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Effects of Carbohydrates on the Hydrodeoxygenation of Lignin-Derived Phenolic Compounds

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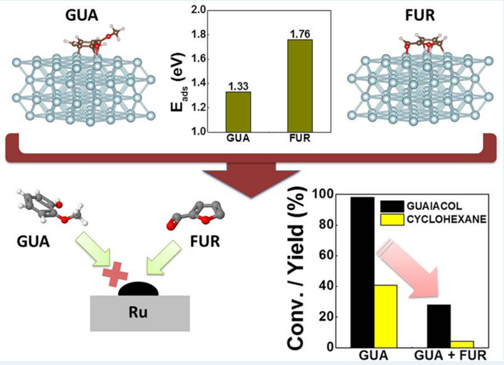
Supporting Information

ABSTRACT: Simulating lignocellulose-derived pyrolysis oil, the effects of carbohydrate derivatives on the hydrodeoxygenation of lignin-derived phenolic compounds, guaiacol in this study, were observed using supported ruthenium catalysts. Among several carbohydrate derivatives which possibly exist in the pyrolysis oil, the addition of furfural and 5-hydroxymethylfurfural (5-HMF) significantly decreased the conversion of guaiacol, with density functional theory (DFT) calculations indicating that guaiacol competes with furfural and 5-HMF to adsorb onto the ruthenium nanoparticle surface, thus suppressing the hydrogenation of guaiacol.



KEYWORDS: *hydrodeoxygenation, guaiacol, furfural, 5-HMF, DFT, ruthenium catalysts*

INTRODUCTION

The thermochemical liquefaction of biomass, including lignocellulose, is a promising technique for producing small hydrocarbon molecules.[1] Depending on the feedstock, fast pyrolysis produces approximately 60−75 wt % of liquid bio-oil, which consists of lignin-derived aromatic and carbohydrate-derived nonaromatic oxygenates.[2,3] Subsequent upgrading processes of the bio-oil through hydrodeoxygenation (HDO) reactions are required to obtain valuable petroleum-like deoxygenated hydrocarbons. The complex nature of the bio-oil mixture, however, makes it difficult to develop efficient upgrading processes.

Carbohydrate-derived compounds in the bio-oil include hydroxyaldehydes, hydroxyketones, carboxylic acids, esters of complex organic acids, and long chain hydrocarbons.[2,4−6] The complex mixture of carbohydrate-derived compounds has undesirable properties, including a low heating value, high viscosity, and thermal and chemical instability.[7] During the upgrading processes, some of these products can be condensed to hydrocarbons with higher carbon numbers or decomposed into lighter fractions, including CO or CO_2, producing coke.[6] Consequently, the fuel precursors from bio-oil are preferably obtained from lignin-derived liquid products, which has initiated numerous efforts to investigate the HDO of lignin-derived monomeric compounds, including phenol,[8−10] guaiacol,[11−14] eugenol,[15−19] and vanillin.[20−22] Although the carbohydrate-derived compounds may not significantly contribute to the final upgraded bio-oil, they may interact with the catalysts and the aromatic compounds during the upgrading process. It is important to study the effects of these carbohydrate-based liquids on the upgrading of lignin-derived aromatic compounds, as doing so can lead to the development of efficient bio-oil upgrading processes. To the best of our knowledge, the effects of carbohydrate-based compounds present in bio-oil and the interactions between these compounds with lignin-derived aromatics in catalysts have not yet been fully explored.

The goal of this study is to elucidate the effects of carbohydrate-derivatives on the HDO of lignin-derivatives. Guaiacol was selected as a representative model compound of lignin-derivatives while furfural, 5-hydroxymethylfurfural (5-HMF), tetrahydrofuran (THF), 2-methylfuran (2-MF), 2-furylmethylketone (FMK), acetic acid, propionic acid, sorbitol, and galactitol were selected as possible compounds obtained from carbohydrates. The HDO of guaiacol in the presence of carbohydrate-derived coreagents was observed using supported noble-metal catalysts. Density functional theory (DFT) was

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introduced to understand the catalysis of these compounds and the effects of the carbohydrate derivatives.

■ RESULTS AND DISCUSSION

The HDO of guaiacol was performed in the presence of furfural, which is produced by the hydrolysis and dehydration of xylan in lignocellulose,[23,24] simulating a mixture of lignin-derived pyrolysis oil (guaiacol) and carbohydrate-derived chemicals (furfural) (Figure 1). As observed in our previous study,[14,25] the phenyl ring of guaiacol was hydrogenated to produce 2-methoxycyclohexanol and further deoxygenated to cyclohexanol, cyclohexanone, and cyclohexane. The formation of phenol and catechol, obtained via the hydrogenolysis of the methyl-oxygen bond of the methoxy group and the further elimination of the hydroxyl group, was also observed.[26] Ring-opening reaction products, including cyclopentane and methylcyclopentane, also formed. Because of the complex mixture of the products, the compounds obtained from guaiacol were classified into three groups, that is, compounds containing no oxygen atom (0-O's), those containing one oxygen atom (1-O's), and those containing two oxygen atoms (2-O's). As described in Table S2, the 0-O's included cyclopentane, methylcyclopentane, and cyclohexane. The major 1-O compounds included cyclohexanol, cyclohexanone, cyclopentanemethanol, methoxybenzene, and phenol. 2-Methoxycyclohexanol, 1,2-cyclohexanediol, and 1,2-benzenediol were the major compounds of the 2-O's.

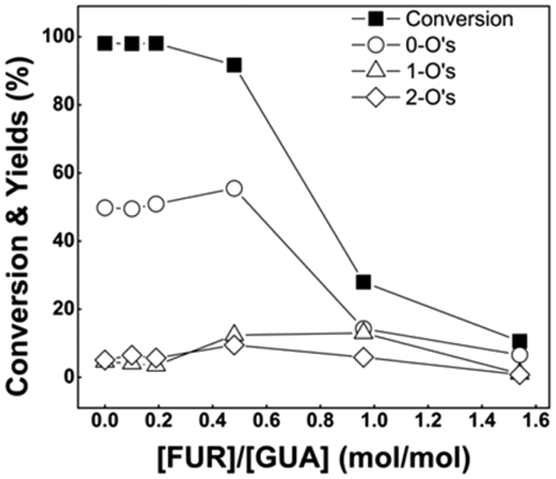

Figure 1. Hydrodeoxygenation of guaiacol in the presence of furfural. A mixture of guaiacol (GUA, 6.277 mmol), furfural (FUR, 0−9.659 mmol), a catalyst (5 wt % Ru/C, 20 mg), water (30 mL), and H_2 (40 bar at room temperature) was stirred (800 rpm) at 270 °C for 1 h.

Furfural can be hydrogenated to furfuryl alcohol and then further converted to tetrahydrofurfuryl alcohol and other ring-opening products (Table S3).[24] The conversion of furfural and its product distribution did not differ significantly regardless of whether guaiacol was present or not. Tetrahydro-2-methylfuran was the major product obtained by the hydrogenation and dehydration of furfural, which was further converted to tetrahydrofuran, cyclopentanol, and cyclopentanone. When guaiacol was present, the yield of cyclopentanol decreased and that of cyclopentanone increased slightly. Cracked products of furfural, including pentanol and butanol, were observed. 1,1′-Bicyclopentyl and bicyclopentyl-2-one, compounds obtained by the contraction of the furan ring, were also observed. Because this study focuses on the effects of carbohydrate-derived compounds on the hydrodeoxygenation of lignin-derived compounds, the products obtained from furfural were not included in the classified product groups.

The presence of furfural significantly affected the conversion of guaiacol and the yields of its products. When furfural was not added, the conversion of guaiacol was 98.1% and the yields of the 0-O's, 1-O's, and 2-O's were 49.8, 4.6, and 5.1%, respectively. When furfural was added to the reaction mixture up to [furfural]/[guaiacol] = 0.47 (mol/mol), neither guaiacol conversion nor the product distribution was significantly adjusted. When the [furfural]/[guaiacol] value was 0.96 (mol/mol), both the conversion of guaiacol and the yield of the 0-O's dropped sharply from 98 and 50% to 28 and 14%, respectively. The yields of the 1-O's and 2-O's increased slightly from 4.6 and 5.1% to 13 and 5.9%, respectively. Increasing the concentration of furfural up to [furfural]/[guaiacol] = 1.5 (mol/mol) decreased the conversion to 11%, while the yields of the 0-O's, 1-O's, and 2-O's were 6.6, 1.1, and 0.8%, respectively. Note that the conversion of furfural was 100% and was practically unchanged in all cases. These results confirm that the reactivity of guaiacol was suppressed by the presence of furfural in the reaction mixture and that the reactivity of furfural was not apparently affected by guaiacol.

The catalytic HDO results of guaiacol in the presence of furfural were then examined using different reaction conditions (Tables 1 and S4), exhibiting the inhibiting effects of furfural on the HDO of guaiacol. Without furfural, increasing the reaction temperature to 300 °C led to 100% conversion of guaiacol with 66.0, 0.2, and 0.3% yields of the 0-O's, 1-O's, and 2-O's, respectively (entry 1). When furfural was added to the reaction mixture at [furfural]/[guaiacol] = 0.96 (mol/mol), significantly reduced catalytic activity was observed and the conversion of

Table 1. HDO Reaction Results of Guaiacol[a]

							yield (%)		
entry	catalyst	amount of catalyst (g)	amount of furfural (mmol)	reaction time (h)	reaction temperature (°C)	conversion of guaiacol (%)	0-O's	1-O's	2-O's
1	Ru/C	0.02	0	1	300	100	66.0	0.2	0.3
2		0.02	6.037	1	300	37.2	7.7	10.1	8.1
3		0.02	0	1	270	98.1	49.8	4.7	5.1
4		0.02	6.307	4	270	52.0	25.3	7.9	2.0
5		0.04	6.307	1	270	91.5	77.4	12.8	7.5
6	Ru/Al2O3	0.02	0	1	300	99.0	63.0	0.6	0.2
7		0.02	6.307	1	300	33.8	1.7	1.9	6.2

[a] Reaction conditions: guaiacol (6.277 mmol) mixed with water (30 mL), initial H_2 pressure at room temperature = 40 bar, stirred at 800 rpm.

guaiacol decreased remarkably to 37.2% (entry 2). Increasing the reaction time from 1 to 4 h at 270 °C did not lead to a significant increase in the guaiacol conversion and the product yields The conversion of furfural was 52.0%, and the yields of the 0-O's, 1-O's, and 2-O's were 25.3, 7.9, and 2.0%, respectively (entries 3 and 4). These observations indicated that the catalytic activity was reduced by furfural and its derivatives at an early stage of the reaction and occupied the active sites of catalysts. For the catalysts poisoned with furfural and its derivatives, the increasing reaction time did not significantly affect the conversion of guaiacol, which may be attributed to the irreversible poisoning of catalysts by the carbon deposition caused by the polymerization of adsorbed furfural and its derivatives. The 4-fold larger amount of carbon deposited on the spent catalysts was measured with the thermogravimetry after the reaction of guaiacol and furfural compared to those after the reaction of guaiacol only (Figure S3), which is attributed to the conversion of guaiacol and strongly adsorbed furfural.[27] The carbon deposition was also observed with powder X-ray diffraction measurements of spent catalysts (Figure S4), which exhibited the formation of amorphous carbon peaks at $2\theta = \sim 23°$ for the catalysts after the reaction of guaiacol and furfural. The irreversible deactivation by adsorbed guaiacol and furfural also explained why the conversion of guaiacol did not increase in the presence of furfural with increasing reaction time. The slightly more sintering of Ru particles after the reaction of guaiacol and furfural was also observed with the CO-chemisorption (Table S1). Increasing the amount of Ru/C from 20 to 40 mg at 270 °C in the presence of the same amount of furfural led to the better HDO activity. The conversion of guaiacol was improved to 91.5%, and the yields of the 0-O's, 1-O's, and 2-O's were 77.5, 12.8, and 7.5%, respectively (entry 5 versus 4). The conversion of guaiacol was less affected by the addition of furfural because the number of active sites for 40 mg of Ru/C was enough to convert guaiacol although some of them were poisoned by furfural molecules, which confirmed the competitive adsorption of carbohydrate-derivatives with guaiacol on the Ru surface. Ru/Al_2O_3 exhibited catalytic activity similar to that of Ru/C in that the presence of furfural suppressed the catalytic conversion of guaiacol (entries 6 and 7).

From the observed results, inhibiting effects of furfural on the reactivity of guaiacol appeared to occur because the reaction of furfural or its derivatives on Ru catalysts was more active at the same active sites of the catalyst where the HDO of guaiacol occurs. The hydrogenation of the aromatic ring of guaiacol to produce 2-methoxycyclohexanol and the deoxygenation of 2-methoxycyclohexanol to form cyclohexanol, cyclohexanone, and cyclohexane most likely occur at metal and acid sites, respectively, on the catalyst surface.[14] The decreasing conversion of guaiacol in the presence of furfural ([furfural]/[guaiacol] = 49% mol/mol) suggests that the hydrogenation of the aromatic ring of guaiacol was suppressed. The fact that the conversion of furfural was practically unchanged in the reaction mixture indicates that furfural or its intermediates captured the active sites for their hydrogenation/hydrodeoxygenation reactions. A similar observation was reported for the conversion of phenol suppressed in the presence of methyl heptanoate.[28]

For a closer examination of the primary reason behind the observed results for the guaiacol and furfural mixture, numerous coreactants, in this study, 5-HMF, acetaldehyde, cyclopentanecarboxaldehyde (Cpc-aldehyde), tolualdehyde, butyraldehyde, THF, 2-MF, FMK, acetone, acetic acid, propionic acid, sorbitol, and galactitol, were studied with regard to the conversion of guaiacol. The selection of these compounds was based on the availability of each in bio-oil and their feasibility when used to represent carbohydrate-derived aldehydes, ketones, carboxylic acids, and alcohols (Figure 2). Each compound was mixed in a reaction mixture with guaiacol, with the molar ratio fixed at 49%. Only the conversion of guaiacol and the yields of cyclohexane were described to simplify the analyses. It is apparent that in the presence of different types of coreactants (excluding furfural and 5-HMF), the conversions of guaiacol were nearly identical, at 98–100%, indicating that the reactivities of guaiacol were not affected in the presence of these compounds. In the presence of some coreactants, it was observed that the yields of cyclohexane increased relative to the yields obtained with guaiacol alone. The yields of cyclohexane were varied, ranging from 40 to 60%. In contrast, when furfural or 5-HMF was mixed as a coreactant in the reaction of guaiacol, substantial decreases of the conversion of guaiacol and the yields of cyclohexane were observed. Note that total yields of cyclohexane counted cyclohexane produced from coreactants for Cpc-aldehyde and tolualdehyde, but the conversion of guaiacol did not significantly change with these coreactants.

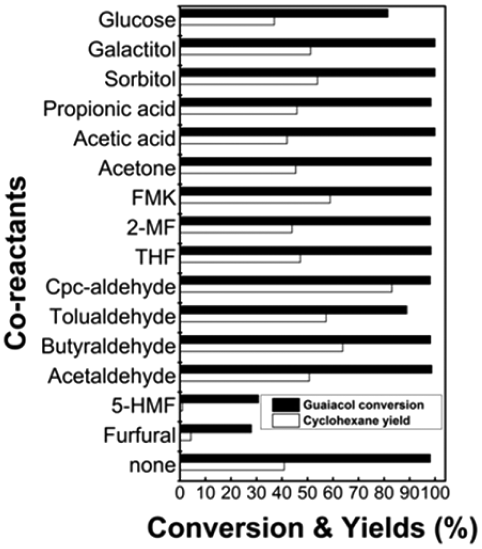

Figure 2. Hydrodeoxygenation of guaiacol in the presence of coreactants. Reaction conditions: guaiacol (6.277 mmol), coreactant (6.037 mmol, the molar ratio of the coreactant in the mixture was 49%), catalyst (5 wt % Ru/C, 20 mg), water (30 mL), initial H_2 pressure at room temperature = 40 bar, 270 °C, 1 h, stirred at 800 rpm. Co-reactants: 5-hydroxymethyl-2-furaldehyde (5-HMF), acetaldehyde, butyraldehyde, tetrahydrofuran (THF), 2-methylfuran (2-MF), 2-furylmethylketone (FMK), acetone, acetic acid, propionic acid, sorbitol, galactitol.

Given the aforementioned results, it is clear that the reactivity of guaiacol is significantly mitigated in the presence of furfural or 5-HMF in the reaction mixture. Our DFT calculation results provide insight into the roles of furfural and 5-HMF in suppressing the conversion of guaiacol.[29−32] Figure 3a summarizes the calculated adsorption energies (E_{ads}) of guaiacol and the six selected coreactants, that is, furfural, 5-HMF, sorbitol, acetic acid, FMK, and THF, on Ru(0001). Among the selected coreactants, only furfural, 5-HMF, and

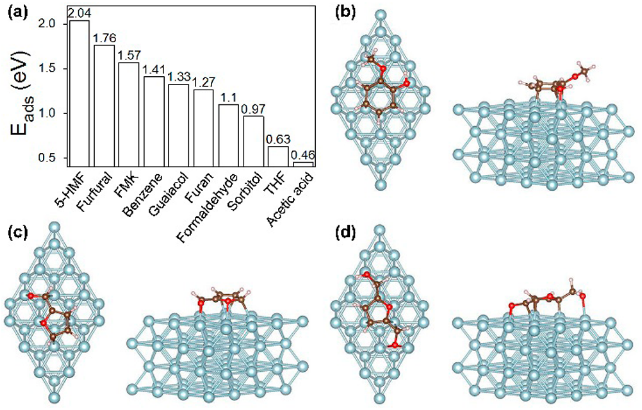

Figure 3. (a) Calculated adsorption energies (E_{ads}) of guaiacol and the selected coreactants on Ru(0001) and their lowest energy adsorption geometries of (b) guaiacol, (c) furfural, and (d) 5-HMF on Ru(0001). In (a), the calculated adsorption energies of benzene, furan, and formaldehyde are also summarized for a further analysis. In (b−d), the blue, brown, red, and white spheres represent the Ru, C, O, and H atoms, respectively.

FMK yield greater adsorption energies than guaiacol, by 0.43, 0.71, and 0.24 eV, respectively. Considering that the guaiacol conversion process is initiated by the adsorption of guaiacol on the Ru surface, the significantly high adsorption energies of furfural and 5-HMF, relative to guaiacol, indicate that the active sites of the Ru surface are likely to be preferentially occupied by furfural or 5-HMF. Such poisoning blocks the adsorption of guaiacol and in turn suppresses the conversion of guaiacol. This suitably accounts for the reduced conversion of guaiacol in the presence of furfural or 5-HMF. One may wonder why a similar suppression of the guaiacol conversion does not occur in the presence of FMK, whose adsorption strength is 0.24 eV greater than that of guaiacol. We anticipate that such a small energy gain by the adsorption of FMK relative to guaiacol can be overcome in an actual catalytic HDO reaction environment, performed at 270−300 °C with agitation, and that the guaiacol conversion process will proceed.

The variations in the adsorption energies of guaiacol and the coreactants can be attributed to the differences in the adsorbate structures and their subsequent interactions with the Ru(0001) surface. Guaiacol and carbohydrate derivatives can be viewed as combinations of several building blocks: (1) ring structures such as benzene, furan, and heterocyclic ether; (2) straight hydrocarbon chains such as hexane; and (3) functional groups such as methyl ($-CH_3$), methoxy ($-OCH_3$), hydroxyl ($-OH$), and carbonyl ($C{=}O$) groups. For example, guaiacol is a benzene derivative in which two hydrogen atoms in a benzene ring are replaced with one methoxy group and one hydroxyl group, whereas furfural and 5-HMF are furan derivatives containing a carbonyl group. To understand the interactions between these building blocks and the Ru surface, we extended our DFT calculations to calculate the adsorption energies of benzene, furan, and formaldehyde on Ru(0001). These results are summarized in Figure 3(b−d), which depict the lowest energy configurations of the adsorbed guaiacol, furfural, and 5-HMF. The Supporting Information provides the configurations of the other coreactants as well as building blocks. From the calculated adsorption energetics and the structural information, we find several key trends, as enumerated below, which determine the overall strength of an adsorbate−surface interaction.

(1) In comparison with the adsorption energy of THF (E_{ads} = 0.63 eV, see Figure S5), the significantly high adsorption energies of benzene (E_{ads} = 1.41 eV, see Figure S9) and furan (E_{ads} = 1.27 eV, see Figure S10) indicate that the aromaticity strengthens the adsorbate−surface binding.

(2) Formaldehyde, the simplest organic compound containing a carbonyl group, exhibits fairly strong adsorption on Ru(0001) with E_{ads} = 1.10 eV (see Figure S11). This, along with the binding pattern between the carbonyl-containing compounds and the Ru(0001) surface, indicates that among the functional groups considered here, the carbonyl group is the most prominent in reinforcing the adsorbate−surface binding, whereas the strengthening effects of the other functional groups are not significant.

(3) Benzene and furan, included in guaiacol and the coreactants, tend to lie flat with respect to the surface in order to maximize the favorable interaction between the aromatic rings and the Ru(0001) surface. In this case, the adsorption typically occurs with an optimum distance of ∼2.2 Å between the ring plane and the Ru surface. Such a binding pattern induces an additional steric effect when benzene/furan-containing compounds have methyl or methoxy groups and adsorb on the Ru surface. In this case, the steric effect works in a direction to weaken the adsorbate−surface binding.

The three aforementioned trends feasibly account for the variation of the adsorption energies in Figure 3a. For instance, the adsorption energy of guaiacol (benzene + methoxy + hydroxyl, E_{ads} = 1.33 eV) downshifts from that of benzene (E_{ads} = 1.41 eV) because of the steric effect of the methoxy group (see the tilted adsorption geometry in Figure 3b), whereas the adsorption energies of furfural (furan + carbonyl, E_{ads} = 1.76 eV) and 5-HMF (furan + carbonyl + hydroxyl, E_{ads} = 2.01 eV) upshift from that of furan (E_{ads} = 1.27 eV) because of the carbonyl−surface interaction. Likewise, the adsorption energy of FMK (furan + carbonyl with methyl group, E_{ads} = 1.58 eV, see Figure S7) upshifts from that of furan mainly because of the carbonyl−surface interaction but to a lower degree compared to those of furfural and 5-HMF because of the steric effect of the methyl group connected to the carbonyl group. On the other hand, the other coreactants, in this case THF (see Figure S5), acetic acid (see Figure S6), and sorbitol (see Figure S8), contain neither an aromatic ring nor a carbonyl functional group and in turn yield much lower adsorption energies than guaiacol. One step further from the direct DFT investigations, we applied the three aforementioned trends to account for the effects of the other carbohydrate derivatives included in our HDO experiments but not investigated directly in our DFT calculations. For instance, tolualdehyde (benzene + carbonyl + methyl) and glucose (hexane +5 hydroxyl + carbonyl/formyl) are expected to have relatively strong adsorbate−surface binding energies mainly because of the presence of a carbonyl group in comparison with the other carbohydrate derivatives, including acetaldehyde, butyraldehyde, cyclopentanecarboxaldehyde, 2-MF, acetone, propionic acid, and galactitol. This estimation is in good agreement with the reduced total conversion of guaiacol in the presence of tolualdehyde (88.9%) and glucose (81.5%). In conclusion, our DFT results and the subsequent analysis suggest that the guaiacol conversion efficiency is determined by the combined effects of (1) the aromaticity (upshift), (2) the carbonyl group (upshift), and (3) the degree of steric hindrance (downshift) by methyl or methoxy groups for the adsorbate−surface binding strength.

CONCLUSIONS

Among the many possible derivatives of carbohydrates, furfural and 5-HMF were observed to inhibit the HDO of lignin-derived phenolic guaiacol. These observations indicate that the presence of furfural or 5-HMF may inhibit the HDO of lignin-derived compounds when the pyrolysis oil of lignocellulose is upgraded. The DFT calculation indicated that the hindering effect of furfural or 5-HMF on the reactivity of guaiacol may contribute to the preferred adsorption of these carbohydrate derivatives on the ruthenium surface. The findings of this study indicate that carbohydrate derivatives can suppress the HDO of phenolic compounds, which must be adjusted in order to improve the HDO of lignin derivatives.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501567x.

Experimental details, catalysis characterization results, and DFT calculation results (PDF)

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Notes

The authors declare no competing financial interest.

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