, it was deemed necessary to acquire basic information about the liver oil obtained from ray species capture in the region.

Hence, the objective of the present study was to analyze the lipid and fatty acids composition, as well as the physicochemical characteristics in liver oil from *Rhinoptera bonasus* (Chucha) *Aetobatus narinari* (Pinta) and *Dasyatis americana* (Bala) rajiform species captured in the State of Campeche, México.

Materials and Methods

Sampling and Oil Extraction

Ray specimens of *R. bonasus* (18 and 9 specimens), *A. narinari* (10 and 7 specimens) were captured in the Gulf of Mexico near Seybaplaya shore in Campeche in the summer (June) and winter (December) of 2006, respectively. Additionally, four *D. americana* specimens were also captured in the winter in the same area. Specimens, as well as their livers were weighed for hepatosomatic index (HSI). Dissected livers were placed in polyethylene bags and frozen at −20 °C for their transportation in coolers to the Centro de Investigación en Alimentación y Desarrollo (Hermosillo, Sonora, México). Livers were stored at −80 °C, for no more than 2 weeks, until oil extraction.

Livers were at thawed at room temperature and homogenized for 2 min using a 14-507-7 M cutter (Fisher Scientific, Pittsburgh, PA). The homogenized liver was heated at 45 °C for 1 h following the procedure described by Kang et al. [10] and centrifuged at 11,300×*g* for 20 min at room temperature in a model J2-21 Beckman centrifuge (Beckman Co., Fullerton, CA). The extracted oil was stored in 15 mL aliquots at −80 °C under nitrogen atmosphere. Oil was analyzed for lipid class, fatty acids, carotenes, tocopherols and its physicochemical properties. In addition, 1 g aliquots of homogenized liver were taken for total lipids content determination following the procedure described by Deprez et al. [11].

Lipids Classes

Qualitative and quantitative analysis of the lipid constituents in the liver oil were carried out by thin layer chromatography (TLC) [12]. We used 20 × 20 cm precoated TLC plates without fluorescent indicator containing silica gel 60 (0.25 mm thick) (Merck-México, S.A.) for the fractionation of hydrocarbons, steryl-esters, diacyl-mono-alkylglycerols, triacylglycerols, sterols and polar lipids. Lipid (600 µg) was spotted over a 1 cm wide line. TLC was carried out at 25 °C in a glass tank (15 × 25 × 25 cm) using, as a carrier agent, a 90:10:1 (v/v/v) mixture of hexane:ethyl ether:acetic acid. Plates were developed by spraying a solution of 5% (w/v) phosphomolybdic acid in ethanol and heated at 110 °C for 15 min. Lipids constituents were identified by comparison of their Rf values with those from corresponding components of the neutral lipid standard mixture (cholesterol oleate, methyl oleate, triolein, oleic acid and cholesterol) (TLC non-polar Lipid mix B, 1130, Matreya, Inc., Pleasant Gap, PA) and oleyl oleate (wax ester) (Sigma, Aldrich Química, México). The TLC plates were densitometrically scanned in a HP Scanjet 4070 Photosmart (Hewlett-Packard Company, Palo Alto, CA) and the peaks areas integrated with Imagen 1.38j software (National Institute of Health, USA). The concentration of the different lipid classes was determined by the area normalization method.

Fatty Acids

Fatty acids were derivatized to their corresponding methyl-esters using 7% BF_3-MeOH, according to method Ce 2-66; AOCS [13]. Identification and quantification of fatty acids methyl-esters (FAME) was obtained by capillary gas chromatography in a Varian 3800 gas chromatograph (Varian Inc., Walnut Creek, CA) fitted with a 30 m × 0.25 mm i.d. CP-Wax 52CB capillary column (Varian, Walnut Creek, CA, USA) and equipped with a flame ionization detector. The initial oven temperature was 140 °C. After 1 min, the temperature was raised to 190 °C at 9 °C/min, the temperature maintained for 1.5 min, then raised to 230 °C at 3 °C per min and and maintained at this temperature for 2 min. Individual components were identified by comparing retention times with those obtained from the FAME mixture standard (Supelco-Sigma cat. No. 4-7885, Aldrich, Química, México). Heptadecanoic acid (C17:0) was used as an internal standard.

Carotenes and Tocopherols

The total carotene analysis in the oil was carried out according to Simpson and Haard [14]. The oil samples (10 mL) were dissolved in petroleum ether and the mixture absorbance determined at 468 nm using a UV–visible spectrophotometer, Perkin Elmer Lambda 2S (Wellesley, MA). The tocopherol determination was carried out according to Medina-Juarez et al. [15] in a Varian 9050 HPLC chromatograph (Walnut Creek, CA), equipped with a Varian 3400 ultraviolet light detector (Walnut Creek, CA) and a Lychrosorb Si 60 column (25 cm × 4 mm × 5 µm) (Supelco-Sigma, Aldrich Química, México) at a wavelength of 292 nm. The mobile phase used for the analysis was a mixture of hexane/isopropanol (99.5:0.5 v/v),

at a flow rate of 1.6 mL/min. The mobile phase was filtered through a 0.45 μm filter before use. Two grams of oil were diluted in 25 mL of hexane and filtered at low pressure through a 0.45 μm filter. The samples (10μL) were injected in triplicate into the HPLC. The chromatographic peaks were identified and quantified by the comparison of the retention time and the areas of standards of α, γ and δ-tocopherol (Sigma, Aldrich Química, México).

Physicochemical Properties in Liver Oil

The density (D), iodine value (IV) and saponification value (SV), were determined following the methods 920.213, 993.20 and 921.160, respectively of the AOCS [16].

Statistical Analysis

Descriptive statistics (mean ± standard deviation) were calculated for each species within season. A one way analysis of variance was carried out in order to identify mean differences between seasons for species. When comparing the means from the three species a Tukey test was carried out. All tests were carried out with an alpha (α) of 5%. The fatty acid content is shown as percentage of total fatty acids for easier comparison with results from other authors. Each ray specimen was considered one replica for the analyses.

Results and Discussion

The hepatosomatic index (HSI) is a useful parameter that shows the relationship between the liver weight and total body weight of the organisms. The HSI from the three specimens studied is presented in Table 1. A significant difference ($p < 0.05$) was found for this parameter between *D. americana* and the other two specimens (*R. bonasus* and *A. narinari*). This result indicates that *R. bonasus* and *A. narinari* specimens showed the highest relationships between liver weight and total body weight. When comparing the effect of the season over the HSI, Table 1 shows that both, *R. bonasus* and *A. narinari* had higher values during the winter than the summer season; however, the effect was only significant ($p < 0.05$) for the *A. narinari* rays. This result can be related to the reproductive cycle of the species. Falch et al. [17] reported significant variations in this parameter for cod (*Gadus morhua*) due to the reproductive cycle of the species. Overall, HSI showed a considerable variation among individuals and species.

The total lipid content in the livers from the three species was not significantly different ($p > 0.05$) with values ranging from 38.2 to 43.0% (Table 1). This shows

Table 1 Lipid classes (triglycerols, phospholipids, diacylglycerols, free sterols, sterols esters) (percent of total lipids) in the oil liver from *Rhinoptera bonasus* (Chucha), *Aetobatus narinari* (Pinta) and *Dasyatis americana* (Bala)

Lipid class and HSI	Chucha (c)		Significant differences ($p < 0.05$)	Pinta (p)		Significant differences ($p < 0.05$)	Chucha (c)	Pinta (p)	Bala (b)	Significant differences ($p < 0.05$)
	Summer	Winter		Summer	Winter		Mean			
Hepatosomatic index (%)	4.3 ± 0.4	5.0 ± 2.4	n.s.	3.1 ± 0.5	4.40 ± 0.6	s	4.8 ± 2.0	3.6 ± 1.7	2.6 ± 0.5	cp > b
Lipid content (%)	40.2 ± 3.3	44.4 ± 2.3	n.s.	48.0 ± 6.4	31.6 ± 9.0	s	43.0 ± 10.0	41.2 ± 11.1	38.2 ± 3.0	n.s.
Lipid classes (%)										
Polar lipids	1.2 ± 0.7	5.2 ± 2.6	s	0.7 ± 0.3	3.1 ± 2.6	s	3.3 ± 8.9	1.7 ± 2.0	5.2 ± 2.8	b > c > p
Diacylglycerols	2.0 ± 0.8	10.8 ± 1.8	s	1.0 ± 0.6	7.7 ± 2.6	s	8.9 ± 4.1	1.9 ± 1.4	1.5 ± 0.2	c > bp
Free sterols	2.7 ± 1.4	4.3 ± 3.8	n.s.	2.3 ± 0.8	3.1 ± 0.7	s	2.3 ± 1.1	2.6 ± 0.9	2.4 ± 0.5	n.s.
Triacylglycerols	70.2 ± 9.3	67.9 ± 6.1	n.s.	90.7 ± 5.0	77.7 ± 7.0	s	69.0 ± 7.7	85.9 ± 8.7	81.6 ± 1.7	bp > c
n.i.	13.9 ± 7.4	6.3 ± 2.6	s	5.2 ± 3.1	3.6 ± 1.7	n.s.	9.0 ± 5.9	4.0 ± 2.0	3.1 ± 1.6	c > pb
Sterols esters	13.4 ± 3.3	8.0 ± 2.8	s	4.2 ± 2.0	4.7 ± 2.4	n.s.	10.6 ± 4.1	4.4 ± 2.1	3.6 ± 1.1	c > pb

c, p, b are abbreviations for the fish species used to presenting the results from the analysis of variance

n.s. not significant, *s* significant, *n.i.* non identified, *HSI* hepatosomatic index (liver weight as a percentage of the whole body weight)

Table 2 Fatty acid composition (percent of total fatty acids) in the liver oil from *Rhinoptera bonasus* (Chucha), *Aetobatus narinari* (Pinta) and *Dasyatis americana* (Bala)

Fatty acid (%)	Chucha (c) Summer	Chucha (c) Winter	Significant differences ($p < 0.05$)	Pinta (p) Summer	Pinta (p) Winter	Significant differences ($p < 0.05$)	Chucha (c) Mean	Pinta (p)	Bala (b)	Significant differences ($p < 0.05$)
14:0	6.2 ± 1.7	4.0 ± 0.5	s	3.1 ± 1.2	1.8 ± 0.4	s	5.1 ± 1.6	2.6 ± 1.2	2.4 ± 0.1	c > pb
14:1	1.3 ± 0.2	1.5 ± 0.3	n.s.	2.0 ± 0.6	2.8 ± 1.2	n.s.	1.4 ± 0.3	2.3 ± 0.9	1.5 ± 0.4	pb > c
16:0	21.1 ± 3.9	16.8 ± 2.9	s	26.3 ± 4.7	25.4 ± 3.1	n.s.	18.9 ± 4.0	25.9 ± 4.0	22.7 ± 4.4	pb > c
16:1	11.1 ± 2.1	8.0 ± 2.0	s	9.8 ± 3.6	6.3 ± 2.0	s	9.5 ± 2.6	8.4 ± 3.5	5.6 ± 0.4	n.s.
18:0	9.0 ± 1.4	10.3 ± 1.2	s	8.6 ± 1.3	8.9 ± 3.1	n.s.	9.7 ± 1.4	8.8 ± 2.1	8.6 ± 0.5	n.s.
18:1	5.6 ± 3.2	6.6 ± 1.7	n.s.	6.9 ± 1.3	6.1 ± 2.2	n.s.	6.1 ± 2.5	6.6 ± 1.7	8.6 ± 2.9	n.s.
18:2	1.8 ± 0.5	1.4 ± 0.3	n.s.	1.5 ± 0.4	1.9 ± 0.6	n.s.	1.6 ± 0.5	1.6 ± 0.5	1.7 ± 0.4	n.s.
18:3	0.6 ± 0.3	0.5 ± 0.1	n.s.	0.3 ± 0.1	0.7 ± 0.2	s	0.6 ± 0.2	0.4 ± 0.3	0.4 ± 0.2	n.s.
18:4	0.8 ± 0.4	0.6 ± 0.3	n.s.	0.3 ± 0.2	0.5 ± 0.3	n.s.	0.7 ± 0.3	0.4 ± 0.2	0.5 ± 0.2	cb > p
20:0	0.3 ± 0.1	0.7 ± 0.2	s	0.3 ± 0.3	2.3 ± 1.0	s	0.5 ± 0.2	1.1 ± 1.2	0.4 ± 0.2	n.s.
20:1	0.5 ± 0.3	0.8 ± 0.4	n.s.	2.0 ± 0.7	1.8 ± 0.6	n.s.	0.6 ± 0.4	1.9 ± 0.6	0.4 ± 0.1	p > cb
20:4	3.2 ± 0.6	3.3 ± 0.6	n.s.	6.6 ± 1.2	8.5 ± 1.5	s	3.3 ± 0.6	7.4 ± 1.6	6.1 ± 0.9	pb > c
20:5	6.6 ± 2.4	7.3 ± 2.1	n.s.	4.2 ± 1.6	3.1 ± 1.5	n.s.	7.0 ± 2.2	3.8 ± 1.6	4.9 ± 2.0	c > pb
22:0	0.1 ± 0.1	0.3 ± 0.1	s	0.1 ± 0.1	1.1 ± 0.3	s	0.2 ± 0.1	0.5 ± 0.6	0.4 ± 0.3	p > cb
22:1	0.1 ± 0.1	0.5 ± 0.3	s	0.1 ± 0.1	1.0 ± 0.7	s	0.3 ± 0.3	0.4 ± 0.6	0.00 ± 0.00	n.s.
22:5	2.9 ± 1.6	3.7 ± 0.6	n.s.	3.3 ± 1.6	5.3 ± 1.4	s	3.3 ± 1.2	4.1 ± 1.8	2.8 ± 0.4	n.s.
22:6	10.4 ± 3.5	13.6 ± 1.9	s	3.0 ± 2.2	3.1 ± 1.4	n.s.	12.1 ± 3.2	3.0 ± 1.8	13.9 ± 2.7	cb > p

c, p, b are abbreviations for the fish species used to presenting the results from the analysis of variance

n.s. not significant, *s* significant

the importance of the liver as a raw material for oil production. Lipid content in *A. narinari* livers was affected by the season ($p < 0.05$) (Table 1), showing higher values during summer than during winter. In elasmobranchs, as well as in other fish species, their livers are the main lipid reservoir and variations in their lipid content depend on various factors such as size, sex, embryonic development, geographic area and season [18]. As expected, the TLC analysis from liver oil showed triacylglycerols as the predominant lipid class in liver oil from the three species studied (Table 1). This observation supports the main way in which lipids are stored in the liver.

Among other constituents, the free and sterified sterols, polar lipids, diacylglycerols and some non identified compounds (Table 1) were found in minor amounts. Diacylglycerols from *R. bonasus* and *A. narinari* were the lipids that were affected the most by the fishing season ($p < 0.05$), resulting in 5.5 and 7.5 times higher values during the winter than in the summer season, respectively (Table 1). In general, *D. americana* oil lipid composition was very similar to *A. narinari* values; however, *D. americana* oil had the smallest HSI of three species studied ($p < 0.05$). Overall results agree with those obtained for other ray species [3, 4] and sharks [14] captured in the Gulf of California.

Individual fatty acid composition in liver oil from *R. bonasus* and *A. narinari* species included 14:0, 16:0 and 18:0 as the major components (Table 2), either from the oil (34–38% of total fatty acids) and from the saturated fraction (96–98%); These fatty acids in oil from *R. bonasus* were most affected by the season ($p < 0.05$), while 14:0 and 16:0 were affected by the species (Table 2). Results agree with others given by Navarro et al. [3, 4], and Val Ould El Kebir et al. [19] for other rajiforms. The most abundant monounsaturated fatty acids found in the oil from all species were the 16:1 and 18:1 (from 76 to 86% of all monounsaturated fatty acids); however, only the 16:1 fatty acid was affected by the season (Table 2) and no species effect was shown in the study. Monounsaturated fatty acids from the oils in the present study showed to be in minor concentration as the ones reported by Navarro et al. [3, 4] from ray species from the Gulf of California. Species differed significantly in PUFAs levels (Table 2). *R. bonasus* and *D. americana* showed values of ω-3 PUFAs (EPA + DHA) three times higher than *A. narinari*. The health benefit of oil consumption with higher ω-3 than ω-6 PUFAs concentrations has been reported by Allen and Harris [20]. In the present study, ω-3/ω-6 ratios found in three oil samples tested were 5.07, 3.04 and 1.33, for *R. bonasus*, *D. americana* and *A. narinari*, respectively.

Table 3 Physical and chemical indices in the liver oil from *Rhinoptera bonasus* (Chucha), *Aetobatus narinari* (Pinta) and *Dasyatis americana* (Bala)

Indices	Chucha (c)		Significant differences ($p < 0.05$)	Pinta (p)		Significant differences ($p < 0.05$))	Chucha (c)	Pinta (p)	Bala (b)	Significant differences ($p < 0.05$)
	Summer	Winter		Summer	Winter		Mean			
Saponification value (mg KOH/g oil)	181.2 ± 3.8	170.7 ± 3.2	s	178.4 ± 2.5	167.4 ± 1.8	s	175.7 ± 6.4	173.9 ± 6.0	174.5 ± 4.3	n.s.
Iodine value (mg I/g oil)	123.0 ± 23.3	141.2 ± 11.2	s	89.6 ± 14.4	99.9 ± 12.9	n.s.	132.7 ± 19.7	93.8 ± 14.3	137.0 ± 18.2	cb > p
Density (g/mL)	$0.916 \pm 3 \times 10^{-3}$	$0.920 \pm 1 \times 10^{-2}$	n.s.	$0.909 \pm 3 \times 10^{-3}$	$0.916 \pm 9 \times 10^{-3}$	n.s.	$0.916 \pm 4 \times 10^{-3}$	$0.912 \pm 7 \times 10^{-3}$	$0.919 \pm 2 \times 10^{-3}$	n.s.
Carotenes (mg/100 g)	10.6 ± 4.2	7.0 ± 1.5	s	8.5 ± 3.9	18.8 ± 10.0	n.s.	8.7 ± 3.5	12.8 ± 8.5	8.0 ± 3.2	n.s.
α-Tocopherols (mg/100 g)	24.2 ± 11.6	18.2 ± 7.1	n.s.	37.9 ± 21.4	59.4 ± 32.8	s	21.0 ± 9.8	46.7 ± 28.0	13.7 ± 4.7	p > cb

c, p, b are abbreviations for the fish species used to presenting the results from the analysis of variance

n.s. not significant, *s* significant

One main aspect in the characterization of fish oils is the determination of their physical and chemical characteristics since they are required for the quality control of their technological processes. With regard to the saponification value of oils tested, no significant differences ($p > 0.05$) were found among species (Table 3); however, season differences ($p < 0.05$) were found for both species studied. Values were slightly lower than the ones reported by Navarro et al. [3, 4]. Iodine values for *R. bonasus* and *D. americana* were significant higher ($p < 0.05$) than *A. narinari* (Table 3), reflecting the highest unsaturation degree of the oils from these species.

Carotenes and tocopherols are among the most effective natural antioxidants. They protect the oil from oxidation as well as from the in vivo peroxidation of the organism that consume them. Rajiforms, not capable of synthesizing carotenes [21], obtain theirs from shrimp or other small crustaceans that are a fundamental part of their diet [22]. Carotenes are stored in the liver and due to their lipophilic nature are extracted with the oil. Carotene contents in the oil from species in the present study are shown in Table 3. No significant differences ($p < 0.05$) were found among the species. Season had an effect only on *R. bonasus* with higher values ($p < 0.05$) in the summer. However, *A. narinari* showed the highest mean value ($p > 0.05$) during the winter, but with the highest standard deviation of all oils (Table 3). Contents were lower than values reported for *D. brevis* and *G. marmorata* [3] and for *R. steindechneri* [4]. Only *A. narinari* showed a season effect ($p < 0.05$) with the highest values of species studied. α-Tocopherol is the main isomer found in the liver of fish [23]; thus, only this type was found in the oil from rajiforms in the present study (Table 3). Tocopherols values were 21.0, 46.7 and 13.7 mg/100 g for *R. bonasus*, *A. narinari* and *D. americana*, respectively. These values are higher than the ones reported for rajiforms *G. marmorata* (2.8 mg/100 g) [3] and *R. steindechneri* (2.8 mg/100 g) [4]. Densities of oils tested were not significantly different ($p > 0.05$), neither from season nor species (Table 3). These values agreed with the one found from oil of *Clupea harengus* [24]. Species in the present study differ in their habitat (i.e., *D. americana* is found mainly on sandy and weedy sea bottoms, *A. narinari* is a benthopelagic species, while *R. bonasus* is a migratory oceanic species) [25–27], thus in their bioavailability of food from the environment. Different habitats could result in the differences found in the lipid composition of the oils from these species.

Conclusions

There is an increasing demand for fish oil, either for aquaculture or for human consumption, due to the benefits

this type of oil offers. The State of Campeche could produce annually an estimated 19,865 kg of fish oil from rajiforms species rich in highly unsaturated fatty acids (22:6, 22:5 and 20:5). Although the concentration of these fatty acids was significantly higher in *R. bonasus* and *D. americana*, all species had good ω-3/ω-6 ratios, making them suitable for human or aquaculture use. An important aspect of these oils is their high α-tocopherol content, an important component that protects the oils from oxidation during their extraction. Finally, the present study shows that livers from these species (*D. americana*, *A. narinari* and *R. bonasus*) should be used for oil extraction and not wasted, as they usually are.

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