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Development of Extracts from Aomori Hiba and Apple Polyphenol as Cosmetics Materials

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Hiba oil and Hiba water can be obtained from sawdust dumped in sawing Aomori Hiba through steam distillation, and hinokitiol can be obtained from Hiba oil and Hiba water through separation and refining. Antimicrobial components such as hinokitiol and aromatic components with a relaxing effect are contained in Hiba oil. Safety, stability, and functionality of Hiba oil, Hiba water, and hinokitiol were studied to use materials obtained from Hiba oil as raw materials for cosmetics.

On the other hand, it is known that polyphenol is contained in lees discharged as industrial waste after apples are crushed into juice. Various functions of apple polyphenol such as an antioxidant, antiallergenic, deodorant and for whitening have been reported. Therefore, the polyphenol components were analyzed and how to efficiently extract polyphenol from apple lees was investigated to utilize the extracted polyphenol as raw materials for cosmetics.

In this paper, research thus conducted on utilizing functional materials which are environmentally friendly such as Hiba oil, Hiba water, hinokitiol and apple polyphenol is reported.

Key words: Hiba oil, Hiba water, hinokitiol, apple polyphenol, cosmetics, environmentally friendly materials

1. INTRODUCTION

Sawdust dumped in sawing Aomori Hiba is discharged as industrial waste. Hiba oil and Hiba water can be obtained from the sawdust through steam distillation, and hinokitiol is obtained from Hiba oil and Hiba water through separation and refining.

In addition to its antibacterial components such as hinokitiol, Hiba oil and Hiba water are characterized by aromatic components with relaxing effects. This suggests that Hiba oil and Hiba water can be used as aromatics for cosmetics. Therefore, the Hiba oil component analysis was conducted to study how Hiba oil disperses in Hiba water.

Hinokitiol of which various effects such as antimicrobial, melanogenesis inhibition, ultraviolet absorption, astriction, and antiphlogistic have been reported is beneficial to skin. However, because of hinokitiol's photo-instability and strong corrosiveness, its use is limited. Therefore, light stability of hinokitiol was investigated by producing a metal complex from hinokitiol.

Lees are also discharged as industrial waste after apples are crushed into juice. It is known that apples contain functional material "polyphenol." Polyphenol is the generic term for materials with two or more hydroxyl groups linked to an aromatic hydrocarbon framework. It concerns the bitterness and astringent taste and color of plants. The components of polyphenol are classified into about 4,000 types. Polyphenol in apples has such effects as an antioxidant, antiallergenic, deodorant, and for whitening.

Therefore, component analysis of apple lees was carried out to develop a method of extracting polyphenol efficiently from apple lees.

This research is thus conducted on extracts from Aomori Hiba and apple polyphenol, which are environmentally friendly materials typical in Aomori Prefecture, to utilize them as cosmetic materials.

2. EXPERIMENTAL METHOD

2.1. EXTRACTS FROM AOMORI HIBA

2.1.1. COMPONENT ANALYSIS OF HIBA OIL

QP-5000 (manufactured by SHIMADZU) was used as GC-MS under the following conditions:

Column: J&W DB-1 0.25mmφ×30mm (film thickness: 0.25μm)

Column temperature: 100 to 230°C (5°C /minute), hold at 250°C for 40 minutes

Introduction temperature: 250°C

Detector temperature: 250°C

Carrier gas: He (total flow rate: 108.4ml/min)

Split ratio: 50 Injection quantity: 1 μl

Detector: TCD

2.1.2. HIBA WATER PARTICLE SIZE

The dynamic light scatting method for particle size measurement (LB-550 manufactured by Horiba) was used to measure Hiba oil particle sizes.

2.1.3. LIGHT STABILITY TESTING OF HINOKITIOL COMPLEXES

1 ml of 1000-ppm acetonic solutions of hinokitiol and its metal complexes formed with various metal ions (-Na、-K、-Ca、-Zn、-Cu、-Mg) were applied on the bottom of laboratory dishes 55 mm in diameter and air-dried in a darkroom.
The decomposition ratio of these samples under 5,000-lux fluorescent light irradiation were measured at specified times with HPLC.

2.1.4. EVALUATION OF ANTIMICROBIAL PROPERTIES OF HIBA OIL AND HINOKITIOL

The minimum inhibition concentrations (MICs) of Hiba oil and hinokitiol effective to inhibit the growth of certain types of fungus and bacterium were measured.

2.2. APPLE POLYPHENOL

2.2.1. COMPONENT ANALYSIS OF APPLE LEES

The Japan Food Research Laboratories analyzed the components of apple lees as requested.

2.2.2. METHOD OF INCREASING POLYPHENOL

Dried apple lee powder (Hichiro apple fiber) was heated (at 150, 160, 170, 180, 190, 200, 250, 260, 270, 280, 290, 300, 310, 320, 330, 340, and 350°C) and the polyphenol quantity in the samples measured according to the Folin-Denis method.

3. RESULTS AND DISCUSSION

3.1. EXTRACTS FROM AOMORI HIBA

3.1.1. COMPONENT ANALYSIS OF HIBA OIL

The results of the Hiba oil component analysis are listed in Table 1.
Hiba oil is separated into acidic oil and neutral oil through alkali treatment.
Antimicrobial components of Hiba oil were found in the acidic oil, including 3 to 6% of such antimicrobial components as β -Dolabrin other than hinokitiol. Aromatic components were found in the neutral oil and Thujopsene accounts for most (55 to 77%) of them.

Table 1 Composition of Hiba oil

Component	Compound name		Content (%)
Neutral oil	Thujopsene		50～60
	Cedrol		5～10
Acidic oil	Tropolone	Hinokitiol	1～2
		β -Dolabrin	1～2
	Citronellic acid		1～2
Others (mainly Sesquiterpene compound)			24～42

3.1.2. MEASUREMENT OF HIBA WATER PARTICLE SIZE

Hiba water may be whitish or transparent, depending on the extraction condition. Particle sizes of whitish Hiba water are shown in Figure 1 and those of transparent Hiba water are shown in Figure 2. The measurement with HPLC showed that 100 ppm of hinokitiol is contained in whitish Hiba water and 70 ppm in transparent Hiba water. Hiba oil is considered to be mixed in the both types of Hiba water and therefore, the difference in appearance is considered to be caused by the mixed Hiba oil particles. The graph in Figures 1 has a peak at about 5,000 nm in addition to the peak at 500 to 1,000 nm in Figures 1 and 2. This suggests that the particles about 5,000 nm in diameter make Hiba water whitish. The cooling temperature to extract whitish Hiba water is lower than that used in extracting transparent Hiba water, suggesting that whitish Hiba water has more Hiba oil than transparent Hiba water. Therefore, transparent Hiba water is considered more stable than whitish Hiba water.

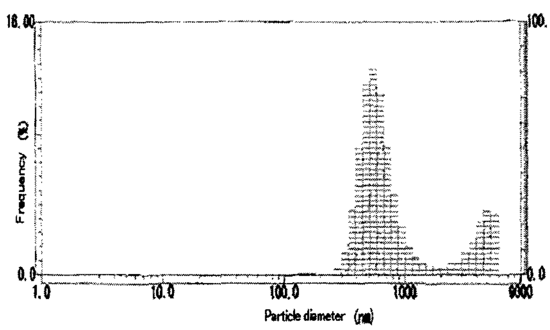

Fig. 1 Whitish Hiba water particle size

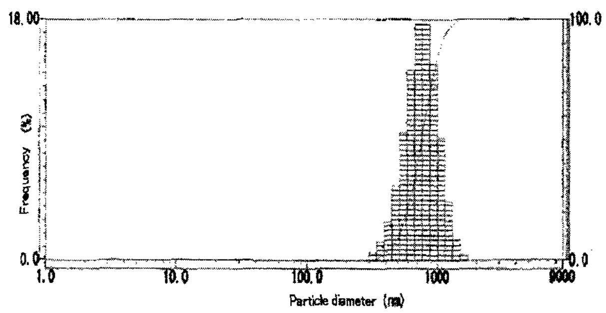

Fig. 2 Transparent Hiba water particle size

3.1.3. LIGHT STABILITY TESTING OF HINOKITIOL COMPLEX

The results of the light stability tests for hinokitiol and its complexes formed with metal ions are shown in Figure 3. Hinokitiol completely decomposed within about 6 hours under 5,000-lux fluorescent light irradiation. It decreased by half after 2.6 hours. Conversely, the time needed for calcium salt to decrease by half was 1.8 days, that for magnesium salt 2.2 days, that for sodium salt 5.1 days, that for zinc salt 6.5 days, and that for copper salt 42.9 days. These results show that hinokitiol becomes photo-stable upon reaction with an appropriate metal ion.

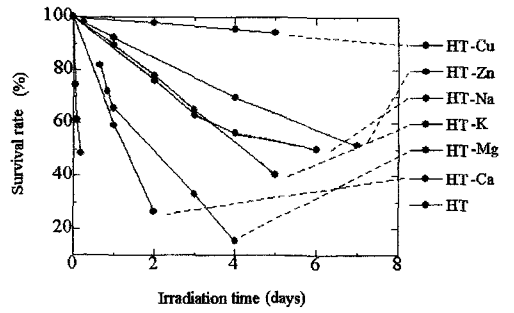

Fig. 3 Light stability of hinokitiol and its complexes

3.1.4. EVALUATION OF ANTIMICROBIAL PROPERTIES OF HIBA OIL AND HINOKITIOL

Table 2 lists the evaluation results (MIC values) of the antimicrobial properties of Hiba oil and hinokitiol. Hiba oil and hinokitiol showed wide antimicrobial spectrums for bacteria and fungi. When considering the content of hinokitiol, other components are thought to exhibit antimicrobial activities, thus strengthening the antimicrobial activity of Hiba oil.

Table 2 Antimicrobial properties of Hiba oil and hinokitiol (minimum inhibition concentration: ppm)

Strain	Hiba oil	Hinokitiol
Staphylococcs aureus IFO 12732	400	25
Escherichia coli IFO 3301	800	25
Aspergillus niger IFO 6341	400	25
Pseudomonas aeruginosa IAM 15	3200	400

3.1.5. SAFETY OF HINOKITIOL

The results of forcibly repeated administering (1, 5, 10, 50 mg/kg) of hinokitiol sodium orally to mice over a period of 6 months revealed an increase in fat particles in the adrenal cortex and the infiltration of mononuclear cells into the hepatic lobule in groups not less than 10 mg/kg of the hinokitiol sodium administered. Therefore, an ingestion of up to 5 mg/kg per day is considered harmless to mice.

In reverse mutation testing of hinokitiol for bacteria, the bacteria generally exhibited negative reactions. Some bacteria (-S9) showed positive reactions for 1.0 mg/disk, although others (+S9) showed negative reactions in a DNA repair test. The chromosome aberration testing of cultured cells revealed the occurrence of chromosome aberration in cells from the -S9 strain with 0.002 mg/ml of hinokitiol, but those from the +S9 strain generally showed negative reactions for up to 0.01 mg/ml. Mice also showed negative reactions for 22.5 to 90.0 mg/kg of hinokitiol in a micronucleus test.

Hinokitiol has also been approved for use as a food preservative and may be mixed in cosmetics with a content of up to 0.1% when the cosmetic is used for only other than mucus without being washed off after application.

3.2. APPLE POLYPHENOL

3.2.1. COMPONENT ANALYSIS OF APPLE LEES

The results of the component analysis of apple lees are listed in Table 3. 0.38 g of polyphenol was found in the apple lees as a functional component. The apple lees were also rich in sugar expected to maintain humidity in skin when used as raw materials for cosmetics.

Table 3 Composition of apple lees

Components	Content
Fructose	26.1g／100g
Glucose	10.3g／100g
Sucrose	2.25g／100g
Sugar	37.6g／100g
Dietary fiber	44.0g／100g
Polyphenol	0.38g／100g

3.2.2. METHOD OF INCREASING POLYPHENOL

The quantity of polyphenol in heated apple lees is graphed in Figure 4. Polyphenol increased in the apple lees after heated to about 230°C and it increased about 3.5-fold at about 250°C. It is considered that sugar changed into polyphenol. Polyphenol decreased gradually after the apple lees were heated to 260°C. This is considered to be a result of gradual carbonization of polyphenol.

4. SUMMARY

Hiba oil and Hiba water extracted from Aomori Hiba and apple polyphenol extracted from apple lees are environmentally friendly materials. In this research, the functionality and safety of these materials were checked to show that they can be used as raw materials for cosmetics.

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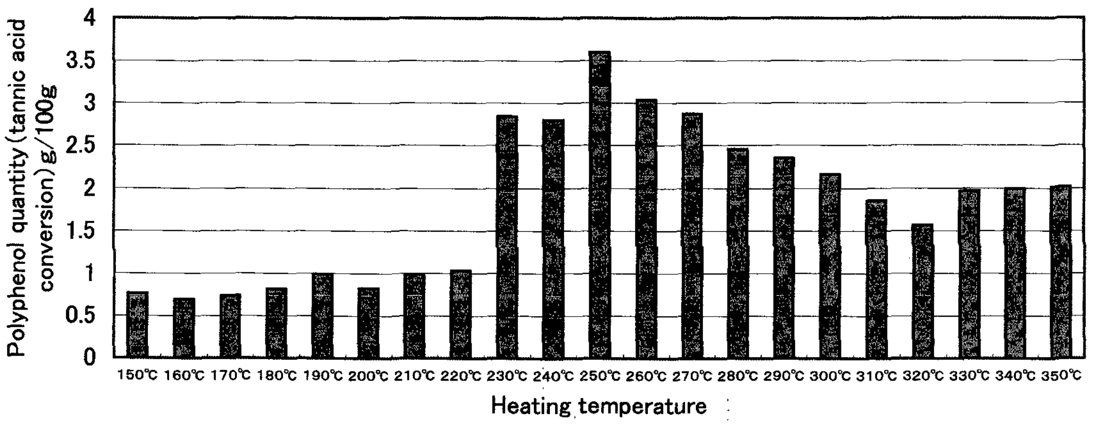

Fig.4 Polyphenol content in heated apple lees

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