Application of Synthetic Acyl Glucopyranosides for White-rot and Brown-rot Fungal Decay Resistance in Aspen and Pine Wood

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Due to its non-toxicity and environmentally friendly nature, carbohydrate-based fatty acid (CFA) esters are encouragingly used as antimicrobials and synthetic intermediates. They also are notably applied in food, surfactant, and pharmaceutical industries. In this respect, methyl 2,6-di-*O*-isopentanoyl-α-D-glucopyranoside (**2**), synthesized in a single step from methyl α-D-glucopyranoside (**1**), was converted into four other 3,4-di-*O*-acyl esters (**3** - **6**). All the newly synthesized CFA esters (**2** - **6**) were applied for the first time to study decay resistances of aspen (*Populus tremula*) and pine (*Pinus sibirica*) wood from decay caused by white-rot (*Polyporous versicolor* L.ex. Fr.) and brown-rot (*Postia placenta* (Fr). Cke.) fungi. Most of these CFA esters protected these woods from fungal attack, reduced deterioration, and preserved the weight percentage of woods at a certain point. It is noted that the CFA esters compounds reduced the deterioration and suppressed the weight percentage loss of wood at a certain point and from low to moderate decay resistances against the selected fungi.

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INTRODUCTION

An increase in environmental awareness, as well as new norms and policies, are driving more businesses to find alternative environmentally friendly materials (Boz *et al.* 2020). Due to their easy biodegradability (both under aerobic and anaerobic conditions), being environment-friendly, and easy availability, carbohydrate-based fatty acid (CFA) esters (acyl sugars or polyol esters) have been used in various fields including food, pharmaceutical, and personal care industries (Matin *et al.* 2020; Teng *et al.* 2021). Additionally, many synthetic and natural CFA esters showed pesticidal (*e.g.*, mites, aphids,

whitefly, psyllid, *etc.*) (Puterka and Severson 1995; Liu *et al.* 1996) and antimicrobial (Muhammad *et al.* 2021; Rahman *et al.* 2022) properties. In the pesticide activities, sugar esters initially dissolve pests' protective waxy coating, leading them to dry out (leakage) and finally to die (US EPA 2002). The CFA esters were produced as metabolites in some plants that are defensive against herbivores and fungal pathogens (*e.g.*, *Alternaria* sp. and *Fusarium* sp.) (Luu *et al.* 2017). More advanced research in this field revealed novel applications of these ester products. For example, in high amylose starch-based wood adhesive (HASWA) these CFA esters highly boost HASWA performance by blocking aggregation of latex particles with increased starch thermal stability (Zia-ud-Din *et al.* 2017).

Modification of the position, size, and length of acyl/ester group, as well as the sugar unit, imposes substantial variation in CFA esters' physical, pesticidal, and antimicrobial activities (Puterka *et al.* 2003; Islam *et al.* 2021a). Various esterification/ modification techniques have been developed and employed successfully (Islam *et al.* 2021b; Matin and Iqbal 2021). However, selective esterification of sugars faced multiple restrictions due to the inherent presence of several hydroxyl groups of almost similar reactivity (Demchenko 2003). In the present study, glucopyranoside esters are prepared with higher yield and selectivity by direct acylation technique under controlled conditions.

The drawbacks of most wood materials are that they tend to absorb moisture from the atmosphere, and this prolonged moisture easily becomes an attraction to fungi and termites. In addition, wood materials have changed their original color and thermal and biological instability (Amit *et al.* 2017). Due to the above-mentioned problem, wood modification is important to produce sustainable materials for the use in next generation. One of the fastest growing categories of materials in the wood business is plasticized or designed wood products, which are ecologically benign, have minimal moisture absorption, and have great resistance against fungi, insects, and UV radiation damage (Jirous-Rajkovic and Miklecic 2021). Plasticized and modified wood is widely utilized in automotive and construction industries, as well as in packing materials among other uses (Mohammed *et al.* 2015). Wood has been treated with several chemicals namely styrene, epoxy resins, urethane, phenol, formaldehyde, methyl methacrylate (MMA), and vinyl or acrylic monomers to improve physicomechanical and morphological properties (Rahman *et al.* 2017, 2018; Jones *et al.* 2020).

In addition, a catalyst is introduced to initiate the polymerization or modification of the wood cell wall (Dube and Salehpour 2013). Treated wood is more resistant to water absorption or resistance to decay, and it significantly increases mechanical characteristics (Rahman *et al.* 2017, 2018; Ferede 2020). Selected wood species, mainly pine and aspen, were chosen for this study. The main disadvantage of utilizing these species is their hydrophilic character, which causes water absorption and resultant product deformation (Kamaly *et al.* 2016; Sepe *et al.* 2018). To overcome this problem, all species were treated with newly synthesized CFA esters **2** through **6** (Fig. 1), as CFA esters are well known for hard water resistance, stabilizing, and foaming properties (Csoka *et al.* 2007) and effectively hinder wood starch/cellulose retrogradation by forming related complexes (Richardson *et al.* 2004). Therefore, the aim of this work is to compare the rate of decay and resistance of untreated and treated wood against the decay by brown- and white-rot fungi. The morphological properties of treated and untreated wood are also reported in this study. In addition, this is the first application of glucopyranoside esters on wood species for fungal decay resistance.

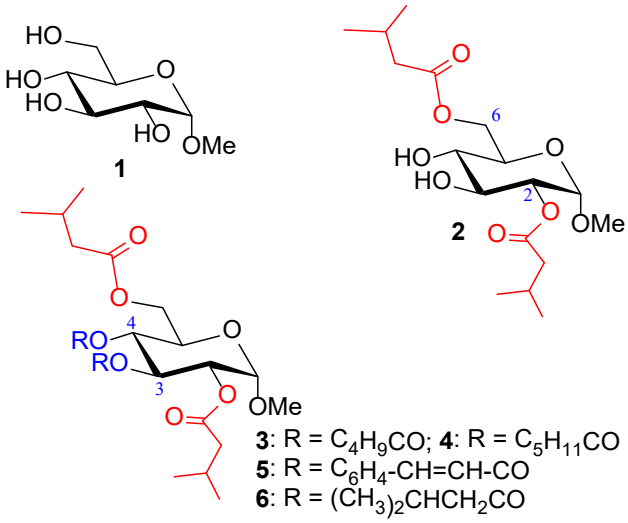


Fig. 1. Structures of the synthesized acyl glucopyranosides **2** through **6**

EXPERIMENTAL

Materials

Aspen (*Populus tremula*) and pine (*Pinus sibirica*) wood were obtained from Vyatka State University, Kirov, Russia Federation. White-rot (*Polyporous versicolor* L.ex. Fr.) ATCC No. 12679 and brown-rot (*Postia placenta* (Fr). Cke.) ATCC No. 11538 were used to study the decay resistances against the newly synthesized glucopyranoside esters, namely methyl 2,6-di-*O*-isopentanoyl-α-D-glucopyranoside (**2**), methyl 2,6-di-*O*-isopentanoyl-3,4-di-*O*-pentanoyl-α-D-glucopyranoside (**3**), methyl 3,4-di-*O*-hexanoyl-2,6-di-*O*-isopentanoyl-α-D-glucopyranoside (**4**), methyl 3,4-di-*O*-cinnamoyl-2,6-di-*O*-isopentanoyl-α-D-glucopyranoside (**5**), and methyl 2,3,4,6-tetra-*O*-isopentanoyl-α-D-glucopyranoside (**6**), which are shown in Fig. 1 and applied against the fungal decay resistance.

Methods

Analytical grade reagents and chemicals (Merck, Darmstadt, Germany) were used. Solvents were distilled before use. Evaporations were conducted at reduced pressure (Buchi rotary evaporator, R-100, Buchi Corrporation, New Castle, DE, USA). For characterization(s) of the synthesized compounds, Fourier transform infrared spectroscopy (FTIR, IR Prestige-21, Shimadzu, Kyoto, Japan), and nuclear magnetic resonance (NMR, ^{1}H: 400 MHz, ^{13}C: 400 MHz) (Bruker DPX-400 spectrometer, Billerica, MA, USA) spectra in deuterated chloroform ($CDCl_3$) solution were used. Correlation spectroscopy (COSY), distortionless enhancement by polarization transfer (DEPT-135), heteronuclear single quantum coherence (HSQC), and heteronuclear multiple bond correlation (HMBC) experiments of several synthesized samples were scanned in the same NMR machine at Wazed Miah Science Research Centre (WMSRC), Jahanginagar University, Savar, Dhaka, Bangladesh. In all cases, chemical shifts are reported in δ (delta) units (ppm). Coupling constant (J) values are reported in Hz (Hertz). For FTIR, wavelength (υ_{max}) is measured in wavenumbers (cm^{-1}) and measured between 5000 and 400 cm^{-1}.

Synthesis of Acyl Glucopyranosides 2 - 6

*Methyl 2,6-di-O-isopentanoyl-α-D-glucopyranoside (**2**)*

A solution of methyl α-D-glucopyranoside (**1**, 1.0 g, 5.15 mmol) in pyridine (15 mL) was cooled to -5 °C, whereupon isopentanoyl chloride (1.366 g, 11.329 mmol) was added drop-wise to this mixture and stirred at this temperature for 6 h. Additional stirring at room temperature for 4 h indicated the formation of a major product along with some mixtures. Usual workup, concentration of solvents, and column chromatography (CC) furnished the title compound **2** in reasonably good yield of 63% (1.175 g) as semi-solid. Its characteristic and spectroscopic data are as follows: R_f = 0.57 (with $CHCl_3$/MeOH = 5/1); FTIR (neat) υ_{max} (cm^{-1}): 3220 to 3450 (OH), 1733, 1722 (CO), 1097 (pyranose ring); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta_H$ppm: 4.90 (d, *J* = 3.6 Hz, 1H, H-1),4.68 (dd, *J* = 10.0 and 3.6 Hz, 1H, H-2), 4.46 (dd, *J* = 12.2 and 4.8 Hz, 1H, H-6a), 4.29 (dd, *J* = 12.2 and 1.6 Hz, 1H, H-6b), 3.95 (t, *J* = 9.6 Hz, 1H, H-3), 3.73 to 3.78 (m, 1H, H-5), 3.42 (t, *J* = 9.6 Hz, 1H, H-4), 3.37 (s, 3H, OC*H*$_3$), 3.15 to 3.22 (br s, 2H, 2 × O*H*), 2.26 to 2.30 [m, 4H, 2 × $(CH_3)_2$CHC*H*$_2$CO], 2.08 to 2.16 [m, 2H, 2 × $(CH_3)_2$C*H*CH_2CO], 0.98, and 0.97 [2 × s, 2 × 6H, 2 × (C*H*$_3$)$_2$CHCH$_2$CO]; ^{13}C NMR (100 MHz, $CDCl_3$) $\delta_C$ppm: 173.9, 173.0 [2 × $(CH_3)_2$CHCH$_2$*C*O], 97.1 (C-1), 72.9 (C-2), 71.3 (C-3), 70.6 (C-5), 69.4 (C-4), 62.9 (C-6), 55.2 (O*C*H$_3$), 43.2(2) [2 × $(CH_3)_2$CH*C*H$_2$CO], 25.8, 25.7 [2 × $(CH_3)_2$*C*HCH$_2$CO], 22.4(2), 22.3 and 22.2 [2 × (*C*H$_3$)$_2$CHCH$_2$CO]. The position of NMR-signals was confirmed by analyzing its COSY, DEPT-135, HSQC, and HMBC experiments.

*General method for the preparation of 3,4-di-O-acylates **3**-**6** of diisopentanoate **2***

To prepare 3,4-di-*O*-acyl esters of **2**, four different acyl halides were used, employing the direct method. In this method **2** (0.2 g, 0.552 mmol) was initially dissolved in pyridine, cooled to 0 °C. The acylating agent was then added followed by the addition of catalytic amount of 4-dimethylamino pyridine (DMAP). Stirring was continued until the completion of the reaction for several hours at 25 °C. The reaction mixture was then quenched with water and extracted with organic solvent (dichloromethane, DCM). Workup, concentration of solvents, and purification through silica gel CC (gradient elution with *n*-hexane to *n*-hexane-EA) gave the desired glucopyranoside esters **3** - **6** in reasonably good yield(s). In all cases, the position of signals was confirmed by analyzing their COSY, DEPT-135, HSQC, and HMBC experiments.

*Methyl 2,6-di-O-isopentanoyl-3,4-di-O-pentanoyl-α-D-glucopyranoside (**3**)*

This compound is obtained as thick liquid in 93%. Its R_f is 0.52 (*n*-hexane/EA = 4/1). Its spectroscopic data are as follows: FTIR (neat) υ_{max} (cm^{-1}): 1750, 1747, 1743, 1733 (CO), 1091 (pyranose ring); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta_H$ppm: 5.48 (t, *J* = 10.0 Hz, 1H, H-3), 5.05 (t, *J* = 10.0 Hz, 1H, H-4), 4.92 (d, *J* = 3.6 Hz, 1H, H-1), 4.85 (dd, *J* = 9.6 and 3.6 Hz, 1H, H-2), 4.10 to 4.19 (m, 2H, H-6a,b), 3.94 to 3.98 (m, 1H, H-5), 3.37 (s, 3H, OC*H*$_3$), 2.15 to 2.32 [m, 8H, 2 × $(CH_3)_2$CHC*H*$_2$CO and 2 × $CH_3(CH_2)_2$C*H*$_2$CO], 2.01 to 2.10 [m, 2H, 2 × $(CH_3)_2$C*H*CH_2CO], 1.46 to 1.58 [m, 4H, 2×CH_3CH_2C*H*$_2CH_2$CO], 1.24 to 1.31 [m, 4H, 2 × CH_3C*H*$_2(CH_2)_2$CO], 0.83 to 0.94 [m, 18H, 2 × (C*H*$_3$)$_2$CHCH$_2$CO and 2 × C*H*$_3(CH_2)_3$CO]; ^{13}C NMR (100 MHz, $CDCl_3$) $\delta_C$ppm: 172.6(2), 172.2(2) [2 × $(CH_3)_2$CHCH$_2$*C*O and 2 × C_4H_9*C*O], 96.8 (C-1), 70.7 (C-2), 69.6 (C-3), 68.3 (C-4), 67.3 (C-5), 61.8 (C-6), 55.3 (O*C*H$_3$), 43.1(2) [2 × $(CH_3)_2$CH*C*H$_2$CO], 33.8, 33.7 [2 × $CH_3(CH_2)_2$*C*H$_2$CO], 26.9, 26.7 (2 × CH_3CH_2*C*H$_2CH_2$CO), 25.6, 25.4 [2 ×

$(CH_3)_2CHCH_2CO$], 22.3(2), 22.2(3), 22.1 [2 × $(CH_3)_2CHCH_2CO$ and 2 × $CH_3CH_2(CH_2)_2CO$], and 13.7(2) [2 × $CH_3(CH_2)_3CO$].

*Methyl 2,6-di-O-isopentanoyl-3,4-di-O-hexanoyl-α-D-glucopyranoside (**4**)*

Compound **4** is obtained as thick syrup in 90% yield. Its R_f is 0.54 (*n*-hexane/EA = 4/1). Its spectroscopic data are as follows: FTIR (neat) υ_{max} (cm^{-1}): 1747, 1736, 1743, 1733 (CO), 1097 (pyranose ring); ^1H NMR (400 MHz, $CDCl_3$) $\delta_H$ppm: 5.32 (t, *J* = 10.0 Hz, 1H, H-3), 4.93 (d, *J* = 3.6 Hz, 1H, H-1), 4.87 (t, *J* = 10.0 Hz, 1H, H-4), 4.49(dd, J = 12.4 and 4.4 Hz, 1H, H-6a), 4.38 (dd, *J* = 9.6 and 3.6 Hz, 1H, H-2), 3.82 to 3.88 (m 1H, H-6b), 3.52-3.58 (m, 1H, H-5), 3.41 (s, 3H, OCH_3), 2.22 to 2.42 [m, 8H, 2 × $(CH_3)_2CHCH_2CO$ and 2 × $CH_3(CH_2)_3CH_2CO$], 2.08 to 2.16 [m, 2H, 2 × $(CH_3)_2CHCH_2CO$], 1.56 to 1.70 [m, 4H, 2 × $CH_3(CH_2)_2CH_2CH_2CO$], 1.25 to 1.37 [m, 8H, 2 × $CH_3(CH_2)_2(CH_2)_2CO$], 0.33 to 1.00 [m, 18H, 2 × $(CH_3)_2CHCH_2CO$ and 2 × $CH_3(CH_2)_4CO$]; ^{13}C NMR (100 MHz, $CDCl_3$) $\delta_C$ppm: 174.7, 173,5, 173.0, 172.3 [2 × $(CH_3)_2CHCH_2CO$ and 2 × $C_5H_{11}CO$],96.9 (C-1),70.4 (C-2), 70.3 (C-3), 69.8 (C-4), 69.6 (C-5), 62.6 (C-6), 55.3 (OCH_3), 43.3, 43.1 [2× $(CH_3)_2CHCH_2CO$], 34.3, 34.1 [2 × $CH_3(CH_2)_3CH_2CO$], 31.3, 31.1 (2 × $CH_3(CH_2)_2CH_2CH_2CO$), 25.7(2) [2 × $(CH_3)_2CHCH_2CO$], 24.6(2), 22.4(3), 22.3, 22.2(2) [2 × $(CH_3)_2CHCH_2CO$ and 2 × $CH_3(CH_2)_2(CH_2)_2CO$], and 13.9(2) [2 × $CH_3(CH_2)_4CO$].

*Methyl 3,4-di-O-cinnamoyl-2,6-di-O-isopentanoyl-α-D-glucopyranoside (**5**)*

This compound **5** is isolated as white solid (mp 197-199 °C) in 85% yield. It has R_f value 0.56 (*n*-hexane/EA = 4/1). Its spectral data are as follows: FTIR (neat) υ_{max} (cm^{-1}): 1733, 1718, 1669, 1637 (CO), 1096 (pyranose ring); ^1H NMR (400 MHz, $CDCl_3$) $\delta_H$ppm: 7.46 to 7.51 (m, 4H, Ar-*H*), 7.38 to 7.42 (m, 6H, Ar-*H*), 6.50 (d, *J* = 16.0 Hz, 1H, =C*H*), 6.44 (d, *J* = 16.0 Hz, 1H, =C*H*), 6.40 (d, *J* = 15.6 Hz, 1H, =C*H*), 6.35 (d, *J* = 15.6 Hz, 1H, =C*H*), 5.88 (t, *J* = 9.8 Hz, 1H, H-3), 5.40 (t, *J* = 9.8 Hz, 1H, H-4), 5.10 to 5.18 (m, 2H, H-1 and H-2), 4.39 to 4.43 (m, 1H, H-6a), 4.18 to 4.28 (m, 2H, H-5 and H-6b), 3.48 (s, 3H, OCH_3), 2.10 to 2.30 [m, 6H, 2 × $(CH_3)_2CHCH_2CO$], 0.90 to 1.00 [m, 12H, 2 × $(CH_3)_2CHCH_2CO$]; ^{13}C NMR (100 MHz, $CDCl_3$) $\delta_C$ppm: 172.7, 172.4 [2 × $(CH_3)_2CHCH_2CO$], 166.1, 166.0 (2 × $C_6H_5CH=CHCO$), 146.5, 146.4, 146.0, 145.6 (2 × *C*H=*C*H), 134.2(4), 1305, 130.4, 128.8(3), 128.3(2), 128.2 (Ar-*C*), 97.1 (C-1), 71.3 (C-2), 70.0 (C-3), 69.0 (C-4), 67.6 (C-5), 62.2 (C-6), 55.4 (OCH_3), 43.2(2) [2 × $(CH_3)_2CHCH_2CO$], 25.8, 25.6 [2 × $(CH_3)_2CHCH_2CO$], 22.4(2), 22.3, and 22.2 [2 × $(CH_3)_2CHCH_2CO$].

*Methyl 2,3,4,6-tetra-O-isopentanoyl-α-D-glucopyranoside (**6**)*

Compound **6** is separated as clear syrup in 94% yield with R_f value 0.53 (*n*-hexane/EA = 4/1). Its spectral data are characterized as- FTIR (neat) υ_{max} (cm^{-1}): 1750, 1740, 1733, 1713 (CO), 1093 (pyranose ring); ^1H NMR (400 MHz, $CDCl_3$) $\delta_H$ppm: 5.55 (t, *J* = 9.8 Hz, 1H, H-3), 5.10 (t, *J* = 9.8 Hz, 1H, H-4), 4.98 (d, *J* = 3.6 Hz, 1H, H-1), 4.86 (dd, *J* = 10.0 and 3.6 Hz, 1H, H-2), 4.16 to 4.19 (m, 2H, H-6a,b), 3.97 to 4.01 (m, 1H, H-5), 3.41 (s, 3H, OCH_3), 1.99 to 2.26 [m, 12H, 4 × $(CH_3)_2CHCH_2CO$], 0.91 to 0.98 [m, 24H, 4 × $(CH_3)_2CHCH_2CO$]; ^{13}C NMR (100 MHz, $CDCl_3$) $\delta_C$ppm: 172.7, 172.2, 171.8, 171.5 [4 × $(CH_3)_2CHCH_2CO$], 96.8 (C-1), 71.0 (C-2), 69.4 (C-3), 68.3 (C-4), 67.4 (C-5), 61.8 (C-6), 55.4 (OCH_3), 43.2, 43.1(2), 43.0 [4 × $(CH_3)_2CHCH_2CO$], 25.6, 25.5, 25.4, 25.3 [4 × $(CH_3)_2CHCH_2CO$], 22.4(4), 22.3(2), and 22.2(2) [4 × $(CH_3)_2CHCH_2CO$].

Sample Preparation

The two wood (aspen and pine) specimens were cut into small pieces of approximately 2 g, with a dimension of 5 mm (width) × 5 mm (length) × 1 mm (thickness). Each of the samples was conditioned to air-dry in a room with a relative humidity of 60% and ambient temperature of approximately 25 °C for a month prior to testing. The white- and brown-rot fungi (Merck, Darmstadt, Germany) were cultivated and were applied to the sample, and left for a month. The wood samples were again weighed and tabulated.

Laboratory Testing of Fungal Decay Resistance

The ASTM D2017-05 (2001) standard method was used to conduct the decay resistance test. Highly resistant heartwood experiences 1.0 to 10 wt% loss, resistance wood 11 to 24 wt% loss, moderately resistant wood 25 to 44 wt% loss, and non-resistance wood experiences loss higher than 45 wt%, according to the ASTM D2017-05 (2001) scale.

Scanning Electron Microscopy with Energy Dispersive Spectroscopy

The samples were scanned using scanning electron microscopy (SEM) and energy dispersive X-ray/spectroscopy (EDX/EDS). The wood samples were examined at a 100x magnification. In addition, a few random spots on the surface of the wood samples were chosen. The elemental composition percentages of the samples were scanned and analysed by automated software (ESPRIT 2, Bruker, Version 2, Billerica, MA, USA). The EDX/EDS was performed many times on each sample at various stages, with the most representative results chosen. A Hitachi TM4000Plus tabletop microscope with a Quantax75TM Series Energy Dispersive X-ray spectrometer (Hitachi Ltd., Tokyo, Japan) was used for the SEM and EDX/EDS analyses of the wood samples to investigate the composition and surface structure.

Fourier Transform Infrared (FTIR) Analysis

The FTIR 'IRAffinity-1' spectroscope (Shimadzu, Kyoto, Japan) was used. The IR spectrum bands from 4000 to 400 cm^{-1} were used to identify the molecular bond structures and the functional groups of the wood specimens. The IR solution software (Shimadzu, v.1.5, Kyoto, Japan) was used to plot the FTIR spectrum.

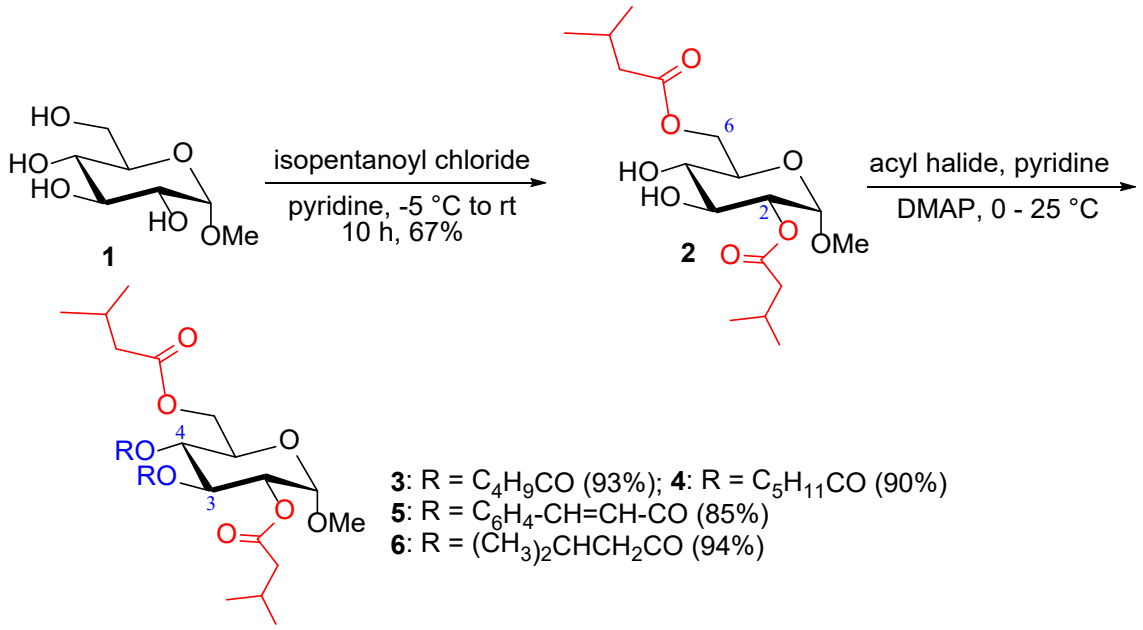
RESULTS AND DISCUSSION

Selective Acrylation of Glucopyranoside: Preparation of 2 Through 6

Initially, dimolar isopentanoylation of methyl α-D-glucopyranoside (**1**) in pyridine at low temperature (-5 °C) was completed that furnished a clear semi-solid mass (Scheme 1). The FTIR analysis of this product revealed the addition of the carbonyl group in the molecule. The ^{1}H NMR indicated the incorporation of 18 extra protons, and ^{13}C NMR indicated the attachment of two carbonyl carbons and eight aliphatic carbons corresponding to two isopentanoyl groups.

Additionally, H-2 and H-6 protons shifted considerably downfield compared to their precursor glucoside **1** (Matin *et al.* 2019; Islam *et al.* 2021b), indicating the attachment of isopentanoyl groups at C-2 and C-6 positions. This was further confirmed by its HMBC experiments where -CO groups correlated to H-2 and H-6 protons. Based on complete spectral analyses (DEPT, COSY, and HSQC), the semi-solid was named as methyl 2,6-di-*O*-isopentanoyl-α-D-glucopyranoside (**2**, Scheme 1).). Formation of **2** also provided the

regioselectivity information of glucopyranoside **1,** which is that 6-OH and 2-OH are more reactive than 3-OH and 4-OH.



Scheme 1. Synthesis of novel 2,6-di-*O*-isopentanoylglucopyranoside esters **2** - **6**

In the next step, the isopentanoate **2** upon dimolar pentanoylation in dry pyridine furnished a thick liquid in excellent yield. The FTIR spectrum indicated the absence of hydroxyl band(s). Its ^{1}H NMR indicated the presence of 18 additional protons in comparison to isopentanoate **2**, informing the attachment of two pentanoyl moieties in the molecule. The ^{13}C NMR, COSY, DEPT, HMBC, and HSQC spectral analyses confirmed the attachment of two new petanoyl groups at C-3 and C-4 positions, and hence, the compound was assigned as methyl 2,6-di-*O*-isopentanoyl-3,4-di-*O*-pentanoyl-α-D-glucopyranoside (**3**, Fig. 1).

Similarly, isopentanoate **2** was separately treated with hexanoyl chloride, cinnamoyl chloride, and isopentanoyl chloride, which upon purification and spectroscopic analyses was established as **4**, **5**, and **6** (Scheme 1), respectively.

Weight Loss Percentage Due to Fungal Attack

Figure 2 shows that the weight loss occurred because of fungal attack. Based on Fig. 2, pine wood showed that methyl 2,3,4,6-tetra-*O*-pentanoyl-α-D-glucopyranoside (**6**) and methyl 3,4-di-*O*-hexanoyl-2,6-di-*O*-isopentanoyl-α-D-glucopyranoside (**4**) provided extra protection against fungal attack, compared with other acyl glucosidic compounds and their raw wood. However, 14% weight loss was exhibited on pine wood after a month of fungal attack compared with the original raw wood. According to the finding, it is clear that methyl 2,3,4,6-tetra-*O*-pentanoyl-α-D-glucopyranoside (**6**) and methyl 3,4-di-*O*-hexanoyl-2,6-di-*O*-isopentanoyl-α-D-glucopyranoside (**4**) strongly resist the fungal decay of this wood. Moreover, for aspen wood, methyl 2,3,4,6-tetra-*O*-pentanoyl-α-D-glucopyranoside (**6**) showed strong decay resistance against fungi compared with other acyl glucosides. It is noted that 16% weight loss was revealed after a month of decay test. Based on this observation, the newly synthesized compounds, methyl 2,3,4,6-tetra-*O*-

pentanoyl-α-D-glucopyranoside (**6**) showed strong decay resistance against fungi for pine and aspen wood species, whereas other compounds showed moderate resistance against fungi for both species (Broda 2020).

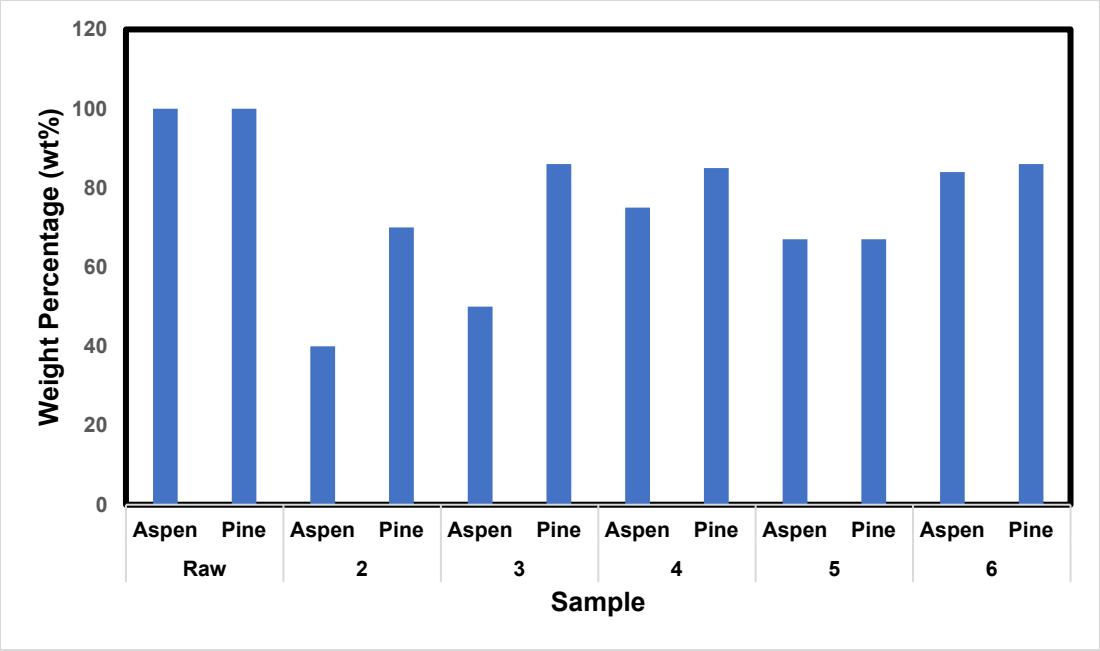


Fig. 2. Weight loss percentage of each wood sample with different acyl glucoside compound

Morphological Properties

Figures 3 to 7 show that the aspen and pine wood treated with methyl 2,6-di-*O*-isopentanoyl-α-D-glucopyranoside (**2**), methyl 2,6-di-*O*-isopentanoyl-3,4-di-*O*-pentanoyl-α-D-glucopyranoside (**3**), methyl 3,4-di-*O*-hexanoyl-2,6-di-*O*-isopentanoyl-α-D-glucopyranoside (**4**), methyl 3,4-di-*O*-cinnamoyl-2,6-di-*O*-isopentanoyl-α-D-glucopyranoside (**5**), and methyl 2,3,4,6-tetra-*O*-pentanoyl-α-D-glucopyranoside (**6**) after the fungal attack.

Figure 8 displays the raw aspen and pine wood after the fungal attack. In Fig. 8, the rough surfaces for both wood species after the fungal attack are noticeable. It can be attributed to the cellulose degradation after fungal attack. However, glucoside **4**-modified aspen and pine showed a smooth surface due to the substantial protection against the decay by fungi.

Moreover, Figs. 5 and 7 indicate a minimal surface area of rough surface on aspen and pine species, which were treated by glucosides **4** and **6**, respectively. This is due to the strong resistance against decay by both compounds. The results showed that 3,4-di-*O*-hexanoyl ester **4** and 2,3,4,6-tetra-*O*-pentanoyl ester **6** are applicable for decay resistance. Meanwhile, 2,6-di-*O*-isopentanoyl ester **2** and 3,4-di-*O*-cinnamoyl ester **5** resulted in moderate decay resistance against the fungi and are shown in Figs. 3 and 5, respectively. The fungi usually attack the weak hemicellulose, cellulose, and lignin structure, while the oil and waxy structures are perserved (Mahilrajan *et al.* 2014; Nazzaro *et al.* 2017).

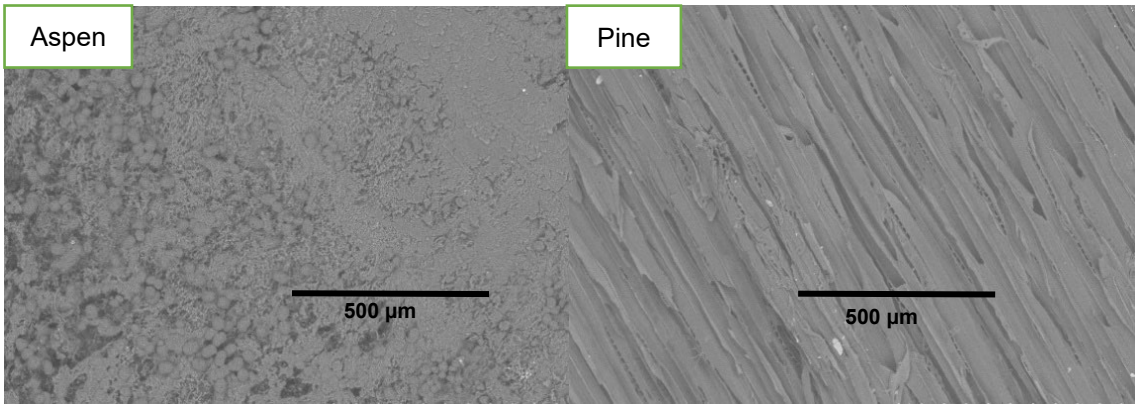


Fig. 3. SEM images of treated aspen and pine with methyl 2,6-di-*O*-isopentanoyl-α-D-glucopyranoside (**2**) after fungal attack

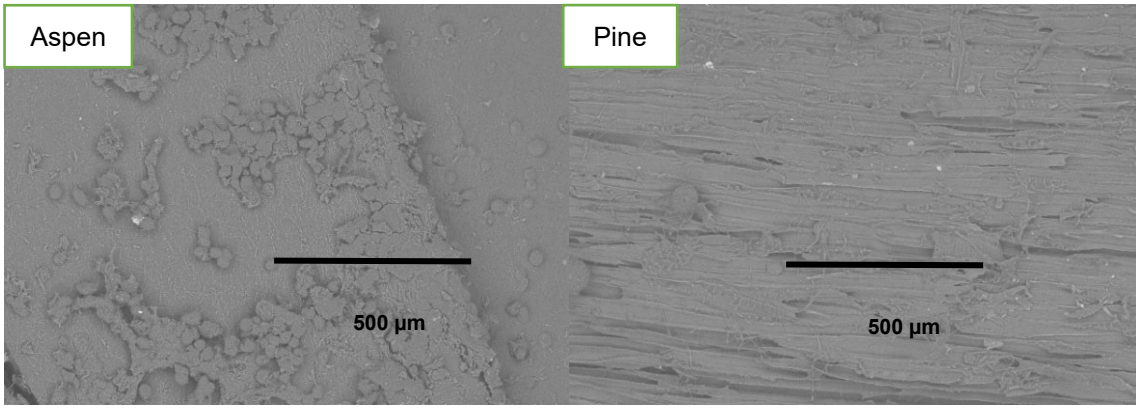


Fig. 4. SEM images of treated aspen and pine with 2,6-di-*O*-isopentanoyl-3,4-di-*O*-pentanoyl-glucopyranoside **3** after fungi attack

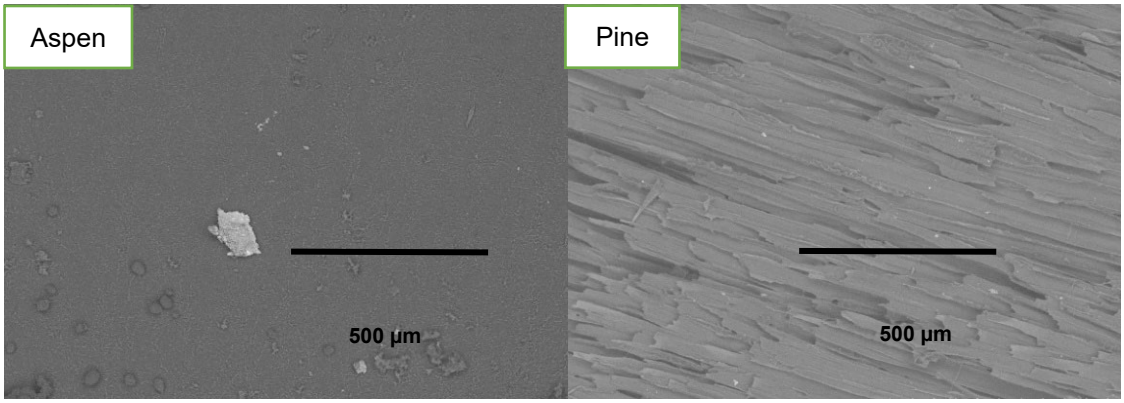


Fig. 5. SEM images of treated aspen and pine with 3,4-di-*O*-hexanoyl-2,6-di-*O*-isopentanoyl-glucopyranoside **4** after fungi attack

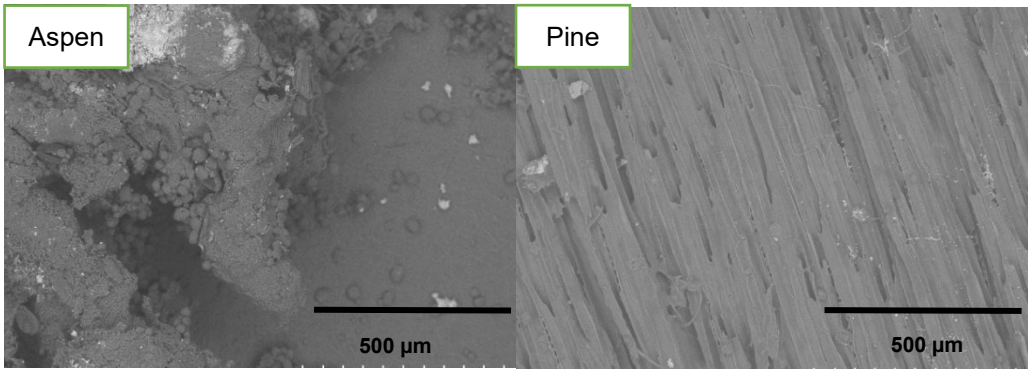


Fig. 6. SEM images of treated aspen and pine with glucopyranoside ester **5**

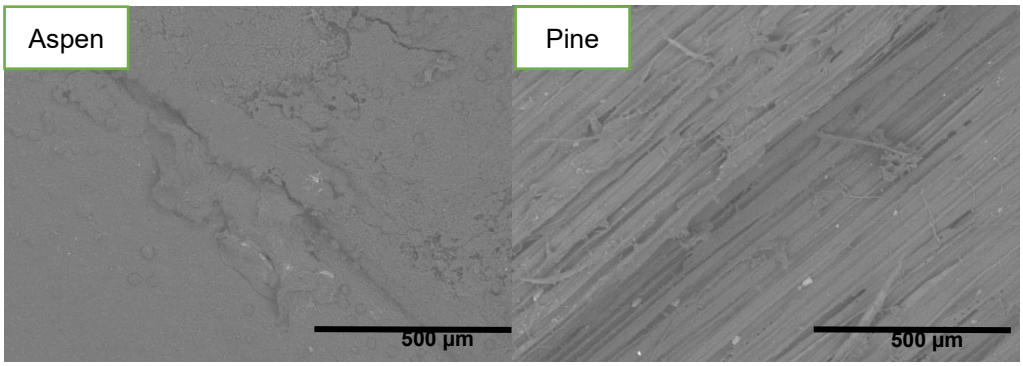


Fig. 7. SEM images of treated aspen and pine with methyl 2,3,4,6-tetra-*O*-pentanoyl-α-D-glucopyranoside (**6**) after fungi attack

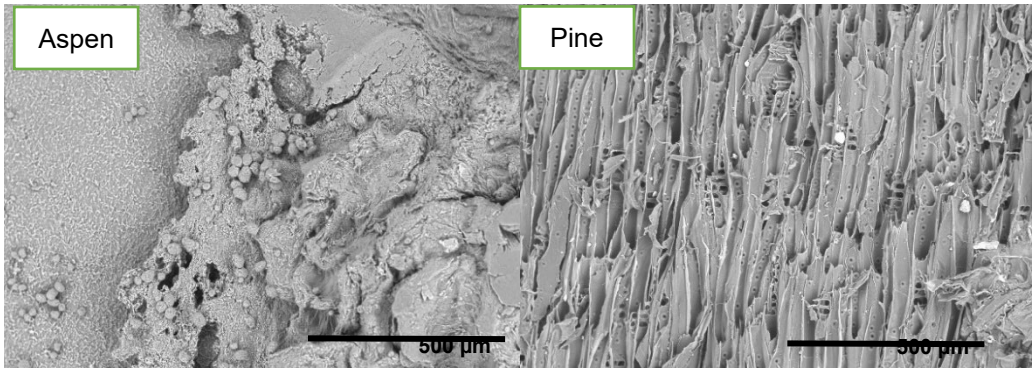


Fig. 8. SEM images of raw aspen and pine after fungi attack

Elemental Properties

Tables 1 and 2 show the elemental compositions of treated aspen and pine wood with compounds **2**, **3**, **4**, **5**, and **6**, along with the raw aspen and pine wood after the fungal attack. It is noted that most of the wood, either raw or coated with the chemical compound, contains mainly carbon and oxygen. It is noticed that the aspen treated with glucopyranoside-**2** contained elements calcium (Ca), sulfur (S), sodium (Na), and phosphorus (P). The presence of these elements was due to the deterioration of cellulose, hemicellulose, and lignin, which was due to nutrient conversion for the fungal digestion (Goodell *et al.* 2020). Therefore, fungal attack caused a reduction in the weight of the wood sample.

Table 1. Elemental Properties of Different Glucopyranoside Esters Treated and Raw Aspen

Compound	Element	Mass (%)	Mass Norm (%)	Atom (%)
2	**C**	56.62	56.62	63.84
	O	42.08	42.08	35.62
	Ca	0.62	0.62	0.21
	S	0.28	0.28	0.11
	Na	0.24	0.24	0.14
	P	0.15	0.15	0.07
3	**C**	54.94	54.94	62.60
	O	41.97	41.97	35.91
	Na	1.09	1.09	0.65
	S	0.97	0.97	0.41
	P	0.52	0.52	0.23
	Cl	0.50	0.50	0.19
4	**C**	49.87	49.87	57.37
	O	48.08	48.08	41.52
	Na	1.35	1.35	1.35
	S	0.71	0.71	0.71
5	**C**	55.43	55.43	62.81
	O	42.62	42.62	36.25
	Na	1.35	1.35	0.80
	Fe	0.60	0.60	0.15
6	**C**	51.84	51.84	59.27
	O	46.23	46.23	39.68
	Na	1.27	1.27	0.79
	Fe	0.66	0.66	0.29
Raw	**C**	53.89	53.89	62.23
	O	43.10	43.10	36.68
	Na	1.40	1.40	0.83
	S	0.60	0.60	0.26

Table 2. Elemental Properties of Different Glucopyranoside Esters Treated and Raw Pine

Compound	Element	Mass (%)	Mass Norm (%)	Atom (%)
2	**C**	54.94	54.94	61.89
	O	45.06	45.06	38.11
3	**C**	61.19	61.19	67.74
	O	38.82	38.82	32.26
4	**C**	57.83	57.83	64.63
	O	42.17	42.17	35.37
5	**C**	62.23	62.23	68.70
	O	37.76	37.76	31.30
6	**C**	58.59	58.59	65.75
	O	39.61	39.61	33.37
	Si	0.98	0.98	0.47
	Al	0.82	0.82	0.41
Raw	**C**	56.62	56.62	63.81
	O	42.24	42.24	35.73
	S	0.67	0.67	0.28
	Cl	0.47	0.47	0.18

Infrared Spectral Properties

Figures 9 through 13 display the FTIR spectra of **2**, **3**, **4**, **5,** and **6** glucopyranosides-treated aspen and pine wood species after fungal attack. The peak intensity at 3200 to 3400 cm^{-1} represents the -OH group in the sample specimen.

Figures 10 through 12 show that there is no peak corresponding to the -OH appearing in the spectrum due to the modified cellulose by the above-mentioned compounds, except **4**. However, -C-H stretching was observed with peak intensities 2922, 2926, 2924, and 2931 cm^{-1} for glucopyranoside esters **3**-, **4**-, **5**-, and **6**-treated wood samples, whereas -C-H stretching did not appear for the glucopyranoside **2**-treated sample. This is due to the prolonged fungal attack, which completely deteriorated the wood specimen.

It is also noted that most of the peak was diminished in the wood sample treated with compound **2**, which causes a reduction in wood weight. Further, fungi reduce moisture, hemicellulose, cellulose, and lignin contents from the wood samples because they use it for their food (Bari *et al.* 2021).

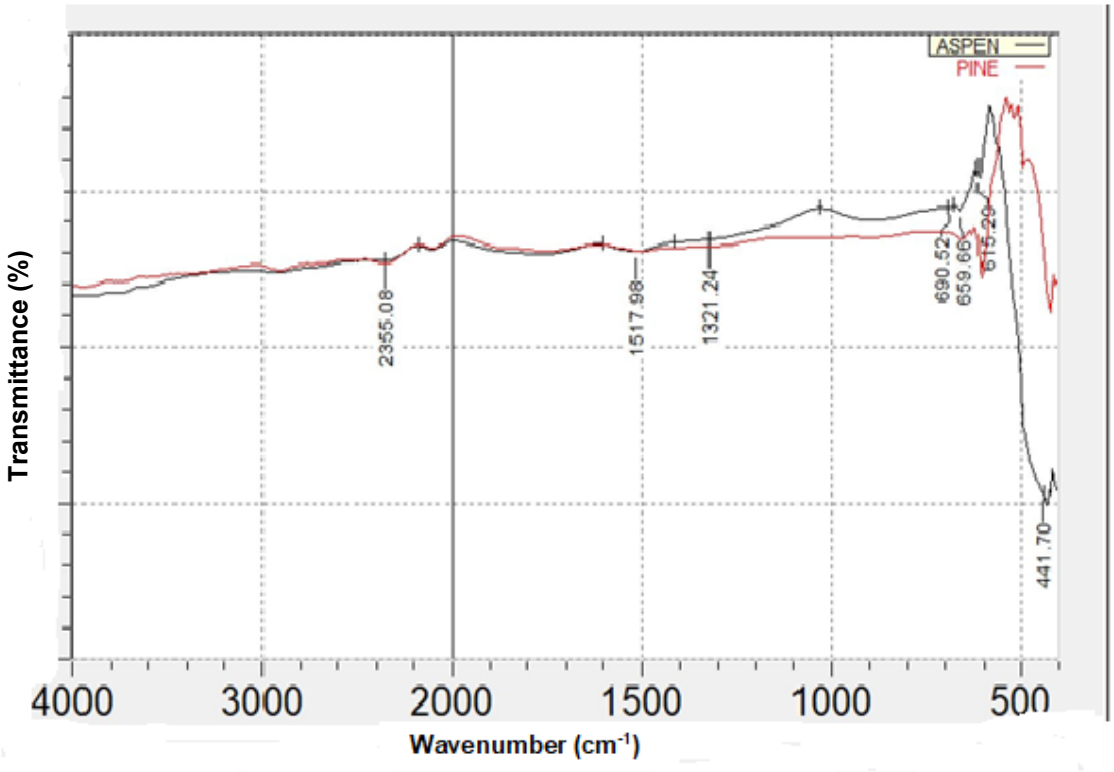


Fig. 9. The FTIR spectrum of methyl 2,6-di-*O*-isopentanoyl-α-D-glucopyranoside (**2**)-treated aspen and pine

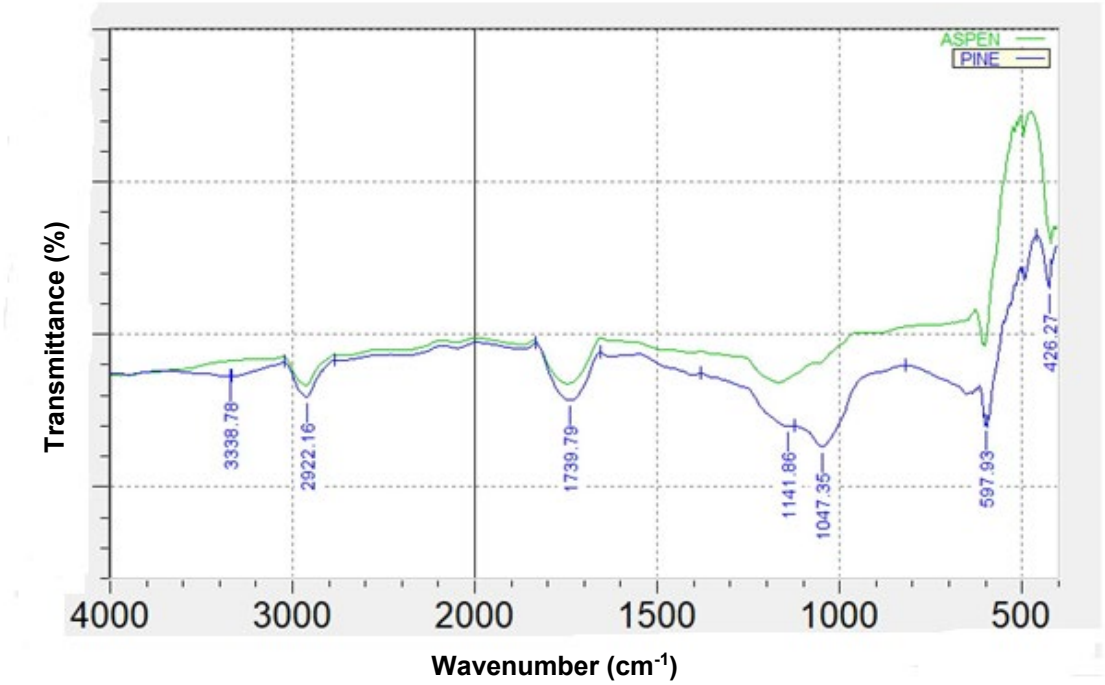


Fig. 10. The FTIR spectrum of methyl 3,4-di-*O*-hexanoyl-2,6-di-*O*-isopentanoyl-α-D-glucopyranoside (**4**)-treated aspen and pine

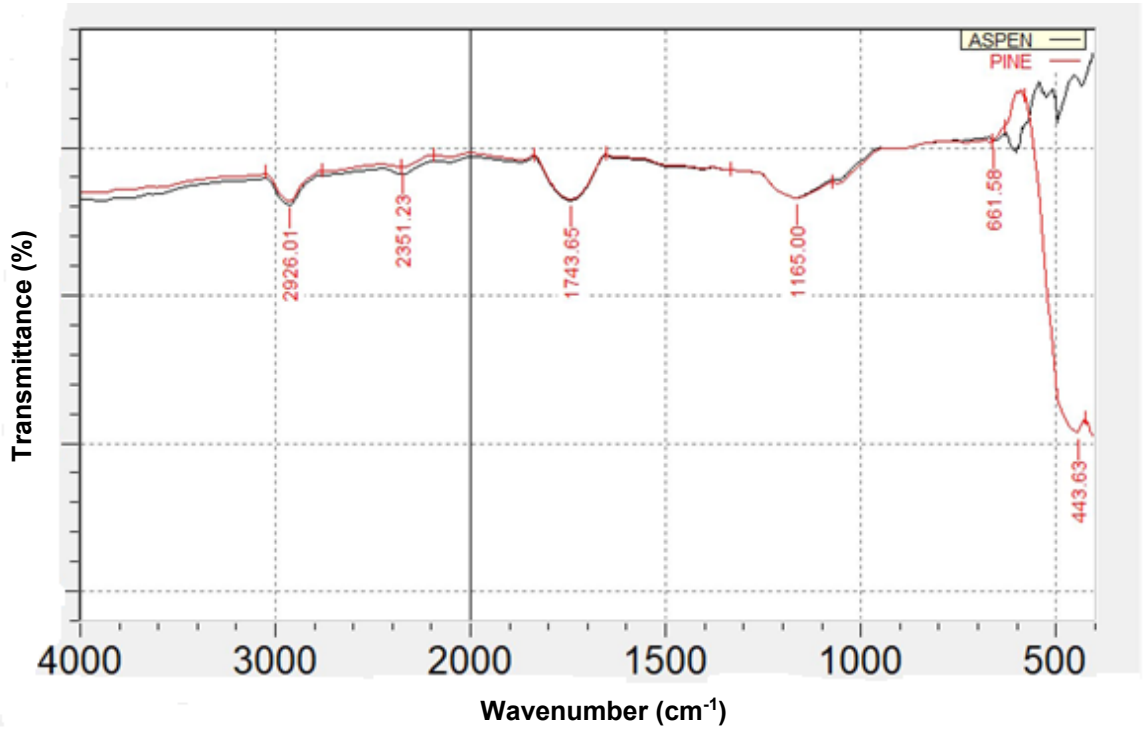


Fig. 11. The FTIR spectrum of methyl 2,6-di-*O*-isopentanoyl-3,4-di-*O*-pentanoyl-α-D-glucopyranoside (**3**)-treated aspen and pine

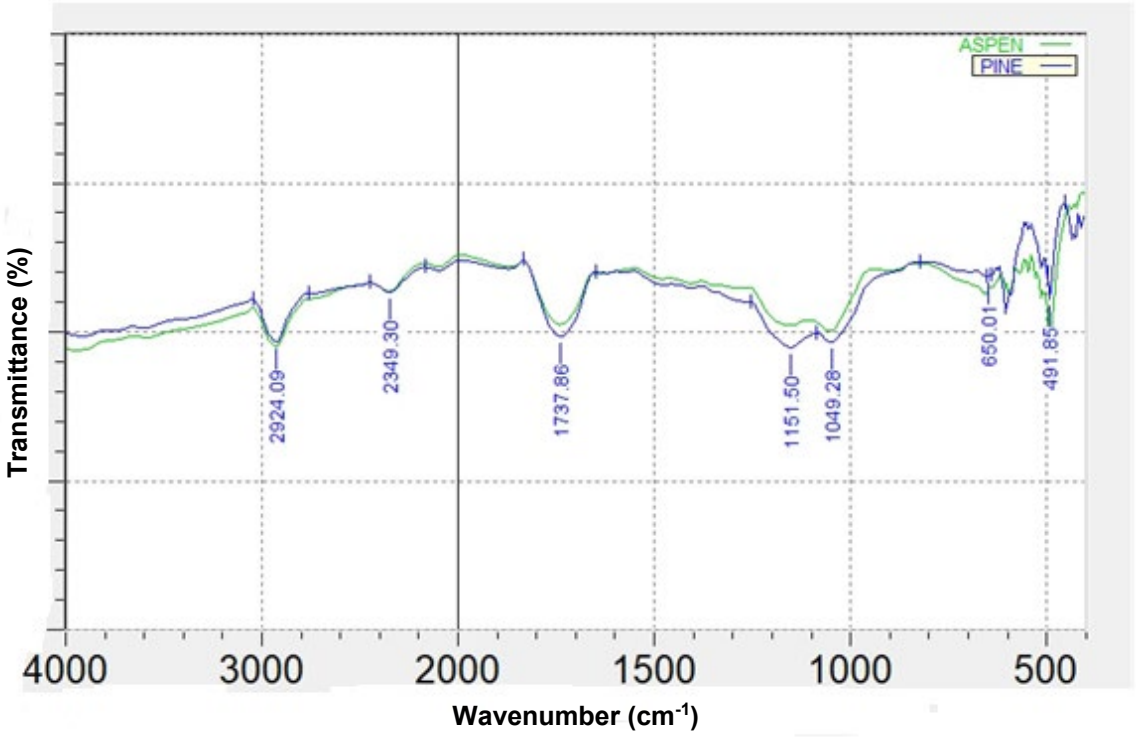


Fig. 12. The FTIR spectrum of methyl 3,4-di-*O*-cinnamoyl-2,6-di-*O*-isopentanoyl-α-D-glucopyranoside (**5**)-treated aspen and pine

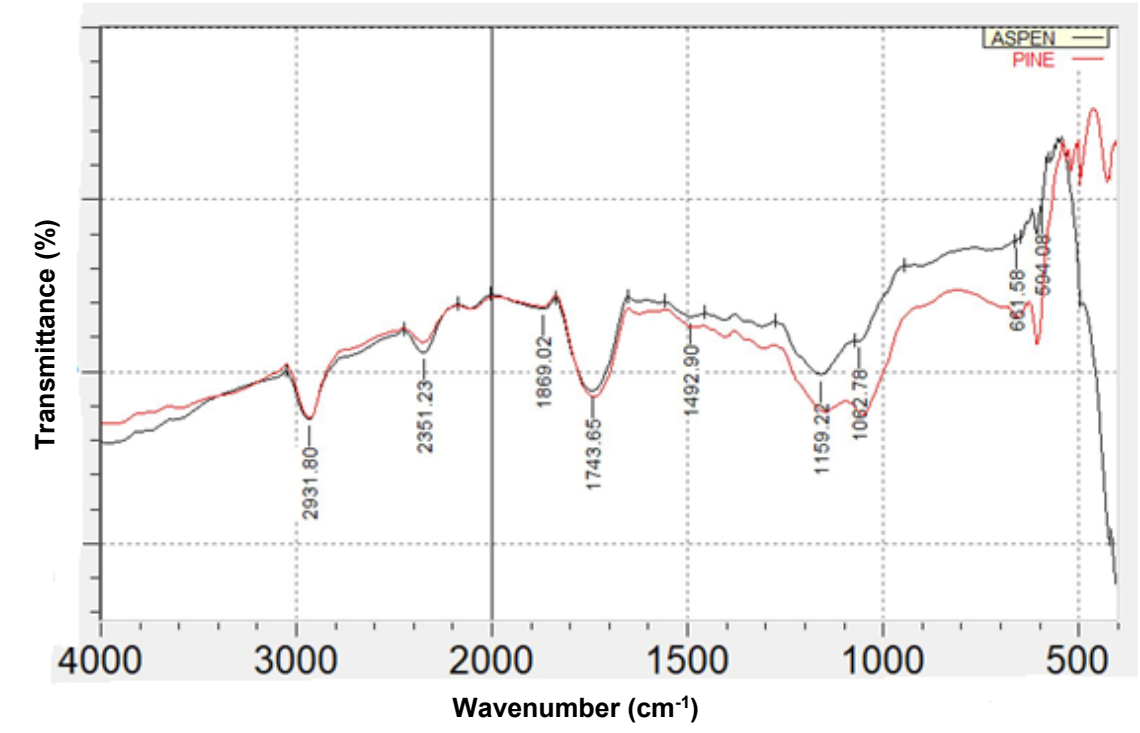


Fig. 13. The FTIR spectrum of methyl 2,3,4,6-tetra-*O*-pentanoyl-α-D-glucopyranoside (**6**)-treated aspen and pine

CONCLUSIONS

A novel application of glucopyranoside esters **2** - **6** for the decay resistances of aspen (*Populus tremula*) and pine (*Pinus sibirica*) wood against white-rot and brown-rot fungi was evaluated successfully in this study.

1. Initially, the glucopyranoside-based sugar esters **2** - **6** were synthesized with selectivity in high yields from methyl α-D-glucopyranoside (**1**). Application of these compounds on aspen and pine wood protects the wood from fungal attacks.
2. It was observed that methyl 2,3,4,6-tetra-*O*-pentanoyl-α-D-glucopyranoside (**6**), methyl 2,6-di-*O*-isopentanoyl-3,4-di-*O*-pentanoyl-α-D-glucopyranoside (**3**), and methyl 3,4-di-*O*-hexanoyl-2,6-di-*O*-isopentanoyl-α-D-glucopyranoside (**4**) compounds reduced the deterioration and suppressed the weight percentage loss of wood at a certain point.
3. In addition, the methyl 2,6-di-*O*-isopentanoyl-α-D-glucopyranoside (**2**), and methyl 3,4-di-*O*-cinnamoyl-2,6-di-*O*-isopentanoyl-α-D-glucopyranoside (**5**) showed moderate decay resistances against the selected fungi.

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