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Analytical Methods

A novel colorimetric sensor array based on boron-dipyrromethene dyes for monitoring the storage time of rice

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ARTICLE INFO

Chemical compounds studied in this article:
18-Crown-6 (PubChem CID: 28557)
5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine (TPP, PubChem CID: 70186)
5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine zinc (TPPZn, PubChem CID: 3580039)
5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine manganese(II) (TPPMn, PubChem CID: 14757041)
5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine manganese (III) Chloride (TPPMnCl, PubChem CID: 91864721)
5,10,15,20-Tetrakis (pentafluorophenyl) porphyrin iron (III) Chloride (FTPPFeCl, PubChem CID: 71431176)
5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine iron (III) Chloride (TPPFeCl, PubChem CID: 67043998)
8-Phenyl-4,4-difluoro-BODIPY (HBDP, PubChem CID: 46868721)
8-(4-Bromophenyl)-4,4-difluoro-BODIPY (NO_2BDP, PubChem CID: 102150779)
8-(4-Nitrophenyl)-4,4-difluoro-BODIPY (BrBDP, PubChem CID: 23631055)

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ABSTRACT

A novel colorimetric sensor array based on boron-dipyrromethene (BODIPY) dyes was developed to monitor the volatile organic compounds (VOCs) of rice at different storage times. The VOCs of rice at different storage times were analyzed through GC–MS combined with multivariate analysis, and the compound 18-crown-6 was found significantly changed during rice aging process. Aimed at 18-crown-6 with particular macrocyclic structure, a series of BODIPYs were targeted synthesized for the selection of sensitive chemically responsive dyes. Four dyes were chosen to construct colorimetric sensor array based on sensitivity to VOCs of aged rice samples. Data acquired from the interactions of dyes and rice VOCs were subjected to the principal components analysis (PCA) and linear discriminant analysis (LDA). The optimal performance obtained by the LDA model was 98.75% in prediction set. Application of BODIPYs in this work has improved the sensitivity and expanded the choices of colorimetric dyes for the specific detection.

1. Introduction

Rice (*Oryza sativa* L.) as a staple food feeds about two-thirds of the world's population, especially in Asia (Choi et al., 2015). Rice plays a crucial role as a primary dietary source of carbohydrates to assure the basic energy and nutrient supply (Tsuzuki et al., 2014). It's no doubt that the quality of rice greatly affects human health. Vast demand for rice and its apparent seasonality make most of the countries store them to guarantee supplies during its lean periods (Park, Kim, Park, & Kim, 2012). In the storage process, the chemical and physical properties of rice change which are termed as aging (Thanathornvarakul, Anuntagool, & Tananuwong, 2016; Zhou, Robards, Helliwell, & Blanchard, 2002). The aging of rice was embodied by following three aspects: the decrease in its nutritive value and culinary quality, and the deterioration in its sensory quality. Flavor is a major rice aging criterion which not only directly reflects the sensor quality, but also relates to the changes in nutrient content and culinary quality (Griglione et al., 2015).

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Sensory and instrumental analyses have long been used to measure the food flavor (Sung, Kim, Kim, & Kim, 2014). Sensory analyses using human nose as a smell assessment instrument provide unique and direct information on food flavor. However, sensor analyses inevitably are affected by subjective factors, such as emotion, physical condition and environment (Radi, Litananda, Rivai, & Purnomo, 2016). Alternatively, the gas chromatography-mass spectrometry (GC–MS) as the most common instrumental analyses method for flavor determination has been widely applied. Although it has been used for qualitative and quantitative analysis of volatile organic compounds, some typical drawbacks appears to limit its application such as: it requires sample preparation, time-consuming, expensive and requires experts for operation. laborious and time-consuming, high costs of implementation and need of skilled personnel (Feng et al., 2011; Sanaeifar, Mohtasebi, Ghasemi-Varnamkhasti, & Ahmadi, 2016).

A new branch of colorimetric sensor array technology proposed by Suslick has been developed and has gained importance since 2000 (Rakow & Suslick, 2000). It is a novel electronic nose system which consisted of a colorimetric sensor array made of chemically responsive dyes with partial specificity and a pattern-recognition system capable of recognizing simple or complex odors (Kim, Li, Lim, Kang, & Park, 2016; Musto & Suslick, 2010). The colorimetric sensor array is composed of chemically responsive dyes that directly influence the detections of volatiles compounds. Nowadays chemically responsive dyes mainly include porphyrins and pH indicators that have been reported to perform intense coloration effect (Huang, Gu, Yao, Teye, & Wen, 2014; Huang, Zou, et al., 2014). Fabricated sensor arrays have been applied to the detection of organic small-molecular compounds such as alcohol (Suslick, Rakow, & Sen, 2004), biogenic amines (Xiaowei et al., 2015), and TVB-N (Huang, Gu, et al., 2014; Huang, Zou, et al., 2014). Therefore, colorimetric sensor array technology has great potential for analyzing the volatile organic compounds (VOCs) of rice with different storage times.

A variety of VOCs would be obtained during the storage process of rice. It is reported that some specific organic compounds such as aldehydes and heterocyclic compounds remarkably changed with prolonged storage time. In this case, the sensitivity of conventional chemically responsive dyes should been investigated in these specific volatile compounds. In fact, it is found that colorimetric sensor array fabricated by conventional dyes (TPP porphyrins and pH indicators) find it difficult to discriminate aging of rice at the early stage (Guan, Zhao, Jin, & Lin, 2016). Given this, improving performance of dyes is of utmost importance. Presumably, sensitive chemically responsive dyes synthesized to target specific samples could change this situation. Besides, application of new chemically responsive dyes will increase the choices available and may provide dyes that will ensure the accurate detection of the VOCs in aging rice.

In this study, a novel colorimetric sensor array was developed to monitor VOCs in the aging process of rice. The specific organic compounds which were identified during rice aging process were analyzed through GC–MS. Different kinds of chemically responsive dyes were synthesized comparatively to characterize the VOCs of aging rice. The process of VOCs exposure to dyes was simulated, and some dyes with simpler structures were specially synthesized to detect the specific VOCs during rice aging. Furthermore, multivariate analysis was employed to discriminate storage time of rice samples.

2. Material and method

2.1. Material

Japonica rice (Wuyujing 3) was grown in a paddy of a local farm in Jiangsu Province, eastern part of China, from May to October 2014. After harvesting, the rice samples were obtained by hulling, separation, selection and stored in shaded plastic bags. Rice samples with different storage times (1, 3, 7 and 10 months) were prepared for the study. Standard 18-crown-6 was purchased from J&K scientific Ltd.

2.2. Method

2.2.1. The synthesis of chemically responsive dyes

Five kinds of general porphyrins were synthesized to determine the characteristic gas of 18-crown-6 and VOCs of rice with different storage times. In view of the special macrocyclic structure of 18-crown-6, eight BODIPYs targeted synthesized with simple chemical structure were also used in this study.

Metalloporphyrins: 0.25 mmol of TPP and 1.25 mmol of different metal salts were dissolved in 50 mL of N, N-Dimethylformamide (DMF) solution, respectively, and refluxed for 24 h under N_2. After solvent evaporation, the residue was dissolved in $CHCl_3$ and rinsed with water for several times. The solution was dried with anhydrous Na_2SO_4. The solvent was re-evaporated and recrystallized using $CHCl_3$ and CH_3OH to get the pure target metalloporphyrin dyes. BODIPYs: Dyes were synthesized according to the classic Lindsey methodology (Loudet & Burgess, 2007; Wu et al., 2012). All reagent used in the synthesis were purchased from Sigma Chemical (USA). Porphyrins and BODIPYs dyes used are listed as follows:

(1) 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine (TPP);
(2) 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine zinc (TPPZn);
(3) 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine manganese(II) (TPPMn);
(4) 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine manganese(III) Chloride (TPPMnCl);
(5) 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin iron (III) Chloride (FTPPFeCl);
(6) 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine iron (III) Chloride (TPPFeCl);
(7) 8-phenyl-4,4-difluoro-BODIPY (HBDP);
(8) 8-(4-bromophenyl)-4,4-difluoro-BODIPY (NO_2BDP);
(9) 8-(4-nitrophenyl)-4,4-difluoro-BODIPY (BrBDP);
(10) 8-(4-nitrophenyl)-6-bromo-4,4-difluoro-BODIPY (NO_2BrBDP);
(11) 8-(4-nitrophenyl)-6,6-dibromo-4,4-difluoro-BODIPY (NO_2Br_2BDP);
(12) 8-(4-methoxylphenyl)-4,4-difluoro-BODIPY (OCH_3BDP);
(13) 8-(6-methoxyl-2-naphthyl)-4,4-difluoro-BODIPY (NaiOCH_3BDP);
(14) 8-(4-carbazolylphenyl)-4,4-difluoro-BODIPY (pCarBDP);

Besides, bromcresol purple (BCP) and dimethyl yellow (DMY) obtained from Sinopharm Chemical Reagent Co., Ltd were also used to characterize the VOCs of rice.

2.2.2. Colorimetric sensor array system

The colorimetric sensor array system is illustrated in Fig. 1. It consists of gas-collecting chamber, vacuum pump, reaction and digital image acquisition system and computer with specific software. In the reaction and digital image acquisition system, a tri-CCD was employed to obtain images of colorimetric sensor array placed inside the reaction chamber whiles the diffuse reflection integrating sphere source provided continuous light with no flashes. All image processing of colorimetric sensor array were executed by the computer with specific software.

Before the analysis, two valves were open and vacuum pump was turned on for 5 min to remove the remaining or other unrelated gases. The method of fabricating a colorimetric sensor array has been described by (Guan, Zhao, Lin, & Zou, 2013). The colorimetric sensor array was placed in the reaction chamber and the before image taken by tri-CCD. Then samples were transferred to a gas-collecting chamber and valves were closed to equilibrate for 5 min. Subsequently, two valves were opened and the vacuum pump was turned on again to extract the VOCs of analyte into the reaction chamber. Finally, digital image of the array after exposure to samples was captured by tri-CCD as after image. A series of image processing including filtering, threshold segmentation, morphological processing, center extraction and additional operations were performed for the next analysis. After that, color change files were produced through subtracting of the corresponding before image from the after image.