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Detection of rice syrup from acacia honey based on lubrication properties measured by tribology technique

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ABSTRACT

Acacia honey and rice syrup's lubrication properties in liquid and crystalline states were tested under rubber friction pairs mimicking oral environment. The results indicated that liquid acacia honey was in elastohydrodynamic lubrication and rice syrup in boundary lubrication. Liquid acacia honey's lubrication state changes into boundary lubrication if adulterated by rice syrup. And the changed friction coefficient is easy to be measured by the tribometer. For crystalline state, even both of them are in boundary lubrication, differences in friction coefficients are three orders of magnitude larger than the test resolution. Therefore, rice syrup can be identified from acacia honey either in liquid or crystalline state. Moreover, the detection mechanism was also interpreted from their wetting performances, microstructures and morphology.

1. Introduction

Honey, a natural sweetener, is brewed by honeybees gathering nectar, honeydew or secretions of plants and mixing them with their own secretions [1]. It is a heterogeneous complex carbohydrate consisting of more than 180 different constituents. It contains 18%–22% water, 75%–80% sugar and 22 carbohydrates with very little content. Besides these major components, honey is composed of many other compositions including organic acids, mineral contents, enzymes, proteins and so on [2]. Due to its unique properties and complex components, honey is of high nutritional value and medical use for human beings [3–8]. For instance, honey is an important energy resource to quickly replenish physical strength and eliminate fatigue especially for athletes. It presents anti-carcinogenic and anti-atherogenic properties owing to the existence of phenolic compositions. Honey is also used to decrease cardiovascular risk without leading to obesity. Moreover, honey can help people to regulate the immune system and treat moderate skin injury especially scalds. Therefore, honey is popular all over the world because of its delicious flavor and multiple applications beneficial to people. It is much better and more expensive than other sweeteners such as cane sugar and various syrups. Illegal honey manufacturers and producers add cheaper adulterants to natural honey to seek higher economic benefits. It raids the honey market and undermines consumers' confidence in honey quality and safety, which is extremely harmful to both customers and producers of real honey. In addition, honey adulterants even may damage people's health due to the increasing of low density lipoprotein and cholesterol. Accordingly, detection techniques of honey adulteration have attracted great interests and attentions among governments, food industry and science around the world.

At present, exogenous syrups, such as corn syrup, glucose syrup and rice syrup, are often used to adulterate natural honey. The contents and ratios of fructose and glucose in these syrups are very close to those of real honey, so they are not easy to be detected. In past decades, researchers have proposed many approaches to identifying adulterants in honey by means of chromatography, isotopic ratio and spectroscopic techniques etc. They include high performance liquid chromatography (HPLC) [9], high performance anion-exchange chromatography pulsed amperometric detection (HPAEC-PAD) [10], gas chromatographic mass spectrometric (GC-MS) [11], thin-layer chromatography (TLC) [12], stable carbon isotopic ratio analysis (SCIRA) [13], infrared spectrum (IR) or near infrared spectroscopy (NIR) [14], Fourier infrared spectroscopy (FTIR) [15], Raman spectroscopy [16], nuclear magnetic resonance (NMR) [17], fluorescence spectrum [18], differential scanning calorimeter (DSC) [19], hyper-spectral imaging [20] and so on. Each method has its own characteristics and applied range not for all syrups.

Compared with syrups from C4 plants, for instance, corn syrup and glucose syrup, rice syrup is extracted from C3 plants. It is much harder to be detected as an adulterant from natural honey, for honey is mostly from C3 plants as well. Nowadays it is a big challenge to identify rice

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syrup from natural honey and there are not many literature about it. Xue et al. [21] used HPLC with diode array detection to test honey adulterated by rice syrup due to a special compound existing in rice syrup. It was called 2-acetylfuran-3-glucopyranoside identified using MS and NMR. Chen et al. [18] employed three-dimensional fluorescence spectroscopy (3DFS) to gather fluorescence information of honey samples and rice syrup. Then the data were compressed by principal component analysis (PCA) and modeled using back propagation neural network. Consequently, rice syrup could be tested from real honey by the combination of 3DFS and multivariate calibration. Sobrino-Gregorio et al. [19] applied DSC to gauge honey and rice syrups' glass transition temperatures. Their ranges were 60.2°C–67.3 °C and 32.8°C-95.8 °C respectively. Subsequently, the data were analyzed by PCA and variance analysis to identify the addition of rice syrup. Although these methods are useful to detect rice syrup from natural honey, they are time-consuming, needing expensive instruments, special skills and complicated analyses. Moreover, more than one techniques are needed to obtain the results. And they usually need to establish models to classify samples using statistical methods, which needs a lot of tests and professionals. Thus it is still necessary to develop a new, simple and effective method to detect rice syrup from natural honey.

In our previous research, we have put forward a novel method for detecting melamine in milk on the basis of oral tribology [22]. It was often used to study food flavor, sensation and texture in food science [23–29], for example, slipperiness, creaminess, astringency and so on [30–33]. Oral tribology has been proved to be very useful and builds a bridge connecting tribology measurement with food sensory science. In addition, the authors of this paper recently applied this approach to identifying melamine in milk according to the differences between their measured friction coefficients. The results indicated it was a simple, fast and effective method and could be used in the detection of food adulteration. The friction coefficients of sample solutions were measured by a tribometer. The results indicated that the friction coefficient of milk became much bigger even if it was adulterated by a little melamine, which was applied to test melamine in milk. This method is very simple without complicated operations, skills and analyses. It does not need sample pretreatment and the test time is only 30 s. Thus, it is very simple, rapid and effective. This research aims to apply this detection method to identify rice syrup from real honey taking the case of acacia honey. In addition, the detection mechanism will be also explored.

2. Experimental

2.1. Sample materials

Natural acacia honey and rice syrup were supplied by State Key Laboratory of Food Science and Technology, Nanchang University. This research used tribology method to detect rice syrup from acacia honey in two states: liquid state and crystalline state. On the one hand, rice syrup was added to natural acacia honey with different mass contents to artificially simulate the adulteration of honey. Both of them are in liquid state, and the mass contents of rice syrup in mixed samples varied from 10% to 90%. On the other hand, acacia honey and rice syrup were placed in a refrigerator at 3 °C for 50 days to make them crystallize. Then they were used to investigate the potential of tribology method for detecting rice syrup from acacia honey in crystalline state.

2.2. Test methods

A test system mimicking the human oral environment was established as shown in Fig. 1. The test equipment is a precise tribometer (Rtec MFT-5000, USA). There are many kinds of test instruments about oral tribology measurement, for instance, a texture analyzer with additional accessories [33], a mini traction machine [34], a high frequency reciprocating rig test device [35] and an optical tribological configuration [36]. Compared with them, the tribometer used in this study is a professional and mature commodity. Moreover, its measurement resolution is very high (0.0001) to ensure the exactitude of test results.

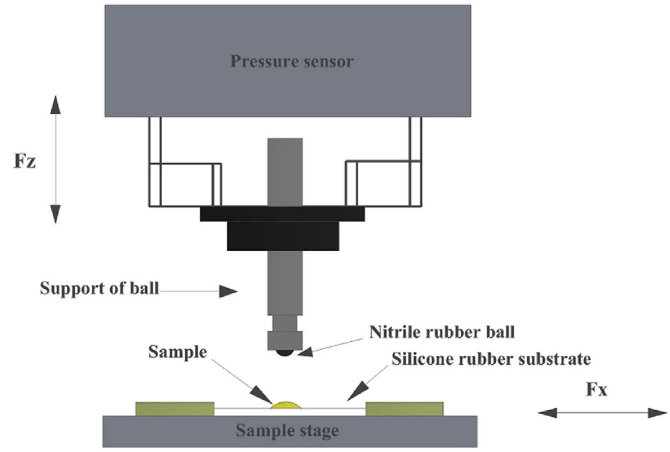

Fig. 1. Test system to detect syrup from honey.

As far as friction pairs are concerned, various materials were used during food tribology tests, including steel, glass, pig's tongue, polydimethylsiloxane (PDMS) and rubber. Among these materials, rubber is a kind of soft and elastic material close to the characteristics of human tongue and palate, so rubber is selected to mimic human oral cavity in this paper. The upper part of friction pairs is a Buna-N rubber ball and its diameter, Young's modulus and Shore hardness are 9.5 mm, 4 MPa and 80 respectively. The lower part is a silicone rubber plate and its corresponding parameters are 43 mm × 28 mm × 2 mm, 7 MPa and 65 respectively. The surface morphology of friction pairs were observed by a scanning laser microscope (Keyence VK-X100, Japan). Their 2D and 3D images were illustrated in Fig. 2. The surface roughnesses of the rubber ball and plate are 15.12 μm and 4.82 μm.

The detection procedures were as follows. 20 mg liquid acacia honey, rice syrup and their mixture solution with different mass contents were put separately on the lower rubber plate. Subsequently, the upper rubber ball pressed onto the sample solution under a certain load and slid against the plate in reciprocating motion. And friction coefficient of the sample was recorded simultaneously. The mass contents of rice syrup in acacia honey were from 10% to 90%. The load and sliding speed were 20 N and 16 mm/s respectively. For crystalline honey and syrup, the test steps are similar and the load and sliding speeds were 15 N and 1–12 mm/s. The mass of crystalline sample was 0.3 g for each test. All tests were conducted in room temperature, test time were 30 s and each test was repeated five times. Then the adulterated acacia honey by rice syrup could be identified by the large difference in friction coefficients between natural honey and adulterated honey.

2.3. Measurements of contact angles

In order to explore the detection mechanism of tribology technique, the contact angles of acacia honey, rice syrup and their mixture solutions were measured by the SPCAX2 contact angle meter (HARKE Testing Instrument Factory, Beijing). A 3 μL droplet of sample solution was placed on the rubber plate, which was the same as used in tribology tests. Afterwards the contact angle was measured by the baseline circle method. The volume of droplet was accurately controlled by the feed system of the contact angle meter. The temperature was 23.5 °C and the humidity was 39%. Each angle was measured three times.

2.4. Microscopic observations of natural honey and rice syrup

Besides measurements of contact angles, we also observed the micro-forms of natural honey and rice syrup combining freeze-drying