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Biosourced Polymetallic Catalysts: An Efficient Means To Synthesize Underexploited Platform Molecules from Carbohydrates

Vincent Escande,^[a, b] Tomasz K. Olszewski,^[c] Eddy Petit,^[d] and Claude Grison^{*[a, b]}

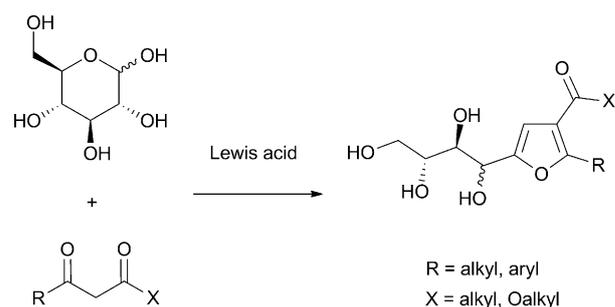
Polymetallic hyperaccumulating plants growing on wastes from former mining activity were used as the starting material in the preparation of novel plant-based Lewis acid catalysts. The preparation of biosourced Lewis acid catalysts is a new way to make use of mining wastes. These catalysts were characterized by X-ray fluorescence, X-ray diffraction, inductively coupled plasma mass spectrometry, and direct infusion electrospray ionization mass spectrometry. These analyses revealed a complex composition of metal species, present mainly as polymetallic chlorides. The catalysts proved to be efficient and recyclable in a solid-state version of the Garcia Gonzalez reaction, which has been underexploited until now in efforts to

use carbohydrates from biomass. This methodology was extended to various carbohydrates to obtain the corresponding polyhydroxyalkyl furans in 38–98% yield. These plant-based catalysts may be a better alternative to classical Lewis acid catalysts that were previously used for the Garcia Gonzalez reaction, such as ZnCl₂, FeCl₃, and CeCl₃, which are often unrecyclable, require aqueous treatments, or rely on metals, the current known reserves of which will be consumed in the coming decades. Moreover, the plant-based catalysts allowed novel control of the Garcia Gonzalez reaction, as two different products were obtained depending on the reaction conditions.

Introduction

As the pressure on raw materials derived from fossil fuels continues unabated and environmental concerns become ever more pervasive, the chemical industry must increasingly focus on obtaining raw materials from renewable resources.^[1] Thus, special emphasis should be put on developing protocols for transforming biomass into fine chemicals and chemicals with high added value.^[1c,2] There is already a considerable range of chemical building blocks derived from renewable resources, such as 5-hydroxymethylfurfural,^[3] γ -valerolactone,^[4] and lactic acid.^[5]

Because of their high synthetic potential, carbohydrates obtained from plant-derived biomass will make a valuable contribution to green chemistry of the future.^[6] The Garcia Gonzalez reaction is a highly valuable route for the synthesis of polyhydroxyalkyl furans starting from carbohydrates (hexoses and



Scheme 1. General concept of the Garcia Gonzalez reaction.

pentoses) and β -dicarbonylated compounds (Scheme 1), but strangely it seems to have been largely forgotten.^[7]

By furnishing a number of useful properties including chirality, rigidity, lipophilicity, hydrophilicity, and flexibility in one system, polyhydroxyalkyl furans represent an interesting scaffold or platform molecule for synthetic chemists to use in the preparation of a variety of diverse structures (Figure 1).

Reported examples of their use include the preparation of free furanic acids having a polyhydroxylated alkyl side chain,^[7] the synthesis of aldehydes by oxidative cleavage of the polyhydroxylated alkyl side chain,^[8] oxidation/reduction of the carbonyl group,^[9] and substitution of the terminal hydroxy groups to form oligomers.^[9]

The Garcia Gonzalez reaction has the potential to meet the modern criteria for green and sustainable chemistry.^[10] This transformation is operationally simple, high yielding, and performed under environmentally friendly conditions (by using

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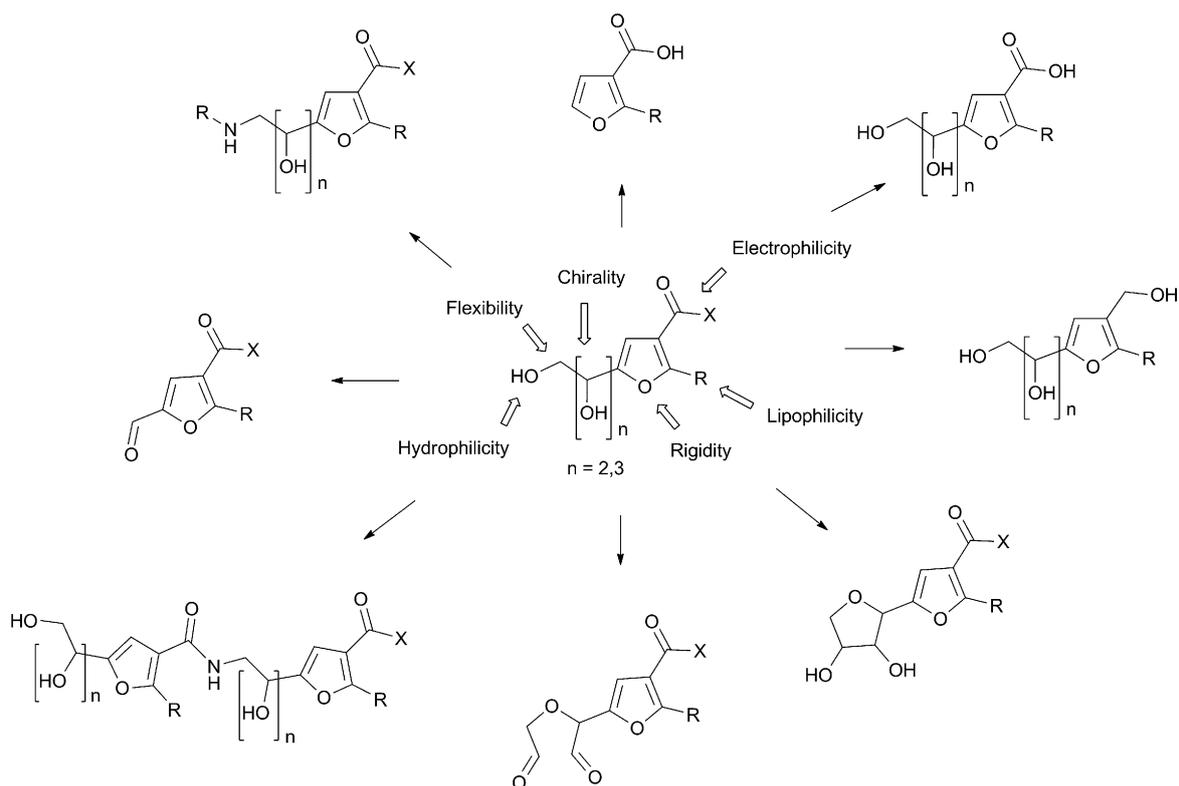


Figure 1. Polyhydroxyalkyl furans as platform molecules for synthetic chemists.

a mixture of H₂O/EtOH as the reaction medium); moreover, it requires a moderate temperature and short reaction time. The reaction is catalyzed by Lewis acids such as ZnCl₂,^[7] FeCl₃,^[11] and CeCl₃.^[8,12] However, these classical catalytic systems are unrecyclable, require aqueous treatment, rely on metals, the current known reserves of which will be consumed in the coming decades,^[13] and do not permit control of the reaction selectivity (in some cases, the polyhydroxylated alkyl side chain undergoes further cyclization).^[11] Owing to the depletion of metal resources^[14] and the emergence of new more stringent regulations,^[15] new catalysts are required that are inexpensive and that are not based on increasingly scarce metals.^[16]

Earlier work by our group led to the development of a new range of plant-based Lewis acid catalysts that are derived from nonconventional biomass, that is, metal hyperaccumulator species. Metal-hyperaccumulating plants, or metallophytes, extract trace metals from soil and concentrate them in their shoots.^[17] Exploring the utility of these plants led to the development of a phytoextraction technique that offers a means to remove the trace metals from contaminated soils, for example, contaminated mine sites, which cause major environmental problems worldwide.^[18] Today, this environmentally compatible process has emerged as the preferred method to reclaim metal-contaminated sites. It is less costly than conventional remediation methods, has a lower environmental impact, and is better accepted by the public.^[19] Potential and specific markets exist for phytoextraction, which also offers an alternative source of non-renewable mineral materials.^[20] Field-scale trials of phytoextrac-

tion by using the practices of farming systems proved the technology's potential on a large scale. It is now possible to access up to several tons of Ni-rich biomass in the USA and in Europe. As an example, crop yields of the nickel hyperaccumulator *Alyssum murale* can reach at least 20 t ha⁻¹ or 400 kg Ni ha⁻¹ with ordinary fertilizers and management practices.^[21] Similar studies are in progress for zinc hyperaccumulator plants. We estimate that a possible biomass production of 5.2 t ha⁻¹ would yield 60 kg ha⁻¹ of Zn, and this is in agreement with the findings of Robinson et al.^[22]

However, numerous efforts are still necessary to exploit the ability to recover and recycle metals from contaminated biomass and fully develop the economic potential of phytoextraction. Innovative technologies are needed to obtain the full benefit of the remediation process. We have found that the unique polymetallic composition of the catalysts derived from metal hyperaccumulating plants allows them to efficiently mediate a diverse set of reactions to afford valuable products in good yields under mild reaction conditions.^[18c,23]

Herein, we describe the use of a novel plant-based Lewis acid catalyst for the Garcia Gonzalez reaction, an innovation that will be of major interest for green chemistry. The key benefits of the proposed catalytic system are the use of a catalyst of plant origin, the possibility to recycle and reuse it, efficiency in terms of yield, the wide range of its applications, ease of control of the reaction outcome, and mild reaction conditions.

Results and Discussion

In this study, we used the two best zinc hyperaccumulator plants, *Noccaea caerulea* (Brassicaceae) and *Anthyllis vulneraria* (Fabaceae), harvested in Les Avinières, a former zinc mining site in Saint-Laurent-Le-Minier, southern France. Both are included in a large program of ecological rehabilitation of this site; they are able to concentrate approximately 120 000 ppm of Zn^{II} in calcinated shoots.^[18c] The plant-based catalysts were prepared by heat treatment of leaves at 400 °C, followed by the addition of HCl (1 M). The potential of zinc hyperaccumulator plants for plant-based catalysis was based on the total mineral composition of contaminated biomass. X-ray fluorescence (XRF) was used to determine the exact chemical composition of the plant extract that was obtained (Table 1).

Element	Composition [wt% ± standard deviation]
Na	1.72 ± 0.021
K	5.72 ± 0.078
Mg	1.6 ± 0.080
Ca	10.3 ± 0.17
Fe	2.75 ± 0.063
Zn	6.75 ± 0.021
Cd	0.19 ± 0.0026
Al	1.5 ± 0.014
Pb	0.44 ± 0.0029
O	15.97 ± 0.50
Cl	43.27 ± 0.23

The XRF data were additionally confirmed by inductively coupled plasma mass spectrometry (ICP-MS). The mineral analysis clearly revealed that Zn was the major transition metal (6.75%), accompanied by an amount of 2.75% of Fe. An amount of 1.50% of Al was also noted. The reproducibility of the composition of the catalyst was investigated, depending on the localization of the crops. Three different samples of leaves were collected at different points in the former mining site, and their content in Lewis acids was analyzed by ICP-MS after their transformation into the catalyst

(Table 2). Whereas the contents of transition metals (Zn, Fe, Cd) and of Al and Pb were stable in the samples, larger differences were observed for Mg and Ca (see also data in Table 1). However, as the use of hyperaccumulating plants is intended as a source of Lewis acids, and particularly of transition metals, this variability in the Mg and Ca content should not compromise the catalytic activity. As a precaution, it is preferable to prepare the catalyst starting from the largest lots of collected plants to homogenize the composition and minimize variation. The biosourced catalyst obtained was characterized by X-ray diffraction (XRD) (Table 3). As the noncrystalline species were

Table 3. Characterization of the plant-based catalyst by XRD.

Mineral	Formula (simplified)
calcium magnesium chloride hydrate anhydrite, <i>syn</i>	CaMg ₂ Cl ₆ (H ₂ O) ₁₂ CaSO ₄
potassium zinc tetrachloride sylvite, <i>syn</i>	K ₂ ZnCl ₄ KCl
magnesium phosphate	MgP ₄ O ₁₁

not detected by XRD, the plant-based catalyst was also characterized by direct infusion in electrospray ionization mass spectrometry (ESI-MS) in the negative mode after dilution in water. Metallic species were detected as chlorides and were identified by their isotopic distribution, as described in Table 4.

The concentration of the solution led to an unusual mixture of mineral species, such as potassium zinc tetrachloride.^[18c] K₂ZnCl₄, the sole mixed zinc chloride that was observed, is a masked form of ZnCl₂.^[18c]

First, we tested the ability of the plant-based catalyst to catalyze the Garcia Gonzalez reaction starting from D-glucose (**1 a**) and ethyl acetoacetate (**2 a**) by using different environmentally benign reaction media previously described in the litera-

Table 4. Characterization of the plant-based catalyst by direct infusion mass spectrometry (ESI⁻).^[a]

<i>m/z</i> (abundance [%])	Ion
159 (6), 161 (100), 162 (2.3), 163 (93.7), 164 (2.2), 165 (30.1), 166 (0.7), 167 (3.3)	Fe ^{II} Cl ₃ ⁻
194 (4.7), 196 (80.8), 197 (1.8), 198 (100), 199 (2.3), 200 (48), 201 (1.1), 202 (10.4)	Fe ^{III} Cl ₄ ⁻
169 (64.7), 171 (100), 172 (5.5), 173 (81.5), 174 (5.3), 175 (39), 176 (1.7), 177 (9.9), 179 (1.1)	Zn ^{II} Cl ₃ ⁻
211 (2.2), 213 (2.2), 215 (23), 216 (22.8), 217 (64.7), 218 (43.9), 219 (100), 220 (28.3), 221 (77.4), 222 (7.6), 223 (30.6), 224 (0.7), 225 (5.9)	Cd ^{II} Cl ₃ ⁻
303 (48), 304 (6.1), 305 (100), 306 (11.8), 307 (88.6), 308 (9.6), 309 (76.5)	MgNa ₃ Cl ₆ ⁻
311 (33.4), 312 (29), 313 (100), 314 (28.2), 315 (76.8), 316 (9.1), 317 (22.7)	Pb ^{II} Cl ₃ ⁻

[a] See the Supporting Information for a comparison of the experimentally observed and predicted isotopic distribution.

Table 2. Mineral composition of different samples of plant-based catalysts, as established by ICP-MS.

Sample of plant-based catalysts	Latitude, longitude data of sampling sites	Composition [wt% ± standard deviation]						
		Mg	Ca	Fe	Zn	Cd	Al	Pb
sample 1	43.933031, 3.666407	3.76 ± 0.10	35.81 ± 0.50	1.80 ± 0.028	6.57 ± 0.059	0.35 ± 0.0040	1.74 ± 0.049	0.73 ± 0.0048
sample 2	43.933514, 3.667212	4.26 ± 0.16	31.15 ± 0.66	1.13 ± 0.030	4.80 ± 0.097	1.12 ± 0.036	1.10 ± 0.056	0.31 ± 0.0076
sample 3	43.932737, 3.666461	11.68 ± 0.18	25.75 ± 0.59	2.95 ± 0.030	9.65 ± 0.045	0.063 ± 0.00060	1.55 ± 0.088	0.11 ± 0.00067

ture.^[7,8,11] Initially, the reaction was performed in water/ethanol, but significant leaching of the metallic elements was noted. To circumvent this problem, we attempted to support the plant-based catalyst on montmorillonite K10 and silica gel by using impregnation methodology.^[24] Those experiments, however, led to a decrease in catalytic activity. To improve our methodology, we conducted the reaction in the solid phase by following methods previously used by Bartoli et al.^[12] Silica gel was used to disperse the catalyst and the reagents. Gentle heating was necessary to achieve total conversion (TLC analysis). Subsequent easy workup was based on washing the solid with ethyl acetate to extract the reaction products (Figure 2). Insoluble

considered conceivable for an economically feasible process, one that furthermore may permit reuse of the catalyst.^[25]

For all reactions, the amount of biosourced polymetallic catalyst was set at 4.0 mol% of Zn or 8.0 mol% of the sum Zn + Fe + Al. Owing to the complex composition of the catalyst, we chose to focus on Zn, Fe, and Al, as these elements have the most pronounced Lewis acidity of the elements present in the catalyst and are the most likely contributors to the catalytic activity. Loadings lower than 8.0 mol% of the sum Zn + Fe + Al resulted in a decrease in the reaction yield (Table 5, entry 3). In turn, higher loadings did not improve the reaction yield, even after prolonged heating.

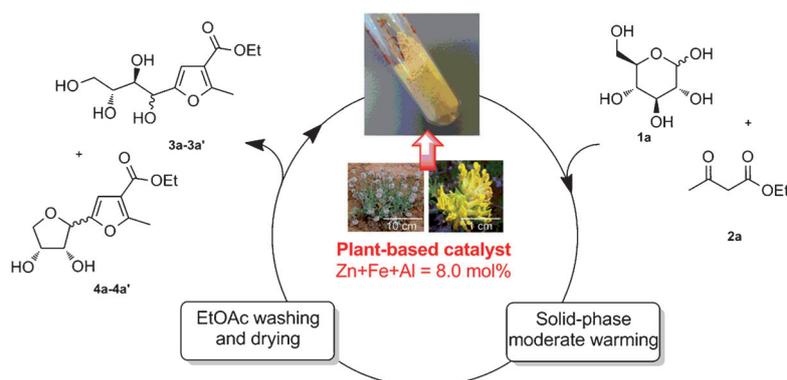


Figure 2. Solid-phase catalytic process with plant-based catalyst.

bility of the metallic elements of the plant-based catalyst in this solvent was noted. This improved methodology was very efficient (Table 5, entries 1 and 2) and avoided contamination of the reaction products with the metallic residue. Bartoli and collaborators used NaI as an activating compound,^[12] but no such additive was necessary if the reaction was catalyzed by the plant-based catalyst. The choice of conditions was also guided by the outcome of the experiment and was therefore

Interestingly, if the reaction time was extended beyond 24 h, the formation of an epimeric mixture of desired polyhydroxyalkyl furans **3a–3a'** was accompanied by the formation of cyclization products **4a–4a'**, which result from the cyclization–dehydration of the initial products.^[26] If the reaction temperature was set at 85 °C, after 24 h only products **4a–4a'** were formed in almost quantitative yield (Scheme 2). In turn, setting the reaction temperature at 50 °C gave the controlled formation of polyhydroxyalkyl furans **3a–3a'** (Scheme 2). Therefore, the application of the plant-based catalyst enabled easy control of the process by simple adjustments of temperature and reaction time.

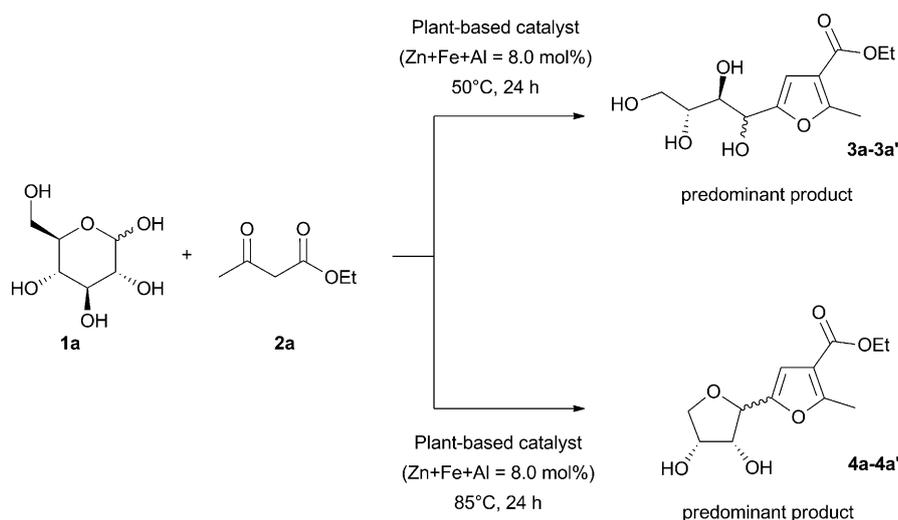
Therefore, this biosourced catalyst has unique flexibility and enables the control of the reaction sequence in comparison to “classical” catalysts and conditions, which lead only to one of the two possible products or to a mixture of **3a–3a'** and **4a–4a'**.

Additionally, the Garcia Gonzalez reaction of **1a** with **2a** performed in the presence of only SiO₂ led to products **3a–3a'** in 8% yield (Table 5, entry 4). Likewise, the use of commercial ZnCl₂/SiO₂ in the same proportion as in the run with the plant-based catalyst (Table 5, entry 1) gave lower yield and selectivity (Table 5, entry 5). The combination of Zn^{II}, Fe^{III}, and Al^{III} conveyed the catalytic activity, but with selectivity opposite to that obtained with the use of the plant-based catalyst (Table 5, entry 6). This is in accordance with previously published data, for which only the furan with a cyclic polyhydroxylic chain was

Table 5. Comparison of the activity of different catalysts in the Garcia Gonzalez reaction.^[a]

Entry	Catalyst	T [°C]	Yield [%]	
			3a–3a'	4a–4a'
1	plant-based catalyst/SiO ₂ ^[b]	50	65	2
2	plant-based catalyst/SiO ₂ ^[b]	85	0	97
3	plant-based catalyst/SiO ₂ ^[c]	50	30	0
4	SiO ₂ ^[d]	50	8	0
5	ZnCl ₂ /SiO ₂ ^[e]	50	11	13
6	ZnCl ₂ + FeCl ₃ + AlCl ₃ /SiO ₂ ^[f]	50	0	49

[a] Reaction performed with D-glucose (10 mmol) and ethyl acetoacetate (12 mmol). [b] Zn (4.0 mol%), Fe (1.9 mol%), Al (2.2 mol%), SiO₂ (500 mg). [c] Zn (1.0 mol%), Fe (0.5 mol%), Al (0.6 mol%), SiO₂ (500 mg). [d] SiO₂ (500 mg). [e] Commercial ZnCl₂ (4.0 mol%), SiO₂ (500 mg). [f] Commercial ZnCl₂ (4.0 mol%), commercial FeCl₃ (1.9 mol%), commercial AlCl₃ (2.2 mol%), SiO₂ (500 mg).



Scheme 2. Controlling the selectivity of the Garcia Gonzalez reaction.

obtained if FeCl_3 was used as the catalyst.^[11] These results show that the catalytic activity lies in the polymetallic composition and in the original species present in the plant-based catalyst.

Subsequently, the optimized reaction conditions were applied to a selected spectrum of hexoses and pentoses and to β -dicarbonyl compounds to test the scope of the presented protocol (Table 6). The use of pentane-2,4-dione (**2b**) as the β -dicarbonyl compound instead of ethyl acetoacetate (**2a**) led selectively to expected polyhydroxyalkyl furans **3b–3b'** in 72% yield if the reaction was performed at 50 °C for 24 h (Table 6, entry 3). In turn, at 85 °C only expected cyclization products **4b–4b'** were obtained in 91% yield (Table 6, entry 4). The use of 1,3-cyclohexanedione (**2c**) in the Garcia Gonzalez reaction has not been previously reported. In our case, with the use of the plant-based catalyst we obtained cyclization products **4c–4c'** in a low yield of 38%, probably as a result of the known dimerization of **2c** (Table 6, entry 5).^[27] A reaction with the use of D-galactose (**1b**) and pentane-2,4-dione (**2b**) did not follow the general pathway and furnished only cyclization products **4d–4d'** in 98% yield (Table 6, entry 6). As described in the literature, owing to the lack of anchimeric assistance of the OH group at the C2' position during the cyclization and probably because of steric effects, the two diastereomers were formed with a modest selectivity of **4d/4d'** = 70:30.^[11] The reaction of pentane-2,4-dione (**2b**) with D-mannose (**1c**) followed the same pathway and furnished only cyclization products **4b–4b'** in 90% yield (Table 6, entry 7). Finally, the biosourced catalyst was found to efficiently mediate the reaction performed with the use of pentoses. Polyhydroxyalkyl furans **3e–3e'** were obtained in 70% yield starting from pentane-2,4-dione (**2b**) and D-ribose (**1d**) or D-xylose (**1e**; Table 6, entries 8 and 9). The lateral chain was too short to undergo cyclization and, thus, only polyhydroxyalkyl furans were obtained.

In the case of cyclic products, the existence of those products as a mixture of diastereomers is well documented.^[11,26a] The ratio of diastereomers observed was moderate owing to

the anchimeric assistance of the OH group at the C2' position or to its absence, depending on the starting carbohydrate.^[11] However, in our case, after acetylation of the obtained uncyclized products, analysis by GC–MS revealed two signals with similar *m/z* values corresponding to two diastereomers. This fact was confirmed by ¹H NMR spectroscopy, for which the signals were doubled in various proportions, depending on the starting carbohydrate.

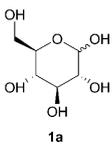
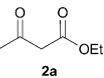
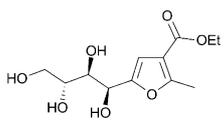
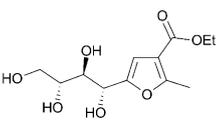
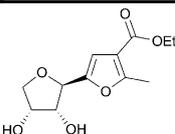
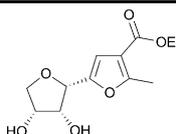
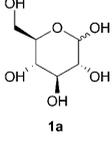
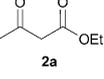
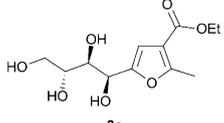
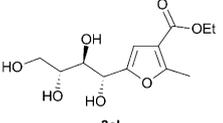
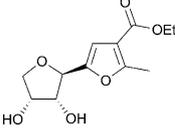
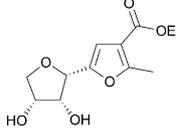
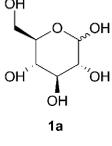
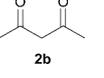
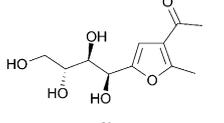
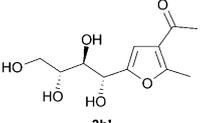
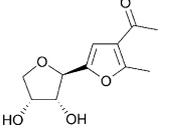
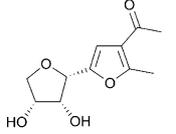
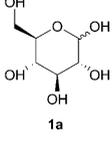
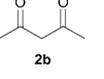
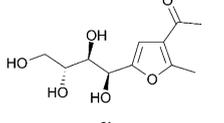
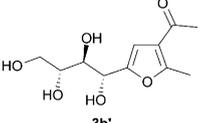
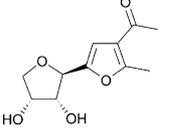
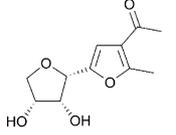
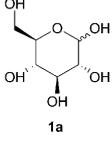
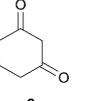
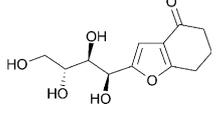
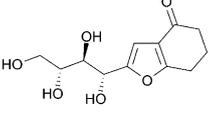
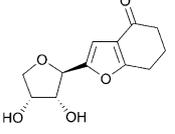
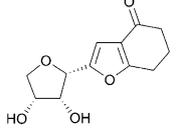
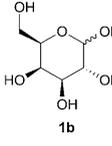
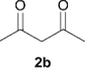
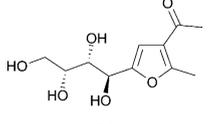
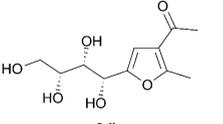
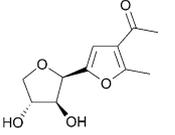
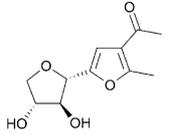
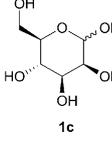
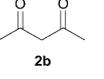
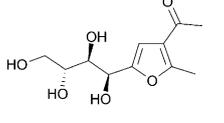
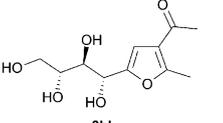
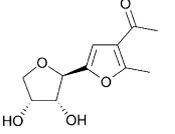
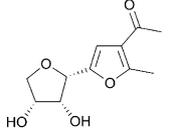
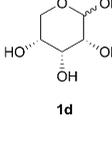
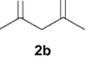
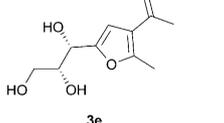
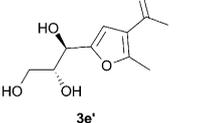
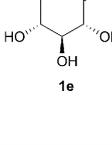
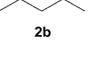
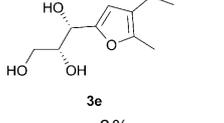
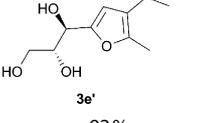
To avoid confusion by the formation of cyclic diastereomers, we studied the polyhydroxyalkyl furans obtained from pentoses, in which the lateral chain is too short to undergo cyclization. Starting from D-ribose, two diastereomers were observed by ¹H NMR spectroscopy for the products that had the linear polyhydroxyalkyl side chain. The diastereomers were most probably formed by epimerization at the C2' position (at which the dehydration is favored in the α position to the furan), following the formation of the carbocation by a mechanism proposed by Sánchez and Roldán,^[26a] for which the linear epimers were until now hypothetical (Scheme 3)

To confirm the formation of those epimers with other catalysts, the synthesis was performed with the use of FeCl_3 and D-ribose as the carbohydrate.^[11] Analysis of the reaction product by ¹H NMR spectroscopy clearly showed the existence of two diastereomers if the reaction was catalyzed by FeCl_3 .

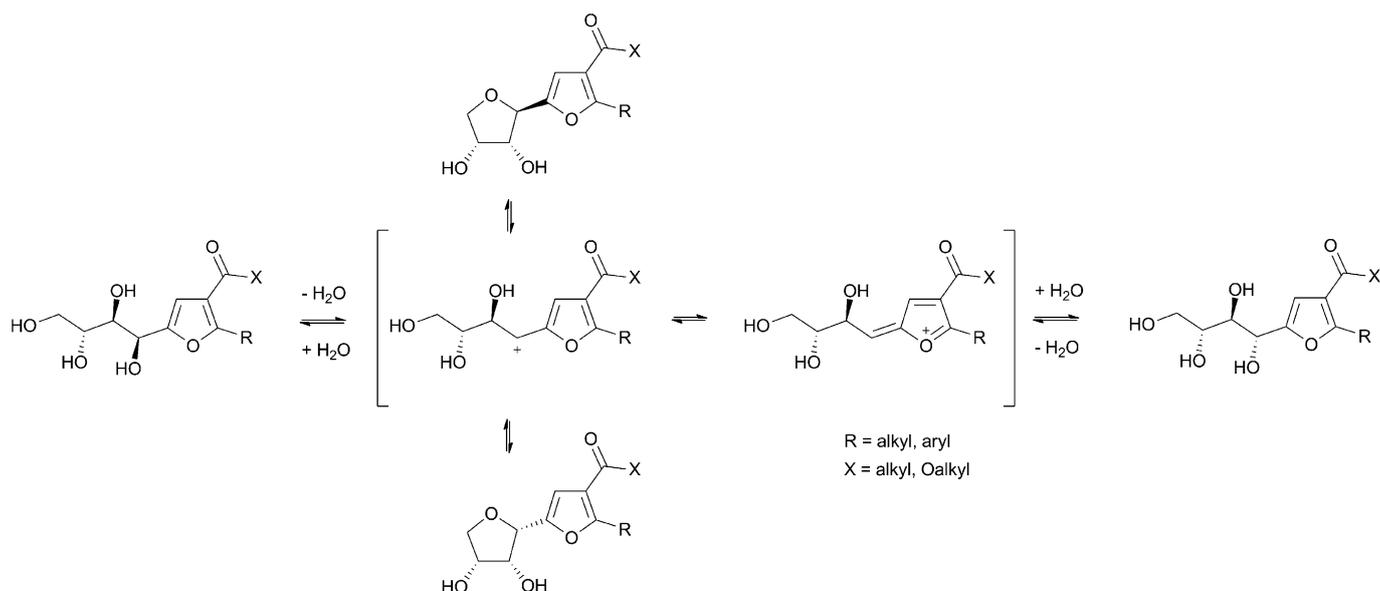
The experimental results (Table 6) showed the following trends concerning the proportions of isomerized products: For uncyclized products, epimerization at C2' with rates of 8 to 25% was observed. In contrast, the rates of isomerization were lower for the cyclized products, as most of the products were observed as β isomers (89–99%). This is probably due to steric effects, as in the α isomer the furan and hydroxyl groups are on the same side of the tetrahydrofuran moiety. Indeed, higher proportions of the α isomer (30%) were observed only for the cyclized product resulting from D-galactose in which the furan and the vicinal hydroxy group are on opposite faces of the tetrahydrofuran moiety (Table 6, entry 6). From a practical point of view, it should be noted that in each case, the different diastereomers of the uncyclized and cyclized products could be separated by fractional crystallization in ethyl acetate.

To test the potential for recycling and reuse of the catalyst, the catalyst was washed with ethyl acetate, dried (120 °C, 5 h), and used in a new run to yield the desired product. As summarized in Table 7, the polymetallic catalyst was used up to four cycles with a marginal decrease in catalytic activity. The batch-to-batch variability of the substrates was monitored by XRF; the mineral composition remained almost the same up to the fourth run. This was determined by comparing the amount

Table 6. Scope of the presented protocol.^[a]

Entry	Carbohydrate	β -Dicarbonyl	T [°C]	Uncyclized products ^[b]		Yield ^[c] [%]	Cyclized products ^[b]		Yield ^[c] [%]
1			50			65			2
				78%	22%		98%	2%	
2			85			0			97
							97%	3%	
3			50			72			5
				75%	25%		89%	11%	
4			85			0			91
							98%	2%	
5			50			0			38
							89%	11%	
6			50			0			98
							70%	30%	
7			50			0			90
							99%	1%	
8			50			70	-	-	-
				77%	23%				
9			50			70	-	-	-
				8%	92%				

[a] Reaction conditions: carbohydrate (10 mmol), β -dicarbonyl compound (12 mmol), plant-based catalyst (Zn + Fe + Al = 8.0% mol), SiO₂ (500 mg), 24 h. [b] Proportions determined by ¹H NMR spectroscopy. [c] Yield of isolated product.



Scheme 3. Epimerization of the uncyclized and cyclized products.

Table 7. Reusability of the plant-based catalyst in the Garcia Gonzalez reaction.

Run	Yield [%] 3 a–3 a'	Composition [wt% ± standard deviation]				
		Zn	Fe	Al	Cd	Pb
first	65	6.75 ± 0.026	2.75 ± 0.042	1.50 ± 0.016	0.19 ± 0.0052	0.44 ± 0.0073
second	60	6.70 ± 0.019	2.47 ± 0.028	1.47 ± 0.049	0.19 ± 0.0066	0.44 ± 0.0020
third	58	6.70 ± 0.041	2.38 ± 0.037	1.45 ± 0.059	0.19 ± 0.0037	0.44 ± 0.0093
fourth	55	6.68 ± 0.028	2.34 ± 0.055	1.45 ± 0.036	0.19 ± 0.0040 ^[a]	0.44 ± 0.0051 ^[b]

[a] Complementary ICP-MS analysis revealed that less than 5 ppm of Cd was lost after the four runs. [b] Complementary ICP-MS analysis revealed that less than 5 ppm of Pb was lost after the four runs.

of Zn, Fe, and Al. These results thus illustrate the stability of the plant-based catalyst and show that there is no leaching of metallic species during the reaction and workup. Only the amount of iron decreased slightly. No trace amounts of cadmium or lead were detected during ICP-MS analysis of the final products. This result is important because these elements are known to be highly toxic.

Conclusions

In conclusion, we described the preparation of a novel plant-based Lewis acid catalyst starting from hyperaccumulating plants collected on former mining sites. The conception of this new type of catalyst can contribute to the recycling of mining wastes. The characterization of this biosourced catalyst revealed that it was composed of mono- and polymetallic species, particularly of transition-metal chlorides known for their Lewis acid character, such as K_2ZnCl_4 . Reproducibility studies showed that the metal content of the catalyst was 4.80–9.65 wt% for Zn, 1.13–2.95 wt% for Fe, and 1.10–1.74 wt% for Al, depending on the localization of the plants used in the preparation of the catalyst. This catalyst proved to be highly efficient in the Garcia Gonzalez reaction by using solid-state

methodology without the use of any additive, which improved the green potential of the reaction. Good to excellent yields (up to 98%) of polyhydroxyalkyl furans were obtained. The plant-based Lewis acid catalyst showed unusual flexibility in catalyzing the Garcia Gonzalez reaction, as furans with an uncyclized or cyclized alkyl chain were obtained simply by adjusting the reaction temperature. Such an activity was not previously described for the catalysis of this reaction. Finally, this study highlighted the epimerization of uncyclized and cyclized polyhydroxyalkyl furans, which was only hypothetical on some points until now.

Experimental Section

General methods

Reagents and solvents were purchased from Sigma–Aldrich and were used without further purification. Flash column chromatography was performed by using Chromagel Carlo Erba Reactifs SDS silica 60A CC 35–70 μ m. Reactions were monitored by using Merck Kieselgel 60 F254 aluminum. TLC plates were visualized by UV fluorescence (254 nm) and one of the following: $KMnO_4$, ninhydrin, phosphomolybdic acid solution, or phosphotungstic acid solution.

Preparation of the polymetallic plant-based catalyst

Leaves of *Noccaea caerulea* and *Anthyllis vulneraria* were harvested before flowering in Les Avinières, a former zinc mining site in Saint-Laurent-Le-Minier, southern France (same mass of the two plants), air dried, and crushed. The obtained solid (150 g) was calcined at 400 °C for 5 h, and the resulting powder (24 g) was added to 1 M HCl solution (100 mL). The solution was heated at 60 °C and stirred for 2 h. The reaction mixture was filtered through Celite. The resulting solution, composed of different metal chlorides, was then concentrated under vacuum. The catalyst was kept in a desiccator under vacuum.

General procedure for the synthesis of uncyclized polyhydroxyalkyl furans

The carbohydrate (10 mmol), plant-based catalyst (390 mg, amount corresponding to 0.40 mmol of Zn, 0.19 mmol Fe, 0.22 mmol Al following ICP-MS dosing), and silica (500 mg, Chromagel Carlo Erba Reactifs SDS silica 60 A CC 35–70 µm) were mixed by grinding in a mortar. The β-dicarbonyl compound (12 mmol) was added, and the resulting solid was homogenized with a spatula. The solid was introduced in a sealed tube (Ace glass tube, 10.2 cm × 25.4 mm) containing a magnetic stirring bar, and the vessel was heated to 50 °C in an oil bath for 24 h until completion of the reaction (TLC monitoring, toluene/acetone = 1:1). The solid mixture was then washed with ethyl acetate (2 × 5 mL) and filtered. The resulting solution was evaporated under reduced pressure to yield a grey powder. This powder was purified by crystallization in hot ethyl acetate to give the uncyclized polyhydroxyalkyl furan as a white solid. The previous catalytic solid (mixture of plant-based catalyst and SiO₂) was recycled by washing with ethyl acetate and drying in an oven (120 °C, 5 h) before being reused in the next run. See the Supporting Information for analytical data.

General procedure for the synthesis of cyclized polyhydroxyalkyl furans

The carbohydrate (10 mmol), plant-based catalyst (390 mg, amount corresponding to 0.40 mmol of Zn, 0.19 mmol Fe, 0.22 mmol Al following ICP-MS dosing), and silica (500 mg, Chromagel Carlo Erba Reactifs SDS silica 60 A CC 35–70 µm) were mixed by grinding in a mortar. The β-dicarbonyl compound (12 mmol) was added, and the resulting solid was homogenized with a spatula. The solid was introduced in a sealed tube (Ace glass tube, 10.2 cm × 25.4 mm) containing a magnetic stirring bar, and the vessel was heated to 85 °C in an oil bath for 24 h until completion of the reaction (TLC monitoring, toluene/acetone = 1:1). The solid mixture was then washed with ethyl acetate (2 × 5 mL) and filtered. The resulting solution was evaporated under reduced pressure to yield a brown oil. This oil was purified by flash column chromatography (toluene/acetone = 1:1) to yield the cyclized polyhydroxyalkyl furan as an off-white solid, which was recrystallized in hot ethyl acetate. The previous catalytic solid (mixture of plant-based catalyst and SiO₂) was recycled by washing with ethyl acetate and drying in an oven (120 °C, 5 h), before being reused in the next run. See the Supporting Information for analytical data.

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- [1] a) A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411–2502; b) P. Gallezot, *Chem. Soc. Rev.* **2012**, *41*, 1538–1558; c) J. J. Bozell, G. R. Petersen, *Green Chem.* **2010**, *12*, 539–554.
- [2] T. Werpy, G. Pedersen, *Top Value Added Chemicals from Biomass*, US Department of Energy, Oak Ridge, **2005**.
- [3] A. A. Rosatella, S. P. Simeonov, R. F. M. Frade, C. A. M. Afonso, *Green Chem.* **2011**, *13*, 754–793.
- [4] D. M. Alonso, S. G. Wettstein, J. A. Dumesic, *Green Chem.* **2013**, *15*, 584–595.
- [5] M. Dusselier, P. Van Wouwe, A. Dewaele, E. Makshina, B. F. Sels, *Energy Environ. Sci.* **2013**, *6*, 1415–1442.
- [6] a) F. W. Lichtenthaler, S. Peters, *C. R. Chim.* **2004**, *7*, 65–90; b) M. J. Climent, A. Corma, S. Iborra, *Green Chem.* **2011**, *13*, 520–540.
- [7] F. G. González, *Adv. Carbohydr. Chem.* **1956**, *11*, 97–143.
- [8] A. K. Misra, G. Agnihotri, *Carbohydr. Res.* **2004**, *339*, 1381–1387.
- [9] A. J. Moreno-Vargas, J. Jiménez-Barbero, I. Robina, *J. Org. Chem.* **2003**, *68*, 4138–4150.
- [10] a) P. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, **1998**; b) R. A. Sheldon, *Chem. Soc. Rev.* **2012**, *41*, 1437–1451; c) R. A. Sheldon, I. W. C. E. Arends, U. Hanefeld, *Green Chemistry and Catalysis*, Wiley-VCH, Weinheim, **2007**.
- [11] L. Nagarapu, M. V. Chary, A. Satyender, B. Supriya, R. Bantu, *Synthesis* **2009**, 2278–2282.
- [12] G. Bartoli, J. G. Fernández-Bolaños, G. Di Antonio, G. Foglia, S. Giuli, R. Gunnella, M. Mancinelli, E. Marcantoni, M. Paoletti, *J. Org. Chem.* **2007**, *72*, 6029–6036.
- [13] A. J. Hunt, T. J. Farmer, J. H. Clark in *Element Recovery and Sustainability*, The Royal Society of Chemistry, Cambridge, **2013**, pp. 1–28.
- [14] a) L. Erdmann, T. E. Graedel, *Environ. Sci. Technol.* **2011**, *45*, 7620–7630; b) I. Sohn, *Resour. Policy* **2005**, *30*, 259–284; c) N. T. Nassar, R. Barr, M. Browning, Z. Diao, E. Friedlander, E. M. Harper, C. Henly, G. Kavlak, S. Kwatra, C. Jun, S. Warren, M.-Y. Yang, T. E. Graedel, *Environ. Sci. Technol.* **2012**, *46*, 1071–1078; d) R. Sinding-Larsen, F.-W. Wellmer in *Non-Renewable Resource Issues* (Eds.: R. Sinding-Larsen, F.-W. Wellmer), Springer, Netherlands, **2012**, pp. 1–19; e) T. E. Graedel, R. Barr, C. Chandler, T. Chase, J. Choi, L. Christoffersen, E. Friedlander, C. Henly, C. Jun, N. T. Nassar, D. Schechner, S. Warren, M.-y. Yang, C. Zhu, *Environ. Sci. Technol.* **2012**, *46*, 1063–1070.
- [15] a) U. Lahl, K. A. Hawxwell, *Environ. Sci. Technol.* **2006**, *40*, 7115–7121; b) M. Wilson, M. Schwarzman, *Environ. Health Perspect.* **2009**, *117*, 1202–1209; c) K. J. M. Matus, J. B. Zimmerman, E. Beach, *Environ. Sci. Technol.* **2010**, *44*, 6022–6023.
- [16] a) *Catalysis without Precious Metals* (Ed.: R. M. Bullock), Wiley-VCH, Weinheim, **2010**; b) S. Enthaler, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2008**, *47*, 3317–3321; *Angew. Chem.* **2008**, *120*, 3363–3367.
- [17] C. W. N. Anderson in *Element Recovery and Sustainability*, The Royal Society of Chemistry, Cambridge, **2013**, pp. 114–139.
- [18] a) C. Grison, J. Escarré, WO2011/064462A1; PCT/FR2009/052312, **2011**; b) C. Grison, J. Escarré, patent references: WO2011/064487A1; PCT/FR2010/052451; CA2781832A1; EP2504096A1, **2011**; c) V. Escande, L. Garoux, C. Grison, Y. Thillier, F. Debart, J.-J. Vasseur, C. Boulanger, C. Grison, *Appl. Catal. B* **2014**, *146*, 279–288; d) G. Losfeld, V. Escande, T. Jaffré, L. L'Huillier, C. Grison, *Chemosphere* **2012**, *89*, 907–910.
- [19] A. Bhargava, F. F. Carmona, M. Bhargava, S. Srivastava, *J. Environ. Manage.* **2012**, *105*, 103–120.
- [20] I. Raskin, B. D. Ensley, *Phytoremediation of Toxic Metals, Using Plants to Clean Up the Environment*, Wiley, New York, **2000**.
- [21] R. L. Chaney, C. L. Broadhurst, T. Centifanty, J. S. Angle, Y. M. Li, C. A. Peters, R. J. Rosenberg, A. P. Davis, A. J. M. Baker, R. D. Reeves, *Abstracts*

- of the International Conference on the Biogeochemistry of Trace Elements, Chihuahua, Mexico, **2009**.
- [22] B. Robinson, M. Leblanc, D. Petit, R. Brooks, J. Kirkman, P. H. Gregg, *Plant Soil* **1998**, *203*, 47–56.
- [23] a) G. Losfeld, P. V. de La Blache, V. Escande, C. Grison, *Green Chem. Lett. Rev.* **2012**, *5*, 451–456; b) G. Losfeld, V. Escande, P. Vidal de La Blache, L. L'Huillier, C. Grison, *Catal. Today* **2012**, *189*, 111–116; c) Y. Thillier, G. Losfeld, V. Escande, C. Dupouy, J.-J. Vasseur, F. Debart, C. Grison, *RSC Adv.* **2013**, *3*, 5204–5212.
- [24] a) P. Laszlo, A. Mathy, *Helv. Chim. Acta* **1987**, *70*, 577–586; b) A. Nasreen, *Synlett* **2001**, 1341–1342.
- [25] W. J. W. Watson, *Green Chem.* **2012**, *14*, 251–259.
- [26] a) A. Gómez Sánchez, A. Rodríguez Roldán, *Carbohydr. Res.* **1972**, *22*, 53–62; b) A. P. Kozikowski, G. Q. Lin, J. P. Springer, *Tetrahedron Lett.* **1987**, *28*, 2211–2214.
- [27] K. Conrow, *J. Org. Chem.* **1966**, *31*, 1050–1053.