Spectroscopy Study of Honey Pineapple Peels Extracted in Different Solvents

Yehezkiel Steven Kurniawan\textsuperscript{a}, Edi Setiyono\textsuperscript{a}, Marcellinus Alfasisurya Setya Adhiwibawa\textsuperscript{a}, Krisfian Tata Aneka Priyangga\textsuperscript{a}, and Leny Yuliati\textsuperscript{a,b}\textsuperscript{*}

\textsuperscript{a} Ma Chung Research Center for Photosynthetic Pigments, Universitas Ma Chung, Malang 65151, East Java, Indonesia
\textsuperscript{b} Department of Chemistry, Faculty of Science and Technology, Universitas Ma Chung, Malang 65151, East Java, Indonesia

*Corresponding Authors: leny.yuliati@machung.ac.id (Tlp. +62-341-550171; Fax +62-341-550175)

Abstract
In the present work, we investigated the extracts of honey pineapple peels in distilled water, ethanol, and acetone solvents. The spectroscopy study of each extract was performed using a Fourier transform infrared (FTIR) spectrometer, an ultraviolet-visible (UV-Vis) spectrophotometer, and a spectrofluorometer. The FTIR spectrum of the distilled water extract showed that it may contain alcohol and/or carboxylic acid compounds. Meanwhile, the ethanolic extract may contain alcohol and/or carboxylic acid and/or ether compounds. On the other hand, the acetone extract may contain alcohol and/or ether and/or aromatic and/or aliphatic compounds. The honey pineapple peels extracted in the distilled water showed a broad absorption signal at the UV region (< 300 nm) while the ethanolic extract showed four absorption signals at the UV region (232–368 nm). On the other hand, the acetone extract showed four absorption signals at the UV region (231–368 nm) with a weak absorption signal at the visible region of 559 nm. The distilled water and acetone extracts gave fluorescence signals, however, the ethanolic extract showed no fluorescence intensity. From the FTIR, UV-Vis, and fluorescence spectra, the extracted natural pigments from the honey pineapple peels in distilled water, ethanol, and acetone solvents were proposed. The distilled water extract may contain polar flavonoid and/or steroid compounds while the ethanolic extract may contain polar carotenoid pigments. On the other hand, the acetone extract may contain carotenoid and chlorophyll pigments as shown by an emission signal at 670 nm.

Pigments in honey pineapple peels: Pineapple peels extracted with different solvents of water, ethanol, and acetone have different types of pigment as investigated through a spectroscopy study. While the water extract may contain either flavonoid or steroid pigments, both ethanol and acetone extracts gave the carotenoid pigments with an additional trace amount of chlorophyll pigments in the acetone extract.

Keywords: maceration, honey pineapple, peels extract, solvent, spectroscopy

INTRODUCTION
Tropical plants are abundantly available in the South East Asia region, especially Indonesia as the country located in the greatest length of the equator line across both land and sea in the world [1,2]. As Indonesia has 10\% of world plant species in 90 ecosystems [3], Indonesia becomes the second largest mega biodiversity country in the world. Because of these abundant natural resources, researches on the isolation and application of tropical plants and fruits have gained a lot of interest [4-6].

Among edible tropical fruits, honey pineapple (Ananas comosus L.) is particularly attractive due to its unique natural product contents [7-10]. Hossain \textit{et al.} (2011) reported that pineapple fruit contains phenolic and flavonoid compounds thus yielding remarkable antioxidant activity [11]. Meanwhile, Debnath \textit{et al.} (2019) reported that the bromelain compound in the pineapple extract gave high anticancer activity [12]. These natural products were extracted and utilized for food supplements [13, 14]. Other applications of these natural products for the advanced materials have been also evaluated such as for solid catalyst [15, 16] and aerogel material [17]. Although honey pineapple gives a remarkable application, in contrast, utilization of its fruit peel is rarely investigated and the peel is usually wasted since the benefit is unexplored.

The first important approach would be investigating the possible compounds in the honey pineapple peels. In our previous work, we evaluated mangosteen, honey pineapple, and red dragon fruit peels for yellow natural coloring agents...
As the solvent affected the type of extracted compounds, in this work we used several solvents to extract the honey pineapple peels. It was revealed that honey pineapple peels extracted in distilled water, ethanol, and acetone solvents are promising to be used as yellow colorants. Therefore, in the present work, we further investigated the Fourier transform infrared (FTIR), ultraviolet-visible (UV-Vis), and fluorescence spectra to investigate the natural pigments in honey pineapple peels extracted in distilled water, ethanol, and acetone solvents.

EXPERIMENTAL

General

Local honey pineapple fruits were purchased from a traditional market in Malang, East Java, Indonesia. Meanwhile, ethanol 96% and acetone in the technical grade were supplied from DJ Labware.

Extraction of Natural Pigments from the Honey Pineapple Peels

The honey pineapple peels extracted in distilled water, ethanol, and acetone solvents were prepared in a similar procedure in our previous report [18]. Briefly, the fruit peel (5.0 g) was then chopped and macerated with distilled water or ethanol or acetone (50 mL) as the macerating solvent at room temperature for 24 h. After the maceration process was completed, each extract was filtered using a WhatmanTM filter paper 1 (diameter 90 mm) to obtain a clear filtrate.

Characterization of Extracts from Honey Pineapple Peel

The FTIR, UV-Vis, and fluorescence spectra of each extract were recorded from an FTIR spectrometer (JASCO FTIR-6800), a UV-Vis spectrophotometer (JASCO V-760), and a spectrofluorometer (JASCO FP-8500), respectively. The FTIR spectrum was recorded at the 400–4000 cm⁻¹ range using an attenuated total reflectance (ATR) technique. The UV-Vis spectrum was investigated in the 200–800 nm range while the fluorescence spectrum was investigated at excitation peaks of 200–700 nm for emission peaks at 300–800 nm.

RESULTS AND DISCUSSION

Extraction of Natural Pigments from the Honey Pineapple Peels

The photographs of honey pineapple peels extracted in distilled water, ethanol, and acetone are shown in Figure 1. Even though the used solvent was different, it was found that all extracts appeared as a clear yellow solution. One could see that the peels indeed are still rich in natural pigments. The similar yellow solution implied that the same yellow pigments could be soluble in different solvents or each solvent dissolved different yellow-colored pigments. To clarify this matter, the honey pineapple peels extracted in different solvents were investigated using FTIR, UV-Vis, and fluorescence spectrometers.

Characterization of Extracts from Honey Pineapple Peel

The FTIR study was conducted to identify the functional groups of the extracted natural pigments from honey pineapple peels extracted in distilled water, ethanol, and acetone. The FTIR spectra of honey pineapple peels extracted in distilled water, ethanol, and acetone are shown in Figure 2. Each extract gave a different pattern of FTIR spectrum, indicating that the extracted pigments were different from each other depending on the used solvent. As depicted in Figure 2(a), the distilled water extract gave six main absorption signals at 3292, 2922, 2850, 1621, 1451, and 1012 cm⁻¹. The broad signal observed at 3292 cm⁻¹ would correspond to C–O stretching while weak signals at 2922 and 2850 cm⁻¹ corresponded to C=O–H stretching. The sharp signal at 1621 cm⁻¹ was assigned to C=O stretching while the weak signal at 1451 and 1012 cm⁻¹ showed the presence of C=C and C=O stretching, respectively. Based on this spectrum, it could be proposed that the distilled water extract may contain alcohol and/or carboxylic acid functional groups.

On the other hand, the acetone extract showed many signals at 3396, 2934, 1597, 1584, 1508, 1301–978, 814, and 518 cm⁻¹ as shown in Figure 2(c). The broad signal at 3396 cm⁻¹ corresponded to O–H stretching while the weak signal at 2934 cm⁻¹ corresponded to C=O–H stretching. The sharp signal at 1597 cm⁻¹ could be assigned to C=O stretching while sharp signals at 1584 and 1508 cm⁻¹ attributed to C=C stretching. The sharp signals at 1301–978 cm⁻¹ may correspond to C–O–C, C=O, C–C, and other functional groups. The sharp signal at
814 cm⁻¹ accounted for Csp³–H bending while the weak signal at 518 cm⁻¹ was for Csp²–H bending. This result showed that the acetone extract may contain alcohol and/or ether and/or aromatic and/or aliphatic functional groups. From the FTIR data, it was confirmed that all extracted compounds in each extract were different from each other.

The UV-Vis study was conducted to identify the absorption signals of the extracted natural pigments from honey pineapple peels in distilled water, ethanol, and acetone. The natural pigments in the extracts were characterized using the UV-Vis spectrophotometer and spectrofluorometer. The UV-Vis spectra of the honey pineapple peels extracted in the distilled water, ethanol, and acetone solvents are shown in Figure 3.

From Figure 3(a), it could be seen that the honey pineapple peels extracted in the distilled water gave an absorption signal at the UV region (< 300 nm) with a shoulder band at 226 nm. On the other hand, the honey pineapple peels extracted in the ethanol have four absorption signals at the UV region, i.e. 232 (shoulder band), 314, 342, and 368 nm, as shown in Figure 3(b). While the honey pineapple peels extracted in the acetone also showed four absorption signals at the UV region, i.e. 231, 314, 344, and 368 nm, it also exhibited a weak absorption signal at the visible region of 559 nm, as depicted in Figure 3(c). The similar absorption signals of both ethanolic and acetone extracts at 231–232, 314, 342–344, and 368 nm indicated that both extracts may contain similar chromophores but different pigment compounds. The UV-Vis data also confirmed that all extracted compounds in each extract were different from each other, which was in agreement with the FTIR data.

The fluorescence study was conducted to identify the excitation and emission signals of the natural pigments extracted from honey pineapple peels in distilled water, ethanol, and acetone. The fluorescence spectra of the extracts are shown in Figure 4. The honey pineapple peels extracted in the distilled water showed the main excitation signal at 350 nm, yielding an emission signal at 420 nm. The honey pineapple peels extracted in the ethanol gave no fluorescence intensity while the honey pineapple peels extracted in the acetone showed two excitation signals at 370 and 400 nm, yielding emission signals at 420 and 670 nm, respectively. In good agreement with other spectroscopy data, the fluorescence data also confirmed that all extracted compounds in various solvents were different from each other.

Based on the FTIR, UV-Vis, and fluorescence spectra, the extracted natural pigments from the honey pineapple peels in distilled water, ethanol, and acetone solvents were proposed. Since the distilled water extract showed O–H functional group in the FTIR spectrum and a shoulder band at 226 nm in the UV-Vis spectrum, the distilled water extract may contain polar flavonoid and/or steroid compounds [20, 21]. It was well-known also that the steroid compounds gave fluorescence signal at 300–450 nm region. Meanwhile, the FTIR and UV-Vis spectra of the ethanolic extract indicated that the extract contained polar carotenoid pigments, which exhibited no fluorescence property as supported by its fluorescence spectrum. On the other hand, the acetone extract would contain carotenoid and trace chlorophyll pigments as shown by an emission signal at 670 nm [22]. It was known that chlorophylls are strong fluorescence compounds and thus, a trace amount of chlorophyll pigments could give fluorescence signals as demonstrated in Figure 4(c). Even though this work gave preliminary knowledge on the possible extracted compounds in each solvent, further investigations to identify and quantify these natural pigments are still required.

![Figure 3. UV-Vis spectra of honey pineapples peels extracted in (a) distilled water, (b) ethanol, and (c) acetone.](image)

![Figure 4. 3D fluorescence spectra of honey pineapple peels extracted in (a) distilled water, (b) ethanol, and (c) acetone.](image)
CONCLUSIONS

Extraction and spectroscopy study of honey pineapple peels extracts using three different solvents of water, ethanol, and acetone were performed and the possible extracted compounds were proposed. All extracts showed a yellow-colored solution, suggesting that they could be utilized as a yellow natural coloring agent. The spectroscopy study suggested that different compounds were successfully extracted when using different solvents. The honey pineapple peels extracted in the water contained alcohol and/or carboxylic acid functional groups, which originated from the flavonoid and/or steroid compounds. The ethanolic extract contained alcohol and/or carboxylic acid and/or ether functional groups, which came from the carotenoid compounds. Meanwhile, the acetone extract contained alcohol and/or ether and/or aromatic and/or aliphatic functional groups which came from the carotenoid and chlorophyll pigments.

Acknowledgements


REFERENCES


Abstrak

Pada penelitian ini, kami mempelajari ekstrak kulit nanas madu dalam pelarut air, etanol, dan aseton. Studi spektroskopi tiap ekstrak dilakukan dengan spektrometer Fourier transform inframerah, spektrofotometer ultraviolet-tampak, dan spektrofluorometer. Spektrum FTIR dari ekstrak air menunjukkan bahwa ekstrak air dapat mengandung senyawa alkohol dan/atau asam karboxilat. Sementara itu, ekstrak etanol dapat mengandung senyawa alkohol atau asam karboxilat atau eter. Di lain sisi, ekstrak aseton dapat mengandung senyawa alkohol dan/atau eter dan/atau senyawa aromatik dan/atau alifatik. Ekstrak kulit nanas madu dalam air menunjukkan sinyal absorpsi melbar pada daerah UV (> 300 nm) sedangkan ekstrak etanol menunjukkan sinyal absorpsi pada daerah UV (231 – 368 nm) di lain sisi, ekstrak aseton menunjukkan empat sinyal absorpsi pada daerah UV (231 – 368 nm) dengan sinyal absorpsi lemah pada daerah tampak (559 nm). Ekstrak air dan aseton memberikan sinyal fluorosensori emisi ekstrak etanol tidak memberikan intensitas fluorosensori. Dari spektrum FTIR, UV-Vis, dan fluorosensori, diusulkan pigment-pigment alam yang terkandung dari kulit nanas madu dalam pelarut air, etanol, dan aseton. Ekstrak air dapat mengandung senyawa flavonoid dan/atau steroid yang polar sedangkan ekstrak etanol dapat mengandung pigment karotenoid polar. Di lain sisi, ekstrak aseton dapat mengandung pigment karotenoid dan klorofil seperti yang ditunjukkan oleh sinyal emisi pada 670 nm.

Kata kunci: maserai, nanas madu, ekstrak kulit, pelarut, spektroskopi