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Characterization of protein and carbohydrate mid-IR spectral features in crop residues

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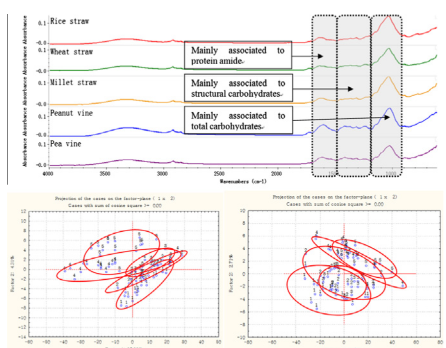
HIGHLIGHTS

- Structural bands associated with protein biopolymer differed among crop residues.
- Structural bands related to carbohydrate conformation varied among crop residues.
- Crop residues had structural similarities in protein and carbohydrate regions.

GRAPHICAL ABSTRACT



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ABSTRACT

To the best of our knowledge, a few studies have been conducted on inherent structure spectral traits related to biopolymers of crop residues. The objective of this study was to characterize protein and carbohydrate structure spectral features of three field crop residues (rice straw, wheat straw and millet straw) in comparison with two crop vines (peanut vine and pea vine) by using Fourier transform infrared spectroscopy (FTIR) technique with attenuated total reflectance (ATR). Also, multivariate analyses were performed on spectral data sets within the regions mainly related to protein and carbohydrate in this study. The results showed that spectral differences existed in mid-IR peak intensities that are mainly related to protein and carbohydrate among these crop residue samples. With regard to protein spectral profile, peanut vine showed the greatest mid-IR band intensities that are related to protein amide and protein secondary structures, followed by pea vine and the rest three field crop straws. The crop vines had 48–134% higher spectral band intensity than the grain straws in spectral features associated with protein. Similar trends were also found in the bands that are mainly related to structural carbohydrates (such as cellulosic compounds). However, the field crop residues had higher peak intensity in total carbohydrates region than the crop vines. Furthermore, spectral ratios varied among the residue samples, indicating that these five crop residues had different internal structural conformation. However, multivariate spectral analyses showed that structural similarities still exhibited among crop residues in the regions associated with protein biopolymers and carbohydrate. Further study is needed to find out whether there is any relationship between spectroscopic information and nutrition supply in various kinds of crop residue when fed to animals.

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Introduction

Grain straws are usually regarded as one of the abundant fibrous waste materials in the world, such as rice straw, wheat straw and millet straw. In accompany with ten kilograms of grain harvested, ten to fifteen kilograms of crop straw are produced [1]. According to FAO statistics, world annual productions of rice, wheat and millet in 2012 are approximately 718, 675 and 256 million tons, respectively. Theoretically, they would generate 256–1077 million tonnes of straw globally. In comparison with cereal grains, peanut and pea are another two important multipurpose crops widely grown in the world, especially in Mediterranean countries [2] and Western Canada [3]. And likewise, substantial amounts of crop residues are produced in the process of peanut and pea harvest.

The crop residues commonly have limited biological value because of their high fiber content and low forage quality. However, a large portion of residues are still used as animal feed [3–5] since it can greatly reduce feeding cost in livestock industry [6], especially for ruminant animals which need forage in their daily rations. Therefore, numerous studies have been designed to find out or discuss the efficient measures for improvement of forage application in ruminant feed [7–9]. In the light of these results, the contents of protein and fiber as well as nutrient degradability in various straw and crop hays differed to a great extent [4,5,10,11]. However, little attention has been paid to the inherent molecular structures which might be highly associated with nutritional values and biodegradation behaviors for ruminant livestock [12–14] in crop residues.

Consequently, the objective of this study was to characterize protein and carbohydrate structural features of three field crop residues (rice straw, wheat straw and millet straw) in comparison with two kinds of crop vine (peanut vine and pea vine) by using Fourier transform infrared spectroscopy (FTIR) technique with attenuated total reflectance (ATR). This spectroscopic method has been already successfully applied to test structural characteristics in feedstuff [12,13,15]. Also, multivariate analyses were performed on spectral data sets within regions related to protein and carbohydrate biopolymers in this study. Our research might be helpful for better understanding of variations in nutritive values as well as biological features of field crop residues when fed to animals.

Materials and method

Crop residue samples

Five kinds of crop residues were selected in this study: rice straw ($n = 4$), wheat straw ($n = 3$), millet straw ($n = 3$), peanut vine ($n = 3$) and pea vine ($n = 3$). Rice straws were obtained from four field grown plots at Chongqing City in 2011. Both wheat straw and pea vine were obtained from grain and vegetable farms in Jingtai County in Gansu Province in 2012. Millet straw was from three local grain farms in Sichuan Province and peanut vine was sampled in Jinlan Dairy Ranch in Shandong Province in 2011. Each sample had several sources. All the crop residues were dried at 55 °C for 12 h and grounded through a 0.5-mm screen (Retsch ZM-1; Brinkmann Instruments, Mississauga, ON, Canada) for spectroscopic scanning.

FTIR spectral data collection

The molecular vibrational spectroscope JASCO FT/IR 4200 with ATR (JASCO Corporation, Tokyo, Japan) was employed for the mid-IR spectroscopic information collection of different sources of crop residue. This spectral experiment was carried out at feed chair molecular structure analysis lab at Department of Animal and Poultry Science, University of Saskatchewan (SK, Canada). Before scanning, we set up the spectral program with 128 co-added scans at 4 cm^{-1} spectral resolution. Each crop residue sample of each source was analyzed five times. Fig. 1 shows typical mid-IR molecular spectra of rice straw, wheat straw, millet straw, peanut vine and pea vine at *ca.* 4000–800 cm^{-1}.

Spectral parameters identification

In this study, we focused on protein and carbohydrate molecular structural parameters including peak height and peak area. Also spectral ratios were calculated based on individual spectral data. For all the peak identifications, OMNIC 7.2 software was a necessary tool and adopted in the study. In the light of detailed description in recent publications [12,13], the regions mainly related to protein and carbohydrate were identified at *ca.* 1718–1482 cm^{-1} and *ca.* 1490–909 cm^{-1}, respectively. Within protein region, there were two main bands related to protein amide I (*ca.* 1626 cm^{-1}) and amide II (*ca.* 1538 cm^{-1}); and protein secondary structures such as α-helix (*ca.* 1651 cm^{-1}) and β-sheet (*ca.* 1635 cm^{-1}) could be identified using two functions (the second derivative and Fourier self-deconvolution (FSD)) in the software. Within carbohydrate region, there were three main parts involved: (1) bands mainly related to cellulosic compounds (CELC, baseline *ca.* 1306–1191 cm^{-1}); (2) bands mainly related to structural carbohydrates (SCHO, baseline *ca.* 1490–1184 cm^{-1}) which were associated with hemi- and cellulosic compounds and (3) bands mainly related to total carbohydrates (CHO, baseline *ca.* 1038–1019 cm^{-1}) which included three peaks with the first, second and third peaks centered at *ca.* 1159, 1103 and 1032 cm^{-1}, respectively .

Multivariate spectral analyses

Agglomerative hierarchical cluster analysis (AHCA) and principal component analysis (PCA) are the two methods successfully

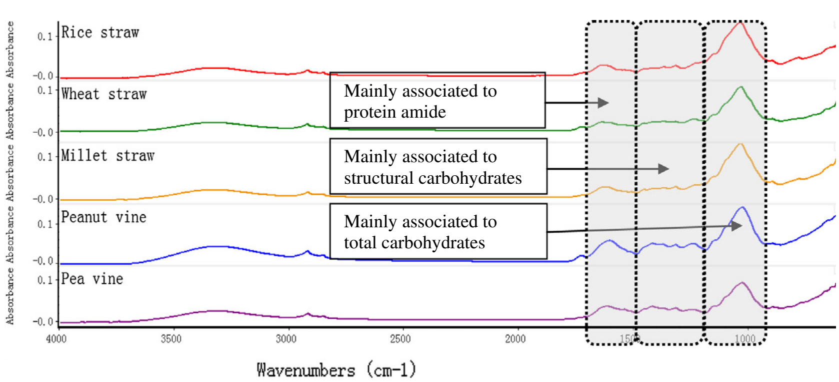

Fig. 1. Typical ATR-FT/IR molecular spectra of five kinds of forage in mid-IR region *ca.* 4000–800 cm^{-1}.