Synthesis of Silsesquioxanes with Methacryloyloxy and Phenyl Groups Using Corn Stover Ash as the Major Precursor

Wenlong Liu, a,b Xingwen Zhang, b,* Hongyu Ren, c,* Xingcheng Hu, b Xinyu Yang, b Baize Zhu, b and Hui Liu a,*

To address the challenges associated with corn stover utilization and the synthesis of phenyl- and methacryloyloxy-based silsesquioxanes (SQs) with difficulty and poor controllability, the authors present a novel approach that combines advanced biorefining techniques and innovative chemical synthesis methods. Spirocyclic alkoxysilane synthesized from corn stover ash was subsequently utilized for the synthesis of phenylSQs. The resulting phenylSQs were then subjected to fluorine ion-catalyzed rearrangement with 3-(trimethoxysilyl)propyl methacrylate (KH570) to yield SQs containing phenyl and methacryloyloxy functional groups. Through manipulating the ratio of phenylSQs and KH570, the authors successfully achieved a desired ratio of functional groups on individual SQ cages. Optimization of the ratio significantly impacted product collection, with a range of 5.5:1 to 8.5:1 recommended for efficient and effective synthesis. This study represents an important advancement in the field of high-value conversion of biomass, offering an easy means of tailoring the structure of phenyl- and methacryloyloxy-based cage SQs.

DOI: 10.15376/biores.18.2.3827-3837

Keywords: Corn stover ash; Corn straw; Biomass; Bioresources; Silsesquioxanes; Biosilica

Contact information: a: School of Energy Science and Engineering, Harbin Institute of Technology, No. 92, West Dazhi Street, Harbin 150001, China; b: School of Chemistry and Chemical Engineering, Harbin Institute of Technology, No. 92, West Dazhi Street, Harbin 150001, China; c: College of Resources and Environment, Northeast Agriculture University, No. 600, Changjiang Street, Harbin 150001, China; * Corresponding authors: zhangxingwen@hit.edu.cn; renhongyu@163.com; liuhui@hit.edu.cn

INTRODUCTION

Corn is one of the most important food crops in the world. Globally, corn ranks among the top in terms of planted area and production. With the development of the economy and the improvement of people’s living standards, the demand for corn is increasing, and the corresponding production of corn stover is also increasing each year. According to statistics, the annual corn stover production in China exceeds 216 million tons (Okoye et al. 2023). Most of the corn stover is still disposed of by open burning (Zhou et al. 2017; Zhang et al. 2023), which leads to serious environmental pollution and waste of biomass resources (Hong et al. 2016; Li et al. 2016; Pan et al. 2021). Therefore, the resource utilization of corn stover has become an issue of great concern to the agricultural and environmental protection sectors (Wang et al. 2010; Ren et al. 2019). The research and development of high value-added technology of corn stover resources has also become an important topic in the field of scientific research.
At the same time, with the progress of science and technology, the aerospace industry is rapidly developing. Among many aerospace materials, cage type silsesquioxanes (SQs) are expensive silica-based polymers because of their high melting point, low volatility, and good thermal stability (Baney et al. 1995; Loy and Shea 1995; Joshi 2008). Cage-type SQs are composed of an inorganic skeleton core with silicon-oxygen bonds and an outer layer of diverse substituents (R) groups (Du et al. 2020).

The number of silicon-oxygen bonds in the inorganic skeleton varies, which in turn affects the size and symmetry of the core of the cage-types of SQs, resulting in differences in the properties of the SQs. The outer R-groups are often organic groups, which can be hydrogen, vinyl, alkyl, phenyl, phenylene, or their derivatives (Cordes et al. 2010; Zhang et al. 2016). The R-groups on a single SQ cage can be identical or composed of different groups, which can be either inert or reactive. The R-groups usually determine the stability, solubility, and compatibility of the SQs structure (Zhang and Müller 2013). The difference in R groups thus determines that such molecules are highly designable.

The type and number of R-groups on SQs have a great influence on the properties of SQs. The synthesis, isolation, and characterization of single R-groups have been well investigated in numerous studies. However, there have been relatively few studies on single SQs cages containing multiple functional groups, and on the regulation of the ratio of functional groups on single SQs cages.

In this study, spirocyclic alkoxysilane first was synthesized using corn stover ash as the precursor. After that, phenylSQs were prepared using spirocyclic alkoxysilane as the reactant. Finally, SQs with phenyl and methacryloyloxy functional groups were successfully synthesized by fluorine ion-catalyzed rearrangement of phenylSQs and KH570. Additionally, the modulation of the ratio of functional groups on individual SQ cages was achieved by adjusting the ratio of phenylSQs and KH570.

Biomass-derived silicon has several potential advantages over using pure reagents. First, biomass is a renewable and abundant resource, whereas pure reagents often require energy-intensive processing and have limited availability. Second, biomass-derived silicon is typically more cost-effective than pure reagents, making it an attractive alternative for industries seeking to reduce costs. Third, the use of biomass-derived silicon can help reduce waste and promote sustainability by converting a waste product (corn stover) into a valuable material. Despite these potential advantages, there are also challenges associated with using biomass as the source of silicon. For example, the purity and quality of the silicon may be lower than that obtained from pure reagents.

EXPERIMENTAL

Materials

Methanol, ethanol, hexane, tetrahydrofuran, dichloromethane, tetrabutyl ammonium fluoride, calcium chloride, 3-(trimethoxysilyl)propyl methacrylate (KH570), and 2-methyl-2,4-pentanediol were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Corn stover ash was received from the Xing Fu Farm (Qiqihar, China). It was synthesized via natural combustion of corn stover in a heating stove under air atmosphere. The BET surface area of corn stover ash is ~10 m²/g.
Methods

Synthesis of spirocyclic alkoxysilane and phenylSQs

Spirocyclic alkoxysilane was synthesized from corn stover ash using a reported method (Liu et al. 2023). In brief, 500 g of corn stover ash was introduced into a 2-L three-necked flask. Subsequently, 1.2 L of 2-methyl-2,4-pentanediol were added to the flask, and the mixture was stirred for 30 min to ensure a homogeneous dispersion of the corn stover ash in the 2-methyl-2,4-pentanediol. The reaction proceeded at 180 °C under a nitrogen atmosphere and was stirred for 48 h to facilitate the formation of spirocyclic alkoxysilane. After the reaction, the spirocyclic alkoxysilane and 2-methyl-2,4-pentanediol mixture were collected through distillation. The mixture was then washed with 1.2 L of hexane and three separate portions of 1.2 L of water. The hexane layer was collected, and sodium sulfate was added to facilitate drying. The sodium sulfate was subsequently filtered out, and the resulting filtrate was placed in a rotary evaporator to remove the hexane solvent. Finally, the desired product, spirocyclic alkoxysilane, was obtained. The yield of the product was 0.67 g per gram of corn stover ash used as the starting material. The phenylSQs was then prepared using spirocyclic alkoxysilane as a precursor by the method reported in the literature (Furgal and Laine 2016).

Synthesis of SQs with phenyl and methacryloyloxy groups

Firstly, 1 g of KH-570 was taken separately in five clean three-necked flasks. Afterwards, phenylSQs were added to the three-necked flasks at mass ratios of 4.5:1, 5.5:1, 6.5:1, 7.5:1, and 8.5:1 of phenylSQs:KH-570. Then, 150 mL of tetrahydrofuran and 1 mL of 1 mol/L tetrabutylammonium fluoride as tetrahydrofuran solution were added to each flask and stirred magnetically for 5 days.

Afterwards, 2 g of CaCl₂ was added to each three-necked flask and the reaction continued for 36 h. The insoluble material was removed by filtration and the filtrate was collected. The solvent was removed from the filtrate by distillation under reduced pressure. Afterwards, 15 mL of tetrahydrofuran was added to the concentrated product to dissolve it completely. The dissolved mixture was added dropwise to 300 mL of methanol solution. At this point, a white powder was seen in the methanol solution. The white product was collected by filtration and dried in a vacuum drying oven.

Characterization

The chemical structure of the spirocyclic alkoxysilane obtained was examined using mass spectrometry (MS, Waters Quattro Premier XE, Milford, MA, USA). The chemical structure of the silsesquioxanes obtained was examined using matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra (Bruker Autoflex III Smartbeam, Bruker, Bremen, Germany).

RESULTS AND DISCUSSION

Synthesis of Spirocyclic Alkoxysilane

The mass spectrometry method was used for characterizing the structure of the product. Figure 1 shows the mass spectrum of spirocyclic alkoxysilane, the mass spectrum of the product synthesized from corn stover ash.
The signal at 261.2 (m/z) corresponded to the molecular weight of spirotcyclic alkoxyalsilane (H⁺ adduct). The signal at 278.4 (m/z) was ascribed to the molecular weight of spirotcyclic alkoxyalsilane (NH₄⁺ adduct). The signal at 283.4 (m/z) was due to the molecular weight of spirotcyclic alkoxyalsilane (Na⁺ adduct). The signal at 299.1 (m/z) was assigned to the molecular weight of spirotcyclic alkoxyalsilane (K⁺ adduct). This confirms the product to be spirotcyclic alkoxyalsilane.

![Mass spectrum of spirotcyclic alkoxyalsilane](image_url)

**Fig. 1. Mass spectrum of spirotcyclic alkoxyalsilane**

**Synthesis of Phenylsilsesquioxanes**

Figure 2 shows the mass spectrum of phenylSQs. The signal at 1056.8 (m/z) corresponded to the molecular weight of (C₆H₅)₈(SiO₁.₅)₈ (Na⁺ adduct). The signal at 1072.2 (m/z) was ascribed to the molecular weight of (C₆H₅)₈(SiO₁.₅)₈ (K⁺ adduct). The signal at 1314.5 (m/z) was assigned to the molecular weight of (C₆H₅)₁₀(SiO₁.₅)₁₀ (Na⁺ adduct). The signal at 1331.0 (m/z) corresponded to the molecular weight of (C₆H₅)₁₀(SiO₁.₅)₁₀ (K⁺ adduct). The signal at 1573.2 (m/z) was ascribed to the molecular weight of (C₆H₅)₁₂(SiO₁.₅)₁₂ (Na⁺ adduct). Among them, (C₆H₅)₈(SiO₁.₅)₈ (Na⁺ adduct) exhibited the highest relative intensity of the signal peak. PhenylSQs are the SQs compounds with (C₆H₅)SiO₃/₂ as the repeating unit. The common structures in phenylSQs are (C₆H₅)₈(SiO₁.₅)₈, (C₆H₅)₁₀(SiO₁.₅)₁₀, and (C₆H₅)₁₂(SiO₁.₅)₁₂ etc. The above results indicate that the spirotcyclic alkoxyalsilane synthesized from corn stover ash can further synthesize phenylSQs.
Fig. 2. Mass spectrum of phenylSQs

Synthesis of SQs with Phenyl and Methacryloyloxy Groups

When the mass ratio of the reactants of phenylSQs and KH570 was 8.5:1, the mass spectra of the synthesized products were as shown in Fig. 3. The signal at 1364.2 (m/z) corresponded to the molecular weight of [CH$_2$=C(CH$_3$)COOC$_3$H$_6$] (C$_6$H$_5$)$_9$(SiO$_{1.5}$)$_{10}$ (Na$^+$ adduct). The signal at 1314.3 (m/z) was ascribed to the molecular weight of (C$_6$H$_5$)$_{10}$(SiO$_{1.5}$)$_{10}$ (Na$^+$ adduct). The signal at 1622.4 (m/z) corresponded to the molecular weight of [CH$_2$=C(CH$_3$)COOC$_3$H$_6$](C$_6$H$_5$)$_{11}$(SiO$_{1.5}$)$_{12}$ (Na$^+$ adduct). From Fig. 3, the signal peak of (C$_6$H$_5$)$_{10}$(SiO$_{1.5}$)$_{10}$ (Na$^+$ adduct) had the highest relative intensity. Further, the signals of the molecular ion peaks of T$_{10}$SQ and T$_{12}$SQ containing single methacryloyloxy group are obvious. The above results indicate that the product contained [CH$_2$=C(CH$_3$)COOC$_3$H$_6$](C$_6$H$_5$)$_9$(SiO$_{1.5}$)$_{10}$, [CH$_2$=C(CH$_3$)COOC$_3$H$_6$](C$_6$H$_5$)$_{11}$(SiO$_{1.5}$)$_{12}$ and (C$_6$H$_5$)$_{10}$(SiO$_{1.5}$)$_{10}$. No signal peak of caged SQ containing more than one methacryloyloxy group was seen in the spectrum. This phenomenon can be related to the large proportion of the reactant phenylSQs. This is because the large proportion of phenylSQs may result in a low proportion of KH570 hydrolysis units available for combination during fluoride ion rearrangement. This leads to a low probability of multiple KH570 hydrolysis units colliding and binding in the same cage at the same time. When the mass ratio of phenylSQs and KH570 exceeds 8.5:1, a large amount of white precipitate will be present in the reaction system. Thus, this ratio of reactants results in a large amount of waste of phenylSQs and post-treatment difficulties.
When the mass ratio of the reactants of phenylSQs and KH570 was 7.5:1, the mass spectra of the synthesized products were as shown in Fig. 4. The signal at 1414.2 (m/z) corresponded to the molecular weight of [CH$_2$=C(CH$_3$)COOC$_6$H$_5$]$\text{[CH}_2\text{]}$2(C$_6$H$_5$)$_6$(SiO$_{1.5}$)$_{10}$ (Na$^+$ adduct). The signal at 1364.3 (m/z) was assigned to the molecular weight of [CH$_2$=C(CH$_3$)COOC$_6$H$_5$](C$_6$H$_5$)$_9$(SiO$_{1.5}$)$_{10}$ (Na$^+$ adduct). The signal at 1314.3 (m/z) corresponded to the molecular weight of (C$_6$H$_5$)$_{10}$(SiO$_{1.5}$)$_{10}$ (Na$^+$ adduct). The signal at 1622.4 (m/z) was ascribed to the molecular weight of [CH$_2$=C(CH$_3$)COOC$_6$H$_5$]$_{-1}$ (SiO$_{1.5}$)$_{12}$ (Na$^+$ adduct). This indicates that the products contained (C$_6$H$_5$)$_{11}$- (SiO$_{1.5}$)$_{12}$ (Na$^+$ adduct). The signal at 1622.4 (m/z) was ascribed to the molecular weight of [CH$_2$=C(CH$_3$)COOC$_6$H$_5$] (C$_6$H$_5$)$_{11}$-(SiO$_{1.5}$)$_{12}$ (Na$^+$ adduct). This indicates that the product contained two methacryloyloxy groups in one SQ cage. However, the signal peaks of the SQ cage structure containing more than two methacryloyloxy groups were not seen in the spectrum. The main reason may be that as the proportion of phenylSQs in the reactants decreases, the probability of combination of two KH570 hydrolyzed monomers in the same cage during the rearrangement process increases. However, the probability that the three KH570 hydrolyzed monomers combine in the same cage during the reaction remains low under this set of reactant ratio conditions. This may also be one of the reasons why no molecular ion peak of the corresponding molecule was seen in the mass spectra.
Fig. 4. Mass spectrum of phenylSQs (7.5:1)

When the mass ratio of the reactants of phenylSQs and KH570 was 6.5:1, the mass spectra of the synthesized products were as shown in Fig. 5. The signal at 1466.0 (m/z) corresponded to the molecular weight of \([\text{CH}_2=\text{C(CH}_3\text{)}\text{COOC}_3\text{H}_6]_3(\text{C}_6\text{H}_5)7(\text{SiO}_{1.5})_{10} (\text{Na}^+ \text{ adduct})\). The signal at 1414.3 (m/z) was ascribed to the molecular weight of \([\text{CH}_2=\text{C(CH}_3\text{)}\text{COOC}_3\text{H}_6]_2(\text{C}_6\text{H}_5)_8(\text{SiO}_{1.5})_{10} (\text{Na}^+ \text{ adduct})\). The signal at 1364.4 (m/z) was assigned to the molecular weight of \([\text{CH}_2=\text{C(CH}_3\text{)}\text{COOC}_3\text{H}_6]_3(\text{C}_6\text{H}_5)_7(\text{SiO}_{1.5})_{10} (\text{Na}^+ \text{ adduct})\). The signal at 1314.2 (m/z) corresponded to the molecular weight of \([\text{CH}_2=\text{C(CH}_3\text{)}\text{COOC}_3\text{H}_6]_2(\text{C}_6\text{H}_5)_8(\text{SiO}_{1.5})_{10} (\text{Na}^+ \text{ adduct})\). The signal at 1622.4 (m/z) was ascribed to the molecular weight of \([\text{CH}_2=\text{C(CH}_3\text{)}\text{COOC}_3\text{H}_6]_3(\text{C}_6\text{H}_5)_7(\text{SiO}_{1.5})_{12} (\text{Na}^+ \text{ adduct})\). The above results indicate that the product contained \([\text{CH}_2=\text{C(CH}_3\text{)}\text{COOC}_3\text{H}_6]_3(\text{C}_6\text{H}_5)_7(\text{SiO}_{1.5})_{10}, (\text{C}_6\text{H}_5)_10 (\text{SiO}_{1.5})_{10}, [\text{CH}_2=\text{C(CH}_3\text{)}\text{COOC}_3\text{H}_6]_2(\text{C}_6\text{H}_5)_8(\text{SiO}_{1.5})_{10}, [\text{CH}_2=\text{C(CH}_3\text{)}\text{COOC}_3\text{H}_6]_3(\text{C}_6\text{H}_5)_7 (\text{SiO}_{1.5})_{10}, and [\text{CH}_2=\text{C(CH}_3\text{)}\text{COOC}_3\text{H}_6]_3(\text{C}_6\text{H}_5)_7(\text{SiO}_{1.5})_{12}\). However, the relative intensity of the signal peak of \([\text{CH}_2=\text{C(CH}_3\text{)}\text{COOC}_3\text{H}_6]_3(\text{C}_6\text{H}_5)_7(\text{SiO}_{1.5})_{12} (\text{Na}^+ \text{ adduct})\) was still the highest. The mass spectrum showed a \([\text{CH}_2=\text{C(CH}_3\text{)}\text{COOC}_3\text{H}_6]_3(\text{C}_6\text{H}_5)_7(\text{SiO}_{1.5})_{10} (\text{Na}^+ \text{ adduct})\) signal peak when the mass ratio of the reactants phenylSQs and KH570 was decreased to 7.5:1. However, the relative intensity of this signal peak was small. This suggests that there were three methacryloyloxy groups within a single SQ cage present in the product. Nevertheless, the mass spectrum did not exhibit signal peaks corresponding to SQ cage structures that contained over three methacryloyloxy groups. One possible explanation is that when the proportion of phenylSQs in the reactants decreases, it becomes more likely for three KH570 hydrolyzed monomers to combine within the same cage during the rearrangement process. However, the probability of four KH570 hydrolyzed monomers combining within the same cage during the reaction remains low under this reactant ratio condition. This could also be a contributing factor to the absence of a molecular ion peak for the corresponding molecule in the mass spectra.
When the mass ratio of the reactants of phenylSQs and KH570 was 5.5:1, the mass spectra of the synthesized products were as shown in Fig. 6. The signal at 1516.0 (m/z) corresponded to the molecular weight of [CH₂=C(CH₃)COOC₅H₈]₄(C₆H₅)₆(SiO₁.₅)₁₀ (Na⁺ adduct). The signal at 1466.0 (m/z) was ascribed to the molecular weight of [CH₂=C(CH₃)COOC₅H₈]₃(C₆H₅)₇(SiO₁.₅)₁₀ (Na⁺ adduct). The signal at 1414.4 (m/z) was assigned to the molecular weight of [CH₂=C(CH₃)COOC₅H₈]₂(C₆H₅)₈(SiO₁.₅)₁₀ (Na⁺ adduct). The signal at 1364.3 (m/z) corresponded to the molecular weight of [CH₂=C(CH₃)COOC₅H₈]₁(C₆H₅)₉(SiO₁.₅)₁₀ (Na⁺ adduct). The signal at 1314.2 (m/z) was ascribed to the molecular weight of (C₆H₅)₁₀(SiO₁.₅)₁₀ (Na⁺ adduct). The signal at 1622.4 (m/z) corresponded to the molecular weight of [CH₂=C(CH₃)COOC₅H₈] (C₆H₅)₁₁(SiO₁.₅)₁₂ (Na⁺ adduct). The signal at 1672.4 (m/z) was assigned to the molecular weight of [CH₂=C(CH₃)COOC₅H₈] (C₆H₅)₁₀(SiO₁.₅)₁₂ (Na⁺ adduct). This shows that the rearranged product contained [CH₂=C(CH₃)COOC₅H₈]₄(C₆H₅)₆(SiO₁.₅)₁₀, (C₆H₅)₁₀(SiO₁.₅)₁₀, [CH₂=C(CH₃)COOC₅H₈]₃(C₆H₅)₇(SiO₁.₅)₁₀, [CH₂=C(CH₃)COOC₅H₈]₂(C₆H₅)₈(SiO₁.₅)₁₀, [CH₂=C(CH₃)COOC₅H₈]₁(C₆H₅)₉(SiO₁.₅)₁₀, [CH₂=C(CH₃)COOC₅H₈] (C₆H₅)₁₀(SiO₁.₅)₁₂, and [CH₂=C(CH₃)COOC₅H₈] (C₆H₅)₁₁(SiO₁.₅)₁₂. The mass spectrum revealed the signal peak for [CH₂=C(CH₃)COOC₅H₈]₄(C₆H₅)₆(SiO₁.₅)₁₀ (Na⁺ adduct) when the mass ratio of phenylSQs and KH570 reagents was reduced to 5.5:1. Nevertheless, the magnitude of this signal peak was relatively low. This indicates that the product contained a single SQ cage with four methacryloyloxy groups, but the mass spectrum did not show any peaks for SQ cage structures with more than four methacryloyloxy groups. One possible explanation is that as the proportion of phenylSQs in the reactants decreases, it becomes more likely for four KH570 hydrolyzed monomers to combine within the same cage during the rearrangement process. However, the likelihood of five KH570 hydrolyzed monomers combining within the same cage remained low under these reactant ratio conditions. This could also contribute to the lack of a molecular ion peak for the corresponding molecule in the mass spectra. Subsequently, the authors decided to further decrease the mass ratio of the phenylSQs:KH570 to 4.5:1 in hopes of achieving a greater proportion of methacryloyloxy in one SQ cage. However, it was difficult to collect the product at this time. If the product can be collected, it would be mostly in a colloidal state.
Methacryloyloxy cage SQ synthesis generally faces two main challenges. Firstly, it is difficult to form a cage of the methacryloyloxy group with cage SQ type. Secondly, even after successful synthesis, isolating the product is difficult because of its physical state. In contrast, phenyl cage SQ exhibits excellent cage-forming properties, and the product can be conveniently isolated as a powder. Nonetheless, one of the drawbacks of phenyl cage SQ is its lack of active functional groups. SQ is predominantly employed as a resin modifier to modify its properties. Consequently, the phenyl cage SQ cannot chemically react with the resin, but it can only physically dope the resin. This may give rise to issues such as agglomeration and compatibility assessment. Accordingly, the aforementioned issues may be addressed through the catalytic rearrangement of phenylSQs and KH570 to synthesize cage SQs that contain two types of functional groups. This approach offers a promising solution to the identified problems. The method described herein has the potential to be utilized for the synthesis of cage SQs molecules that contain phenyl and other reactive functional groups. This may be accomplished through the replacement of other silane coupling agents with KH570, thus enabling the incorporation of desired functional groups into the resulting cage SQs. As such, this approach offers a versatile means of tailoring the properties of cage SQs for various applications.

CONCLUSIONS

1. This study successfully synthesized cage silsesquioxanes (SQs) containing phenyl and methacryloyloxy types of functional groups using corn stover ash as the major precursor. This marks a great achievement in the field of high-value conversion of biomass.

2. Manipulating the ratios of phenylSQs and the catalyst KH570 through fluorine ion-catalyzed rearrangement is an effective approach for modulating the ratio of two functional groups on cage SQs. In particular, an increase in the proportion of KH570
can improve the probability of obtaining the desired ratio of methacryloyloxy groups on a single cage.

3. The ratio of phenylSQs and KH570 has a large impact on the synthesis process and product collection. Based on the study results, it is recommended optimizing the ratio within the range of 5.5:1 to 8.5:1 for efficient and effective product collection.

4. This approach offers an easy means of tailoring the structure of phenyl and methacryloyloxy cage SQs. Therefore, this study holds important potential in the field of molecular design.

ACKNOWLEDGMENTS

The authors are grateful for the financial support of the Harbin Institute of Technology.

REFERENCES CITED


Article submitted: Feb. 28, 2023; Peer review completed: March 25, 2023; Revised version received: April 7; Accepted: April 14, 2023; Published: April 18, 2023. DOI: 10.15376/biores.18.2.3827-3837