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Raman spectroscopic comparison of zearalenone and its derivatives for non-destructive rapid detection

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Abstract

Raman spectroscopy is used to investigate the absorption and dispersion of zearalenone (ZEN) and its derivatives. The C=C stretching vibration modes of ZEN and zearalenol (ZENOL) were appeared at 975–990 cm⁻¹. The C=O vibration mode was present at 1680–1690 cm⁻¹ for ZEN and zearalanone (ZAN), but it was absent for ZENOL and zearalanol (ZANOL) which have –OH group instead of –C=O group in ZEN and ZAN molecular structures. On the basis of this characterization, Raman spectra of specific chemical groups and linkages corresponding to the structural difference of ZEN and its derivatives were identified. These results indicated that Raman spectroscopy can apply for the identification of ZEN and its derivatives and has a potential for the non-destructive rapid detection of these compounds in food.

Keywords Raman spectroscopy, Mycotoxins, Zearalenone, Characterization

Introduction

Mycotoxins produced by *Fusarium* spp. are generally classified into two types: ones are the nonestrogenic trichotecenes including deoxynivalenone (DON), nivalenol, T-2 toxin, and diacetoxyscripenol, and the others are the mycoestrogens including Zearalenone (ZEN) and its derivatives, such as Zearalanone (ZAN), Zearalenol (ZENOL), and Zearalanol (ZANOL) (Bennett and Klich 2003). ZEN and its derivatives are known as one of strong mycotoxins with potent estrogenic activities, and frequent contaminants of cereal crops, such as

maize, barley, oats, wheat and other grains throughout the world (Darra et al. 2019). Consequence of animal feedings of those crops, many cases have been observed estrogenic effects from diverse animals, such as bird, pig, cattle, and other domestic animals. Although the poultry is known to show relatively less sensitive reaction to these mycotoxins, the swine reacts the most severely among all domestic species. In case of the cattle, the infertility, reduced milk production, and hyperestrogenism have been reported due to association with these mycotoxins. While increasing consumption of processed foods such as cereals and ready to consume grains, their estrogenic activity is becoming a potential risk to human as well. Because of the potential toxic effects of ZEN and its derivatives for human health, the foods for human and animal feeds are closely monitored and tested for the presence of these toxins. Furthermore, many countries have established guidelines for maximum tolerance range of these mycotoxins from 30 to 1000 µg/kg in grains depends on the type of foods (Appell et al. 2022).

Recently the potential toxicity of ZEN and its derivatives on the reproductive structural and functional

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parameters have been intensely studied by many groups (Minervini et al. 2001; Zinedine et al. 2007). The estrogenic activities of ZEN and related compounds have been reviewed (Takemura et al. 2007). In the report, the authors claimed that sensitivity to the mycotoxins is related to species-dependent biotransformation pathways and these reactions show similarities to process in steroid metabolism. There are two metabolic pathways including hepatocytes and intestinal cells. Through these pathways, ZEN and its derivatives are metabolized to ZENOL with hydroxyl group by hydroxysteroid dehydrogenase (HSD). The high sensitivity to ZEN-mediated oestrogenic effects shown in some animals is related to this metabolic transformation of hydroxyl group. It has been proved that the higher oestrogenicity of ZENOL in pig and rat is related to its strong binding affinity to the cytoplasmic oestrogenic receptor (Minervini et al. 2006). As many studies showed, the small difference in structures of ZEN and its derivatives is one of the important factors for the species-dependent sensitivity. It also induces in the different binding affinity to the cytoplasmic receptor, resulting in difference symptom and sensitivity. In the previous studies, it was reported that the diverse analysis techniques based on chromatography and immunoassay are applied to detect these mycotoxins (Josephs et al. 2001; Krška et al. 2005). Particularly, chromatographic techniques including thin-layer chromatography (TLC) (Josephs et al. 2001; Schaafsma et al. 1998), gas-liquid chromatography (Josephs et al. 2001), gas chromatography-mass spectrometry (Tanaka et al. 2000; Zhang et al. 2006), HPLC (Saeger et al. 2003), and HPLC-mass spectrometry (Pallaroni and Holst 2003) are considered as a strong candidate method for the detection and determination of these mycotoxins. In addition, recently immunosensors and surface plasmon resonance (SPR) sensor have been employed to detect food contaminants with high sensitivity and fast analytical time (Abouziied and Pestka 1994; Choi et al. 2009). However, these methods often involve expensive, time-consuming pretreatment steps, including solid-phase extraction, separation, detection, and sample clean-up. Furthermore, they cannot provide detailed structural information of mycotoxins which are closely related in their structures. It is well known that spectroscopic method is non-destructive, rapid, and reliable experimental technique with minimal sample treatment. In previous studies, optical spectroscopic methods were proved as highly sensitive analytical techniques to obtain the structural information of target mycotoxins without complicated extraction steps (Gordon et al. 1998; Dowell et al. 1999; Pettersson and Åberg 2003; Delwiche and Hareland 2004; Delwiche 2008). Among the optical spectroscopic methods, Raman spectroscopy is suitable to study the structural differences at the molecular level.

Because Raman spectra contain the detailed information of molecular structure, it has been employed as quite effective probes to investigate process-induced changes and to monitor quality of food (Li-Chan 1996; Belton 1993; Scotter 1997).

In this study, Raman spectroscopic technique was used to characterize the mycotoxin ZEN and its derivatives. Comprehensive characterization of Raman spectra of four mycotoxins (ZEN, ZAN, ZENOL and ZANOL) was conducted. From full spectral range of the spectra of those molecules, specific chemical groups and linkages corresponding to the subtle differences in their structures were identified. The main objectives of this research are to provide detailed spectroscopic data of the mycotoxins of ZEN and its derivatives.

Experiment

Zearalenone, β -zearalenol, 4earalenone, and β -zearalanolone, were purchased from Sigma (St. Louis, MO, USA). The molecular structures of ZEN and its derivatives are shown in Fig. 1. To determine the three-dimensional structure of ZEN and its derivatives, their theoretical calculation was performed by mean of computer simulation with MM2 (ChemBioOffice, ver.11.0). The molecule was set at a minimum energy position of 0 K for MM2. And then, molecular dynamics was carried out with a step size of 1 fs at a constant temperature of 298 K. And data analysis was performed for 300 ps.

The Raman spectrum was obtained from the powder sample at room temperature (25 ± 2 °C). Raman spectra were collected using a triple monochromator coupled with a CCD array detector (Triplemate 1877, Spex Industries, Edison, NJ, USA). The laser power used for all experiments was 15 mW at 514.5 nm (Innova 70 Ar+laser, Coherent Co., Santa Clara, CA., USA). The laser light was passed through a premonochromator to remove plasma emission lines. The scattered light was collected in a 45° angle geometry. Spectra obtained with 514.5 nm excitation were recorded using a 1800 grooves/mm holographic grating. All spectra were obtained in the Raman shift range between 300 and 3700 cm^{-1} at room temperature (298 K).

Results and discussion

The theoretical calculation of molecular dynamics for the ZEN and its derivatives was performed by MM2 at a constant temperature of 298 K and the determined three-dimensional structures of them are shown in Fig. 2. As shown in Fig. 2, optimized geometry of ZEN and its derivatives well represented their three-dimensional characteristics due to the structural similarity and difference. The similarity of molecular structure between ZEN and its derivatives is not only having a benzene ring

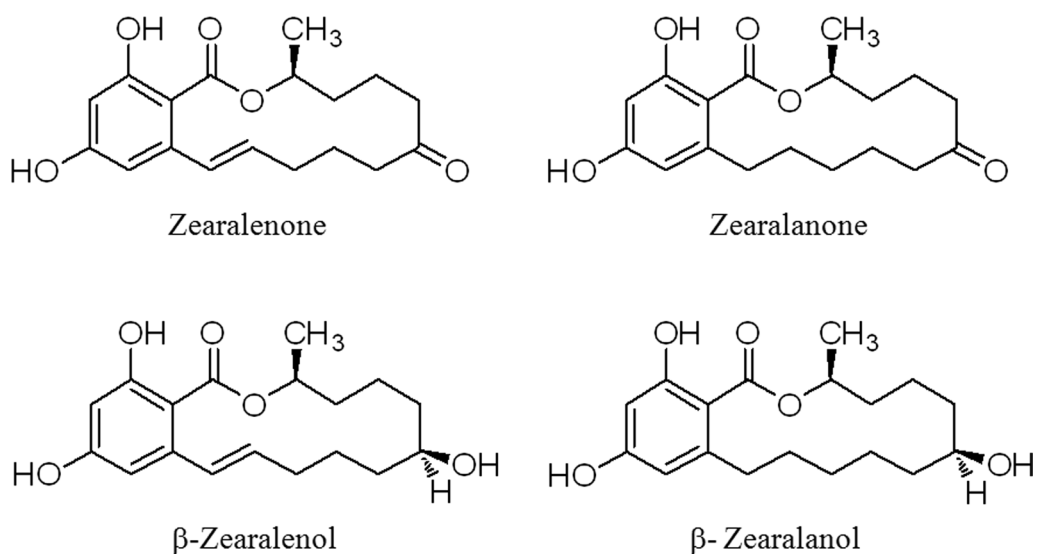


Fig. 1 Molecular structure of ZEN and its derivatives

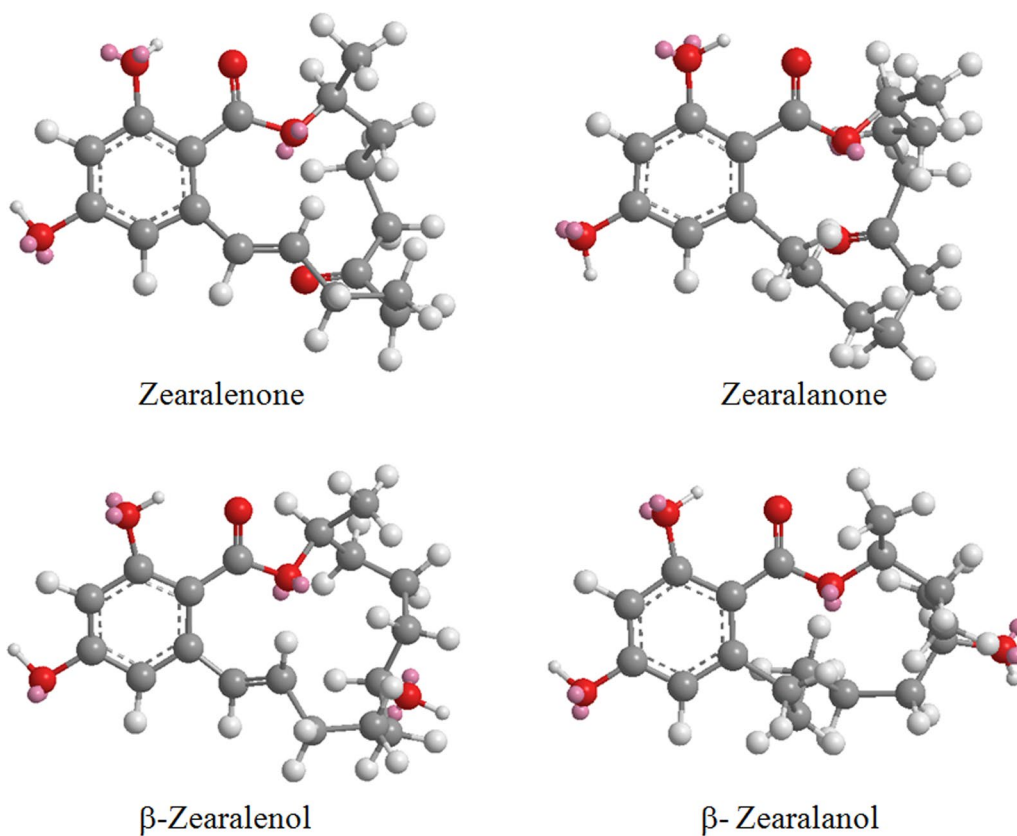


Fig. 2 The optimized geometry of ZEN and its derivatives, calculated by means of MM2

with two hydroxyl groups but also, having a ring-shaped circular carbon chain structure. This structural similarity is well represented in their optimized geometry in

Fig. 2. Moreover, it was demonstrated well through the peak assignment of $\nu(\text{C-H})$ aromatic ring, $\nu(\text{C=C})$ aromatic ring, and $\nu(\text{C-C})$ aromatic ring in Table 1. While,

Table 1 Spectrum band position and assignment of zearalenone and its derivatives

Zearalenone	Zearalanone	β -Zearalenol	β -Zearalanol	Assignments
889	880	885	875	$\nu(\text{C}-\text{C})$
980	–	976	–	$\nu(\text{C}=\text{C})$ aryl
1019	1021	1025	1019	$\nu(\text{C}-\text{C})$ aromatic ring
–	–	1128	1126	$\nu(\text{C}-\text{OH})$
1329	1332	1328	1327	$\nu(\text{C}-\text{OH})$
1363	1362	1370	1368	$\delta(\text{CH}_3)$ sym
1473	1468	1460	1460	$\delta(\text{CH}_2)$ sym, $\delta(\text{CH}_3)$ asym
1624	–	1621	–	$\nu(\text{C}=\text{C})$ aryl
1649	1653	1651	1644	$\nu(\text{C}=\text{C})$ aromatic ring
1693	1688	–	–	$\nu(\text{C}=\text{O})$
2848–3027	2851–3022	2849–3023	2857–3028	$\nu(-\text{CH}_2)$, $\nu(-\text{CH}_3)$
3075	3077	3085	3083	$\nu(=\text{C}-\text{H})$
3229	3229	3230	3228	$\nu(\text{C}-\text{H})$ aromatic ring
3484	3485	3484	3483	$\nu(\text{O}-\text{H})$ $\text{R}-\text{OH}\cdots\text{O}=\text{C}<$

the main difference between ZEN and its derivatives with estrogenic activity is the existence of C=C double bond and C=O residue in a circular carbon chain structure. Firstly, ZEN and ZENOL have a C=C double bond at near the benzene ring and this C=C double bond shows more rigid properties than that of C–C single bond. Therefore, it is expected that these structural rigidity due to the C=C double bond decrease the degree of freedom of circular carbon chain structure and result in the difference of three-dimensional structure against ZAN and ZANOL with C–C single bond at the same position. Their optimized geometries in Fig. 2 clearly represent these structural differences between ZEN/ZENOL and ZAN/ZANOL. The Raman spectra were measured in the range from 200 cm^{-1} to 3700 cm^{-1} . Figure 3 shows the Raman spectra of ZEN and its derivatives; while the peak positions along with the appropriate vibrational assignments are listed in Table 1.

As shown in Fig. 3 and Table 1, the CH_2 stretching vibration modes and CH_3 stretching vibration modes of ZEN and its derivatives appeared at 2848–3028 cm^{-1} . The peak at 3075–3085 cm^{-1} could be attributed to the $=\text{C}-\text{H}$ stretching vibration mode. Raman peak at 3228–3230 cm^{-1} were C–H stretching vibration mode in aromatic ring (Duley and Williams 1983; Jones et al. 1983; Barrett 1981; Vasko et al. 1972). The peak at 3483–3485 cm^{-1} could be attributed to the $-\text{OH}$ stretching vibration mode of aromatic ring in the ortho-position forming (Shaw et al. 1990). As shown in Fig. 4, the C–C stretching vibration modes of ZEN and its derivatives appeared at 875–889 cm^{-1} (Korolevich et al. 1990). Meanwhile, the C=C stretching vibration modes of ZEN and ZENOL

appeared at 976–980 cm^{-1} and the peak at 1621–1624 cm^{-1} could be attributed to the C=C stretching mode (Table 1) (Potts and Nyquist 1959; Wexler 1967). Because the $\nu(\text{C}=\text{C})$ aryl peaks at 976–980 cm^{-1} and 1621–1624 cm^{-1} are the structure specific Raman peaks which can distinguish ZEN and ZENOL from ZAN and ZANOL, these peaks can be used as one of spectroscopic fingerprint for the determination of ZEN and ZENOL among the related mycotoxin species. Raman peak at 1019–1025 cm^{-1} were C–C stretching vibration mode in aromatic ring (Korolevich et al. 1990; Wexler 1967; Kacuráková and Mathlouthi 1996), and the peak at 1327–1332 cm^{-1} could be attributed to the C–OH stretching vibration mode of aromatic ring in the para- position forming (Barrett 1981). The C–OH stretching vibration modes of ZENOL and ZANOL were appeared at 1126–1128 cm^{-1} (Green et al. 1971). The CH_3 bending mode of ZEN and its derivatives were appeared at 1362–1370 cm^{-1} , and the peaks at 1460–1473 cm^{-1} were attributed to contribution of two main vibrational modes, such as CH_2 bending and CH_3 bending (Nava et al. 1996; Bourée et al. 1996). Raman peak at 1644–1653 cm^{-1} corresponds to C=C stretching vibration mode in aromatic ring (Potts and Nyquist 1959; Wexler 1967). ZEN and ZAN have a C=O residue in the middle of circular carbon chain structure. The existence of C=O residue is one of main reason for the difference of three-dimensional structure between ZEN and its derivatives, along with the C=C double bond. As shown in Fig. 4 and Table 1, the C=O vibration mode appeared at 1688–1693 cm^{-1} (Schrader et al. 1997) for ZEN and ZAN, but did not appear for ZANOL and ZENOL which have $-\text{OH}$ group instead of $-\text{C}=\text{O}$ group

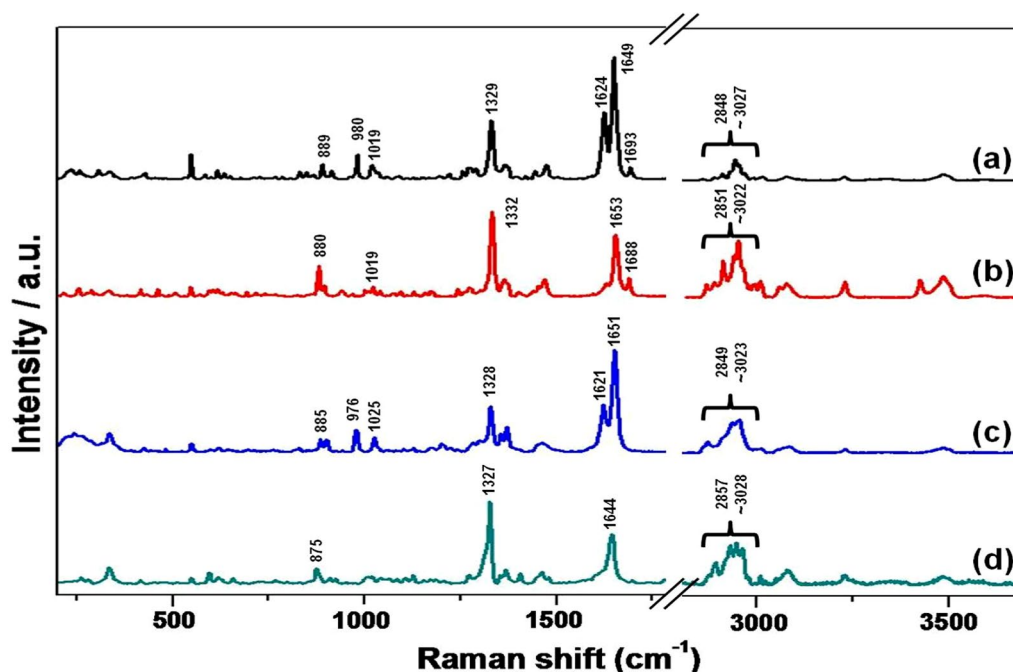


Fig. 3 Raman spectra of zearalenone and its derivatives (zearalenone (a), zearalanone (b), zearalenol (c), zearalanol (d)). The spectral region between 1800 and 2800 cm^{-1} was omitted due to the lack of spectra information

in ZEN and ZAN molecular structures. Because the $\nu(\text{C}=\text{O})$ peaks at 1688–1693 cm^{-1} are the structure specific Raman peaks which can distinguish ZEN and ZAN from ZENOL and ZANOL, therefore, we expect that these peaks can be used as one of spectroscopic fingerprint for the determination of ZEN and ZAN among the related mycotoxin species.

The optimized geometrical images of ZEN and its derivatives in Fig. 2 well represented their structural differences. These differences due to the three-dimensional structure of molecules frequently bring different inter- or intra-molecular interaction. The widths and intensities of the spectral bands marked small changes depending on the difference of molecular structures. Firstly, the $\text{C}=\text{O}$ band in ZAN was shifted to lower wavenumber (1688 cm^{-1}) compared to that of ZEN (1693 cm^{-1}). This seems to be mainly due to the inter-molecular interactions between the $\text{C}=\text{O}$ group and $\text{C}-\text{H}$ group of neighboring molecules (Yu et al. 2002). When the CO group of ZEN and ZAN belong to the inter-molecular interaction, they can form hydrogen bonding with $\text{C}-\text{H}$ group of neighboring molecules. At that time, there are two $\text{C}-\text{H}$ candidate groups which can participate in inter-molecular hydrogen bonding. One is aromatic $\text{C}-\text{H}$ in benzene ring and the other is aryl $\text{C}-\text{H}$ in circular carbon chain. In case of aryl $\text{C}-\text{H}$ group, the Raman peak appears as symmetric and asymmetric CH_2 stretching mode. If the $\text{C}-\text{H}$ group belongs to the inter-molecular hydrogen bond,

it will be expected that the symmetric CH_2 mode will decrease while the asymmetric CH_2 mode will increase because of the interference of CO group of neighboring molecules. In our results, the CH_2 sym peaks of ZEN and ZAN showed very lower intensity than that of ZENOL and ZANOL. The restriction of CH_2 symmetric vibration mode is due to the inter-molecular interaction between $\text{C}=\text{O}$ group (Raman peak at 2848–3028 cm^{-1}) and $\text{C}-\text{H}$ group in the circular carbon chain. Meanwhile, a previous report explained that aromatic ($\text{C}-\text{H}$) peak would shift to a lower frequency by hydrogen bond formation due to the weakening of $\text{C}-\text{H}$ bond and it would shift to a higher frequency upon breaking down the hydrogen bonding since the weakened $\text{C}-\text{H}$ bond would be reinforced (Yu et al. 2002). In our results, there is no remarkable shift of aromatic ($\text{C}-\text{H}$) peak to the lower frequency. These results indicate that $\text{C}-\text{H}$ group of aromatic ring was weakly participating to the intra-molecular interaction between other adjacent molecules. Moreover, $\text{R}-\text{OH}\cdots\text{O}=\text{C}$ peak can be affected by intra-molecular interaction between aromatic $\text{R}-\text{OH}$ in benzene ring and $\text{C}=\text{O}$ group in circular carbon chain, appeared at 3483–3485 cm^{-1} and did not show frequency shifts. These results indicate that the changes due to the $\text{C}=\text{C}$ double bonding and $\text{C}=\text{O}/\text{C}-\text{OH}$ group exchanging, give just very small effect to the intra-molecular interaction between $\text{R}-\text{OH}$ in benzene ring and $\text{C}=\text{O}$ group in circular carbon.

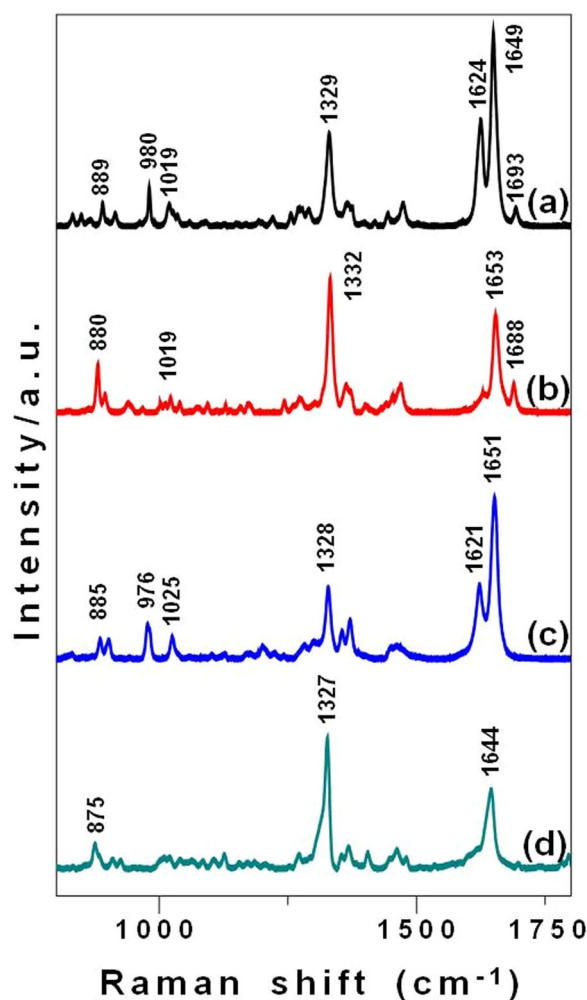


Fig. 4 Raman spectra of zearalenone and its derivatives in the 800–1800 cm^{-1} region (zearalenone (a), zearalanone (b), zearalenol (c), zearalanol (d))

Conclusion

In this study, we characterized some specific Raman peaks of ZEN and its derivatives based on their structural differences. The C=C stretching vibration modes of ZEN and ZENOL were appeared at 975–990 cm^{-1} . The C=O vibration mode was present at 1680–1690 cm^{-1} for ZEN and ZAN, but it was absent for ZANOL and ZENOL which have –OH group instead of –C=O group in ZEN and ZAN molecular structures. On the basis of this characterization, Raman spectra of specific chemical groups and linkages corresponding to the structural difference of ZEN and its derivatives were identified. These results indicated that Raman can apply for the identification of ZEN and its derivatives and has a potential for the non-destructive rapid detection of ZEN and its derivatives in food. Our studies are

in progress to deepen understanding the spectroscopic difference between ZEN and its derivatives in low frequency range under 200 cm^{-1} . Moreover, we will study the Raman spectroscopy of mixed sample with corn and wheat for the non-destructive rapid detection of mycotoxin, as a future work.

Abbreviations

ZEN	Zearalenone
ZENOL	Zearalenol
ZAN	Zearalanone
DON	Deoxynivalenone
HSD	Dehydrogenase
SPR	Surface plasmon resonance

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Not applicable.

Author contributions

Conceptualization, W.-S.K., J.-H.K., and J.-H.L.; methodology, S.-W. Choi and H.-S.K.; analysis, W.-S.K., S.-W. Choi, and J.-H.L.; writing—original draft preparation, W.-S.K. and J.-H.L.; writing review and editing, J.-H.K. and J.-H.L.; all authors have read and agreed to the published version of the manuscript.

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Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Declarations

Competing interests

All authors declare that they have no conflict of interest.

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References

- Abouzi MM, Pestka JJ. Simultaneous screening of fumonisin B1, aflatoxin B1, and zearalenone by line immunoblot: a computer-assisted multianalyte assay system. *J AOAC Int.* 1994;77:495–501.
- Appell M, Compton DL, Bosma WB. Raman Spectral analysis for rapid determination of zearalenone and alpha-zearalanol. *Spectrochimica Acta Part A Mol Biomol Spectroscopy.* 2022;270:120842.
- Barrett TW. Laser Raman spectra of mono-, oligo- and polysaccharides in solution. *Spectrochim Acta a.* 1981;37:233–9.
- Belton PS. New methods for monitoring changes in proteins. *Food Rev Int.* 1993;9:551–73.
- Bennett JW, Klich M. Mycotoxins. *Clin Microbiol Rev.* 2003;16:497–516.
- Bourée JE, Godet C, Etemadi R, Drévilon B. Dual-mode plasma-enhanced chemical vapor deposition (PECVD) of polymer-like a-C: H films: vibrational and optical properties. *Synth Met.* 1996;76:191–4.
- Choi SW, Chang HJ, Lee N, Kim JH, Chun HS. Detection of mycoestrogen zearalenone by a molecularly imprinted polypyrrole-based surface plasmon resonance (SPR) sensor. *J Agric Food Chem.* 2009;57:1113–8.

- Darra NE, Gambacorta L, Solfrizzo M. Multimycotoxins occurrence in spices and herbs commercialized in Lebanon. *Food Control*. 2019;95:63–70.
- De Saeger S, Sibanda L, Van Peteghem C. Analysis of zearalenone and α -zearalenol in animal feed using high-performance liquid chromatography. *Anal Chim Acta*. 2003;487:137–43.
- Delwiche SR. High-speed bichromatic inspection of wheat kernels for mold and color class using high-power pulsed LEDs. *Sens Instrum Food Qual*. 2008;2:103–10.
- Delwiche SR, Hareland GA. Detection of scab-damaged hard red spring wheat kernels by near-infrared reflectance. *Cereal Chem*. 2004;81:643–9.
- Dowell FE, Ram MS, Seitz LM. Predicting Scab, Vomitoxin, and Ergosterol in Single Wheat Kernels Using Near-Infrared Spectroscopy. *Cereal Chem*. 1999;76:573–6.
- Duley WW, Williams DA. A 3.4 micron absorption band in amorphous carbon Implications for interstellar dust. *MNRAS*. 1983;205:67–70.
- Gordon SH, Wheeler BC, Schudy RB, Wicklow DT, Greene RV. Neural network pattern recognition of photoacoustic FTIR spectra and knowledge-based techniques for detection of mycotoxigenic fungi in food grains. *J Food Prot*. 1998;61:221–30.
- Green JHS, Harrison DJ, Kynaston W. Vibrational spectra of benzene derivatives—XIV: mono substituted phenols. *Spectrochim Acta A*. 1971;27:2199–217.
- Jones TJ, Hyland AR, Allen DA. 3 μ m spectroscopy of IRS7 towards the Galactic Centre. *MNRAS*. 1983;205:187–91.
- Josephs RD, Schuhmacher R, Kraska R. International interlaboratory study for the determination of the Fusarium mycotoxins zearalenone and deoxynivalenol in agricultural commodities. *Food Addit Contam*. 2001;18:417–30.
- Kacuráková M, Mathlouthi M. FTIR and laser-Raman spectra of oligosaccharides in water: characterization of the glycosidic bond. *Carbohydr Res*. 1996;284:145–57.
- Korolevich MV, Zhabankov RG, Sivchik VV. Calculation of absorption band frequencies and intensities in the IR spectrum of α -D-glucose in a cluster. *J Mol Struct*. 1990;220:301–13.
- Kraska R, Welzig E, Berthiller F, Molinelli A, Mizaikoff B. Advances in the analysis of mycotoxins and its quality assurance. *Food Addit Contam*. 2005;22:345–53.
- Li-Chan ECY. The applications of Raman spectroscopy in food science. *Trends Food Sci Technol*. 1996;7:361–70.
- Minervini F, Dell'Aquila ME, Maritato F, Minoia P, Visconti A. Toxic effects of the mycotoxin zearalenone and its derivatives on in vitro maturation of bovine oocytes and 17 beta-estradiol levels in mural granulosa cell cultures. *Toxicol in Vitro*. 2001;15:489–95.
- Minervini F, Giannoccaro A, Fornelli F, Dell'Aquila ME, Minoia P, Visconti A. Influence of mycotoxin zearalenone and its derivatives (α and β zearalenol) on apoptosis and proliferation of cultured granulosa cells from equine ovaries. *Reprod Biol Endocrinol*. 2006;4:62.
- Nava D, Rajmankina de Parada T, González E, Boscàn N, De la cruz C. An infrared spectroscopic comparison of cis- and trans-CH=CH and vinyl CH=CH₂ group frequencies of some hexenes, heptenes, and stereospecific and non-stereospecific polybutadienes. *Spectrochim Acta A Mol Biomol*. 1996;52:1201–10.
- Pallaroni LL, von Holst C. Determination of zearalenone from wheat and corn by pressurized liquid extraction and liquid chromatography-electrospray mass spectrometry. *J Chromatogr A*. 2003;993:39–45.
- Pettersson H, Åberg L. Near infrared spectroscopy for determination of mycotoxins in cereals. *Food Control*. 2003;14:229–32.
- Potts WJ, Nyquist RA. Factors affecting the out-of-plane hydrogen deformation frequencies in olefins and their derivatives. *Spectrochim Acta*. 1959;15:679–708.
- Schaafsma AW, Nicol RW, Savard ME, Sinha RC, Reid LM, Rottinghaus G. Analysis of Fusarium toxins in maize and wheat using thin layer chromatography. *Mycopathologia*. 1998;142:107–13.
- Schrader B, Dippel B, Fendel S, Keller S, Löchte T, Riedl M, Schulte R, Tatsch E. spectroscopy—a new tool in medical diagnostics. *J Mol Struct*. 1997;408:23–31.
- Scotter CNG. Non-destructive spectroscopic techniques for the measurement of food quality. *Trends Food Sci Technol*. 1997;8:285–92.
- Shaw RA, Wieser H, Dutler R, Rauk A. Vibrational optical activity of (S)-1-d-ethanol. *J Am Chem Soc*. 1990;112:5401–10.
- Takemura H, Shimb J-Y, Sayamac K, Tsubura A, Zhue BT, Shimoi K. Characterization of the estrogenic activities of zearalenone and zeranin in vivo and in vitro. *J Steroid Biochem Mol Biol*. 2007;103:170–7.
- Tanaka T, Yoneda A, Inoue S, Sugiura Y, Ueno Y. Simultaneous determination of trichothecene mycotoxins and zearalenone in cereals by gas chromatography–mass spectrometry. *J Chromatogr A*. 2000;882:23–8.
- Vasko PD, Blackwell J, Koenig JL. Infrared and raman spectroscopy of carbohydrates. *Carbohydr Res*. 1972;23:407–16.
- Wexler AS. Integrated intensities of absorption bands in infrared spectroscopy. *Appl Spectrosc Rev*. 1967;1:29–98.
- Yu KH, Rhee JM, Lim J-H, Yu S-C. Raman study of the intermolecular interactions between thermotropic liquid-crystalline oligomers: comparison of the effect of Poly(Propylene Oxide) and Poly(Ethylene Oxide). *Bull Korean Chem Soc*. 2002;23:633–6.
- Zhang W, Wang H, Wang J, Li X, Jiang H, Shen J. Multiresidue determination of zeranin and related compounds in bovine muscle by gas chromatography/mass spectrometry with immunoaffinity cleanup. *J AOAC Int*. 2006;89:1677–81.
- Zinedine A, Soriano JM, Moltó JC, Mañes J. Review on the toxicity, occurrence, metabolism, detoxification, regulations and intake of zearalenone: an oestrogenic mycotoxin. *Food Chem Toxicol*. 2007;45:1–18.

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