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Quality of Cuban shark liver oil. Comparison with Icelandic cod liver oil. (Calidad del aceite de hígado de tiburón cubano. Comparación con el aceite de hígado de bacalao Islandés)

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Resumen.

A través del contenido de vitaminas A, D y E, dioxinas, metales pesados y escualeno, se estudió la calidad del aceite de hígado de tiburón obtenido a partir de un pool de hígados de tres especies de tiburones (*Ginglimostoma cirratum, Carcharhinus longimanus,* y *Carcharhinus falciformis*) capturados en costas cubanas. Se evalúan los contenidos de hierro y cobre como indicadores de posible oxidación en el aceite. Se determinan los niveles de rancidez del aceite mediante análisis sensoriales. Las dioxinas y los bifenilos policlorados (BPC) son químicos muy persistentes responsables de la contaminación en los aceites de pescado, cuyo contenido es también evaluado. También se estudió el aceite de hígado de bacalao de la especie *Gadus morhua* y otras especies de Gadus del sur-oeste de Islandia, con el fin de comparar ambos aceites en términos de su calidad. En el aceite de hígado de tiburón cubano se detectó un bajo contenido de escualeno. Su contenido de vitaminas E y A indica que puede ser potencialmente utilizado como suplemento nutricional, contribuyendo a una completa utilización de los hígados de tiburones cubanos. No se detectó vitamina D. El contenido de hierro y cobre indica que el aceite constituye una buena fuente de estos minerales. Los análisis sensoriales revelaron niveles ligeramente más elevados de rancidez en el aceite de bacalao islandés que en el aceite de hígado de tiburón cubano. No se detectó un alto contenido de dioxinas en el aceite de hígado de tiburón cubano (3.69 $ngkg^{-1}$), menor que los limites permisibles para aceites crudos, (Food Standard Agency, 2002). Las dioxinas como PCBs detectadas en el aceite (14.3 $ngkg^{-1}$) pueden ser removidas durante los procesos de purificación en la producción.

Palabras claves: tiburones cubanos | aceite de hígado de tiburón | calidad.

Abstract.

The quality of shark liver oil obtained from a pool of livers of three sharks species (*Ginglimostoma cirratum, Carcharhinus longimanus,* and *Carcharhinus falciformis)* caught in the Cuban coast was studied by measuring some chemical characteristics: content of vitamins A, D and E, dioxins, heavy metals and squalene. The content of copper and iron was used as indicators of the possible oil oxidation. The rancidity level of the oil was evaluated by sensory analysis. Dioxins and dioxin-like PCBs are very persistent chemicals responsible for the contamination in fish oils. Its content was also evaluated. Cod liver oil from *Gadus morhua* and other species of *Gadus* from South-West Iceland was also evaluated in order to establish comparison between both oils in terms of its quality. A low content of squalene was detected in Cuban shark liver oil. Its amount of vitamin E and A indicate that it can be potentially used as a nutritional supplement, contributing to a complete use of the Cuban shark's livers. Vitamin D was not detected. Iron and copper content indicate that the oil is a good source of these minerals. Sensory analysis showed a little higher rancidity level in cod liver oil than in Cuban shark liver oil. A not high content of dioxins (3.69 ngkg^{-1}) was detected in Cuban shark liver oil, lower that the limit permissible for crude oils, (Food Standard Agency, 2002). Dioxins like PCBs (14.3 ngkg^{-1}) found in the oil, can be removed during the production by purification process.

Key words: Cuban sharks | shark liver oil | quality, calidad

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1. INTRODUCTION

Sharks are among the most important commercial fish stocks in Cuban waters nowadays and there are 23 commercial species which have been caught for the past 100 years (Garcia 2005). Levels of shark catches in Cuban waters have varied during the years in terms of fishing effort. Catch levels are actually around the 500 to 1000 tones per year. The intention is to increase these levels, in sustainable way, up to the 2000 tones per year.

Fish oils may also help protect the brain from cognitive problems associated with Alzheimer's disease, as demonstrated in a study from Louisiana State University in September 2005 (Lukiw 2005). Incorporating fish oil in foods, is not only a very effective way to increase the value of fish oils, but is also an important way to increase the consumption of fatty acids contained in these oils (Medina *et al.* 2003). Is well known that EPA and DHA, which are most often found in fish oils, are very beneficial to human's health (Aidos 2002, Market Biosciences Corporation 2007).

Shark liver oil (also known as shark oil) is extracted from the livers of various species of sharks. Oil is yellow to brown, it has a strong flavour, and it is insoluble in water. It is used as a source of Vitamin A and Omega-3, and has a high level of squalene, which is used in biochemical research.

Studies have been conducted on oil extracted from shark livers of Cuba since the 1940s. Some exports of the product were carried out and its physical, chemical and microbiological properties were studied. It is known (Lopez 2007, personal communication) that comparative studies were made between shark oil and the Atlantic cod liver oil, showing the similarity between both of them in terms of their properties. Unfortunately there are no references published on the matter. However, after 1959 investigations concerning Cuban sharks were reopened and there are some studies on their populations (Espinosa 1983, 1987, 1994, 1997), taxonomic characterization, status of exploitation of the species, representative species and general characteristics of each one (Guitart 1975).

Although liver is a good source of oil in sharks, it is currently considered a waste in Cuba. Therefore interest is now in Cuba to investigate the possibilities of using shark liver oil as a health product, as well as developing new technological processes for extracting quality liver oil and to develop new food products for human consumption (Garcia 2005). Converting shark by-products into shark oil is an opportunity of adding value to by-products.

It was mentioned by Kreuzer and Ahmed (1999) and Vannucini (1999) that height and weight in shark livers vary depending on the species and time of year. In some sharks, liver can be up to 20% of the total animal weight and it can be the 5% of the body weight in other species (Navarro *et al.* 2000).

Since only artisanal production of shark liver oil exists in Cuba at this moment, advanced processing is not possible. For this reason, to evaluate the quality of the oil is a very important aspect to guarantee its safety as a nutritional supplement for human consumption. One plant (supported by WWF) is almost ready to work on developing methods to process the shark oil as a by-product in Cuba. Once it begins the shark liver oil production, it will be possible to refine it with the aim of using it as a nutritional supplement for the Cuban population (Garcia 2007, personal communication).

The focus of this research was to study the quality of Cuban shark liver oil obtained from a pool of livers from sharks captured in Cuban waters, as well as to provide a comparison between Cuban shark liver oil and Icelandic cod liver oil. Three species of sharks (caught in the

Cuban coast) were used to extract the oil: *Ginglimostoma cirratum, Carcharhinus longimanus,* and *Carcharhinus falciformis.*

1. MATERIALS AND METHODS

1.1 Raw material

The shark liver oil was obtained from a pool of livers from sharks *(Ginglimostoma cirratum, Carcharhinus longimanus,* and *Carcharhinus falciformis)* captured in Cuban waters under artisanal conditions of production. The oil was sent from Cuba (through Spain) to Iceland and the shipping took nine days. The cod liver oil was obtained by rendering fresh liver of cod (*Gadus morhua*) and other species of Gadus from South-West Iceland. No refining of the oil from shark and cod had taken place.

By keeping both oils (poured into brown bottles) at two different temperatures (0°C and 30°C), during three weeks, the storage test was done. The reference sample was kept at -80°C. Kept samples were used to measure volatiles, peroxides and for sensory analysis.

1.2 Chemical properties of shark liver oil

Vitamins A, E, D were measured by HPLC in-house method developed at Lysi Ltd., Reykjavik, Iceland.

Squalene content in Cuban shark liver oil was determined by Gas Chromatography (GC) in-house method developed at Lysi Ltd., Reykjavik, Iceland.

Iron and copper concentrations in shark liver oil and cod liver oil were determined by an inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7500ce, Waldbronn, Germany) in the full quantitative mode after mineralization, and complete destruction of the organic matrix of samples with closed vessel acid digestion. Dogfish Muscle Certified Reference Material for Trace Metals (DORM-2) measurement control was used. The analysis was done at MATIS Laboratory of Marine Research Institute, Reykjavik, Iceland.

1.3 Sensory analysis

Sensory evaluation methods are very useful to determine quality of fish and fish oils (Ramos 2004). In this work, Cuban shark liver oil and Icelandic cod liver oil were sensorial analyzed by Icelandic trained panellists once a week during three weeks in order to evaluate its rancidity levels. The analysis was done at Sensory Laboratory of Marine

Research Institute, Reykjavik, Iceland. Samples were evaluated by using a 6-point category scale with a description of intensity of rancid odour at each score (ISO 1985, 1987): 0 = no rancidity; 0.5 = thresholds or just detectable; 1 = very slight; 2 = slight; 3 = moderate; 4 = very rancid.

The sensory panellists were trained in odour analysis to assess shark and cod liver oils in three sessions. Some of the panellists have several years of experience in evaluating rancidity of fish, fish oils, and vegetable oils and have been trained according to international standards including detection and recognition of odours. The order of samples presentation to the panellists was balanced to minimize possible carryover effects between samples. All observations were conducted under standardized conditions, with as little interruption as possible, at room temperature, and under white fluorescent light.

1.4 Pollutants of shark liver oil

In order to know its content of dioxins, Cuban shark liver oil was analyzed by partner laboratory Eurofins GfA, Hamburg in Germany, by using Method: EN 1948 modified HRMS for Polychlorinated dibenzodioxins and -furans (PCDDs/PCDFs) and HRMS for Dioxin-like PCBs (DL-PCBs).

2. RESULTS

The results for squalene and vitamins (A, E, D) are shown in Table 1.

Table 1. *Quality properties (squalene, vitamins A, E, D) of shark liver oil.*

Property	Value
Squalene (%)	0.03
Vitamin A (mgg^{-1})	439.5
Vitamin E (mgg^{-1})	0.76
Vitamin D (mgg^{-1})	Not detected

Iron (Fe) and copper (Cu) were evaluated in shark liver oil. Content of same metals was also measured in cod liver oil to establish comparison between both oils content (Table 2). The results are presented as mean±s.d. in milligrams per kilogram of product.

Table 2. *Iron (mgkg⁻¹) and copper (mgkg⁻¹) content in shark and cod liver oil. Values presented as mean±s.d.*

Samples	Fe (mgkg^{-1})	Cu (mgkg^{-1})
Cod liver oil	0.754 ± 0.176	0.030 ± 0.005
Shark liver oil	1.02 ± 0.17	0.52 0.021

Intensity of rancid odour, according to the 6-point category scale (referring to shark and cod liver oils) is shown in Table 3. Values are presented as mean±s.d.

Table 3. *Rancidity levels in cod and shark liver oils at two different temperatures: 0°C and 30°C during three weeks of storage. Values expressed as mean ± s.d.*

Days of storage	0°C	30°C	-80°C (standard)
Shark			
0	0.65 (0.80)	0.55 (0.72)	0.40 (0.45)
5	0.50 (0.59)	0.39 (0.63)	0.21 (0.38)
15	0.58 (0.80)	0.67 (0.82)	0.08 (0.20)
Cod			
0	0.10 (0.35)	0.20 (0.32)	0.20 (0.35)
5	0.50 (0.23)	0.64 (0.52)	0.14 (0.23)
15	0.85 (0.66)	1.10 (1.18)	0.60 (0.66)

The results for rancidity levels of shark and cod liver oil during the storage time at two different temperatures (0°C and 30°C) are shown in Figure 1 and 2, respectively.

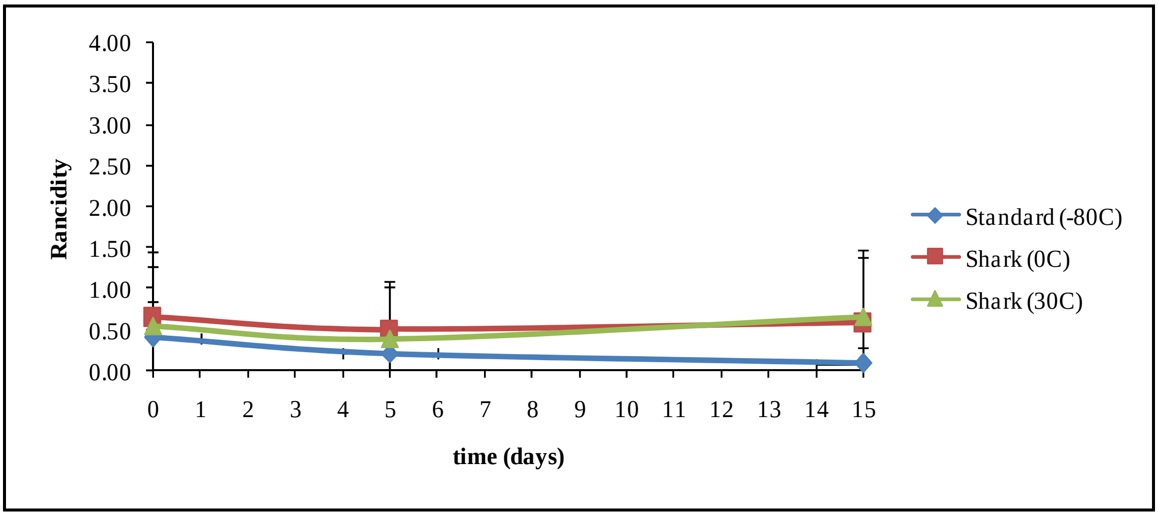

Figure 1. *Rancidity levels for shark liver oil at two different temperatures: 0°C and 30°C (standard at -80°C) during three weeks of storage.*

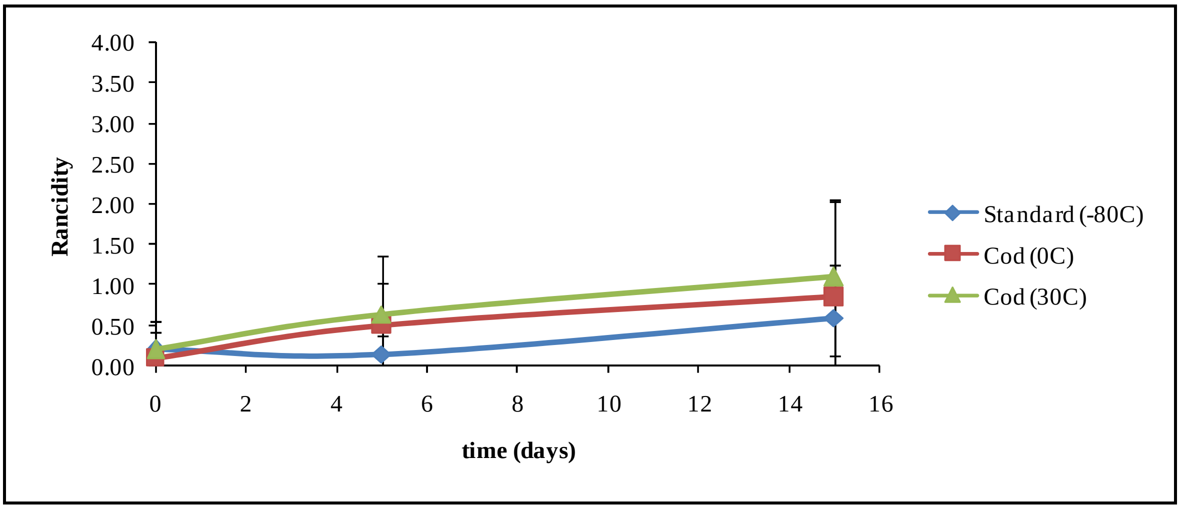

Figure 2. *Rancidity levels for cod liver oil at two different temperatures: 0°C and 30°C (standard at -80°C) during three weeks of storage.*

Contaminants (dioxins) were evaluated in shark liver oil. The results are presented in nanograms per kilograms of product (Table 4).

Table 4. *Content of dioxins (ngkg^{-1}) in shark liver oil.*

Dioxins	value (ngkg^{-1})
Dioxins PCDD/F incl. LOQ	3.69
Dioxin-like PCBs incl. LOQ	14.3

3. DISCUSSION

As part of the objectives of this paper, squalene and vitamins (A, D and E), were measured in order to study the quality of Cuban shark liver oil. These parameters are compared with standard values, carried out in previous investigations.

It is known that shark liver oil is recommended as a nutritional supplement because of his content of hydrocarbon squalene. Cuban shark liver oil was analyzed and its squalene content is reported as a 0.03% in this study (Table 1), which is considered low. The most abundant source of squalene is from the livers of deep sea sharks (found at depths of as much as 1500 metres). Therefore it is understandable that the shark species studied (caught in the Cuban coast) do not have a high content of squalene. Due to its low squalene content the shark liver oil must be minimally processed to ensure that the squalene content and all of its natural trace elements are maintained.

Vitamin D was not detected in the shark liver oil analyzed (Table 1). However, the oil was found to have a high amount of vitamin A (439.5 mgg^{-1}). Vitamin A (as a fat soluble vitamin) is considered good for human health and provides shark liver oil with some essential properties to help human health (Berdanier 1997), as it is essential for the maintenance of healthy epithelial tissue which is found in the skin, eyes, respiratory system, GI and urinary tracts. Its detection in the shark oil is considered a good quality parameter. As well as the recommended daily allowance for men and women (Office of Dietary Supplements 2007), is 900-700 microgram/day, one spoon of the shark liver oil studied gives the 50% of the RDI.

On the other hand, vitamin E was found (0.76 mgg^{-1}) in the shark liver oil (Table 1) and is known that this vitamin plays an important role as a powerful biological antioxidant (Traber *et al.* 1999), (Farrell *et al.* 1994). Fish and fish oils are one of the best known sources of this vitamin (Bauernfeind 1980).

Content of iron (Fe) and copper (Cu) in shark liver oil were 1.02 $mgkg^{-1}$ and 0.052 $mgkg^{-1}$ respectively (Table 2). Cod liver oil had, on the other hand, lower values of Fe (0.754$mgkg^{-1}$) and Cu (0.030$mgkg^{-1}$) in this study. The iron (as reported by Benedet J. and Shibamoto T., 2007) is an important catalyst in the formation of the OH radical, which is the most relevant initiator of the lipid peroxidation in fish oils. Iron is, however, an essential nutrient and it is not a negative property in the oil studied. If high value of iron were found, it can be removed by alkali refining and bleaching during the purification step of the oil production. Copper, in this amount, can be considerate an important mineral in protecting against free radical production.

Rancidity levels in shark and cod liver oil kept at 0°C and 30°C during three weeks were analyzed by a sensory panel. Since the time of the storage was quite short, the evaluation was very difficult to carry out. Shark and cod liver oils have a very characteristic smell and it was complicated for the panellist to recognize the rancidity level in the samples. However, the results (Figure 1 and Figure 2) show a small increase of rancidity level in cod liver oil in comparison with the shark liver oil. Significant differences were not found in the oils samples analyzed (P_{shark}=0.464 and P_{cod}=0,671) as can be seen in Table 3.

It is a global trend to reduce dioxin levels in fish oils, in order to ensure the reliability of suppliers face to consumers (International Fish Oil Standards 2006b).

Even though dioxins and PCBs are usually high in fish oils, especially in fish liver oils, the present study indicates that Cuban shark liver oil has a not so high content of dioxins. Its value (3.69 $ngkg^{-1}$) is lower than the permissible limit for crude oils (4.99 $ngkg^{-1}$ for pure cod liver oil), (Food Standard Agency, 2002). Dioxins like PCBs (14.3 $ngkg^{-1}$) found in the oil, can be removed during the production by purification process.

4. CONCLUSIONS

Even though Cuban shark liver oil presented a not high content of squalene (which is well documented for not deep sea sharks), its amount of vitamin E and vitamin A indicate that it can be potentially used as a nutritional supplement, contributing to a complete use of the Cuban shark's livers. Due to its low levels, iron and copper are not considerate negative quality factors in shark liver oil, but they seems to be a good minerals source in this product.

Sensory analysis showed a little high rancidity level in cod liver oil in comparison with the shark liver oil. Significant differences were not found in the oils samples analyzed.

Cuban shark liver oil presented a not so high content of dioxins (3.69 $ngkg^{-1}$), lower that the limit permissible for crude oils (4.99 $ngkg^{-1}$), (Food Standard Agency, 2002). Dioxins like PCBs (14.3 $ngkg^{-1}$) found in the oil, can be removed during the production by purification process.

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