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ARAŞTIRMA MAKALESİ

Fatty acid profile and proximate composition of the thornback ray (*Raja clavata*, L. 1758) from the Sinop coast in the Black Sea

Hülya TURAN[1*], Gülşah SÖNMEZ[1] and Yalçın KAYA[1]

1 University of Ondokuz Mayıs, Faculty of Fisheries, Department of Fishing and Processing Technology, Sinop, Turkey.

Abstract: The fatty acid and proximate composition in the flesh of thornback ray (*Raja clavata*, L. 1758) collected in the coast of Sinop in Turkey were evaluated. Proximate analyses of thornback ray are rich in protein (20.02%) and low in lipid (0.51%). The crude ash and moisture contents were found as 1.38% and 77.47%, respectively. The total SFA, MUFA and PUFA content were 48.27%, 13.98% and 24.10% of total fatty acids, respectively. Palmitic acid ($C_{16:0}$, 26.45%) and stearic acid ($C_{18:0}$, 10.62%) were the dominant saturated fatty acids. The major unsaturated fatty acids were determined as docosahexaenoic acid ($C_{22:6\ n3}$, 12.21%), oleic acid ($C_{18:1}$, 8.88%) and linoleic acid ($C_{18:2}$, 3.43%). The results of this study have showed that thornback rays are good sources of protein. The atherogenic index (AI) and index of thrombogenicity (IT) were calculated as 2.37 and 0.63, respectively.

Keywords: Thornback ray, proximate analysis, fatty acids

[*] **Correspondence to:** Hülya TURAN University of Ondokuz Mayıs, Faculty of Fisheries, Department of Fishing and Processing Technology Sinop, Turkey Tel: 0 368 2606254 Fax: 0 368 2606255
E-mail: hturan@omu.edu.tr

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Introduction

The thornback ray is most likely one of the most common rays encountered by divers. Like all rays it has a flattened body with broad, wing like pectoral fins. The body is kite-shaped with a long, thorny tail. The back is covered in numerous thorny spines. Adult fish can grow up to 1m in length although most are less than 85 cm. The thornback ray is usually found on sediment type seabeds such as mud, sand or gravel at depths between 10-60 m (Anonymous, 2006).

In Turkey, 540 tons of the thornback rays were caught as by-catch in 2003 (Anonymous, 2004). Although it is a relatively low-priced fish, Turkish people do not appreciate due to its shape and taste. Therefore, it is not used for human consumption and generally exported to other countries. Global catches should be utilised better because of overexploitation and the increasing demand for fish and fishery products (Howgate, 2007).

There is a little information on proximate composition of thornback ray from Turkey while there is no information on the fatty acids compositions of thornback ray. Therefore, the aim of this study was to investigate the fatty acid profile and proximate composition of the thornback ray caught in the coast of Sinop in Black Sea.

Materials and Methods

Fresh thornback rays weighing a total of 95 kg were obtained from a fish market in Sinop, Turkey. They were immediately transported to the laboratory in plastic boxes within 30 min after cutting their tails to flow blood in order to remove odour of ammonia from fish. The fish were hung to proper height with hooked bars of steel and fins were cut. The skin was completely removed and fillets were made. The fillets were washed with tap water and strained in a shifter for 20 minutes. The thornback ray flesh was homogenized with Yellowline D25 Basic homogenizer at the high speed (24000 rpm).

The moisture (method 952.08), crude ash (method 938.08), crude lipid (method 948.16) and crude protein (method 968.06) contents were determined by AOAC (1990). Crude protein content was calculated multiplying N by factor 6.25 and result was expressed as percentage. Each analysis was conducted in triplicate.

Fatty acid analyses were carried out using the IUPAC II.D.19 method (IUPAC, 1979). Fatty acids of the thornback ray were analyzed using a Perkin Elmer Auto system XL Gas Chromatograph equipped with SP-2330 and a flame ionization detector (FID). Separation of fatty acid methyl esters was achieved by using fused silica capillary column (30mx0.25mmx0.20µm film thickness). The oven temperature was set at 120°C for 2 min then reached to 220°C with a ramp rate of 5°C/min, and then held for 15 min. The injector and detector temperatures were maintained at 240°C and 250°C, respectively. The carrier gas was helium 10psi with a split ratio of 1/50. The air and hydrogen of pressure were 338 ml/min and 45 ml/min respectively. Results were expressed as the percentage of each fatty acid with respect to the total fatty acids. The fatty acid analyses were conducted in duplicate.

Lipid quality indices were calculated according to Ulbricht and Southgate (1991). The atherogenic index (AI) was calculated as fallows:

$$AI = \frac{[12:0+4(14:0+16:0)]}{[(n6+n3)PUFA+18:1+\Sigma MUFA]}$$

The index of thrombogenicity (IT) was calculated as follows:

$$IT = \frac{(14:0+16:0+18:0)}{[(0.5x18:1)+0.5(\Sigma MUFA)+0.5(n6PUFA)+3(n3PUFA)+(n3PUFA/n6PUFA)]}$$

Results and Discussion

Proximate composition - Proximate composition of thornback ray was presented in Table 1. Moisture, crude protein, crude ash and crude fat contents of thornback ray were determined as 77.47%, 20.02%, 1.38% and 0.51%, respectively.

Table 1. Proximate composition of the thornback ray (*Raja clavata*, L. 1758)

Parameters	%
Moisture	77.47±0.07
Crude protein	20.02±0.00
Crude ash	1.38±0.00
Crude fat	0.51±0.07

n=3 ±SE (standard error)

According to Göğüş and Kolsarıcı (1992), thornback ray has high protein (18.2-24.2%) and low fat (0.1-1.6%) content. The results obtained in this study also were within levels reported by Göğüş and Kolsarıcı (1992). In addition, Erkoyuncu and Samsun (1988) and Yılmaz and Akpınar (2003) determined the protein content 19.46% for thornback ray (*Raja clavata*) and 16.63% for common guitarfish (*Rhinobatos rhinobatos*), respectively. In this research, it was determined that the thornback ray has high protein content as well as other sea fish species. Thornback rays can be used as a good protein source (20.02%) for functional products such as surimi, sausage and fish protein concentrate. Fish are usually categorized as lean, moderately fat, and fat according to its fat content, which is less than 5 percent, from 5 to 10 percent, and greater than 10 percent, respectively (Dean, 1990). Thus, thornback ray can be classified as a lean fish with its low fat content (<5%). Erkoyuncu and Samsun (1988) and Yılmaz and Akpınar (2003) determined the lipid content 1.3% for thornback ray and 0.7% for common guitarfish, respectively. In this study the moisture and crude ash content of thornback ray were determined as 77.47% and 1.38%, respectively. These results were similar with results determined by Erkoyuncu and Samsun (1988).

Fatty acids- Table 2 shows the fatty acid composition of the thornback ray.

Total SFA content of thornback ray lipids was 48.28%. Palmitic acid (C16:0) was the primary saturated fatty acid followed by stearic acid (C18:0), contributing 55% and 22% of total saturated fatty acid content of thornback ray. Palmitic acid was found to be the most abundant in different fish species (Alasalvar et al., 2002; Çelik and Gökçe, 2003; Şengör et al., 2003; Wheeler and Morrissey, 2003; De Silva et al., 2004; Rossano et al., 2005; Bayır et al., 2006; Senso et al., 2007).

The major classes of unsaturated fatty acids in nature are omega-9, omega-6 and omega-3, represented by oleic, linoleic and α-linolenic acids, respectively (Gordon and Ratliff, 1992). Total MUFA content of lipids of thornback ray was 13.98%. Oleic acid (C18:1 n9c) was identified as the primary monounsaturated fatty acid (about 63% of total MUFA). Similar results for other fish species have also been reported in the literature (Alasalvar et al., 2002; Çelik and Gökçe, 2003; Wheeler and Morrissey, 2003; De Silva et al., 2004; Rossano et al., 2005; Bayır et al., 2006; Senso et al., 2007).

Total PUFA content of thornback ray lipid was 24.11%. Fish is known to be a rich source of the unique polyunsaturated fatty acids of the omega-3 family, including both eicosapentaenoic acid (EPA, 20:5n-3) and docosahexaenoic acid (DHA, 22:6n-3). Recent studies have suggested that the dietary consumption of fish/fish oils containing omega-3 fatty acids may favourably influence a number of biological factors associated with cardiovascular disease (independent of blood-cholesterol lowering). In addition to cardiovascular disorders, there is evidence to suggest that the consumption of fish or derived omega-3 fatty acids (EPA and/or DHA) may offer benefits in the management of individuals with inflammatory disorders such as rheumatoid arthritis, psoriasis, etc. (Holub, 1992). The omega-3 fatty acids EPA and DHA accumulate in seafood via the food chain. These fatty acids, synthesized by various forms of sea algae and then consumed by plankton and other small marine animals, are probably also essential for ocean life. A major reason for their critical importance in marine physiology may be their ability to remain fluid at cold temperatures (Gordon and Ratliff, 1992). Atlantic salmon, anchovies and herring contain 12.2, 9.0 and 6.0% DHA, respectively (Jonsson et al., 1997; Sargent, 1997). According to Bayır et al (2006) EPA and DHA values in some marine fish species living in Turkish waters were 6.18% and 12.15% for bluefish, 8.74% and 20.55% for gilthead sea bream, 11.68% and 28.85% for anchovy, 7.48% and 10.57% for horse mackerel, 8.7% and 22.71% for grey mullet, 8.21% and 19.61% for atlantic bonito, 10.22% and 12.7% for mackerel, 6.14 and 34.92% for garfish, respectively. In this research, EPA and DHA contents of thornback ray were found as 1.52%, and 12.21% respectively.

Table 2. Fatty acid composition of the thornback ray

Fatty acids	%
$C_{8:0}$	2.71 ±0.04
$C_{12:0}$	0.41 ±0.00
$C_{14:0}$	1.48 ±0.01
$C_{15:0}$	1.09 ±0.00
$C_{16:0}$	26.45 ±0.17
$C_{17:0}$	2.92 ±0.62
$C_{18:0}$	10.62 ±0.06
$C_{20:0}$	0.52 ±0.01
$C_{21:0}$	0.77 ±0.01
$C_{23:0}$	0.31 ±0.31
$C_{24:0}$	1.00 ±0.06
Total SFA	**48.28 ±0.99**
$C_{14:1}$	0.23 ±0.00
$C_{15:1}$	0.56 ±0.01
$C_{16:1}$	1.43 ±0.00
$C_{17:1}$	0.89 ±0.00
$C_{18:1\ n9t}$	0.37 ±0.00
$C_{18:1\ n9c}$	8.88 ±0.09
$C_{20:1\ n9}$	0.74 ±0.00
$C_{22:1\ n9}$	0.36 ±0.02
$C_{24:1\ n9}$	0.53 ±0.04
Total MUFA	**13.99 ±0.17**
$C_{18:2\ n6t}$	0.27 ±0.02
$C_{18:2\ n6c}$	3.43 ±0.04
$C_{18:3\ n3}$	0.63 ±0.01
$C_{20:2}$	0.80 ±0.00
$C_{20:3\ n3}$	0.52 ±0.00
$C_{22:2}$	2.79 ±0.06
$C_{20:4\ n6}$	1.94 ±0.08
$C_{20:5\ n3}$	1.52 ±0.01
$C_{22:6\ n3}$	12.21 ±0.06
Total PUFA	**24.11 ±0.28**
EPA+DHA	**13.73**
Σn3	**14.88**
Σn6	**9.23**
n3/n6	**1.61**
AI value	**2.37**
IT	**0.63**

n= 2 ± standard error
SFA: Saturated fatty acids
MUFA: Monounsaturated fatty acids
PUFA: Polyunsaturated fatty acids

Pigott and Tucker (1990) suggested that the n3/n6 ratio is a better index in comparing relative nutritional value of fish oils of different species. A n3/n6 ratio of 1:1 is considered to be optimal for nutritional purposes (Simopoulos, 1989). As shown in Table 2, the n3/n6 ratio of thornback ray was 1.61. n3/n6 ratio in gilthead sea bream was found between 1.6 to 3.6 in different months (Senso et al., 2007). Gökçe et al., (2004) determined that n3/n6 ratio for common sole was between 1.45 with 3.84 in different months. Bayır et al., (2006) determined the n3/n6 value in some selected marine fish species living in Turkish waters: bluefish (7.30), gilthead sea bream (2.67), anchovy (8.27), horse mackerel (12.61), gray mullet (8.64), Atlantic bonito (9.91), mackerel (5.63), and garfish (12.2).

A minimum value of PUFA/SFA ratio recommended is 0.45 (HMSO 1994), which was obtained in *Raja clavata* with value of 0.50.

Ulbricht and Southgate (1991) proposed that an atherogenicity index (AI) for the composition of a fat based on current information about the effect of various fatty acids on serum cholesterol that is low-and high-density lipoprotein concentrations. According to this equation, only saturated fatty acids with chain lengths of 12 to 16 are atherogenic and myristic acid is considered four times more atherogenic than the other two. All unsaturated fatty acids, regardless of their double bond number, position, or configuration, are considered equally effective in decreasing atherogenicity primarily for lack of reliable information to assign more suitable coefficients to the various structures. When applied to various fats and oils, this equation gives AI values of 13-20 for coconut oil, 7 for palm kernel oil, 0.7 for cocoa butter, and<0.5 for other vegetable oils. Meat fats vary from 0.5-1. Anti-atherogenic lipids inhibited the aggregation of plaque and diminishing the levels of esterified fatty acid, cholesterol, and phospholipids, thereby preventing the appearance of micro- and macrocoronary diseases. In this research, atherogenicity and thrombogenicity index values were 2.37 and 0.63, respectively. Valfre et al., (2003) reported that IT and AI values were 0.45 and 1.35 for anchovy, 0.32 and 0.94 for eel, 0.37 and 0.57 for rainbow trout, 0.25 and 0.45 for seabass. Rueda et al., (1997) reported that IT and AI values were 0.2 and 0.4 for wild red porgy and 0.2 and 0.5 for reared red porgy. Rueda et al., (2001) determined that IT and AI values were 0.24 and 0.51 for reared sharpsnout seabream, 0.35 and 0.53 for wild sharpsnout seabream.

Conclusion

The results presented in this work show that thornback rays are rich in protein and low in lipid content. The major fatty acids identified in *Raja clavata* were 16:0 (palmitic), 18:0 (stearic), 18:1n9 (oleic), 18:2n6 (linoleic) and 22:6n3 (DHA). By-catches are a valuable source for fish processors. However, a great portion of thornback ray caught in Turkey is discarded. But, thornback ray can be used for functional products such as surimi, fish protein concentrate, salami, sausage.

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