QUALITY ANALYSIS AND IDENTIFICATION OF FUNCTIONAL GROUPS OF SWEET ORANGE (*Citrus sinensis*) PEEL ESSENTIAL OIL USING FTIR

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ABSTRACT
Organic waste in the form of citrus fruit peels has not been handled seriously, causing environmental pollution, such as the emergence of unpleasant odors. Therefore, waste management becomes a more valuable product or item. Citrus peel oil counterfeiting often occurs because there is no Indonesian National Standard (SNI) for citrus peel oil as a quality standard, making it difficult to identify the falsity of finished citrus peel oil products in the market. Research was conducted to test the quality of sweet orange peel oil so that it could be used as a standard to identify the content of sweet orange peel oil using the FTIR method. Oil quality testing included an organoleptic test, specific gravity, refractive index, and acid number. The oil quality test results showed clear yellow oil with a distinctive sweet orange peel aroma, specific gravity of 0.845, refractive index of 9.263, and acid number of 1.1. FTIR analysis revealed spectra that appeared in the region of 1490 with strong intensity (C-H aromatic), 1645 with medium intensity (C=C), and 2860 with medium intensity (C-H aliphatic). FTIR spectra of sweet orange peel oil showed similarity with limonene with a hit quality value of 958, the content of sweet orange peel oil is dominated by limonene compounds.

Keywords: sweet orange peel, Essential oil, FTIR, Limonene, Oil quality

INTRODUCTION

Organic waste in the form of citrus fruit peels has not been handled seriously, causing environmental pollution and resulting in an unpleasant smell (Cahyati et al., 2016). However, increasing the amount of waste is a problem that must be solved. Therefore, waste management becomes a product of greater value. Sweet orange peel waste can be used as a valuable product and as a deodorizer by extracting the essential oil of orange peel (Kartika Fitri & Proborini, 2018).

Citrus peel is one of the sources of essential oils, and citrus fruit peel is often discarded as waste, which has potential as an essential oil that is not optimally utilized (Yuda et al., 2017). Orange peel essential oil has a main limonene content of 95%, and other compounds such as myrcene, noctanal, pinene, linanool, decanal, sabiene, geranial, dodecanal, and neral. Limonene in orange peel causes orange peel oil to have a distinctive aroma; therefore, it is widely used as a mosquito repellent when burned (Megawati and Kurniawan, 2015). Limonene is a hydrocarbon compound in the terpene cycle. Limonene is physically characterized as a colorless liquid with a very strong citrus odor at room temperature (Mujdalipah et al., 2020). Limonene and linalool are the main components of orange peel; thus, orange peel can be used pharmacologically as an antioxidant, antiviral, anti-aging, and antibacterial agent (Suardhika et al., 2018).

Essential oil is a secondary metabolite that is widely obtained from plants through extraction processes such as the enflurge method, distillation, extraction using non-polar solvents, and the supercritical fluid extraction (SFE) method. Many essential oil extraction processes are performed by distillation. Distillation separates analytes from their components based on the principle of boiling point differences. There are three types of distillation processes: water distillation, steam distillation, and steam-water distillation (Suardhika et al., 2018). The counterfeiting of orange peel oil in the market often occurs because there is no standard Nasional Indonesia (SNI) for orange peel oil as a quality standard, making it difficult to identify the falsity of orange peel oil finished products. (Latifah et al., 2023). Fourier transform infrared spectroscopy (FTIR) was used to identify the compound content in the sweet orange peel oil.

Fourier-transform infrared spectroscopy (FTIR) is an analytical method used to identify plants with multicomponent content. FTIR is the most inexpensive, simple, and fast identification method; therefore, it is often used as an efficient method to ensure the quality of natural materials in terms of identifying the characteristics of plant species (Puspitasari et al., 2021). In this study, sweet orange peel was extracted using water vapor distillation to obtain its essential oil. Quality testing of orange peel oil was carried out because sweet orange peel essential oil does not yet have a standard; therefore, the results of testing the quality of sweet orange peel oil can be set as a standard. The sweet orange peel oil content was determined using FTIR.

RESEARCH METHODS

Tools and Materials

Tools: A series of water vapor distillation devices; FTIR ATR (BRUKER ALPHA II), a set of glassware (pyrex), pycnometer, refractometer, burette, pH meter, analytical balance (OHAUS), chamber.

Materials: Sweet orange peel, sweet orange peel oil, Na2SO4, phenolphthalein 1%, NaOH, ethanol, and distilled water.

Course of Research

1. Determination of citrus peel

Sweet orange peel was determined at the Ahmad Dahlan University Biology Laboratory by sending fresh whole samples, including sweet orange fruit and peel, to ensure the correct identity of the sweet orange peel.

2. Preparation of sweet orange peel oil

The orange peel samples were cut into pieces and dried at 50°C for 24 hours. A total of 534 g of dried orange peel Simplisia was placed in the sample collection drum. Water was placed in a steam-generator flask. The distillator was assembled, and the distillation process was carried out by heating the water in the steam generator flask; when steam started to form, the three-neck flask was heated, and the distillation rate was set. The distillate yield is calculated using the following formula:

$$\%\,Yield = \frac{Oil\,Volume\,(ml)}{sample\,weight\,(gr)} \times 100\%$$

3. Oil Quality Test

The quality test of sweet orange peel oil was carried out in the form of organoleptic observations, including color, odor, refractive index, and acid number (Irfan et al., 2022).

   a. Organoleptic (color and odor)

   Observations were made visually on the color using the sense of sight and the smell of sweet orange, lime and lemon oil using the sense of smell (Irfan et al., 2022).

   b. Specific gravity (BJ)

   Specific gravity testing was performed using a 25 µL pycnometer. The specific gravities of sweet orange peel oil, lime, and lemon were tested by comparing the weight of the oil at the same volume and temperature of 20°C. In this test, 2 replicates were performed. The specific gravity value was calculated using the BJ formula with the temperature during operation, which was converted to a temperature of 20 °C (Irfan et al., 2022). Specific gravity was calculated as follows:

$$BJ = \frac{A1 - B}{A2 - B} + (0{,}0007 \times (t - 20°C)$$

Conditions:
A1 = Weight of pycnometer with sample
A2 = Weight of pycnometer with water
B = Weight of empty pycnometer
t = temperature at the time of work

c. Refractive index

Refractive index testing was performed using an Abbe refractometer. The refractive index was determined by directly measuring the refractive angle of oil, which was maintained at a fixed temperature of 20°C. In this test, 2 replicates were performed.

d. Acid Number Determination

A total of 0.4 g of sweet orange peel oil is put in a 250 ml Erlenmeyer flask, and 10 ml of ethanol and 5 drops of 1% phenolphthalein indicator solution were added. Perform titration using 0.01 N NaOH solution until the titrate is pink, and the end point of the titration is marked by a color that does not change (Zaimah, 2016). The acid Numbers were calculated using the following formula:

$$\text{Acid Numbers} = \frac{V\ titration\ X\ N\ NaOH\ X\ BM\ NaOH}{m}$$

Description:
V titration = Volume of NaOH Solution
N = Normality of NaOH Solution
BM = Molecular Weight of NaOH
m = weight of oil sample used

e. FTIR Analysis

Place 1 drop of sweet orange peel oil was placed on the ATR crystal plate and the FTIR device was run. Specific spectra on the fingerprint of sweet orange peel oil are observed in the wavenumber region 3500-500 cm-1(Septiani & Roswien, 2018).

RESULT AND DISCUSSION

1. Determination of Citrus Peel

Determination of citrus fruit peels used in this study were obtained from the Biology Laboratory, Ahmad Dahlan University. The name of the citrus fruit species used in this study is Citrus sinensis (L.) Osbeck.

2. Sweet Orange Peel Oil Preparation

Sweet orange peel oil is prepared using the steam-water distillation method because distillation is carried out without direct contact with water, thus preventing the degradation of the oil components, which is quite simple and economical. Distillation of sweet orange peel was carried out for 2 days, and the resulting yield was 8.68%. The sweet orange peel used in the distillation stage is in the form of dry simplisia because based on research, the yield is 8.68% Muhtadin et al (2013) The drying process can increase the amount of yield produced. Based on Badan Standarisasi Nasional (2014) on the parameters of essential oil of kaffir lime leaves, the minimum percentage of yield produced is 1.42%, so that the percentage of oil yield produced from steam-water distillation of sweet orange peel meets the requirements.

3. Oil Quality Test

The results of the oil quality test on sweet orange peel oil can be seen in Table I.

Table I. Sweet Orange Peel Oil Quality Test Results

No	test		Replication	Result	Average±SD
1	Organoleptic	Color	-	Clear Yellow	-
		Odor	-	Characteristic citrus odor	-
2	Specific gravity		1	0.845 g/ml	0.845 ± 0 g/ml
			2	0.845 g/ml	
3	Refractive index		1	1.469	1.469 ± 0
			2	1.469	
4	Acid Numbers		1	1.2 mg/g	1.1 ± 0,1 mg/g
			2	1.1 mg/g	
			3	1 mg/g	

Standar Nasional Indonesia (SNI) sweet orange peel oil has not been established; therefore, there is no standardized standard for the quality of sweet orange peel oil (Latifah et al., 2023). Therefore, the test results on the quality of sweet orange peel oil can be used as a reference for quality standards of sweet orange peel oil. The results of organoleptic testing of sweet orange peel oil in accordance with the research conducted by Fekadu et al. (2020) showed that orange peel oil is orange yellow in color with a fresh and sharp odor. The average specific gravity test result is 0.845 g/ml, these results are in line with the specific gravity value of kaffir lime leaf oil 0.837 - 0.845 g/ml (Khasanah et al., 2015). The test results for the refractive index of sweet orange peel oil 1, 469, this value almost meets the refractive index standard of the Essential Oil Association (EOA), which is 1.471-1.475. The average result of the acid number test with three replications was 1.1, which is different from the research conducted by Fekadu et al. (2020), where the acid number of orange peel oil was 4.2.

4. FTIR Analysis

Analysis of sweet orange peel oil using Fourier transform infrared attenuated total reflectance was conducted for qualitative analysis of the essential oil content of the sweet orange peel (Septiani & Roswien, 2018). FTIR spectrophotometry is a simple, nondestructive, and fast analysis method that can display the chemical properties of samples in the form of spectra (Puspitasari et al., 2021). The results of FTIR analysis of orange peel oil can be seen in

Figure **1**, Figure 2 and Figure 3.

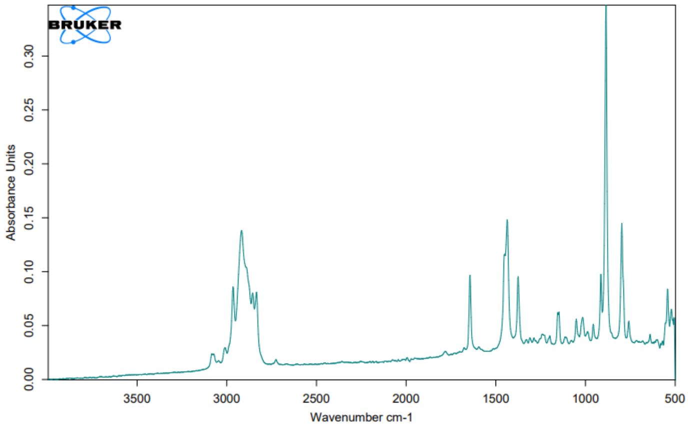

Figure 1. Replication 1 FTIR-ATR spectra

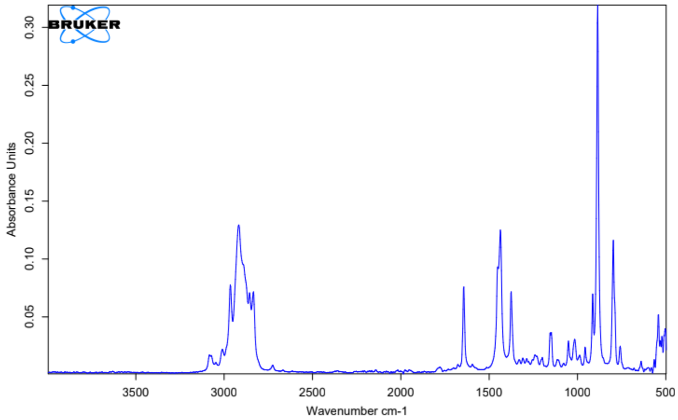

Figure 2. Replication 2 FTIR-ATR spectra

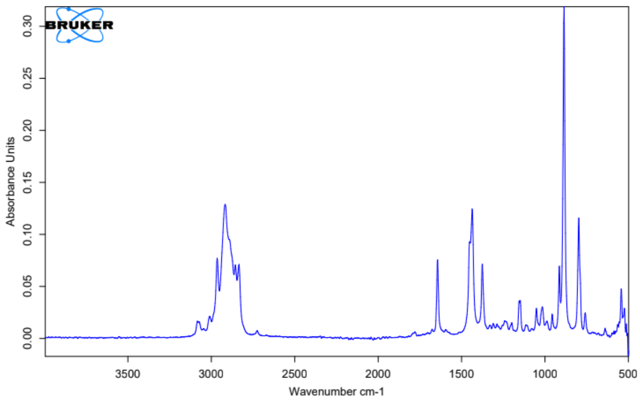

Figure 3. Replication 2 FTIR-ATR spectra

Based on the results of the FTIR-ATR spectral profile of sweet orange peel oil with three replications, it can be seen that a typical spectral pattern is formed and is similar to each other. There were differences in the absorbance values of the FTIR spectra. The spectra reading results in the form of functional groups obtained from the analysis of sweet orange peel oil samples are presented in Table II.

Table II. Functional Groups of Sweet Orange Peel Oil

No	Wave Number	Wave Numbers (cm^{-1}) literature	Intensity	Suspected functional groups

		(Winter, 1984)		
1	1490	1450-1650	strong	C-H aromatic
2	1645	1640-1680	medium	C=C
3	2860	2850-2975	medium	C-H aliphatic
4	1700	1660-1820	medium	C=O Carbonyl

Based on the table above, the functional groups possessed by the sample were similar to those possessed by limonene compounds. This was confirmed by the FTIR spectra of sweet orange peel oil compared to the FTIR spectra of limonene compounds in Figure 4.

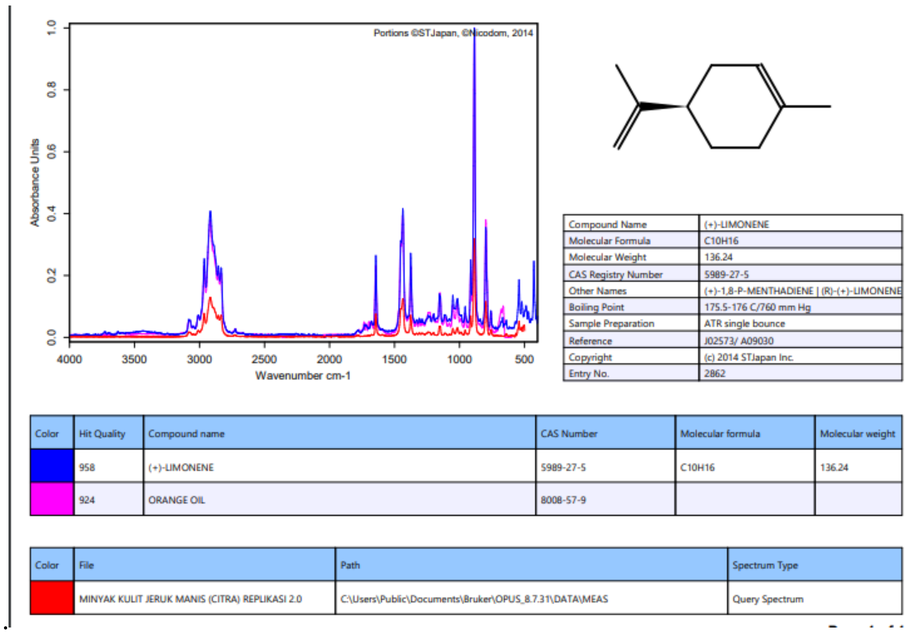

Figure 4. FTIR Spectra Of Sweet Orange Peel Oil Compared With Spectra Of Limonene And Orange Oil

The similarity of the FTIR spectra results of sweet orange peel oil with limonene FTIR spectra shows a hit quality number of 958, indicating that the content of sweet orange peel oil is dominated by limonene compounds. This is in accordance with research conducted by Megawati & Kurniawan (2015) on the largest content of sweet orange peel oil is limonene (96.69%) and pinene (3.31%).

CONCLUSION

In this study, steam-water distillation was carried out to distill the essential oil of sweet orange peel and an essential oil yield of 8.68 ± 64.57% was obtained. The test results of sweet orange peel oil obtained included a clear yellow color, typical odor of sweet orange peel, specific gravity (BJ) of 0.845 ± 0 g/ml, refractive index of 1.469 ± 0, and acid number 1.1 of 0.1 mg/g. The results of testing sweet orange peel oil using FTIR-ATR showed that the content of sweet orange peel oil was dominated by limonene.

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