Extraction of Stingray Liver Oil (Dasyatis Sp) with Alkaline Digestion Method

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Abstract. Stingray liver oil extraction method (Dasyatis sp) using alkaline digestion method with the addition of 2% concentrated NaOH reagent and HCL to maintain pH 8-9 by heating at 50°C for 3 hours can produce a yield of 35.74±0.38%. then with the addition of 3% magnesol XL adsorbent and centrifuged for 15 minutes at a speed of 5000 rpm can improve the quality of stingray liver oil (Dasyatis sp) by producing an FFA value of 0.40%±0.02, PV of 2.37±0.05 mEq/kg, p-anisidin 5.72±1.95 mEq/kg, TOTOX 8.27±1.80 mEq/kg, AV 1.74±0.01 mg NaOH/kg, clarity 75.19±1.7%.

1. Introduction
Fish oil can be extracted from fish with high fat content or from fish liver by cooking, processing, enzymatically or using organic solvents [1]. The process of extracting oil from fish liver or from other materials includes removing oil from the tissue by breaking/breaking its structure and separating the oil from the mixed mass. Tissue is broken down by heating or by heating or by crushing.

Stingray (Dasyatis sp) is one of the fish with high fat content, and the liver of this type of fish is only used for processed foods such as fish liver paste, even if the catch is too much, the stingray liver is often thrown away or as waste. Several studies on stingray liver oil have been carried out in Indonesia, including determining the best temperature using the steam jacket method on Mondol stingrays (White Spot Whipray Rays) [2], researchers who revealed a high proportion of oil in stingray liver [3]. Stingray liver oil is rich in fat (54%) by weight of raw materials with unsaturated fatty acid content of EPA (4%) and and DHA (16%)[4]. The most research on fish livers conducted in Indonesia is shark liver, such as banana shavings[5][6], bottle shavings [8], [9]

Research on extraction methods for fish liver oil includes wet-rendering [10], dry rendering [11], by heating [8], extraction using the Bligh and Dyer [6], wet rendering method with temperature difference treatment [12] Steam jacket method [2] all of which aim to obtain the best quality fish oil. This study also aims to produce better quality stingray liver oil but with the alkaline digestion method with 2% NaOH concentrated reagent and HCL to maintain pH 8-9 and temperature using 50°C.

2. Materials and Methods
2.1 Material
The material used is fresh stingray liver (Dasyatis sp) obtained from smoked fish processing waste in Karangsari and Kingking villages, Tuban District, East Java. Fish weight ranges from 1-3 kg. liver weight is about 50-70 g per head. Stingray liver was placed in a styrofoam box which was given ice
flakes at a ratio of 2:1 to maintain the quality of the stingray liver. Other ingredients are concentrated NaOH and HCL.

2.2. Method

The extraction method of stingray liver oil (Dasyatis sp) has been tested through preliminary research, namely the Hot Method and Alkali Digestion Method, of the 2 (two) methods can be used as a basic reference, which method is suitable for stingray liver. From preliminary research, it can be seen that the use of alkaline digestion is better than the use of the Hot Method, because after purification with magnesol XL as an adsorbent centrifuged at 5,000 rpm for 15 minutes, if left for 1 week for the Hot Method, the color changes and clots, so that the use of the alkaline digestion method used in further research. In general, the extraction method of stingray liver oil (Dasyatis sp), is as follows:

The first thing to do is to wash 250 grams of stingray liver by removing the gall, then chop and grind it in a meat grinder.

Weigh 200 grams of stingray liver that has been ground and put in a glass pyrex beaker (300 – 400 ml). Then add water 50% of the weight of the liver that has been milled, then add 2% concentrated NaOH then add HCL until the pH of the mixture is between 8-9.

Fill the Pyrex glass beaker (1000 ml) with 500 ml of water, then put the glass beaker containing the milled liver into the glass beaker and its contents for one hour with a temperature between 50°C, during heating, stirring continuously using a glass rod.

After one hour of heating, the temperature is raised to 60-750°C and maintained at a constant temperature and heated again for 1-2 hours.

Take out a small glass beaker containing stingray liver, cool for 15 minutes, then put the contents in a centrifuge tube and add 3% magnesol XL then centrifuge for 15 minutes at a speed of 5,000 rpm.

3. Results and discussion

Extraction method of stingray liver oil (Dasyatis sp) with alkaline digestion method to produce better quality stingray liver oil. The quality reference here is the percentage of free fatty acids (FFA), acid number (AV) and the percentage of clarity. The yield of the extraction of stingray liver by the extraction method is highly dependent on the temperature and time of extraction. The yield resulting from the method described in the brief description of the invention resulted in the highest oil yield of 20% at a temperature of 50°C with an extraction time of 3 hours of 35.74±0.38%.

Oxidation parameters include Peroxide Value (PV), p-Anisidin value 9p-AV) and TOTOX Value. Oxidation value is very important as an indicator of oil quality, the lower the oxidation value, the better the quality of the oil. The International Fish Oil Standard (IFOS) stipulates a peroxide value of 3.75 meq/Kg as a standard for edible oil. Good quality oil should have a p-anisidin value below 20 mEq/Kg [5], 4-60 mEq/Kg [13], 15 mEq/kg [14]. The total oxidation value is the sum of x 2 values of peroxide and panicidin [15]. Oterhals states the TOTOX value for edible oil is between 10-60 mEq/Kg. Meanwhile, IFOS states that edible oil must have a TOTOX value below 20 mEq/Kg. Rozi [16] stated that purification using centrifugation and the addition of synthetic adsorbents has the potential to improve the quality of fish oil. Bleaching is done to remove pigment components (carotenoids, tocopherols) so as to improve the color of the oil.

Table 1 shows the peroxide value of crude oil extracted at 50°C at 8.05±0.35 mEq/kg, while the peroxide value after the addition of 3% magnesol XI (bleaching) was 2.37±0.05 mEq/kg. The p-anisidin value of crude oil extracted at 50°C was 17.85±1.20 mEq/kg, while the p-anisidin value after bleaching was 5.72±1.95 mEq/kg. The total oxidation value of crude oil extracted at 50°C was 32.83±0.75 mEq/kg, while the total oxidation value after bleaching was 8.27±1.80 mEq/kg. Bleaching using magnesol XL can improve the quality of crude fish oil.
### Table 1. Peroxide analysis of stingray liver oil \((Dasyatis\; sp)\) with the addition of 3% magnesol XI

| Analysis | Crude oil | Pure Oil (addition of 3% magnesol XI) | Percentage of quality improvement | Standart* |
|----------|-----------|--------------------------------------|-----------------------------------|-----------|
| PV       | 8.05±0.35 | 2.37±0.05                            | 70.56%                            | ≤3.75     |
| p-anisidin| 17.85±1.20 | 5.72±1.95                           | 67.80%                            | ≤15       |
| TOTOX    | 32.83±0.75 | 8.27±1.80                           | 74.80%                            | ≤20       |

Remarks: PV (mEq/kg), p-anisidin (mEq/kg), TOTOX (mEq/kg). *IFOS (2011)

Table 2 shows the value of the percentage of free fatty acids, the value of the acid number, and the value of the percentage of oil clarity before and after using 3% magnesol XL bleaching. The value of free fatty acids of crude oil extracted at 50°C was 0.80±0.07%, while the value of free fatty acids after bleaching was 0.40±0.02%. FFA is a product of triacylglyceride hydrolysis reaction which is closely related to the storage process. The FFA value is closely related to the amount of alkali to be used in the purification process. Oils that have a high percentage of free fatty acids will have an unpleasant aroma and taste[17,18]

The acid value of crude oil extracted at 50°C was 2.45±0.22%, while the value of free fatty acids after bleaching was 1.74±0.01%. Acid number is an important parameter to determine the presence of FFA value and other non-fatty acid components. The acid number is highly dependent on the composition of the oil, the extraction method, and the freshness of the raw material [19]

A high percentage of transmission value indicates that fish oil has a good level of clarity. The clarity of crude oil extracted at 50°C was 65.22±3.56%, while the value of oil clarity after bleaching was 75.19±1.85%. The wavelength used in the clarity test was 450 nm.

### Table 2. Percentage of free fatty acids (FFA), acid number (AV), and percentage clarity of stingray liver oil \((Dasyatis\; sp)\) with the addition of 3% magnesol XI

| Analysis | Crude oil | Pure Oil (addition of 3% magnesol XI) | Percentage of quality improvement | Standart* |
|----------|-----------|--------------------------------------|-----------------------------------|-----------|
| FFA      | 0.80±0.07 | 0.40±0.02                            | 50.00%                            | ≤1.13     |
| AV       | 2.45±0.22 | 1.74±0.01                            | 60.00%                            | ≤3        |
| Kejernihan| 65.22±3.56 | 75.19±1.85                            | 15.57%                            |           |

Remarks: FFA (%), AV (mg NaOH/kg), clarity transmission (%). *IFOS (2011)

### 4. Conclusions

The results showed the yield of the extracted stingray liver \((Dasyatis\; sp)\) using the alkaline digestion method (acid digestion method) with 2% NaOH concentrated reagent and HCL to maintain pH 8-9 and by heating at 50°C for 3 hours. of 35.74±0.38%, the addition of 3% magnesol XL adsorbent and centrifuged for 15 minutes at a speed of 5000 rpm can improve the quality of stingray liver oil \((Dasyatis\; sp)\).

### 5. References

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