様　式　C－19、F－19－1、Z－19　(共通)

科研費 KAKENHI

科学研究費助成事業　　研究成果報告書

令和　５年　６月２８日現在

機関番号：１８００１
研究種目：若手研究
研究期間：2019～2022
課題番号：１９Ｋ１５７８４
研究課題名（和文）Multi-omics authentication of global and adulterated Japanese non-centrifugal brown sugars

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研究代表者
ＡＳＩＫＩＮ　ＹＯＮＡＴＨＡＮ（ASIKIN, YONATHAN）

琉球大学・農学部・准教授

研究者番号：２０７９９６８９

交付決定額（研究期間全体）：（直接経費）　　3,300,000円

研究成果の概要（和文）：サトウキビやヤシを原料とする含糖蜜は品質的な特徴があり、特に黒糖はヤシ糖やココナッツシュガーよりもポリフェノール含量が高く、抗酸化性能が高いことがわかった。伝統的な製法で作られる黒糖は、一般的な工業製品と比較し、メイラード反応生成物（MRP）を高く含有するが、一方で酢酸含量は減少した。また、製造産地は黒糖中のミネラルや香気成分の組成に影響するとし、国産とASEAN諸国の黒糖についてMS-e-nose法を用いた香気成分プロファイリングを実施した。さらに、沖縄県産黒糖は、粗糖の混合比率が増加すると、色味の輝度は増し、香気成分、MRP、有機酸含量が減少すると、官能特性も変化することがわかった。

研究成果の学術的意義や社会的意義
本研究成果は、原料材料や原料産地の異なる黒糖における栄養学的、食品機能性、香気特性等の特徴を示す重要な情報を提供するものである。これらデータは、食品・飲料の製造において黒糖を原材料とする場合、官能特性や嗜好性を着目した商品開発や改良するための基礎的知見として活用できる。さらに、この研究では、黒糖への粗糖混合比率を判別するためのマルチオミックス分析手法の開発も行っており、これら手法を用いることで、多角的に沖縄県産黒糖の品質価値を国際的に示すことにもつながると考えている。

研究成果の概要（英文）：Unrefined-solidified sugars which are derived from various plant sources, including sugarcane, palm, and coconut, had diverse key quality traits. Non-centrifugal cane sugar (NCS) had higher polyphenol contents and antioxidant activities than in palm- and coconut-sugars. Traditionally made NCS contained greater Maillard reaction products (MRPs) and less acetic acid than in industrially manufactured NCS. Production origin also greatly affected mineral and volatile organic compound (VOC) compositions of NCS. MS-e-nose analysis showed comparable VOC profiles between NCSs of Japan and ASEAN origins. Moreover, Okinawan specialty NCS (kokuto) can be adulterated with raw sugar, forming a processed NCS (kako-kokuto). The color of adulterated NCS became lighter as raw sugar proportion increased, and it contained less VOCs, MRPs, and organic acids. The adulteration also lowered sourness and roasted aroma intensities, and thus distinctly altered its flavor quality and retronasal olfaction traits.

研究分野：Food science

キーワード：Food flavor quality　Mineral composition　MS-e-nose profiling　Multi-omics profiling　Non-centrifugal sugar　Brown sugar　Product adulteration　Food authentication

1. Research Background

Unrefined-solidified brown sugars are produced worldwide by dehydrating sugar syrup without centrifugation. These unrefined-solidified sugars which are derived from various plant sources, including sugarcane, palm, and coconut, have different quality traits. The commonly known term for unrefined brown sugar from sugarcane syrup is non-centrifugal cane sugar (NCS), and this cane brown sugar is manufactured without molasses removal. However, there is little information on assessment of nutrient and flavor components in unrefined brown sugars across countries. Because adequate comparisons between quality attributes from different plant resources and origins are not available, interested parties and consumers with specific quality requirements could have difficulty selecting suitable brown sugars, particularly for products from Japan and developing nations, such as ASEAN countries. On the other hand, the global trade era has urge domestic brown sugar industries to take measure on fraud and adulteration threats.

2. Research Objectives

This study aimed to elucidate key nutrient and flavor characteristics of unrefined-solidified sugars of different plant sources and origins, and to determine the flavor quality between pure and adulterated NCS (processed brown sugar) using multi-omics analytical techniques. The study was divided into three parts: (1) Characterization of physicochemical traits, antioxidant potentials, volatile organic compounds (VOCs) of unrefined-solidified sugars of different plant sources; (2) Characterization of minerals and VOCs of NCS products from Japan and ASEAN countries; and (3) Determination of flavor components and retronasal olfaction profiles of simulated NCS adulteration model.

3. Methodology

(1) Differentiation of plant sources

Unrefined-solidified sugars of different plant sources, viz. sugarcane (NCS), palm, and coconut, were collected from Japan (Okinawa), Thailand, and Indonesia. Among NCS products, three were of traditional produces and four were industrially made sugars. The color index of unrefined-solidified sugars was determined according to the International Commission for Uniform Methods of Sugar Analysis (ICUMSA). Total phenolic and flavonoid contents of unrefined sugars were determined, and their antioxidant potentials (1,1-diphenyl-2-picrylhydrazyl radical scavenging activity and oxygen radical absorbance capacity) were measured. VOCs and their aroma profiles were examined using headspace–gas chromatography–mass spectrometry (GC-MS) and mass spectrometry-based electronic-nose (MS-e-nose) analyses, respectively.

(2) Differentiation of geographical origins

NCS products comprising 20 samples were obtained from Japan and three ASEAN countries: ten NCSs were obtained from Japan, representing four prefectures (Aichi, Kochi, Kagoshima, and Okinawa); five from Vietnam (Ha Giang, Hanoi, Nghe An, Quang Ngai, and Son La); three from Malaysia (Kedah, Negeri Sembilan, and Perak); and two from Indonesia (Central Java and East Java). The mineral composition of the NCS products was analyzed using inductively coupled plasma–atomic emission spectroscopy, whereas the VOCs were analyzed using solid-phase microextraction (SPME)-GC-MS. Additionally, aroma profiles were evaluated using the MS-e-nose method and chemometric data analysis.

(3) Simulated NCS adulteration model

The NCS adulteration model (processed NCS or kako-kokuto) was produced by simulating sugar syrup blend (50 °Brix) composed of Okinawan brown sugar/kokuto syrup in four concentration levels, i.e., 10, 50, 75, and 90% (w/w), and raw cane sugar syrup. The ICUMSA color index and L*a*b* color spaces of adulterated NCS were measured. The food components were measured using ^{1}H-NMR analysis. VOCs and retronasal olfaction (flavor release) profiles were determined using SPME-GC-MS and proton transfer reaction–time of flight–MS (PTR-TOF-MS) analyses, respectively. Additionally, the perceived sensory properties of adulterated NCS were assessed.

4. Results and Discussion

(1) Physicochemical traits, antioxidant activities, and VOCs of unrefined-solidified sugars of different plant sources

Unrefined-solidified sugars from cane (NCS) had significantly higher ICUMSA color value than palm and coconut sugars, yet they possessed comparable total soluble solid levels (Weerawatanakorn et al., 2021). NCS products also presented superior phenolic and flavonoid contents and antioxidant activities, particularly in Thai and Japanese products. Each unrefined sugar had distinct volatile flavor composition, comprising Maillard reaction products (MRPs: pyrazines, furans, and pyranones), acids, aldehydes, alcohols, and sulfurs. All traditionally made NCS products had significantly greater MRPs and less acetic acid than in industrially manufactured NCS products. MS-e-nose profiling detection and chemometric computation via principal component analysis (PCA) provided specific ion masses from various volatile components as potential chemical markers in monitoring aroma characteristic of unrefined sugars and differentiated these sugars based on their materials and origins (Figure 1). Thoroughly, palm sugars from Thailand and Indonesia, as well as NCS products from Thailand and Japan, had comparable volatile profiles. These outcomes suggest that plant source and geographical origin greatly influences the quality traits of unrefined-solidified sugars.

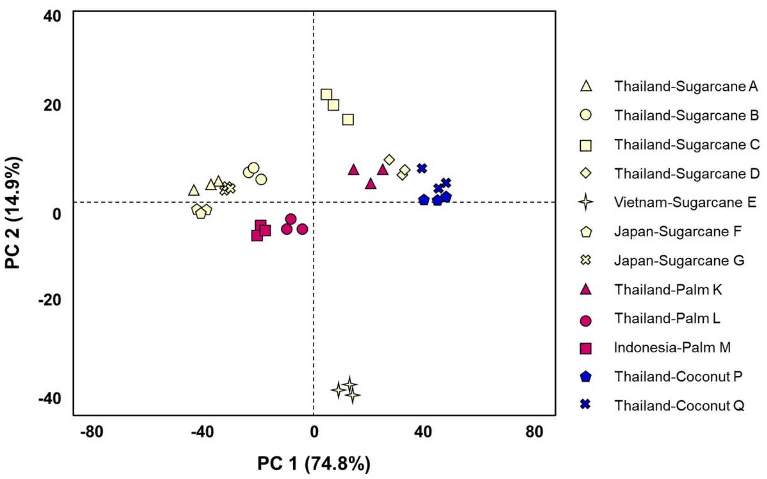

Figure 1. Principal component scores of volatile profiles of unrefined-solidified sugars.

(2) Composition of minerals and VOCs of NCS products from Japan and ASEAN countries

There was great variation in the mineral content of NCS products of Japanese and ASEAN origin, wherein a distinction was observed domestically and between countries (Ayustaningwarno et al., 2023). The average mineral content was 962.87, 984.67, and 928.47 mg/100 g in Japanese, Malaysian, and Indonesian products, respectively, and was mainly composed of K, Ca, Mg, P, and Na, followed by small amounts of Fe, Zn, Mn, and Cu. Forty-four VOCs were identified, of which concentrations of MRPS such as pyrazines, furans, and pyranones varied significantly among the NCSs (Figure 2). Additionally, the MS-e-nose analysis provided a multivariate differentiation profile of the NCS products based on differences in the intensities of the VOC ion masses. Nine statistical clusters were presented, wherein certain NCS products of ASEAN origin had volatile profiles comparable to those of the Japanese products (Figure 3). These outcomes suggest that the origin of production greatly influences the mineral and VOC compositions of NCS, affecting their quality traits.

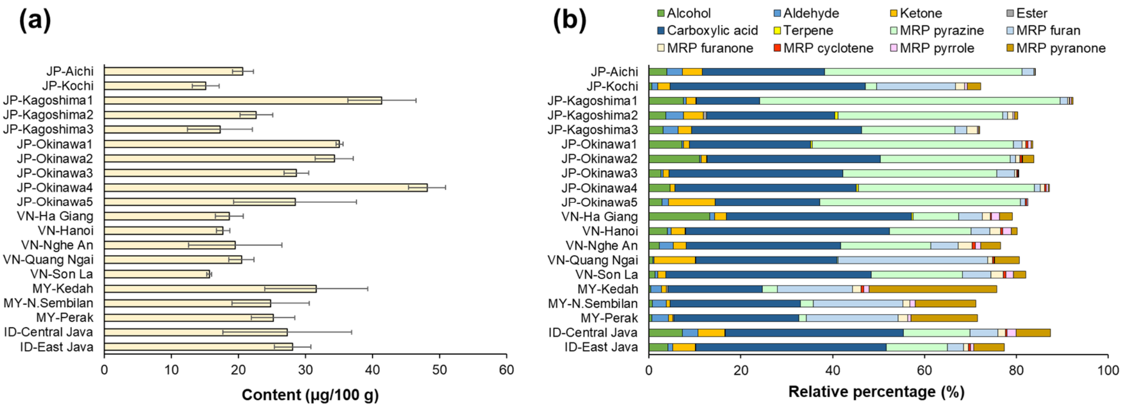

Figure 2. (a) Total content and (b) relative percentage of VOCs of NCS products from Japan and ASEAN countries.

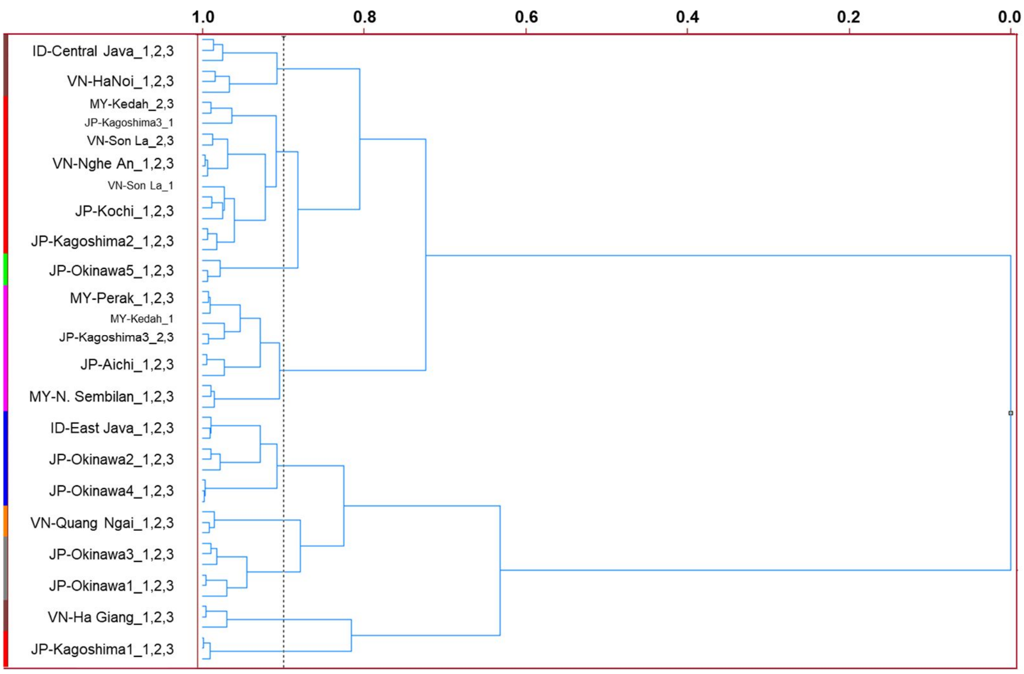

Figure 3. Hierarchical cluster analysis dendrogram of MS-e-nose profiles of NCS products from Japan and ASEAN countries.

(3) Flavor components and retronasal olfaction profiles of simulated NCS adulteration model

ICUMSA color index of adulterated NCS decreased along with the addition of adulterant (raw sugar), and there were strong Pearson's negative correlations between ICUMSA index with L* and b* color spaces, indicating raw sugar adulteration causes the color of final product to become lighter. On the other hand, there was no changes in sucrose concentration among adulterated NCS models, but their glucose contents tended to decline as brown sugar-syrup ratio decreased (or raw sugar proportion increased). Moreover, there were significant declines in the concentrations of threonine and organic acids (acetate, trans-aconitate, and succinate) along with raw sugar addition. The blends also reduced total VOCs, particularly MRPs such as pyrazines, furans, and furanones, indicating lower likeable nutty/roasted odor characteristics could have effect in the final product due to raw sugar adulteration (Figure 4). Additionally, the flavor release evaluation showed alteration of retronasal odors such as pyrazine, 2-furanmethanol, and other MRPs in adulterated NCS models. Lastly, raw sugar adulteration could lower the intensities of perceived sour taste and roasted aroma of Okinawan NCS, and thus distinctly alters its flavor characteristics and retronasal olfaction attributes.

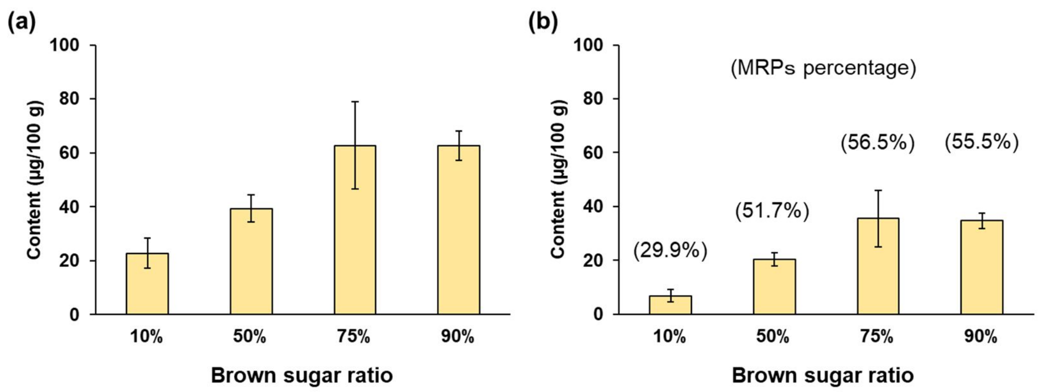

Figure 4. (a) Total VOCs and (b) MRPs of raw sugar-adulterated NCS models.

Taken together, the flavor quality of unrefined non-centrifugal sugars, including NCS, is greatly affected by its plant source and geographical production origin. On the other hand, adulteration to Okinawan specialty brown sugar with raw sugar affects its flavor properties. The results of this study provide important information regarding key physicochemical, nutritional, functionality, and favor attributes of unrefined non-centrifugal sugars that could be used as a valuable basis for further preference and sensory studies for practical applications when they are used as sugar materials in food and beverage production. Moreover, the study established a multi-omics analytical technique for distinguishing adulterated NCS that could be further utilized as an effective measurement to advance the building efforts of international product identity for local NCS products such as Okinawan specialty brown sugar against adulteration threats.

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５．主な発表論文等

〔雑誌論文〕　計3件（うち査読付論文　3件／うち国際共著　3件／うちオープンアクセス　2件）

１．著者名 Monthana Weerawatanakorn, Yonathan Asikin, Kanyaphat Meerod, Hajime Tamaki, Koji Wada	４．巻 15 (2)
２．論文標題 Physicochemical, antioxidant, volatile component, and mass spectrometry-based electronic nose analyses differentiated unrefined non-centrifugal cane, palm, and coconut sugars	５．発行年 2021年
３．雑誌名 Journal of Food Measurement and Characterization	６．最初と最後の頁 1563-1577
掲載論文のDOI（デジタルオブジェクト識別子） 10.1007/s11694-020-00749-x	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Fitriyono Ayustaningwarno, Yonathan Asikin, Ryo Amano, Vu Tuan Nam, Siti Hajar-Azhari, Gemala Anjani, Kensaku Takara, Koji Wada	４．巻 12
２．論文標題 Composition of minerals and volatile organic components of non-centrifugal cane sugars from Japan and ASEAN countries	５．発行年 2023年
３．雑誌名 Foods	６．最初と最後の頁 1406～1406
掲載論文のDOI（デジタルオブジェクト識別子） 10.3390/foods12071406	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

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掲載論文のDOI（デジタルオブジェクト識別子） 10.3390/app13116402	査読の有無 有
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４．発表年 2019年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

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