Natural Dye Extraction from Brown Algae using the Microwave Assisted Extraction

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Abstract. This paper discusses the extraction of natural dyes from brown algae Sargassum sp. using the Microwave assisted extraction method. Brown algae Sargassum sp. used in this study were taken from Wane Beach, Bima Regency. The sampel is washed and dried with aerated and then ground to form powder. Sargassum sp. powder mixed with distilled water (1:4 w/v) then extracted in the microwave for 1 minute. Extraction is done by varying the power level at 10; 20; 30; 40 and 50. Extracts of the dyes produced were then characterized using UV-Vis and GC-MS spectrophotometers. The results of the analysis using UV-Vis showed that the maximum dye extract was obtained at power level 30. The results of the analysis using GC-MS showed that the compound content in the Sargassum sp. Extract. using distilled water there are 15 peaks and the largest content is Hexadecanoic acid, methyl ester compound with a peak area of 79.72%. While the content of compounds in Sargassum sp. using methanol solvent there are 32 peaks and the largest content is Hexadecanoic acid, methyl ester which is 29.39%.

1. Introduction

Utilization of brown algae (Phaeopyceae) as a source of dyes is very promising to be developed considering that brown algae contain fucosantin and chlorophyll and do not compete with food. The excess of brown algae is able to regenerate continuously without requiring a lot of cost and shorter harvest time compared to plants in general that require nutrients, expensive maintenance costs and a long time to grow [1]. The pigment component in Sargassum sp. can be obtained by extraction. Extraction is the process of withdrawal or separation of components or active substances of a samplisia using certain solvents. Extraction with solvents is based on the polarity of the substances in the solvent at the time of extraction. Polar compounds will only dissolve in polar solvents and non-polar compounds will only dissolve in non-polar solvents [2]. A variety of methods have been used in the extraction of dyes including maceration, reflux, and soxlets. Development of extraction methods to speed up extraction time and reduce the amount of solvent needed. Lately, the Microwave Assisted Extraction (MAE) extraction method has been widely used to extract active compounds in natural substances [3]. MAE extraction method utilizes microwave radiation to accelerate selective extraction by heating the solvent quickly and efficiently. The advantages of extraction using the MAE method are reduced extraction time and the use of fewer chemical solutions [4]. According to some research results, the MAE method increases the efficiency and effectiveness of the extraction of active ingredients of various types of spices, herbal plants and fruits [5]. MAE method has advantages such as shorter time needed,

less solvent needed, reducing energy consumption, suitable for thermolable components, giving higher extraction results, higher accuracy and precision [6]. Microwave extraction method can accelerate the extraction of target compounds compared to conventional heating methods [7]. Kartikasari (2013), isolated phenolic compounds from Euceuma Cottonii seaweed using microwaves with optimum conditions at a temperature of 60 ^{o}C with extraction time of 6 minutes [8].

This article will discuss the extraction of dyes from brown algae Sargassum sp. using the method of heating with the help of microwave radiation. By using this method, the extraction process can be done in a short time and low cost.

2. Experimental Section

2.1. Preparaton of Brown Algae

Brown algae Sargassum sp. wash with water thoroughly then immersed in 1% HCl for 2 hours and rinsed with water to neutral pH. Furthermore, seaweed is dried with aerated and then blended until seaweed powder is obtained.

2.2. Extraction of Natural Dye

A total of 20 grams of brown algae powder Sargassum sp. mixed with 100 mL of distilled water then cooked in the microwave at power level 100 for 1 minute. The mixture is then cooled and filtered. The filtrate obtained is measured its absorbance. The same treatment is used for the extraction of dyes at power level 20; 30; 40 and 50 and methanol solvents.

2.3. Characterization

Characterization of the natural dyes was carried out by UV-Vis spectrophotometer analysis and GC-MS method.

3. Discussion

Brown algae Sargassum sp. used in this study were taken from seaweed farmers in Wane beach, Bima Regency. Sargassum sp. fresh ones are washed thoroughly using fresh water to remove mud, coral and residual salt that sticks to the algae. Then immersed in a solution of HCl to dissolve minerals that are not soluble in water. Then rinse with distilled water to neutralize the brown algae sample. Samples that have been washed, then dried by aerated. The dried sample is then ground to a powder. Sargassum sp. Aquades are mixed and extracted using microwaves at different power levels. the measurement results of the absorbance of the dye using a UV-Vis spectrophotometer as shown in Figure 1.

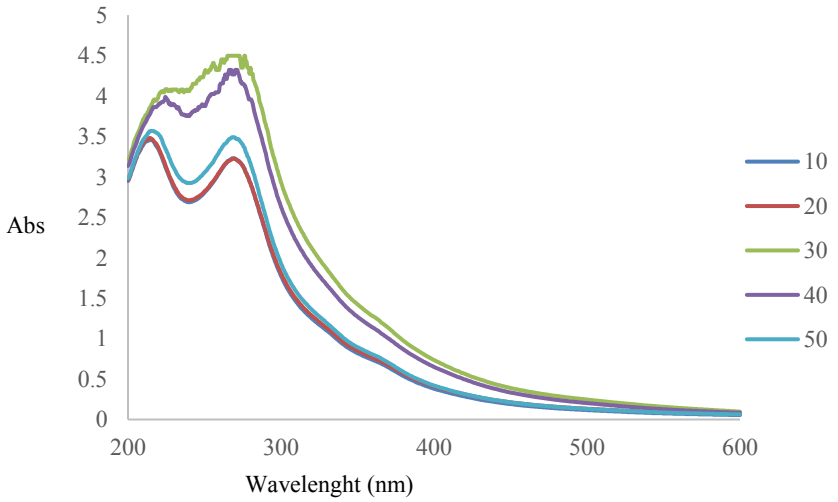

Figure 1. UV-Vis Graph of Sargassum sp. Extract at Power Level Variation

Based on the graph shows that the optimum conditions for the extraction of dyes from Sargassum sp. performed at power level 30 for 1 minute. The absorption peak occurs at a wavelength of 269 nm with an absorbance of 4.498. The use of microwaves in the extraction of dyes from brown algae Sargassum sp. can be said to be better because the extraction process takes place quickly and maximum results. Wiraningtyas research results (2019), explained the extraction of dyes from Sargassum sp by maceration method produces extracts with absorbance of 3,883 with extraction time of 2 days while extraction by microwave method produced extracts with absorbance of 3,371 with extraction time of 20 minutes [1]. The advantages of the microwave method being an alternative as a substitute for conventional heating, where heat transfer occurs through the heat gradient. Whereas in microwave, heating occurs through direct collisions between polar material and microwaves which are regulated by two phenomena, namely ionic conduction and dipole rotation which take place simultaneously. As a result, energy transfer takes place faster and has the potential to improve product quality [9]. Microwave helps the process of extracting dyes by giving energy directly to the material. With the direct energy to the material, the direction of energy transfer and mass transfer becomes the same direction, so that the extraction process is faster [10].

Whereas at the same wavelength obtained low absorbance values at power levels 40 and 50 are 4,323 and 3,492. The decrease in absorbance may be due to excessive heat degradation of the dye. The same was stated by Handayani (2014) that polyphenol compounds will degrade if excessive heating occurs [8]. At too high a power can cause degradation of dyestuff compounds so that the resulting product is getting smaller [11].

Effect of solvents on the extraction of dyes from sargassum sp. performed using distilled water and methanol as shown in Figure 2. Extraction of dyes using methanol has a absorption peak at a wavelength of 425 nm with an absorbance of 2,297, whereas the distilled water solvent has an absorption peak at a wavelength of 269 nm with an absorbance of 4,498 . The difference in wavelength and absorbance value in methanol and distilled water solvents is caused by the two solvents having different levels of polarity.

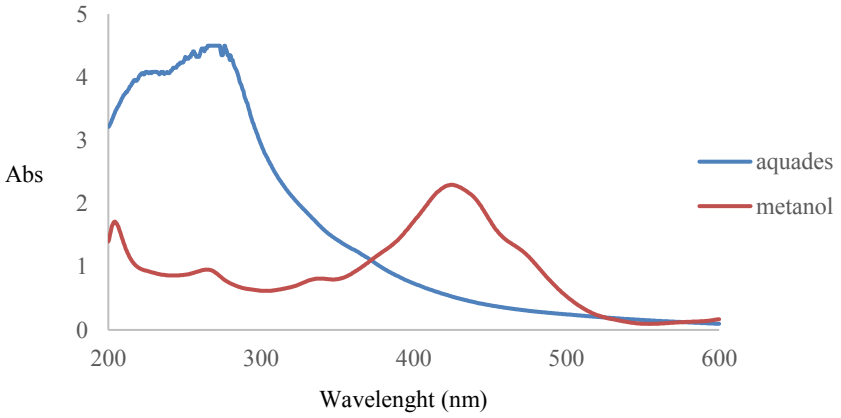

Figure 2. UV Vis graph of Sargassum sp extract on aquades and methanol solvents

To find out the content and structure of compounds contained in the extract of Sargassum sp. the extraction results were carried out by analysis using Gas Chromatography-Mass Spectroscopy (GC-MS). The samples analyzed were extracted from Sargassum sp. using methanol and distilled water assisted microwaves at power level 30 for 1 minute. Chromatogram of Sargassum sp. using distilled water as shown in figure 3.

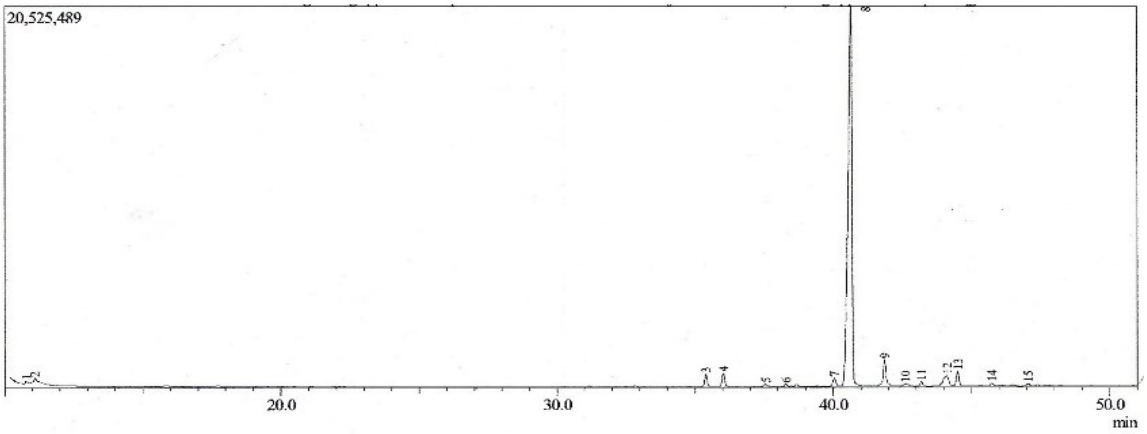

Figure 3. Chromatogram of Sargassum sp. using distilled water

Based on Figure 3, it was found that Sargassum sp. using aquades solvent shows 15 peaks detected. Based on the chromatogram, there is one of the most dominant peaks seen from the percent area, namely Hexadecanoic acid, methyl ester which is 79.72%. Data on the content of compounds in Sargassum sp. as in table 1.

Table 1. Compound Content in Sargassum sp. Extract. using distilled water

Peak	Retensi Time	Compound Name	Formula	Mol Weight	Peak area %
1	10.783	1-nonena	C_9H_{18}	126	0,43
2	11.083	nonena	C_9H_{20}	128	1,34
3	35.383	hexadecane	$C_{16}H_{34}$	226	1,69
4	36.016	Decanoic Acid, methyl ester	$C_{11}H_{22}O_2$	186	1.99
5	37.540	1-Hexadecanethiol	$C_{16}H_{34}S$	258	0.54
6	38.288	Tetradecanoic acid, methyl ester	$C_{15}H_{30}O_2$	242	0.42
7	40.047	9-Octadecanoic acid, methyl ester	$C_{19}H_{36}O_2$	296	1.40
8	40.655	Hexadecanoic acid, methyl ester.	$C_{17}H_{34}O_2$	270	79.72
9	41.857	Nonadecanoid acid, methyl ester	$C_{21}H_{42}O_2$	326	4.10
10	42.602	1-Decanol	$C_{15}H_{30}O_3$	258	0.75
11	43.197	2-Norpinanol,3,6,6-trimethyl	$C_{10}H_{18}O$	154	0.67
12	44.130	9-Hexadecanoic acid, methyl ester	$C_{17}H_{32}O_2$	268	3.40
13	44.506	Octadecanoic acid, methyl ester	$C_{19}H_{38}O_2$	298	2.50
14	45.743	6-octadecrnoid acid, methyl ester	$C_{19}H_{36}O_2$	296	0.61
15	47.057	Methyl arachidonate	$C_{21}H_{34}O_2$	318	0.46

While the chromatogram from Sargassum sp. using methanol as a solvent as shown in figure 4.

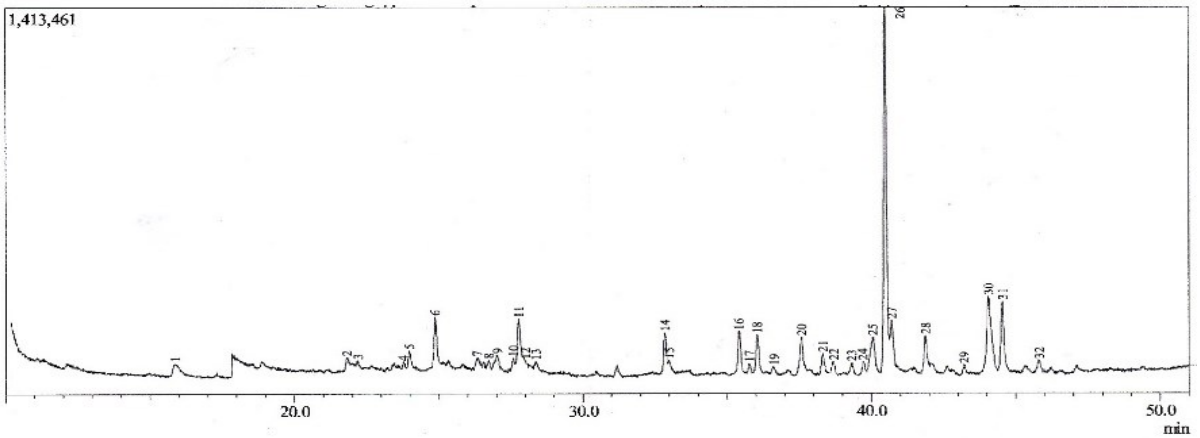

Figure 4. Chromatogram of Sargassum sp. using methanol

Based on the chromatogram in figure 4, that extract of Sargassum sp. using a methanol solvent showing 32 peaks detected. Based on the chromatogram, there is one of the most dominant peaks seen from the percent area, namely Hexadecanoic acid, methyl ester which is 29.39%. Data on the content of compounds in Sargassum sp. as in table 2.

Table 2. Compound Content in Sargassum sp. Extract. using methanol

Peak	Retensi Time	Compound Name	Formula	Moleculer Weight	Peak area %
1	15.858	1,4 dichloro benzene	$C_6H_4Cl_2$	146	1.40
2	21.817	Tetradecane	$C_{14}H_{30}$	198	0.64
3	22.183	Dodecane	$C_{12}H_{26}$	142	0.37
4	23,775	2-methyl Octane	C_9H_{20}	128	0.41
5	23.992	2-methyl Decane	$C_{11}H_{24}$	156	1.42
6	24,883	Tetradecane	$C_{14}H_{30}$	198	3.81
7	26,333	1-Eicosanol	$C_{20}H_{40}O$	296	1.95
8	26,725	2-Methyl Undecane	$C_{12}H_{26}$	170	0.86
9	27,025	2,6,11-trimethyl Dodecane	$C_{15}H_{32}$	212	1.72
10	27,583	Octyl-Cycloprepane	$C_{11}H_{30}O_3$	258	0.73
11	27,775	Dodecane	$C_{12}H_{26}$	170	5.02
12	28,017	4-Bromomethyl cyclohexene	$C_{17}H_{11}Br$	174	0.61
13	28,375	Octadecanoic acid, methyl ester	$C_{19}H_{18}O$	142	0.73
14	32,833	1-Tetradecene	$C_{14}H_{28}$	196	3.42
15	32,922	2,2-dimethyl 3-Hexanone	$C_8H_{16}O$	128	0.90
16	35,408	1-chloro Octadecane	$C_{18}H_{37}Cl$	288	3.48
17	35,767	1,1 dimethoxy-Tetradecane	$C_{16}H_{34}O_2$	258	0.69
18	36,042	Decanoic acid, Methyl ester	$C_{11}H_{22}O_2$	186	3.17
19	36,600	1-hexadecenyl methyl Eter	$C_{17}H_{34}O$	254	0.63
20	37,575	Tricholoroeicosyl-Silane	$C_{20}H_{41}Cl_3Si$	414	3.57
21	38,308	Decanoic acid, methyl ester	$C_{11}H_{22}O_2$	186	1.75
22	38,692	2,2,-Dimethyl-1-Octanol	$C_{10}H_{22}O$	158	1.39
23	39,308	Dodecanal dimethyl acetal	$C_{14}H_{30}O_2$	230	0.63
24	39,708	(Hexadecyloxy)methyl Oxirane	$C_{19}H_{38}O_2$	298	1.05
25	40,042	9-Hexadecenoic acid, methyl ester	$C_{17}H_{32}O_2$	268	4.79

Peak	Retensi Time	Compound Name	Formula	Moleculer Weight	Peak area %
26	40,492	Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	270	29.39
27	40,708	1,1'-11,12-bis (1,1-dimethylethyl) tricyclo 5.2.2.12,6 dodeca-3,8-diene-4,8-diyl bis 2,2-dimethyl-1-propanone	$C_{30}H_{48}O_2$	440	4.49
28	41,875	Pentadecanoic acid, 4,6,10,14-tetramethyl- methyl ester	$C_{20}H_{40}O_2$	312	2.60
29	43,225	2H-Pyran, tetrahydro-2-(12-pentadecynyloxy)-	$C_{20}H_{36}O_2$	308	0.67
30	44,058	11-Octadecanoic acid, methyl ester (CAS) Methyl 11-octadecenoate	$C_{19}H_{36}O_2$	296	10.23
31	44,550	Octadecanoic acid, methyl ester	$C_{19}H_{38}O_2$	298	6.48
32	45,808	1-Docosene	$C_{22}H_{44}$	308	0.99

Based on the data in tables 3 and 4, it appears that saturated fatty acids have the highest content compared to unsaturated fatty acids. These fatty acids dissolve in both polar and non-polar solvents. The longer the carbon chain on the triglycerides, the lower the oil / fat solubility. This is consistent with the results of Gunawan's research (2012) which states that unsaturated fatty acids are more soluble than saturated fatty acids with the same chain length, thus fatty acids with higher unsaturation degrees will be more soluble [12].

4. Conclusion

Sargassum sp. Brown algae extract can be extracted using the Microwave Assisted Extraction (MAE) method. Extraction by the MAE method was carried out in a short time and optimum results. Extraction using distilled water has an absorption peak at a wavelength of 269 nm and an absorbance value of 4,495, while extraction using methanol has an absorption peak at a wavelength of 425 nm with an absorbance value of 2,297. The results of the analysis using GC-MS showed that the compound content in the Sargassum sp. Extract. using distilled water there are 15 peaks and the largest content is Hexadecanoic acid compound, methyl ester with a peak area of 79.72%. While the content of compounds in Sargassum sp. using methanol solvent there are 32 peaks and the largest content is Hexadecanoic acid, methyl ester which is 29.39%.

5. References

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