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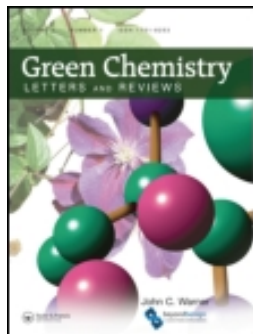
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RESEARCH LETTER

Zinc hyperaccumulating plants as renewable resources for the chlorination process of alcohols

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Green Lucas reagent was prepared from Zinc hyperaccumulating plant, *Thlaspi caerulescens*. It is an effective and reusable reagent for the chlorination of tertiary, secondary, and primary alcohols. The results are the first use of contaminated biomass in organic synthesis and can constitute an encouragement for the economic development of phytoextraction and remediation programs for metal-bearing soils.

Keywords: green catalysts; hyperaccumulating plants; chlorination; green Lucas reaction; biomass valorization

Introduction

Metal hyperaccumulating plants can extract, transport, and concentrate metals from soils into their roots and aboveground shoots. By definition, a hyperaccumulating can accumulate at least 100 mg kg⁻¹ Cd or As or 1000 mg kg⁻¹ Co, Cu, Cr, Pb or Ni or 10,000 mg kg⁻¹ Mn or Zn (1). The hyperaccumulation mechanism is active with transport from soils to roots, and translocation from roots to leaves. It naturally occurs as an adaptive response to metal stress and does not diminish hyperaccumulating's fitness (2). In the case of zinc hyperaccumulating species *Thlaspi caerulescens*, leaves concentration up to 1% were measured on soils (former mine sites) which contained up to 0.2% available zinc (EDTA extraction). This increase in zinc content from soil to plant tissues is referred to as the enrichment coefficient: it is usually higher than 1 for metal hyperaccumulating and reaches 5 for *T. caerulescens* (3).

The discovery of these plants suggested using them for the remediation of heavy metal-contaminated soils. This approach to environmental restoration has been termed phytoextraction. It has attracted the interest of researchers and more recently of public and regulatory agencies. This environmentally compatible process emerges today as the preferred method to reclaim metal contaminated sites (1). It is less costly than conventional remediation methods with the lowest environmental impact and showed better public acceptance (1). Potential and

specific markets exist for phytoextraction, which also offers an alternative to non-renewable mineral materials. Field-scale demonstrations of phytoextraction combining agronomic practices and farming systems proved the potential of the technology. It is now possible to access to tons of Ni rich biomass in the USA and in Europe. As an example, crop yields of the nickel hyperaccumulating *Alyssum murale* can reach at least 20 t ha⁻¹ or 400 kg Ni/ha with ordinary fertilizers and management practices (4). Similar studies are under process for zinc hyperaccumulating plants *T. caerulescens* and *Anthyllis vulneraria*. We estimate a possible biomass production of 5.2 t ha⁻¹ would yield 60 kg ha⁻¹ of Zn, which is in accord with the findings of Robinson et al. (3).

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 for the valorization of the remediation process.

The most common method of recycling metals contained in the biomass is phytomining: metal hyperaccumulating plants are considered as "bio-ores" and treated by conventional mining methods. Phytomining now seems to have limited applications, and the economic viability of the process is not evident (5). Although new processes emerge (6,7), the valorization of phytoextraction remains a challenging task as long as there are no general outlet for contaminated biomass.

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Results and discussion

Herein we suggest the use of the biomass from metal hyperaccumulating plant *T. caerulescens* as a promising and sustainable source of Lewis acids. The use of Lewis acids in organic synthesis has recently been one of the most rapidly developing fields in synthetic organic chemistry (8). Lewis acid catalysis is one of the key technologies for catalysis, green chemistry and asymmetric synthesis and it is used for fine chemistry as well as for large-scale production (9,10). Because of the high concentrations of transition metals in their tissues, hyperaccumulating plants represent an interesting renewable resource of various Lewis acids (9). The synthesis of aliphatic chlorides with Lucas' reagent constitutes an interesting model reaction to test this new process. This first chemical application of using contaminated biomass is illustrated with the well-known zinc hyperaccumulating *T. caerulescens* harvested in Les Avinières, a former zinc mine site in Saint-Laurent-le-Minier, southern France.

Lucas' reagent is a very useful analytical tool to distinguish primary, secondary, and tertiary alcohols. It is also well known that the reaction of ZnCl_2/HCl is an efficient method to prepare alkyl chlorides from aliphatic alcohols on an industrial scale. However, the wide use of the Lucas' reagent is limited due to the cost of ZnCl_2 (10).

The production of ZnCl_2 from *T. caerulescens* to prepare alkyl chlorides can become economically competitive compared to classical techniques. This new process is also attractive for other reasons: it represents a real opportunity to prevent the looming depletion of zinc resources (11).

This new chemical application can also constitute an incentive for the economic development of phytoextraction and remediation programs on metal-bearing soils.

The prerequisite for successful chlorination of alcohols is the preparation of ZnCl_2 from biomass. The challenge was to develop a cleaner chemical methodology, avoiding the use of organic solvents and separation agents that are hazardous substances for the environment. The selection of conditions was

guided toward a simple, low-cost and efficient process, transposable to an industrial scale. In a first step, a thermal treatment was applied to *T. caerulescens* leaves at 400 °C in order to destroy all organic compounds. The ashes were then treated with 1–10 M HCl to finish the destruction the remaining organic residues and to convert metallic oxides into metal chlorides. The reaction mixture was stirred for 2 h at 60 °C, and filtered on celite. The resulting solutions were composed of different metal chlorides. An analysis of the mineral composition of the prepared mixtures was conducted by inductively coupled plasma mass spectrometry (ICP-MS). The most noteworthy results are summarized in Table 1. Zn(II), Cd(II), and Pb(II) result from heavy-metal hyperaccumulation capacities of *T. caerulescens* while the other metal cations are present as they are essential for plant growth [Na(I), K(I), Ca(II), Mg(II), Fe(III), Cu(II), Mn(II)]. Oxidation state of Fe(III) was confirmed by colorimetric reaction with ammonium thiocyanate (12). Pulse polarographic analysis confirmed unequivocally this result and the concentration established using ICP-MS (13). HCl concentration was a significant parameter in the metal recovery process. Ten M HCl dissolved all metal oxides, including Zn ferrite, forming the corresponding dissolved chloride. One M HCl showed a selective dissolution and led to the crystallization of zinc ferrite. It was possible to isolate crystals of magnetic spinel ZnFe_2O_4 with a magnet without notably affecting the amount of Zn(II). Energy Dispersive X-ray Spectroscopy (EDXS) analysis confirmed the structure of isolated crystals.

The second step was to achieve a successful conversion of aliphatic alcohols into chloride derivatives to show that the mixture of metal chlorides demonstrates interesting catalytic properties in the chlorination of alcohols. Unlike conventional processes, we postulated that there is no advantage to obtain pure ZnCl_2 . Hence, we investigated a partial purification to concentrate ZnCl_2 and to eliminate cations that do not present interesting Lewis acid properties. In a first time, we investigated two classic processes: solid–liquid separation and liquid–liquid

Table 1. Mineral composition for different mixtures established by ICP-MS.

Mixture	Na ^a	K ^a	Mg ^a	Al ^a	Ca ^a	Mn ^a	Fe ^a	Cu ^a	Zn ^a	Cd ^a	Pb ^a
Crude mixture of metal chlorides ^b	145	177	83	57	528	2	253	3	385	23	106
Crude mixture of metal chlorides ^c	152	180	74	56	649	1	79	2	350	22	92
Green solid catalyst	2	3	8	8	96	0	120	1	373	22	86

^aWeight (mg) calculated from 5.25 g of dehydrated leaves.

^bMixture obtained after treatment with HCl 10 M.

^cMixture obtained after treatment with HCl 1 M.

extraction. Solid–liquid separation was obtained with pH adjustment for selective precipitation of metal hydroxides followed by suitable separation and acidification. Separation by selective precipitation of metal fluorides was also considered in our investigations. Then, we attempted an unsuccessful liquid–liquid extraction system based on reactive extraction by trioctylamine (TOA) dissolved in toluene, and selective complexation with (2-ethylhexyl) phosphoric acid (DEHPA). The two methods resulted in partial separation only and poor yields. However, LC-MS analysis of different isolated fractions confirmed the metal speciation. The main species are chloride metals but small amounts of mixed chloride-phosphate metals were also detected.

Finally, the separation by ion exchange was found to be the most effective and rapid process. The acidic solution of the different solvated metal chlorides was treated in order to remove undesired metals ions with exchange resin. The use of Amberlite IRA 400 resulted in an adsorption of Zn(II) (90% min) on the resin, and elution of alkali and alkaline earth cations. A treatment with 0.5 M HCl eliminated a part of Fe(III) fixed on the resin before the elution of heavy metals [Zn(II), Cd(II), Pb(II)] with 0.005 M HCl (Figure 1).

The ion exchange product was a metal mixture enriched in ZnCl_2 . It has been successfully used in the chlorination of alcohols: the green Lucas' reagent consisted in anhydrous "green catalytic solid" dissolved in concentrated hydrochloric acid (about 1.6 g per gram of 10 M HCl). Taking into account that green Lucas' reagent is unusual; it was useful to examine its action toward reactive alcohols. Thus, tertiary and benzyl alcohols were converted to the corresponding chlorides by treatment with the green Lucas' reagent. The reactions were easily monitored by gas chromatography and mass spectrometry (GC-MS); alkyl chlorides were characterized analytically by comparison with previously obtained

samples. As clearly indicated by GC-MS, the alcohols were completely consumed after 30 min at room temperature. Contrarily to the reported classic procedure, the concentration of HCl is not crucial for the reaction. The technical acid was sufficiently concentrated to give good yields. This result indicated the activity of metal chlorides in the mixture green Lucas' reagent. To improve the sustainability of process, we studied the reactivity of the crude mixture obtained from the *T. caerulescens* biomass after treatment with 10 M HCl and without purification. The conversion of alcohols was quantitative after stirring for 8 h (Figure 2).

After demonstrating that the green Lucas' reagent and the crude mixture of metal chlorides gave possible and non-ambiguous access to alkyl chlorides, we investigated the chlorination of secondary and primary alcohols. The best reaction conditions were obtained with the purified green Lucas' reagent. As deduced from the GC-MS data, the reaction was complete after 8 h. No side products were detected. It appeared that the facility of isomerization roughly increased in the following order $2 > 4 > 5 > 3 > 1$ as it is commonly observed for the classic chlorination. The regiosomers were separated by distillation according to Vogel (14). The chloride derivatives were distilled twice from a Claisen flask with fractioning side-arm. Having successfully achieved the chlorination of secondary alcohols, all efforts were focused on *L*(-)-menthol, which represents an attractive example for the chemical industry (10).

The results mainly indicated the formation of *L*(-)-menthyl chloride. Small amounts of 3-menthene **4'b** and 2-menthene **4'c** were observed, which may result from E_2 elimination of menthyl and neo-menthyl chlorides (14). *L*(-)-menthyl chloride **4'a** was purified by distillation using a fractioning column (bp 101 °C at 21 mmHg). Primary alcohols have also been the object of chlorination reactions with green Lucas' reagent. One-hexanol has been used as a model substrate. As expected, chlorohexanes **5'a** and **5'b** were obtained in modest yield after distillation. The sulfuric acid treatment removed high-boiling impurities which are not easily separated by distillation (14).

After completion of the reaction, the organic layer was diluted with petroleum ether and separated from the aqueous phase. A solventless option was possible from 0.5 g of alcohols; for this, alkyl chloride is directly isolated by decantation of the reaction mixture and separated from the aqueous layer. The crude product was washed with water. In these conditions, no quantifiable amount of metallic residue was detected in the final product. The green Lucas' reagent could be recycled easily by simple

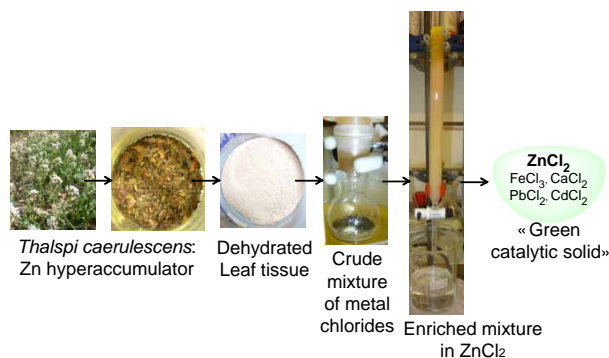


Figure 1. Preparation of enriched mixture in ZnCl_2/HCl and the "green catalytic solid."

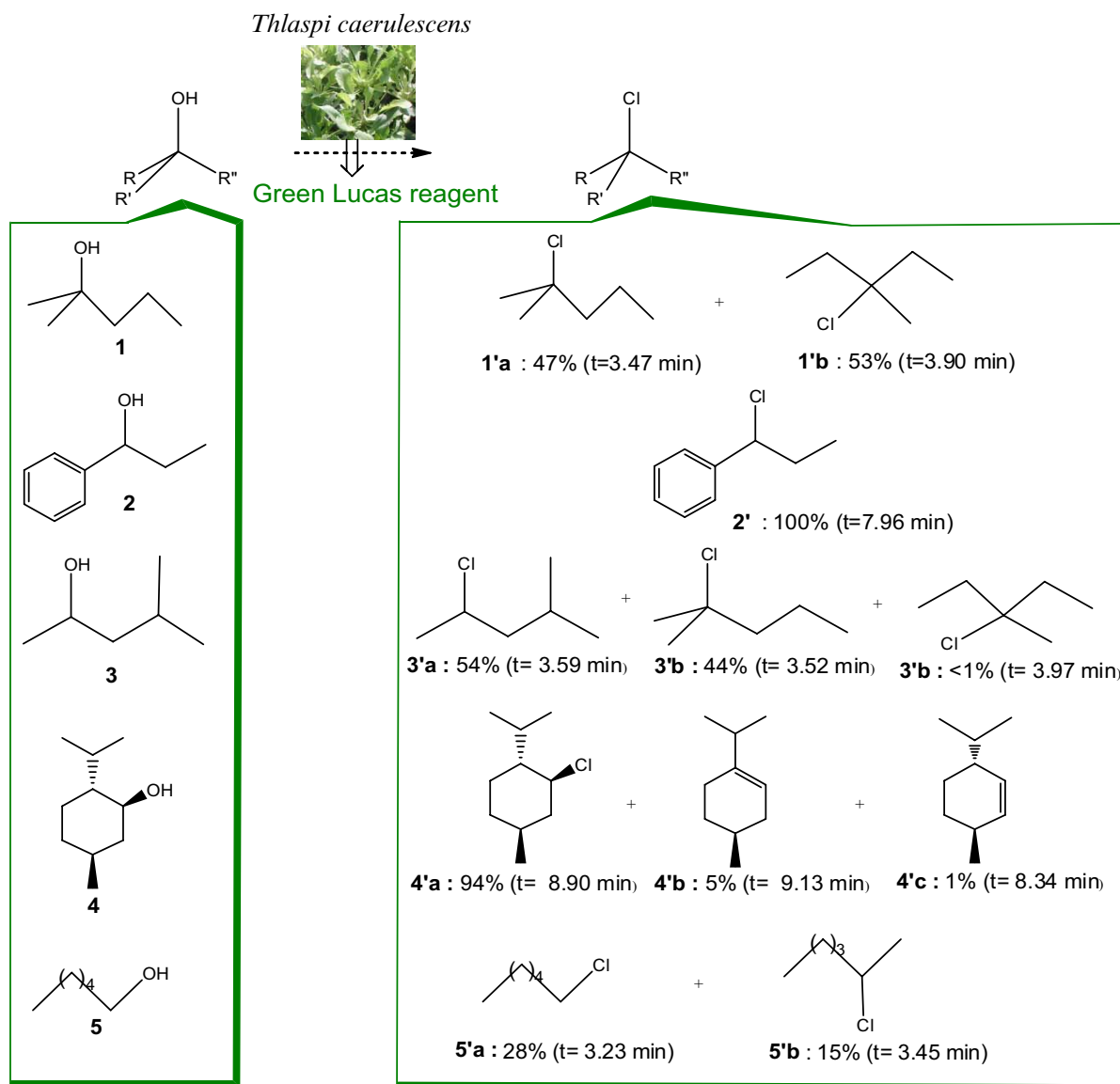


Figure 2. Chlorination of alcohol with green Lucas reagent derived from *T. caerulescens*.

concentration of the aqueous layer at 110 °C. The solid residue was kept in a stove at 90 °C. It can be used as “green catalytic solid” under the same conditions and retained optimum activity until four cycles. The batch to batch variability of reagent was controlled by ICP-MS; the mineral composition remained almost the same after four-run, which was illustrated with the compared amount of Zn(II) (from 21.96 mg for the first run to 21.56 mg for the fourth run).

Experimental

Gas chromatography and mass spectrometry analyses were performed using electronic impact (EI) ionization mode on a Varian Saturn 2000 ion trap

instrument, interfaced with a Varian CP-3800 apparatus. The Varian CP-3800 was equipped with a 1079 split-splitless injector (206 °C) and a 30 m × 0.25 mm × 0.25 µm film thickness ID WCOT CPSil-8CB fused silica capillary column (Chrompack®, Bergen op Zoom, The Netherlands), with helium as carrier gas (1 mL min⁻¹), and programmed 2 min isothermal at 50 °C, then increasing from 50 to 220 °C at 4 °C min⁻¹. Mass spectra were recorded in EI at 70 eV, and identified by comparison with data of the NIST 98 software library (Varian, Palo Alto, CA) and by comparison of the retention time of the standard compounds.

Samples of ferrite were studied using a Philips CM 20 TEM with a LaB₆ cathode operating at 200 kV.

Pulse polarography was performed according to Ref. (13).

Liquid chromatography-mass spectrometry (LC-MS) analyses were performed with a Mass spectrometer in Electrospray mode coupled to HPLC (Quattro micro QAB 1822), under the following conditions: SM: 1.03 eV, ES⁻; LC: chromatographic column Onyx, 1 mL min⁻¹, 50/50 H₂O/CH₃CN.

ICP-MS analyses were performed using the metal analysis of total dissolved solutes in water. The samples were acidified with nitric acid 2.5% and stirred for 30 min. The digestates were diluted to 0.005 g L⁻¹. Three blanks are recorded for each step of the digestion and dilution procedure on a HR-ICP-MS Thermo Scientific Element XR.

Representative experimental procedure for the preparation of the green Lucas' reagent

T. caerulea leaves were collected from plants growing on the Les Avinières mine site, Saint-Laurent-Le-Minier, Gard, France. Leaves were harvested before flowering, air-dried, and crushed. The obtained solid (150 g) was calcined at 400 °C for 5 h and the resulting powder (148 g) was added to 1 L of a solution of hydrochloric acid (~10 M). The solution was heated at 60 °C and stirred for 2 h. The reaction mixture was cooled at room temperature, filtered, and introduced at the top surface of the Amberlite IRA 400 (about 60 g of resin per gram of solid). Operating conditions of purification were as follows: elution of alkali and alkaline earth metals with 0.5 M HCl (3 mL per min.); then elution of heavy metals with 0.005 M HCl.

Representative experimental procedure for the chlorination of alcohols

Alcohol (10 mM) was added to 20 mL of Green Lucas' reagent. The reaction mixture was then stirred at 25 °C. The stirring was maintained for 7–10 h. A sample of the reaction mixture was taken for GC-MS analysis. Conversion and selectivity were determined based on area normalization without any purification. Products were identified by GC-MS, and by comparison of their GC retention times and MS analysis with those of authentic samples. When GC showed that the conversion of alcohol was more than 99%, 50 mL of petrol ether were added. After separating the resulting two layers, the organic phases washed with a solution of NaHCO₃. The organic layer was dried with calcium chloride and the solvent was removed. The aqueous solution was concentrated by rotary evaporator, dried under heated desiccant at

150 °C and the solid residue was kept in a stove at 90 °C until a new experiment. Crucial data were reconfirmed by ¹H NMR after work-up. The chlorinated products were purified by according to (14).

Conclusion

In summary, this work was the first application of hyperaccumulating plants in organic synthesis. The obtained results demonstrated that "green Lucas' reagent" derived from *T. caerulea* is an efficient catalyst for the chlorination of alcohols. Under optimal conditions, aliphatic chlorides were obtained in high yields within 8 h. The process combines three "green" aspects:

1. "Green Lucas' reagent" can be produced from renewable resources, using plants to clean up the environment. The process is based on the recycling of metallic wastes.
2. In comparison with the hydro or pyrometallurgical ZnCl₂ production pathways, this method is environmentally benign and economical for the conversion of biomass-based derivatives; moreover the process does not require the use of auxiliary substances (solvent or separation agents).
3. After the reaction, the catalyst could easily be separated from the reaction mixture for reuse. It was recycled in a new chlorination of alcohols.

Further research and application of this solid acid catalyst in sustainable chemistry should be developed in the future.

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