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Graphical Abstract

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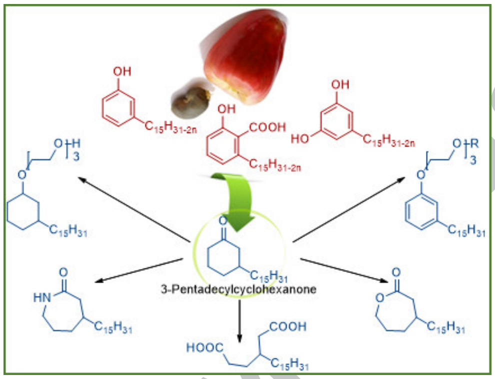

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ABSTRACT

A unique advanced intermediate: 3-pentadecylcyclohexanone was synthetized from the crude product which contained a mixture of cardanol, cardol and 2-methylcardol, which was hydrogenated onto Pd/C at 80°C. From this alkylated cyclohexanone: C15 alkylated adipic acid, caprolactam, caprolactone, were synthetized in high yields, such products may have many potentially applications in polymer chemistry. The condensation of the 3-pentadecyl-cyclohexanone and triethylene glycol in oxidative or reductive conditions gave aryl ether and cyclohexyl ether, this may be a way to prepare intermediate for surfactant chemistry. Therefore we show that Cashew Nut Shell Liquid (CNSL) may lead to numerous useful compounds thank to the preparation of a unique advanced intermediate.

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1. Introduction

Industrial ecology is one of the most important concepts developed in the so call "green chemistry". In industrial ecology the waste of one factory should become the starting material of a second factory. So use of starting material and energy and ultimate waste production should be minimized.[1] Fruit industry appears to be one of promising areas for the development of such concept. Indeed, fruit industry is collecting large amount of raw materials and use only a fraction of the collected fruits. Peels, hulls and in some case seeds are burned or landfill.[2] Over the world the production of Cashew Nuts is higher than 2.2 millions of tons.[3] These nuts contain 30% of kernel and 70% of Hulls.[2] Cashew hulls could be easily extracted with hexane to give a liquid with a very original composition including one of the rare natural sources of non-polymerized aromatic rings (**Fig 1**).[4] Indeed CNSL is clearly one of the best candidate for valorisation and several recent articles and reviews have described its application in different areas. Antibacterial and larvicidal properties of CNSL, and in particular of derivatives of anacardic acid and cardanol were demonstrated.[5] Antioxidant properties of CNSL constituents were also studied [6] and applications in curing of natural rubber or as additive for biofuel were proposed.[7] Oxidation of cardanol with peroxides allows the formation of materials with good temperature stability and medium flame retardant properties.[8]

CNSL was also used for the synthesis of resins with various aldehydes or these materials were transformed into polyurethane.[9] Epoxide resins were also prepared using either the phenol or the alkene groups to introduce the epoxide functions.[1]

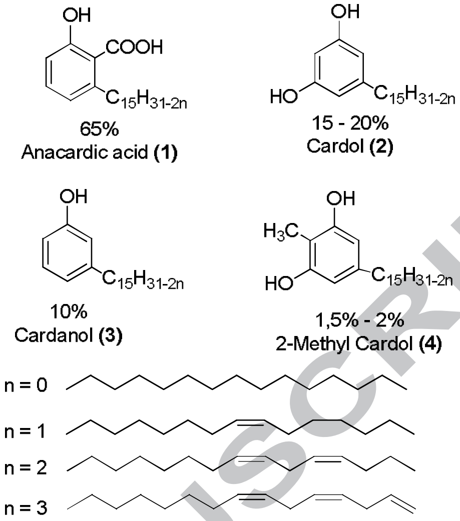
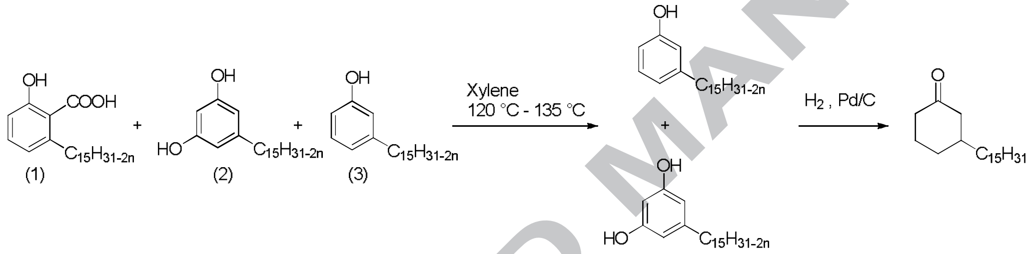


Fig 1 Main constituents of the Cashew Nut Shell Liquid



Scheme 1 Preparation of 3-Pentadecylcyclohexanone from the CNSL mixture

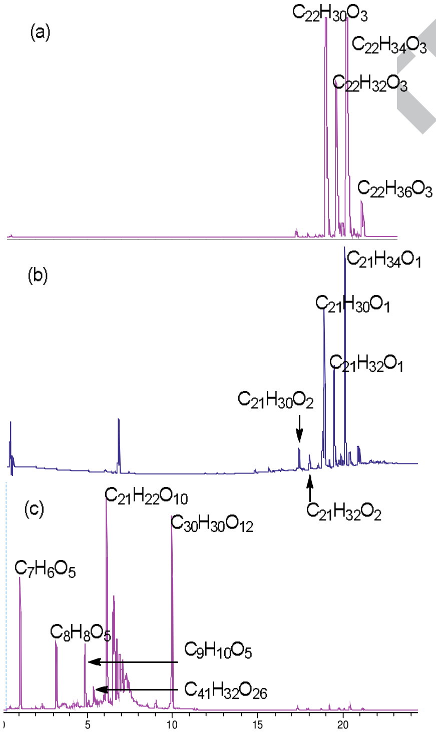


Fig 2 Chromatogramof (a) Malagasy CNSL, (b) decarboxylated CNSL, (c) Mixture of Gallic acid and tannin.

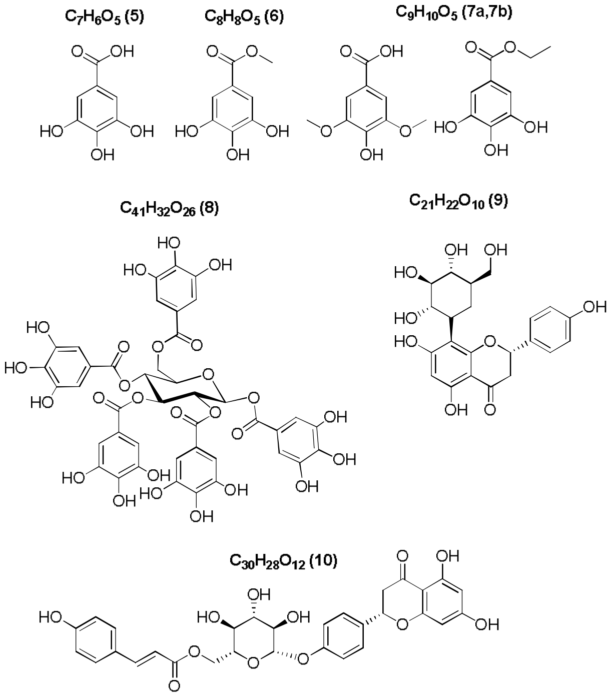


Fig. 3. Main constituents of ethanol extract

Table 1. Results of UPLC – HRMS analysis coupled with a high resolution mass spectrometer

[M-H] Ion Formula	m/z	Structure proposition
$C_7H_5O_5$	169.0142	Gallicacid

$C_8H_7O_5$	183.0299	Methyl gallate
C_9H_9O5	197.0455	Syringicacid
$C_{41}H_{31}O_{26}$	939.1109	Penta-O-galloyl-D-glucose
$C_{21}H_{21}O_{10}$	433.114	Iso hemiphloin
$C_{30}H_{29}O_{12}$	581.1654	Leufolin

Finally, the aromatic ring of cardanol was transformed into diacid, then the reaction with diamine *via* a 6 steps gave the polyamides.

Although promising, these applications are still limited and cardanol should be separated from cardol and others derivatives and is mainly used as renewable source of alkylated phenol ring

This strategy suffers from the comparatively very low price of the petro-sourced phenols. One of the main difficulties, when working with agro-industry wastes, is linked to the complex composition of the crude material with often significant seasonal variations. From this general point of view, CNSL contain aromatic compounds with one or two phenol groups, no or one carboxylic group, no or one methyl group and finally a C15 alkyl chain with one, two or three double bonds.

In this article we describe a strategy allowing the access to a unique advanced intermediate (3-Pentadecylcyclohexanone, **Scheme 1**) and then the preparation of several building blocks of high potential for polymer science and technology.

2. Result and discussion

2.1. Extraction of CNSL

Although production of Cashew nut in Madagascar is important and increasing 4660 metric tons/years, Malagasy CNSL is not valorised for the moment. We have worked on hulls obtained from cashew trees (*Anacardium occidentale* L.) of Boeny Region, Madagascar. More precisely, using Soxhlet extraction with hexane, we obtained 39 wt% of a dark brown liquid from the crushed cashew hulls. The composition is given above and contains mainly 4 families of products with only difference at the number and the position of CC double bonds on the alkenyl chains: Anacardic acid 71 % (**1**), Cardol 19 % (**2**), Cardanol 4 % (**3**) and 2-Methyl cardol 1,2 % (**4**). Another extraction of cashew nut shell residue by ethanol supplied 5.8% of a mixture of gallic acid and tannin (**Fig 3**).

These compounds and its derivatives are commonly used in tannery, for the production of ink and as starting materials for chemical industry.[12] As a consequence, we focused this study on the valorization of anacardic derivatives.

2.2. Decarboxylation of CNSL

A way of simplifying the mixture of CNSL consists in decarboxylating the anacardic acid derivatives following the Tejas conditions in reflux of toluene.[13] Nevertheless, Antananarivo is located at a height of 1276 m, consequently the boiling point of toluene is too low at this place to perform the reaction in a reasonable speed. Therefore, we used the reflux of xylene instead of toluene and we obtained a mixture of cardanol, methyl cardol and cardol derivatives with 94 % yield.

2.3. Synthesis and purification of 3-Pentadecylcyclohexanone

In order to obtain an even more simplified mixture by the formation of cyclohexanone derivative, we reduced the aromatic core and the alkyl chain. First of all, we separated the cardanol derivatives from the cardol and methyl cardol using chromatography (silica gel, hexane, ethyl acetate) with 80 %, 14,8 %, 1,1 % isolated yields respectively. These samples contained 3-alkenyl phenol, 3-alkenyl methyl resorcinol and 3-alkenyl resorcinol with variations on the alkenyl chain.

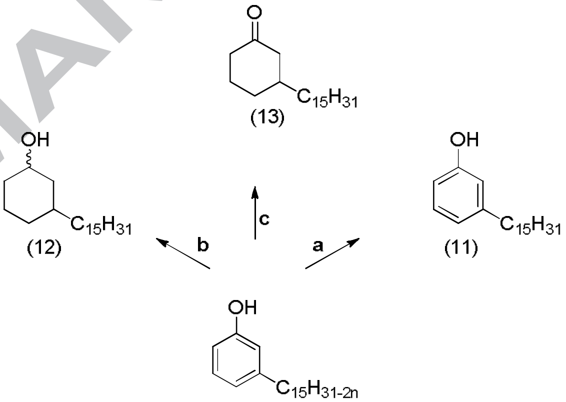
2.4. Reduction of cardanol

Firstly, we reduced pure cardanol using different catalysts and hydrogen under pressure since the reduction of phenol may lead to the formation of cyclohexanone which can be considered as a useful advanced intermediate (**Scheme 2**).[14] Although the aromatic ring could be easily reduced using ruthenium or rhodium metal nanoparticles or colloids,[15] we chose, to facilitate the separation and the recycling of the catalyst, to use commercially available transition metal on support.

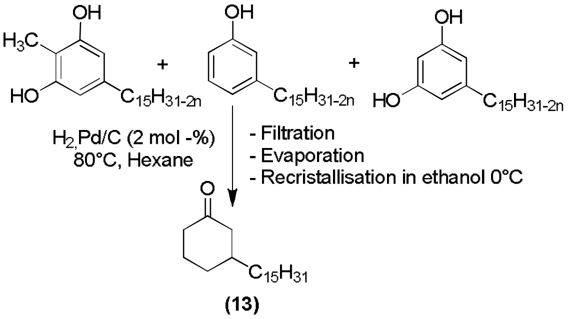
Attempts with silica or alumina as support for ruthenium particles prove to be inefficient conversely ruthenium and palladium onto hydrophobic support such as carbon were active catalysts. Ruthenium catalysts clearly exhibited poor selectivity toward the 3-Pentadecylcyclohexanone: at low temperature the main product is the 3-pentadecyclphenol and at a higher temperature both the aromatic ring and the ketone were reduced: the two isomers of 3-pentadecylcyclohexanol are obtained as major products. Conversely complete reduction of the aromatic ring and few reduction of the ketone were observed when using palladium even at 80 °C.[16]

2.5. Reduction of cardol

Finally, we have reduced the cardol derivatives in similar conditions and we were very pleased to observe that the main product obtained was also the 3-Pentadecylcyclohexanone.



Scheme 2 Reduction of cardanol using different catalysts. Reactions conditions: (a) H_2, Ru/C (1 mol-%), Hexane, 20 Bar, rt, 5h; (b) H_2, Ru/C (1 mol-%), Hexane, 20 Bar, 70°C, 5h; (c) H_2, Pd/C(2 mol-%), Hexane, 30 Bar, 80°C, 3h.



Scheme 3 Hydrogenation of CNSL

This could be explained by the reduction of the resorcinol ring into diketone then hydroxyl ketone, dehydration, followed by the reduction of the CC double bond to give the cyclohexanone. In this particular case, the 3-Pentadecylcyclohexanone was obtained after chromatography purification with 36 % yield.

Therefore it was possible to transform the two main products of decarboxylated CNSL into a single product. The main drawback of this method is the use of solvent with high ecological impact (methylene chloride), nevertheless this is only due to the poor solubility of the pure cardanol and cardol in alkane. We have furthermore demonstrated a higher solubility of the crude decarboxylated CNSL and the possibility of using alkane as solvent for the reduction of the natural mixture (see below).

2.6. Reduction of the decarboxylated Cashew Nut Shell Liquid

Attempt in reducing the crude cashew nut shell liquid directly after decarboxylation was unsuccessful; this is probably due to the poisoning effect of highly polar compounds similar to that obtained by ethanol extraction (see above). Indeed after elimination of such polar compounds by filtration through a pad of silica (ethyl acetate 95% yield), the reduction was performed in hexane and similar conditions that of pure cardanol.

To validate the poisoning effect of polar molecules, a reduction was performed with addition of 20 wt.% of crude polar compounds obtained during the ethanol extraction (see above) under hydrogen pressure with 1 mmol of 3-pentadecylphenol, 2 mol-% of Pd/C at 80°C. The conversion was in this case incomplete.

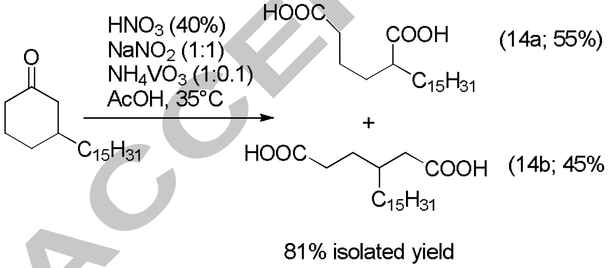
Moreover it was possible to use hexane (or better heptane) (**Scheme 3**) as solvent for this reaction with the mixture of natural CNSL.

The purification of the crude product after reduction by chromatography allowed us to obtain pure 3-Pentadecylcyclohexanone with 58 % (mp 43 °C) of yield but more simply, recrystallizing in ethanol leaded to a white solid in more of 90 % purity and with 70 % yield. Methyl cardol derivatives are only partly reduced and are soluble in ethanol as well as the major part of the isomers of 3-pentadecyl-cyclohexanol. Therefore our strategy gave access to a unique advanced intermediate with overall (two steps) yield of 67 % from the crude Cashew Nut Shell Liquid. It was possible to propose many potential synthetic applications for this alkylated cyclohexanone, we have already evaluated some of them.

2.7. Potential applications of 3-Pentadecylcyclohexanone

2.7.1. Synthesis of alkylated adipic acid

The preparation of diacid from cyclohexanone, is an important industrial process for the preparation of adipic acid.[17] We evaluated conditions similar to that already used for adipic acid synthesis in order to obtain the diacid with C15 chain as pendant group.



Scheme 4 Synthesis of 3- pentadecyl-adipic acid

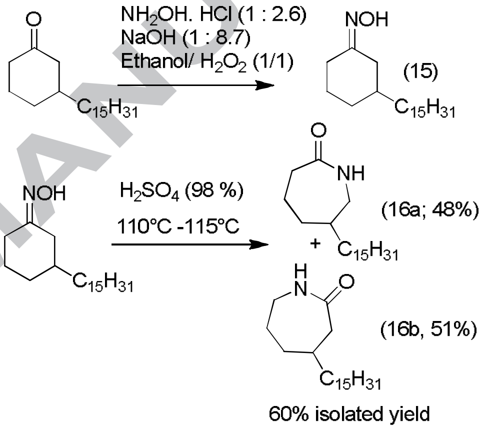
The difficulty in using nitric acid in water and sodium nitrite with a hydrophobic substrate such as 3-Pentadecylcyclohexanone could be overcome by using acetic acid as co-solvent. We obtained the desired products after hexane crystallizing as a mixture 1/1 of two regioisomers with 81 % yield (**Scheme 4**) (white solid mp 78°C).

2.7.2. Alkylated caprolactam

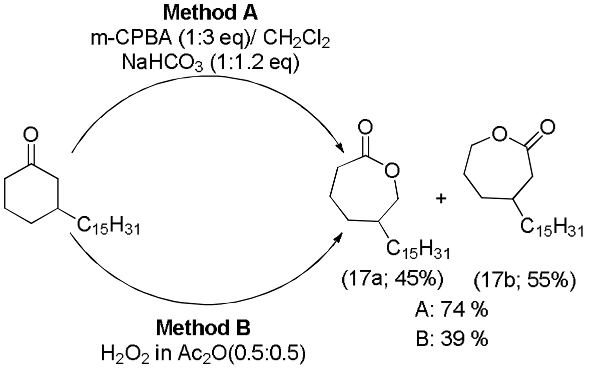
Similarly, the preparation of caprolactam with pendant alkyl chain could be performed by the same method used for caprolactam itself.[18] Oxime could be prepared by using hydroxylamine chlorohydrate then Beckman transposition was performed in sulfuric acid. The first step was tested in two conditions: the first one, using a solution of free hydroxylamine (2 eq) in ethanol at 60°C that gave a low conversion. And a second one, using the same amount of hydroxylamine chlorohydrate in the presence of sodium hydroxide in ethanol a yield of 94 % of the *syn* and *anti* oxime was obtained (Shedge et al., 2005)[16]. Similarly, for the second step, the Beckmann transposition was firstly tested using 70 % sulfuric acid and such conditions allowed the formation of the desired product with only low yield and hydrolysis into the previous ketone was the main reaction. On the opposite, the use of 1 mol /mol of 100 % sulfuric allowed the formation of the two desired lactams (**Scheme 5**), (white solid mp 81°C) with 61 % yield after purification by chromatography.

2.7.3. Alkylated caprolactone

Caprolactone is an important monomer for the synthesis of poly(esters). The alkylated cyclohexanone was treated with *m*-CPBA in solvent at 25 C (**Scheme 6**, **Method A**), after purification by extraction with sodium carbonate and chromatography, 74 % yield of a white solid (mp 42 C). In order to avoid the formation of large amount of *m*-chlorobenzoic acid as by-product and the use of methylene chloride, we performed the reaction using 30 % hydrogen peroxide in acetic anhydride (**Scheme 6**; **Method B**), the desired lactone was obtained in 39 % yield.



Scheme 5 Synthesis of alkylated caprolactam



Scheme 6 Synthesis of alkylated caprolactone

2.7.4. Alkylated phenyl ether

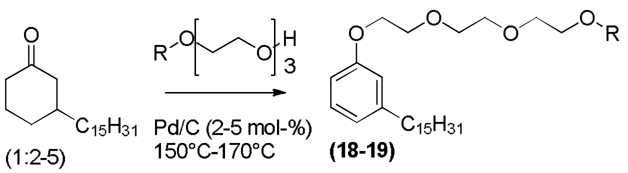
Phenyl ethers are interesting building blocks as solvent and potentially as surfactant or plasticizer. Generally, phenyl ethers are obtained by Williamson type synthesis[19] or by aromatic nucleophilic substitution catalysed either by copper[19] or palladium.[20] Although very useful, these reactions suffer from several drawbacks such as production of salts as by-products, the use of toxic solvent and/or expansive catalyst.

More recently the use of oxidative alkylation of cyclohexanone was proven to be an efficient alternative with lower ecological impact.[21] In this reaction the formation of ketal or enol ether is followed by deshydrogenation over activated palladium. The formed hydrogen was scavenged either by an alkene or by air.[21]

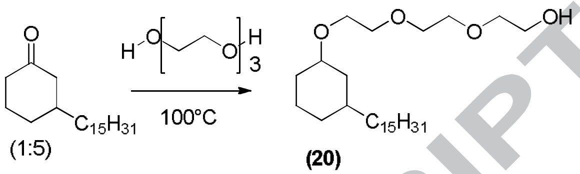
In the case of 3-Pentadecylcyclohexanone the difficulty is linked to the high hydrophobicity of the substrate hardly compatible with polar alcohol, nevertheless we performed the reaction at 150°C, with the presence of an excess of triethylene glycol and after 36 hours we isolated only 9 % of the desired product (**18**) (**Scheme 7**).

This low isolated yield makes, (for the moment) the method useless from a practical point of view. Therefore, we tested the reductive alkylation following the conditions developed in Lyon laboratory. The reductive alkylation [22] of 3-Pentadecylcyclohexanone with triethylene glycol in a 1:5 molar ratio at 100 °C was performed (**Scheme 8**), as shown in Table 2.

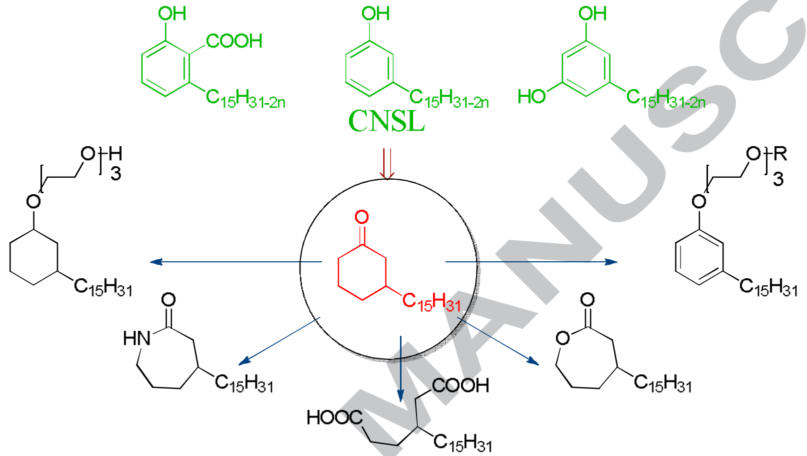
In the reaction the competition between reduction of cyclohexanone into cyclohexanol and the desired reductive alkylation could be limited by using a large excess of the alcohol and by limiting both the hydrogen pressure and the catalyst load.



Scheme 7 Synthesis of oxyethylen ether of 3-pentadecylphenol



Scheme 8. Synthesis of oxyethylen ether of 3-pentadecylcyclohexanol



Scheme 9 Examples of potential valorizations of CNSL via 3-Pentadecylcyclohexanone

Table 2. Reductive alkylation of the 3-Pentadecylcyclohexanone

Entry	Pressure (Bar)	Time (h)	Yield (%)[b]
1	40	14	48
2	30	22	55
3	20	28	57
4	40[c]	16	58

[a]Condition: molar ratio of 3-Pentadecylcyclohexanone/triethylene glycol = 1/5, Pd/C (5mol-%), 100 °C under hydrogen pressure.

[b]Yields were determined on Column chromatography.

[c]Condition: molar ratio of 3-Pentadecylcyclohexanone/triethylene glycol = 1/10

When the reactants were used in a molar ratio alcohol/ketone of 1/10, the ether was obtained in 58% (Table 2, entry 4).

3. Conclusions

Although CNSL is, like most of the natural products and agroindustry wastes, a complex mixture, we found a strategy allowing the preparation of unique advanced intermediate in two steps and with high yield. This 3-Pentadecylcyclohexanone has structural similarity with the cyclohexanone which is a very important building block of the petro-based chemical industry in general and polymer industry in particular. Examples of several potential applications in these areas are presented here. Indeed, chemical transformations similar to that already realized in industry could be performed on this new bio-sourced building block.

Di-acid, lactam, lactone and ethers (**Scheme 9**) were obtained in few steps and good yields. Taking into account the very large potential production of CNSL (million tons!) these may be of importance in term of chemical ecology.

Acknowledgments

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Supplementary Material

Supplementary data associated with…

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- The synthesis of one advanced intermediate is proposed.
- The hydrogenation of the crude cardanol-cardol mixture gave the corresponding ketone.
- The 3-Pentadecylcyclohexanone has structural similarity with the cyclohexanone
- Di-acid, lactam, lactone and ethers were obtained in few steps and good yields.