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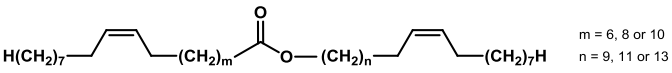
Synthesis of Diols from Jojoba Oil via Rhodium-Catalyzed Reductive Hydroformylation: a Smart Way to Access Biobased Polyurethanes

Chryslain Becquet[a], Michel Ferreira[a], Hervé Bricout[a], Baptiste Quienne[b], Sylvain Caillol[b], Eric Monflier[a] and Sébastien Tilloy[a*]

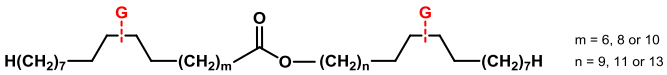
Jojoba oil ester has been functionalized with alcohol groups via hydrohydroxymethylation (HHM) catalyzed by a Rh/amine system. In the optimized conditions, a full conversion together with a 99% yield in alcohol products were obtained. The catalytic system has been recycled via a chromatographic technique at least 10 times without notable loss of activity. The hydrohydroxymethylated products have been succesfully used as monomers for the synthesis of a new biobased polyurethane possessing good thermal and mechanical properties.

In the context of the transition to a post-petroleum chemistry, chemists are increasingly turning to the development of innovative materials from biobased resources such as oils.[1] Among the various vegetable oils available on the market, there is jojoba oil, whose world annual production is about 4000 tonnes.[2] Jojoba plants (*Simmondsia chinensis*) are native to the desert and are highly resistant to arid environments. Jojoba oil is a mixture of esters with two linear monounsaturated carbon chains (Scheme 1).



Scheme 1. Fatty ester structure of jojoba oil.

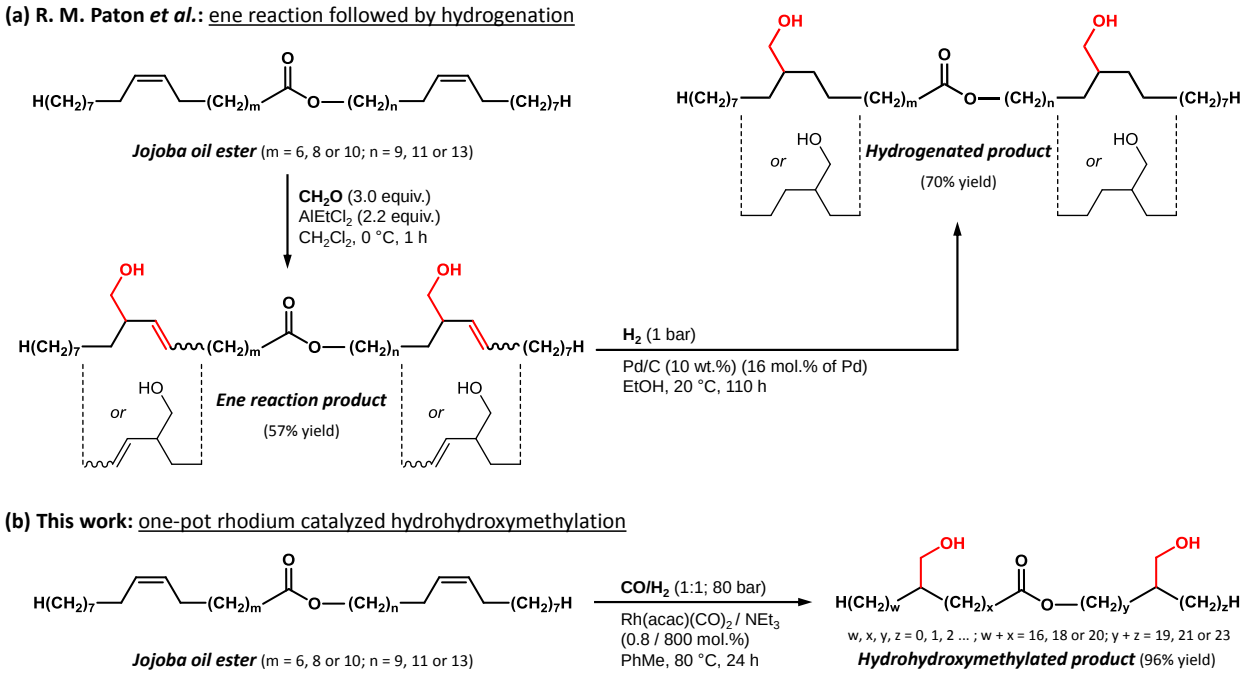
The first of these chains consists of 18 to 22 carbons on the carboxylic acid side of the ester. The second chain has 20 to 24 carbons on the alcohol side. On each of these carbon chains, a C=C double bond of Z stereochemistry is present in the ninth bond from the methyl end group. This oil has therefore a different structure from other vegetable oils, which usually consist mainly of triglycerides. One way to add value to jojoba oil is through C=C unsaturations conversion into different functions (aldehyde, carboxylic acid, amine, alcohol...). More specifically, functionalization of the C=C of jojoba oil by alcohol functions is of great interest in order to produce plasticizers, lubricants or monomers for the synthesis of polymers (such as polyesters or polyurethanes).[3,4] For instance, some of us have reported the introduction of primary alcohol functions on jojoba oil double bonds by addition of 2-mercaptoethanol using thiol-ene coupling.[5] The obtained diol (Scheme 2 with –G = –S–CH_2–CH_2–OH) was reacted with different isocyanates to form polyurethanes with good properties.



Scheme 2. Jojoba oil ester functionalized with G groups.

The synthesis of another interesting diol based on jojoba oil was published by J. F. McLellan *et al.* in 1994 (Scheme 2 with –G = –CH_2–OH). This compound was obtained in two steps. In the first step, jojoba oil was reacted in an ene reaction with formaldehyde and a Lewis acid ($EtAlCl_2$) both in excess (Scheme 3 (a)).[6,7] An esters mixture of mono and di-adducts was obtained, with an isolated yield in di-adducts of 57%. The second step involved the double bond hydrogenation using palladium on carbon under H_2 atmosphere with a yield of 70%, giving a global yield of only 40% for the conversion of jojoba oil ester into the targeted diol. In order to develop a synthesis route of this diol compound more in line with industry requirements (no stoichiometric reagents such as $EtAlCl_2$, high reaction selectivity), a catalytic way involving a rhodium/tertiary amine system was used in this study (Scheme 3 (b)). Such Rh/tertiary amine catalytic systems have proven to be highly active in the reductive hydroformylation of various oleochemicals,[8,9,10,11] carbohydrates[12] or petroleum based olefins[13,14,15,16,17,18].

In this respect, the catalytic system combining $Rh(acac)(CO)_2$ and triethylamine was evaluated in the HHM of jojoba oil. It is important to note that jojoba oil has never been functionalized via this process.



Scheme 3: Synthesis of bis-primary alcohols from jojoba oil ester.

During this reaction, C=C double bonds may be isomerized, hydrogenated or hydroformylated into aldehyde functions further transformed into primary alcohols (equation in table 1). At the end of the reaction, the catalyst was originally and successfully recycled via a chromatographic method. Finally, the bis-primary alcohol synthesized via the Rh-HHM of jojoba oil ester was used as monomer for the synthesis of a biobased polyurethane to evaluate the potential of this diol in polymer chemistry.

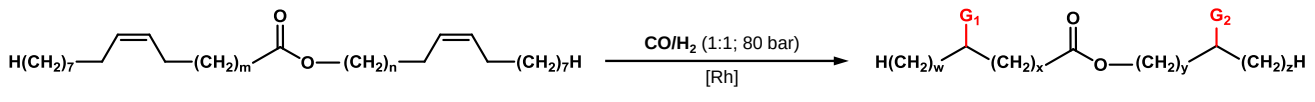
Hydrohydroxymethylation performance tests of the catalytic system

The catalytic system combining $Rh(acac)(CO)_2$ as the rhodium precursor (0.8% substrate molar ratio) and triethylamine (=TEA, 2000 molar equivalent towards Rh) as both a ligand and solvent was firstly tested at different temperatures under 80 bar of CO/H_2 (table 1, entry 1-3). Yields in alcohols (Alc.) were high in all experiments but the best temperature to reach a combined high conversion and high selectivity in alcohols was 80 °C. At a lower temperature of 60 °C, the conversion and alcohols yield dropped from 93% to 53% and from 90% to 47% respectively (compare entries 1 and 2). On the other hand, at a higher temperature of 100 °C, despite a slight increase in the alcohols yield (93%), a twice yield in hydrogenated double bonds (Sat.) was obtained (entry 3). Entry 4 was conducted without any nitrogen ligand indicating its importance for the hydrogenation to proceed. Indeed, no conversion in alcohols was observed while 97% yield in aldehydes was obtained.
The combined use of toluene as solvent and TEA as nitrogen ligand, at constant rhodium concentration compared to entries 1-3, permitted to reach an almost full selectivity in primary alcohols together with a full conversion in 48 h (entry 5 and 6). Such behaviour has already been observed when ethyl ricinoleate was hydrohydroxymethylated by the same catalytic system.[11]

Recycling experiments

The main issue of the system used in this study is the recycling of the catalyst. Indeed, the reaction was done in homogeneous conditions which render the catalyst recovery difficult to some extent. From a sustainable chemistry point of view, recycling the expensive catalyst is highly desirable. Few examples of recycling rhodium reductive hydroformylation systems based on the use of hydrosoluble hydroxyalkylamines[19,20] or CO_2 switchable solvent[21] achieving a biphasic medium at the end of the reaction have already been used. Heterogenization of the rhodium catalyst on a support containing amino groups has also been exploited as a strategy to reuse the catalyst.[14,22,23,24,25,26,27]

Table 1. Rhodium-catalyzed reductive hydroformylation of jojoba oil in various conditions.



Jojoba oil ester

m = 6, 8 or 10; n = 9, 11 or 13

-G_1, -G_2 = **-CHO** (Ald.), **-CH_2OH** (Alc), or **-H** (Sat.)

w, x, y, z = 0, 1, 2 … ; w + x = 16, 18 or 20; y + z = 19, 21 or 23

Entry	T (°C)	Solvent	Amine equiv.[a]	C(%)[b]	$Y_{Ald.}$(%)[c]	$Y_{Alc.}$(%)[c]	$Y_{Sat.}$(%)[c]
1	60	TEA	2000	53	3	47	3
2	80	TEA	2000	93	1	90	2
3	100	TEA	2000	98	1	93	4
4	80	Toluene	0	99	97	0	2
5	80	Toluene/TEA[d]	1000	97	0	96	1
6[d]	80	Toluene/TEA[d]	1000	100	0	99	1

Experimental conditions: Rh(acac)$(CO)_2$ (6 mg, 23 µmol, 1 eq.), jojoba oil ester (1.73 g, 2.87 mmol, 125 eq.), solvent (6.5 mL, 50/50 v/v when the Toluene/TEA mixture was used), 80 bar CO/H_2 (1/1), 1500 rpm, reaction time = 24 h. [a]amine/Rh molar ratio. [b]C = global CC double bond conversion = total amount of CC double bonds in the starting jojoba oil ester and in the CC double bond isomerized ester that have been transformed into other products (Ald., Alc. and Sat.). [c]Y_x = yield in X with respect to CC double bonds, determined by ^{1}H NMR. [d]reaction time = 48 h.

In our case, given that the catalytic active system has been identified as to be composed of ionic species,[11,18] an original approach based on a chromatographic technique to recycle the catalyst has been set up. The protocol is quite easy to realise and was done under atmospheric conditions. For technical reasons, these recycling tests were done on an upscaled reactor of 100 mL, with starting material 6-fold higher than the preliminary experiments. The reaction conditions of each run were selected as the optimal previous conditions (*i.e.* 80 °C, 80 bar CO/H_2, 24 h). The recycling experiments were done as follows: at the end of the reaction, the medium was in a first step eluted through a silica gel column with toluene in order to recover the different products of the reaction, mainly alcohols. During this first elution step, a dark purple sample was stacked on the silica gel column and a light-yellow liquid was obtained as the eluted solution (Figure 1(a)). In order to recover the more polar species, a second elution step was realized with acetone as solvent. This second step coincided with a complete discolouration of the silica gel column, implying recovery of the whole rhodium catalytic species in the autoclave (Figure 1(b)). At this point, the autoclave was sealed and a reduced pressure was applied until a dry residue was obtained. Then, a new jojoba oil/TEA/PhMe mixture was introduced and the reaction was started again by pressurizing the autoclave with syngas at 80 °C. Ten recycling experiments with the same strategy were conducted in order to check the robustness of the proposed system (Figure 2). The 1st run showed that the reaction could be upscaled without any modifications in conversion and yields.

During each recycling test, the reaction medium was sampled at 4 h and extended to 24 h. A blank experiment, conducted without catalyst, was realized after the 4th recycling to check the non-wall contamination of the autoclave. During this 24 h "blank" experiment, the 4th recycled catalyst, recovered in a separated Schlenk after the 2nd elution step, was kept in acetone under air atmosphere. The great stability of this 4th recycled catalyst was confirmed by the 5th recycling run (post-blank run) which did not show any specific loss in conversion and alcohol yield.

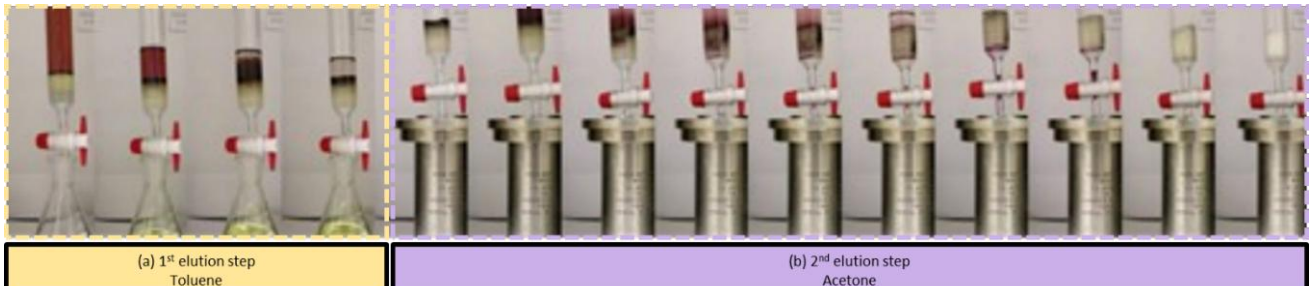


Figure 1. Photographs of the catalyst recycling protocol. (a) Migration of reaction products with toluene as eluting solvent (dark rhodium species stay at the top of the column), (b) Migration of the dark rhodium species with acetone as eluting solvent, with total silica column discolouration and direct recovery in the autoclave reactor.

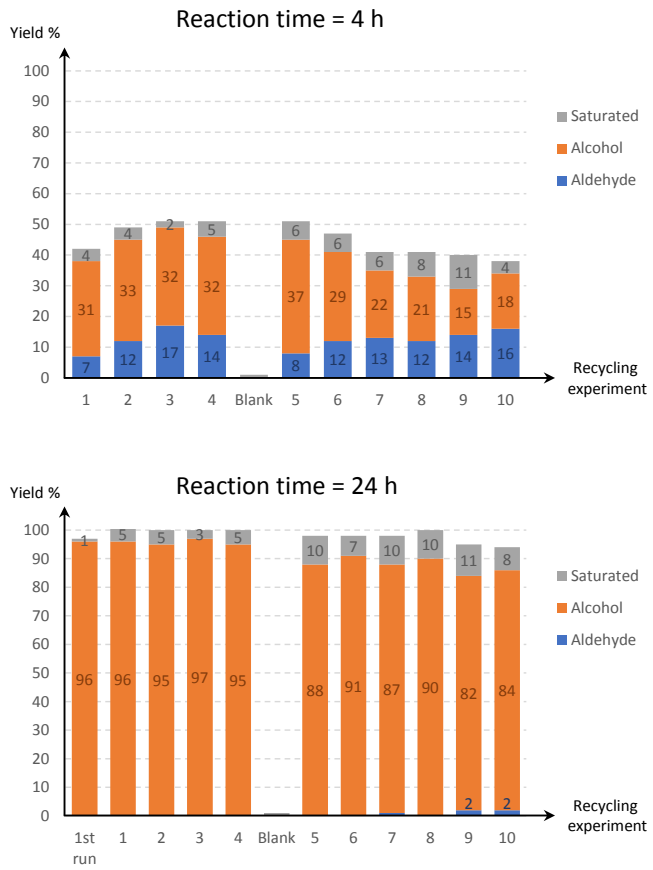


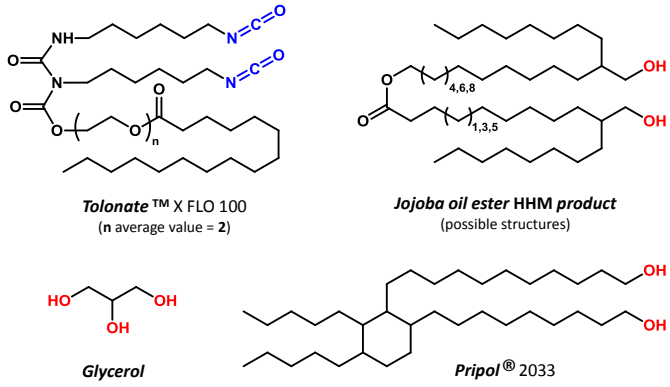
Figure 2. Repeated catalyst recycling by the chromatographic method. *Experimental conditions*: Rh(acac)$(CO)_2$ (36 mg, 140 µmol, 1 eq.), jojoba oil ester (10.53 g, 17.4 mmol, 125 eq.), TEA (14.2 g, 140 mmol, 1000 eq.), toluene (19.5 mL), 80 bar CO/H_2 (1/1), 80 °C, 1500 rpm.

By using this chromatographic method, the catalyst could be, at least, reused 10 times without loss of significant activity and yield in alcohols after 24 h of reaction (Figure 2). However, a small decrease in conversion was observed after the 5th recycling at 4 h reaction time presuming a loss in rhodium. Indeed, conversion of jojoba oil ester fell from 51% in the 5th run to 38% in the 10th run. This loss in rhodium probably came from the chromatographic elution given that rhodium ICP quantitation obtained in the 3rd and 5th recycled organic phases were particularly low (0.3% and 0.7% of the starting rhodium respectively). The global catalyst activity, measured after the ten recyclings, was satisfying with a turnover number (TON) value of around 2700 and a 5% rhodium loss. The organic phases of each recycling run were then combined and evaporated to dryness to yield a crude oil that was subsequently flash chromatographed to obtain an alcohol mixture directly used as starting monomer for the next step.

The market demand for biobased polymers, and particularly polyurethanes (PUs) which are synthesized from polyols and polyisocyanates is increasing. Recently, some biobased polyisocyanates have emerged on the market, allowing to increase the renewable carbon content of PU beyond 90%.[28,29] Until now, the major renewable part of PUs was only due to the biobased polyols used for their synthesis, since only fossil-based polyisocyanates were commercially available. To highlight the potential of HHM jojoba oil esters as a biobased diol for the synthesis of biobased PU, and the desire to develop greener materials, PU thermosets have been synthesized using a recently developed biobased diisocyanate.

Thermosets synthesis

Two biobased PUs have been synthesized. The first one (PU1) using the previous hydrohydroxymethylated product of jojoba oil and the second one (PU2) using Pripol® 2033, a fully biobased dimer of fatty alcohols (Scheme 4) already used in biobased PU synthesis.[30]



Scheme 4. Monomers structures.

In both cases, glycerol was used as crosslinker and Tolonate™ X FLO 100 as a biobased diisocyanate containing 32% of renewable carbons. Finally, the two PUs were obtained with a biobased carbon content of 61% and 60%, for PU1 and PU2 respectively (Table 2; see also ESI, Tables S3 and S4). Their crosslinking was confirmed by FTIR analyses with the disappearance of the isocyanate band at 2271 cm^{-1} and the appearance of the urethane band at 1714 cm^{-1} (see ESI, Figure S13). Moreover, no residual exothermy was observed by DSC and high gel contents (GC) of 93 % and 95 % were respectively obtained, confirming that both materials were fully cured (see Figure S15 in ESI and Table 3).

Table 2: Formulation and biobased carbon content of PUs.

	Tolonate™ X FLO 100 (eq.)	Glycerol (eq.)	HHM Jojoba oil ester (eq.)	Pripol® 2033 (eq.)	Biobased carbon content (%)
PU1	1	0.3 [a]	0.7 [b]	-	61
PU2	1	0.3 [a]	-	0.7 [b]	60

[a] means 0.3 hydroxyl function of glycerol for 1 isocyanate function of Tolonate™ X FLO 100; [b] means 0.7 hydroxyl function of HHM jojoba oil ester or of Pripol®2033 for 1 isocyanate function of Tolonate™ X FLO 100.

Thermomechanical properties

Both PUs have Tg under room temperature, −35 °C and −27 °C for PU1 and PU2 respectively, resulting in soft materials (Table 3 and see Figure S15 in ESI for DSC thermograms).

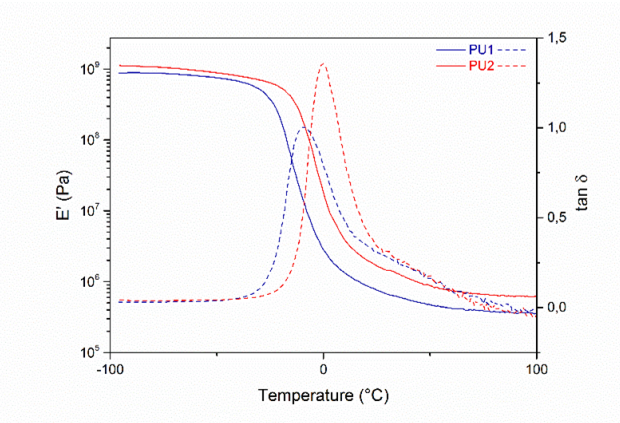


Figure 3. DMA analyses of PUs.

Since both PUs are composed of the same ratio of glycerol and isocyanate, the network difference depends on the diol used. Indeed, the hydrohydroxymethylated product of jojoba oil ester is mainly composed of long fatty acids forming esters from 40 to 48 carbons while Pripol® 2033 is composed of 36 carbons, allowing to reach higher crosslinking density for PU2. For the same reason, Tα measured by DMA was lower for PU1 than PU2 with −21 °C and −11 °C respectively (Figure 3). The lower crosslinking density of PU1 was also confirmed with swelling indexes (SI). The swelling index is higher for PU1 than for PU2, with respectively 960% and 710% (Table 3). It demonstrates that crosslinking nodes of PU1 are further apart and lead to a looser network, as confirmed with calculated v' of 93 mol/m^3 and 141 mol/m^3 for PU1 and PU2 respectively. Finally, the lower crosslinking density of PU1 led to softer material as demonstrated by its lower E' values compared to PU2 (Table 3). Nevertheless, both PUs presented a quite similar thermal resistance since their $T_{d5\%}$ were 295 °C and 284 °C, for PU1 and PU2 respectively (see ESI, Figure S14, for the TGA thermograms).

Table 3. Thermomechanical properties of PUs.

	T_g (°C)	T_α (°C)	$T_{d5\%}$ (%)	E'_{glassy} (GPa)	$E'_{rubbery}$ (MPa)	v' (mol/m^3)	SI (%)	GC (%)
PU1	−35	−21	295	0.86	0.7	93	960	93
PU2	−27	−11	284	0.97	1.1	141	710	95

Conclusions

In summary, we have developed an efficient protocol for the hydrohydroxymethylation of jojoba oil ester. Optimal reaction conditions permitted to reach an almost full conversion in alcohols. The whole process has been optimized by recycling, at least ten times, the rhodium HHM catalyst without loss of significant activity and with an overall TON of 2700. The diol obtained was then used to synthesize a biobased polyurethane thermoset PU1 with a biobased diisocyanate. Finally, HHM jojoba oil ester brought flexibility and thermomechanical properties to PU quite comparable to the commercial Pripol®2033 highlighting its potentiality in the polymer field.

Author Contributions

Conceptualization S.C., S.T. and E.M.; Methodology, C.B., B.Q. and H.B.; Validation, M.F., S.C., H.B., S.T. and E.M.; Formal analysis, C.B., B.Q. and H.B.; Investigation, C.B., B.Q. and H.B.; Resources, M.F., H.B., S.C., E.M. and S.T.; Data curation, C.B., B.Q. and H.B.; Writing—original draft preparation, M.F., H.B., S.T. and E.M.; Writing—review and editing, M.F., S.C., H.B., S.T. and E.M.; Supervision, S.C., S.T. and E.M.; Project administration, S.C., S.T. and E.M.; Funding acquisition, S.T. and E.M. All authors have given approval to the final version of the manuscript.

Acknowledgments

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Conflicts of interest

"There are no conflicts to declare"

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