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Characterization of Chemical Quality of Tuna Fish Skin Oil (*Thunnus Sp.*)

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Abstract
The chemical physical properties of tuna fish oil include 25% saturated fat, 75% unsaturated fat, density 967.96 kg/m3, iodine number 170, saponification number 188, refractive index 25 oC 1.4785, unsaponifiable number 0.1% and types of fatty acids contained in tuna fish oil, namely palmitic, stearic, oleic and linoleic acids. Tuna fish waste, which includes heads, bones and skin, if not handled, will quickly deteriorate and become rotten, so further processing is needed to be utilized as well as possible into products such as oil from tuna fish processing waste. At present, oil from tuna fish waste, which is a derivative product of tuna fish with selling value, has not been widely developed and commercialized. Therefore, a more in-depth study of the processing of tuna fish waste is needed, including to determine the physico-chemical properties contained in oil from tuna fish waste. This study aims to analyze how the value of refractive index, peroxide number, free fatty acids and iodine number in tuna fish skin oil. The results showed that the chemical quality characterization of tuna fish skin oil obtained a refractive index value of 1.638, free fatty acids (FFA) 0.03%, peroxide number 0.2 meq / kg material and Iod number 44.74 g I2 / 100 g material.

Keywords: chemical properties, tuna skin oil, refractive index, peroxide number, free fatty acids, iodine number.

Introduction

Fish oil is one of the nutrients that contain beneficial fatty acids, because it contains about 25% saturated fatty acids and 75% unsaturated fatty acids. The polyunsaturated fatty acids (PUFA) in it will help the process of brain growth and development (intelligence), as well as the development of the sense of sight and the immune system of infants and toddlers. In addition, fish oil contains vitamins A and D, two types of fat-soluble vitamins in high amounts. The benefit of vitamin A is to help the process of eye development, while vitamin D is to help the process of growth and formation of strong bones. The levels of these vitamins in the fish body will increase with age. Generally, vitamin A levels in fish oil range from 1,000 - 1,000,000 SI (International Standard) per gram, while vitamin D is about 50 - 30,000 SI per gram.

Fish oil has three types of fatty acids, namely, saturated fatty acids, which are fatty acids that do not have double bonds in their carbon chains, such as palmitic. Monounsaturated fatty acids are fatty acids that have one double bond in the carbon chain, such as oleic. Polyunsaturated fatty acids are fatty acids that have one double bond in the carbon chain, such as linoleic, elkosapentanoic acid (EPA) and docosahexanoic acid (DHA). The combined carbon atom

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configuration of DHA and EPA is known as omega-3. Types of marine fish that are rich in omega-3 content include salmon, tuna, sardine, and shellfish. (De Man, 1997).

The chemical physical properties of tuna fish oil include 25% saturated fat, 75% unsaturated fat, density 967.96 kg/m3, iodine number 170, saponification number 188, refractive index 25 oC 1.4785, unsaponifiable number 0.1% and types of fatty acids contained in tuna fish oil, namely palmitic, stearic, oleic and linoleic acids. However, there has been no research on fish oil derived from tuna fish waste, therefore the author chose tuna fish waste to determine its physico-chemical properties because tuna fish has quite a lot of waste and has a high nutritional value.

Recent research on the central nervous system has shown that DHA is important for early human development. In infancy, DHA is highly concentrated in brain and retinal tissue. DHA accumulates from fetal life through infancy. (Medina et al., 1995). Waste from tuna fish includes heads, bones and skin, but if it is not handled, it will quickly deteriorate and become rotten, so processing is needed, therefore we need to make the best use of this tuna fish waste so that it is not wasted, for example, such as taking oil from tuna fish processing waste. At this time, tuna fish waste is very few people who can use it, however, oil from tuna fish waste, which is a derivative product of tuna fish that has a selling value, has not been widely developed and commercialized. The problem needs to be overcome so that it is necessary to process tuna fish waste to determine the physico-chemical properties contained in oil from tuna fish waste. This study aims to analyze how the value of refractive index, peroxide number, free fatty acids and iodine number in tuna fish skin oil. It is expected that from this research, the quality value obtained can be a reference for further development of milkfish oil into products that provide health effects.

Literature Review

1. Tuna Fish Waste

Tuna fish waste is a by-product of fisheries industry processing and is expected to be utilized as an alternative feed ingredient for livestock food. Fish waste consisting of heads, entrails, skin, and bones amounts to 271,000 tons per year (BPS, 2001). The waste is perishable, so it needs processing. Processing is aimed at producing high-protein products that do not experience significant damage during storage for several months or even years (Kompiang, 1990). Fisheries development that is being promoted today in addition to producing products that can be utilized to meet food, industrial and income needs that produce waste in the form of solids, liquids and gases. Until now, these wastes have generally not been managed and utilized properly, but disposed of into the sea, rivers and other places (Anonymous, 1994).

Inadequate waste handling can be a source of pollution that endangers health. Waste generated from the food processing process can be in the form of solid waste and liquid waste. This waste generally still contains organic materials that can be utilized by microbes such as bacteria, fungi, parasites or insects and rodents (Purnawijayanti, 2001). Processed food waste is included in organic waste materials. This waste often causes a foul odor that stings the nose. If processed food waste contains protein and amino groups, then during degradation by microbes it will break down into volatile and foul-smelling compounds (Wardhana, 1995).

Fish waste is the whole fish after the fish meat is taken so that what is left is a part consisting of the head, tail, bones and thorns. Among the fish waste that is quite large in number besides the head is fish skin, which is about 14.78% of the weight of the whole fish. Fish skin has considerable potential to be utilized because it is a considerable source of fat. So far, fish waste is only used as agricultural fertilizer and fishmeal for animal feed (Anonymous, 2005). Efforts to

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reduce pollution are to develop fisheries waste management. The steps taken include increasing efficiency by handling and processing fishery products, as well as maximizing the utilization of waste so that the waste produced can be reduced to a minimum. In addition, it is necessary to treat waste that is no longer utilized so that it is below the predetermined threshold, so that if the waste is disposed of it will not pollute the environment. (Anonymous, 1994).

2. Fish Oil

Quality fish oil is fish oil that is rich in fatty acids that are beneficial to health. Omega-3 is one of the essential unsaturated fatty acids for the body and is needed especially for people with high cholesterol. EPA and DHA are the most dominant types of omega-3 in fish oil. EPA and DHA are not produced by fish, but by marine plants such as algae. The EPA and DHA content in fish is due to the fish consuming algae that contain both fatty acids (Haris, 2004). Therefore, it is not surprising that herbivorous fish such as lemuru, anchovies will have higher EPA and DHA content compared to carnivorous fish such as sharks, tuna, and kites. Long-term consumption of EPA and DHA has been shown to have a positive impact on people with coronary heart disease, which can reduce the risk of sudden death by 45% when compared to people who do not consume EPA and DHA (Haris, 2004). EPA and DHA are also beneficial for healing keloid symptoms (Olaitan et al., 2011), lowering cholesterol in the blood, especially LDL, anti-platelet aggregation, and anti-inflammatory (Haris, 2004). Consumption of foods rich in omega-3 has also been shown to be effective in reducing the risk of heart attack.

Based on research, it is known that the sudden death rate due to heart attack in the Eskimo race is at the lowest level compared to other races in the world. This is apparently closely related to the Eskimo race's habit of consuming a menu rich in omega-3 compared to other races (Hanafiah et al., 2007). The quality of an oil is determined through the determination of acid number and peroxide number. The acid number indicates the presence of free fatty acid content in the oil. While the peroxide number shows the level of damage to fish oil. An oil that can last a long time if the free fatty acid content in the oil is a maximum of 0.5% (equivalent to oleic acid) or a maximum acid number of 1 mg KOH per gram of sample (Haas, 2005). However, based on the requirements set by BPOM, the maximum acid number in fish oil to be used in pharmaceutical preparations is 0.6 mg/g KOH. Free fatty acid content that is still above the maximum limit can be improved through the purification process with the neutralization method (Rasyid, 2003) until the fatty acid content meets the requirements. In addition, the maximum limit of peroxide number of an oil according to BPOM is 5 meq O2/kg. Fish oil will also be very beneficial for health if the oil is rich in omega-3 fatty acids such as EPA and DHA. However, an oil will also be bad for health if it contains a lot of saturated fatty acids and trans fatty acids. This is because saturated fatty acids can cause obesity while trans fatty acids can trigger risk factors for cancer (Mozaffarin et al., 2006).

Fats and oils are triglycerides and triacylglycerols. Natural triglycerides are trimesters of long-chain fatty acids (C12 to C24) and glycerol, are the main constituents of animal fats and vegetable oils. Triglycerides through transesterification reactions with glycerol are converted into monoglycerides and diglycerides with the help of catalysts such as sodium methoxide and other Lewis bases. However, this process produces a mixture consisting of 40-80% monoglycerides, 30-40% diglycerides, 5-10% triglycerides, 0.2-9% free fatty acids and 4-8% glycerol (Juliati, 2002). There are solid animal fats that are usually derived from land animal fats such as milk fat, beef fat, lard. Marine animal fats such as whale oil, cod liver oil, herring oil are liquid and are called oils (Winarno, 1997).

Fish oil is an oil derived from the oily tissues of fish. Fish oil is recommended for a

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healthy diet because it contains omega-3 fatty acids, EPA (eicosapentaenoic), DHA (docosahexaenoic) which can reduce inflammation in the body. Not all fish produce omega-3 fatty acids but only fish that consume microalgae can produce these fatty acids, for example, herring and sardines or predatory fish that prey on fish that contain omega-3 fatty acids such as freshwater fish, lake fish, sprawling sea fish, tuna and salmon may contain high omega-3 fatty acids. Fish oil contains various fatty acids. The saturated fatty acid content is low while the unsaturated fatty acids are high, especially the long-chain unsaturated fatty acids containing 20 or 22 or more C atoms. Some of these acids include EPA and DHA (De Man, 1997).

3. Fatty Acid Content of Oil

Oil is known to have a high vapor point due to its constituent substance in the form of triacylglycerol. Therefore, before being analyzed by gas chromatography mass spectroscopy (KGSM), each oil sample is first transesterified to form a unit of fatty acid methyl ester or known as FAME (Fatty Acid Methyl Ester) with the help of a base catalyst and boron trifluoride (BF3). This transesterification process involves two stages, namely the hydrolysis stage of triacylglycerol in the presence of a base catalyst and the esterification stage of fatty acids with methyl groups from methanol assisted by boron trifluoride (BF3) catalyst.

Research Method

This research will be conducted in May 2024. Sample preparation was carried out at the Biochemistry Laboratory, Department of Agricultural Technology, Pangkep State Agricultural Polytechnic. Quality analysis of fish skin oil was carried out at Ujung Pandang State Polytechnic Laboratory.

1. Tools and Materials

The main material used in this research is tuna fish waste, namely tuna fish skin. Tuna fish skin waste was obtained from PT Nirvana Niaga Sejahtera Makassar. The tuna fish skin was taken after separation from the parts used and then cleaned and stored in the freezer before oil separation.

Chemicals used were chloroform, N-hexane, 0.1 N KOH, Wijs reagent, 15% KI solution, starch indicator, 95% ethanol, pp indicator, glacial acetic acid, saturated KI, and filter paper.

The tools used in this study include, water bath, analytical balance, pycnometer, thermometer, measuring flask, burette, measuring cup, erlenmeyer, measuring pipette, beaker glass, upright cooler, hot plate, paper chromatography.

2. Implementation of Research

The implementation of this research goes through several stages, namely the preparation of tuna fish waste raw materials, then the material is dried by freeze-drying which aims to remove moisture content and freeze the oil contained in tuna fish waste, after which tuna fish waste is extracted with soxhlet which aims to separate oil from tuna fish waste.

3. Freeze-drying

Freeze-drying is drying by sublimation of ice from frozen products. Because in this process to reduce water content and low temperatures are used, so that microbiological reactions can be stopped. Four stages are important in the freeze-drying process: cooling, vacuum, sublimation and condensation. Sublimation uses high energy, the total energy taken in the process is 45%. The reduced fish waste material is then freeze-dried at -50 ^{o}C for 24 hours. This aims to

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freeze the oil in the fish waste.

4. Extraction With Solvent (Soxhlet Method)

In this extraction process there are three parts that will be extracted separately first on the head, second on the skin, third on the bones. The goal is to see the difference in oil contained in the body parts of tuna fish. The principle of this process is extraction by dissolving oil in oil and fat solvents. The oil or fat solvent that can be used in the extraction process with vaporized solvents is n-hexane.

It should be noted that the amount of solvent evaporated or lost should not be more than 5%. If more, the entire extraction solvent system needs to be re-examined. Extraction with soxhlet gives a higher yield of extracts because in this way heating is used which is thought to improve the solubility of the extract. Compared to maceration, soxhlet extraction gives higher extract yields. The more polar the solvent, the more extractable material was not different for the two extraction methods.

5. Experiment procedure

a. Fat flask in the oven and weighed

b. A 5 g sample was weighed and put into a filter paper sleeve.

c. The sleeve is inserted into the soxhlet apparatus + 3 hours and the fat flask which has known weight is mounted on the soxhlet apparatus.

d. 50 ml of hexane was added to the soxhlet apparatus.

e. The sample was extracted with hexane solvent

b. The fat flask was dried in a 105 ^{o}C oven for 30 minutes, until the aroma of hexane was not smelled.

c. The fat obtained was then collected.

d. The resulting oil/fat is ready for analysis.

6. Soxhletation mechanism

Samples that have been mashed, weighed 5 g and then wrapped or placed in a thimble (sleeve where the sample). The solvent used is hexane with a boiling point of 60-80^{o}C. Hexane is used because fat is soluble in organic solvents. Thimble that has been filled with samples is inserted into the soxhlet.

The soxhlet is connected to the flask and placed in an electric heating device and condenser. A cooling device is connected to the soxhlet. Water for cooling is run and the fat extraction device starts to heat up. As the solvent is brought to a boil, the effort rises through the soxhlet to the cooling pipe. Cold water passed through the outside of the condenser condenses the solvent vapor so that it returns to the liquid phase, then drips into the thimble. This principle is the principle of condensation. The solvent dissolves the fat in the thimble, this juice solution collects in the thimble and when the volume is sufficient, the juice will be flowed through the siphon to the flask. The process from condensation to jetting is referred to as reflux.

The fat extraction process, crude distillation is carried out for 3 hours. After the extraction process is complete, the solvent and fat are separated through a distillation process and dried. The fat flask that will be used, must previously be in the oven first. This aims to remove the water

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content and fat attached to the flask. After the oven, the fat flask is stored in a desiccator containing silica gel. Silica gel serves as a water absorber and balances the temperature of the fat flask so that it is cold when weighing. After the soxhletation process is complete, the fat flask must be dried in a 105 oC oven for 30 minutes until the aroma of hexane is not smelled (Ketaren, 2008).

Results and Discussion

1. Index of Bias

The refractive index is the degree of deviation of light passed through a bright medium. The refractive index of a substance is the ratio of the sine of the incident ray angle and the sine of the refractive ray angle of light through a substance. Refractive index is used as a quality test parameter in this tuna skin oil research in order to provide information on how to easily determine the quality level of fish oil quality through the physical properties of refractive index.

The refractive index value of fish oil depends on its density, the smaller the density, the light will easily penetrate the oil. Vice versa, the higher the density, the light will be difficult to penetrate the oil. Based on research conducted by (Sutiah, 2008). The refractive index value produced from tuna skin oil is 1.638. These results indicate that the refractive index value of tuna skin oil is still high.

The refractive index value of fish oil indicates the quality of the fish oil. A high refractive index value is an indicator that the fish oil has not been oxidized by processing factors such as temperature. Fish oil that has been oxidized twice its density has been reduced due to heating, so the speed of light in the fish oil is greater which results in a smaller refractive index value. Fish oil that has not been oxidized has the largest refractive index value because the oil has a greater density, so the speed of light in the oil is smaller and results in a larger refractive index value.

2. Iod Numbers

Iod number is the amount (grams) of iodine that can be absorbed by 100 grams of oil. Iod number can express the degree of unsaturation of oil or fat. The greater the iod number, the higher the degree of unsaturation and the softer the oil, because saturated fatty acids are usually solid and unsaturated fatty acids are liquid.

The test result of the Iod number of oil from tuna fish skin is 44.77 g Iod/100 g of material. When compared with the Iod number of oil from tilapia fish waste which is 56.6% -73.5 g Iod/100g (Nugroho, 2014), the Iod number of tuna skin oil obtained is low. The Iod number of shark liver oil from the results of Damongilala's research (2008) was 33.39 g Iod/100 g material - 35.33 g Iod/100 g material. The maximum standard Iod number of commercial products is 130g/100g.

Unsaturated fatty acid compounds are able to bind iodine and form saturated compounds. The amount of iodine bound indicates the number of double bonds. Thus the more iodine that is bound the higher the degree of unsaturation (Sudarmadji, 2007). The high degree of unsaturation of fish oil causes fish oil to oxidize more easily. If fish oil is easily oxidized, the degree of unsaturation decreases because the double bond has been broken so that the iodine number is getting smaller.

3. Peroxide Numbers

Peroxide number is an indicator of damage to fat or oil. Oil damage is caused by enzymatic and non-enzymatic reactions. Peroxide numbers are expressed as milliequivalents.

Peroxide numbers indicate changes in primary oxidation products to secondary oxidation products that occur in oil. Peroxide number testing is carried out to determine the presence of hydroperoxide content in oil which is the primary product of the oxidation process. The hydroperoxide content is directly proportional to the damage that occurs in fish oil, the greater the hydroperoxide content, the greater the level of damage to the fish oil.

Based on the analysis of the peroxide number of tuna skin oil is 0.02 meq/100 g of material or 0.2 meq / kg. IFOS (International Fish Oil Standard) standard set for peroxide number is ≤ 5 mEq/kg. These results indicate that tuna skin oil has a peroxide number that meets the IFOS standard. Peroxide values that exceed the standard and are very high can cause the body to experience poisoning if consumed (Ketaren, 2012), accelerate rancidity and unwanted flavors, and are toxic to the body if the peroxide value is> 100 mEq / kg (Nurhasnawati et al., 2015).

4. Free Fatty Acids

Free fatty acids (FFA) are acids that are free and not bound as triglycerides. Acid value is related to the value of free fatty acids (FFA). The free fatty acid test results in this study were 0.03%, indicating that the FFA value produced still met the IFOS standard of <1.5%.

Factors that can affect the value of free fatty acids are poor storage that can cause fatty acid levels to increase (Gunawan et al. 2003). Fatty acid oxidation is highly dependent on the number of double bonds and is also influenced by temperature, oxygen concentration, metals, water activity, prooxidants, antioxidants, and catalysts. Compound unsaturated fatty acids (PUFA) found in fish oil have a long number of double bonds that are easily oxidized, when compared to habbatussauda oil which has monounsaturated fatty acids.

Conclusion

The results of the chemical quality characterization of tuna skin oil obtained a refractive index value of 1.638, free fatty acids (FFA) 0.03%, peroxide number 0.2 meq / kg material and Iod number 44.74 g I2 / 100 g material.

Suggestion

For further research, it is necessary to utilize other waste sources besides the skin of tuna fish, considering the potential for utilizing tuna fish waste into fish oil is very large.

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