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Synthesis of bio-based surfactants from cashew nutshell liquid in water

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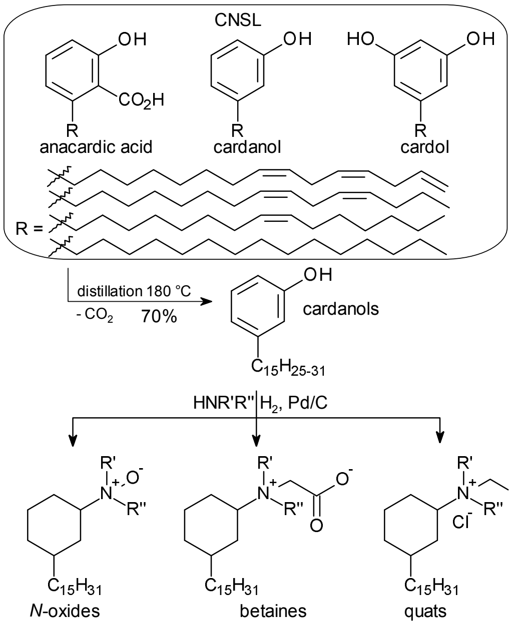
3-Pentadecylcyclohexylamines were synthesised via Pd/C-catalysed reductive amination of crude cashew nutshell liquid, an underused waste product, with hydrogen in water. The short, modular, and waste-minimised synthetic approach enables accessing structurally diverse neutral, cationic, and zwitterionic tenside derivatives.

Cashew nutshell liquid (CNSL, Scheme 1) is an inedible waste product of cashew nut production, obtained on a scale of 1 megaton per year.[1] Cashew nutshells contain a mixture of anacardic acids, substituted phenols, cardanol, and cardol, each bearing a 15-carbon side chain with different degrees of unsaturation. CNSL is obtained by pressing the nutshells at elevated temperatures, causing decarboxylation of the acid components. The resulting oil consists mainly of cardanols. The use of cardanol as a chemical feedstock is highly advantageous because it does not compete with land use for food production.[2–4] However, most current applications of this raw material lead to low-value products. Cardanol has been used in the synthesis of aromatic amines,[5,6] modifiers of epoxy resins,[7] rubber plasticisers,[8] and adhesives.[9]

The long alkyl chain makes cardanol a promising source for surfactants. Indeed, it has been converted to anionic surfactants such as sulfonates, sulfates, carboxylates, as well as non-ionic polyethoxylate surfactants.[7,10–18] However, these structures retain the aromatic ring, which is known to lead to toxicity and bioaccumulation, and are particularly harmful for the aquatic habitat.[19–26] In this respect, they are inferior to state-of-the-art surfactants, which are, however, mostly prepared from petrochemical sources or fatty acids valuable for food use.

The global consumption of surfactants as softeners, detergents, cosmetics and personal care products, paints, and agrochemicals is close to 20 megatons.[27,28] Cationic (*quats*), zwitterionic (betaines), and non-ionic surfactants (*N*-oxides), all based on long-chain amines, are expensive and used for high-end applications.[29,30] They are characterised by low toxicity and skin irritation, good foam stability, and rapid biodegradation, and are therefore used in detergents, shampoos, cosmetics and personal care products.[31–34]



Scheme 1. Targeted conversion of CNSL into amine-based surfactants.

Exceptionally high value creation with maximal sustainability would thus be achieved if a short and waste-minimised synthesis of non-aromatic amine surfactants could be devised starting from technical CNSL (Scheme 1). The recent discovery of reductive amination processes of phenols to cyclohexyl amines (Scheme 2) seemed to open up a window of synthetic opportunity for the valorisation of cardanols. Thus, Li[35] and Taddei[36] reported a Pd/C-catalysed reductive

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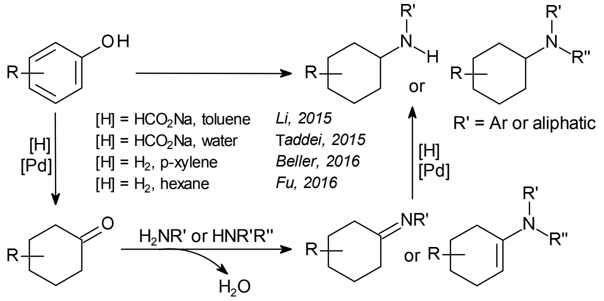
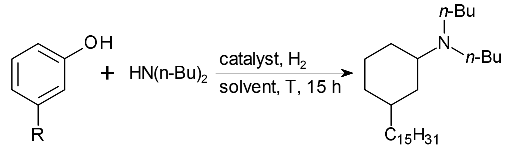
amination of simple phenols using aqueous HCO_2Na as the reducing agent, leading aromatic or aliphatic amines, respectively. Beller[37] and Fu[38] used H_2 as reducing agent, albeit in organic solvents.



Scheme 2. Reductive amination of phenols to cyclohexyl amine derivatives.

The use of hydrogen in combination with a Pd/C catalyst and an ecologically benign solvent would be optimal for large-scale applications. We thus began investigating the coupling of technical CNSL (**1**) with di-*n*-butyl amine (**2a**) as a model reaction using 2 mol% Pd/C at 10 bar H_2 pressure at 100 °C (Table 1). Compared to structurally simple and highly purified phenols, dark-brown, oily CNSL proved to be a challenging substrate.

Table 1. Optimisation of the reductive amination conditions. [a]



1 **2a** **3a**

Entry	Catalyst	Solvent	Yield of **3a** (%)
1	Pd/C	EtOH	15
2	"	^{i}PrOH	11
3	"	toluene	17
4	"	cyclohexane	15
5	"	mesitylene	11
6	"	diglyme	5
7	"	H_2O/^{i}PrOH	51
8	"	H_2O	90
9	Rh/C	"	49
10	Ru/C	"	n.d.
11	Al/Ni	"	n.d.
12	Pd/Al_2O_3	"	trace
13	Pd/$BaSO_4$	"	n.d.
14[b]	Pd/C	"	18
15[c]	"	"	40
16[d]	"	"	90
17[e]	"	"	60

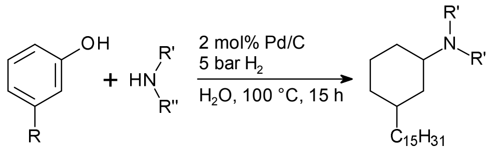
[a] Reaction conditions: 0.5 mmol **1**, 0.55 mmol **2a**, 2 mol% catalyst, 10 bar H_2, 2 mL solvent, 100 °C, 15 h. Yields were determined by GC using *n*-hexadecane as internal standard and calculated based on CNSL weight. [b] 1 mol% catalyst. [c] 80 °C. [d] 5 bar H_2. . [e] 1 bar H_2. n.d. = not detected.

In non-polar and polar, aprotic and protic organic solvents, the yields were low (entries 1-6). This was not improved by addition of Lewis acids or alternative solid supports for Pd (see the supporting information). However, the yields drastically improved when switching to aqueous solvents (entry 7). To our delight, the desired product **3a** was obtained in almost quantitative yield in water (entry 8). In this solvent, Pd/C was superior to all other metals (rhodium, ruthenium, platinum, Raney nickel) and solid supports (charcoal, alumina, barium carbonate) tested (entries 9-13 and Table S1). A catalyst loading of 2 mol%, a temperature of 100 °C, and a H_2 pressure of 5 bar are necessary to obtain 90% yield (entries 14-16). Under ambient H_2 pressure **3a** could obtained in only 60% yield (entry 17). Considered that the yields were calculated based on the weight of technical CNSL, this is likely to be a quantitative yield based on the cardanols. The reaction likely proceeds via phenol hydrogenation followed by a classical reductive amination (Scheme 2).[37,39] In control experiments, no product was formed when starting from the cyclohexanol, whereas quantitative conversion was observed when starting from the cyclohexanone (Scheme S1).

We next investigated the generality of this reductive amination (Table 2). Cyclic, mono- and dialkylamines were all converted in good yields. Functionalities including methoxy, acetal, or dialkylamino groups were well tolerated. This confirms that this reaction step is suitable for designing structurally diverse tensides for various applications.

The scalability of the reaction was demonstrated by synthesizing *N*,*N*-dibutyl-3-pentadecyl cyclohexylamine (**3a**, 66% yield) and *N*,*N*-dimethyl-3-pentadecyl cyclohexylamine (**3b**, 64% yield) on 15-20 g scale.

Table 2. Substrate scope for the reductive amination of cardanol.[a]



1 **2a-l** **3a-l**

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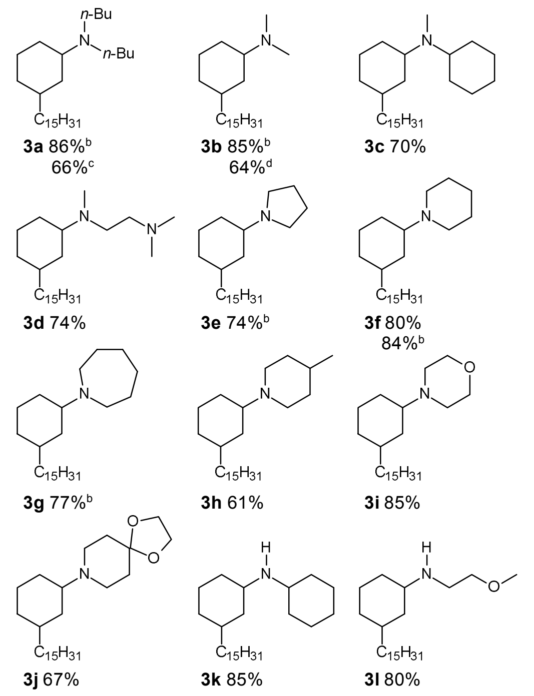
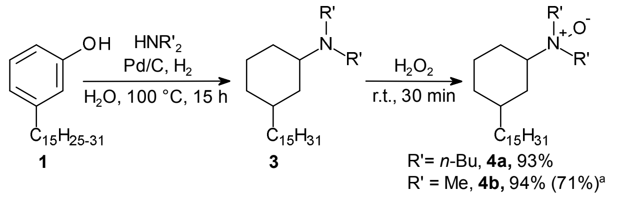


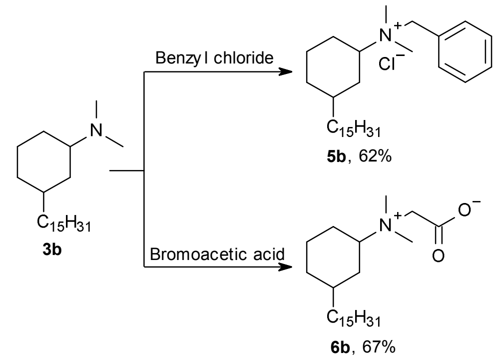
[a] Reaction conditions: 1 mmol **1**, 1.1 mmol **2**, 2 mol% Pd/C, 5 bar H_2, 3 mL H_2O, 100 °C, 15 h. Isolated yields after purification. [b] 10 bar H_2. [c] 50 mmol scale. [d] 68 mmol scale.

The oxidation of amines **3a** and **3b** to the corresponding *N*-oxides proceeded in quantitative yields using hydrogen peroxide (Scheme 3). Moreover, both reaction steps were successfully combined into one pot. The resulting process involves reductive amination of cardanol and dimethylamine in the presence of Pd/C at 10 bar H_2 and 100 °C in water. After 15 h, the intermediate amine was oxidized with H_2O_2 at room temperature. Water and pentane were added after 30 minutes, and the aqueous phase was concentrated, yielding **4b** in 71% yield. Unreacted amine and 3-pentadecylphenol side-product remained in the organic layer, and the catalyst was recovered by filtration. This way, an E-factor of 2 (total kg of waste per kg product, see SI) was reached which for large-scale manufacture can certainly be improved further.[40,41]



Scheme 3. Synthesis of *N*-oxides from cardanols. [a] yield of one pot procedure.

Amine **3b** was also successfully converted to the benzylquat *N*-benzyl-*N*,*N*-dimethyl-3-pentadecylcyclohexan-1-aminium (**5b**) and to the betaine 2-(dimethyl(3-pentadecylcyclohexyl)ammonio)acetate (**6b**) in reasonable yields following standard procedures (Scheme 4).[42,43]



Scheme 4. Synthesis of quaternary ammonium salt and betaine.

The surface tension and aggregation behaviour of **4b**, **5b**, and **6b** were explored using drop shape analysis. Their critical micellar concentration (CMC) was found to be 28 μM, 0.5 μM, and 10 μM respectively (see SI for the data). These values compare favourably with those of the state-of-the-art commercial fatty acid-derived tensides lauryldimethylamine oxide (1.7 mM),[44] stearyldimethylbenzylammonium chloride (0.31 mM),[45] and lauryl betaine (2.86 x 10^{-3} mM),[46] proving their exceptional potential as surfactants. These results form an excellent basis for the targeted design of cardanol-derived amine-based tensides for various applications.

Conclusions

A straightforward, eco-friendly and waste-minimised concept for the synthesis of amine-based surfactants from CNSL, an inedible waste product of the cashew nut industry, has been devised. The *N*-oxide, betaine, and quaternary ammonium salt tensides thus obtained show comparable or better properties than state-of-the-art commercial surfactants. The key step, a catalytic reductive amination, is carried out in water using molecular H_2 as reductant. In the case of the particularly valuable *N*-oxide surfactant, the entire reaction sequence can be performed in one pot with water as the sole solvent, resulting in a remarkably low E-factor.

Acknowledgements

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Conflicts of interest

The authors declare no conflict of interest.

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