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Mechanochemical synthesis of (4S)-*N*-alkyl-4,5-bis-sulfooxypentanamide *via* a one-pot sequential aminolysis-sulfation reaction of (S)- γ -hydroxymethyl- γ -butyrolactone (2H-HBO)

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To valorize further the highly valuable bio-based platform (S)- γ -hydroxymethyl- γ -butyrolactone (2H-HBO), whose sustainable kiloscale-synthesis from cellulose-derived levoglucosenone (LGO) has been validated, a mechanochemical strategy was developed to produce new potential bio-based surfactants in solventless conditions. First, the reaction of 2H-HBO with primary or secondary amines was investigated followed by a sulfation reaction on the isolated *N*-alkyl-amide derivatives to obtain the corresponding *N*-alkyl sulfated compounds. These latter were then obtained by an optimized one-pot sequential aminolysis-sulfation in a planetary ball mill with excellent efficiency. For the first time, sulfated compounds arising from bio-based/renewable resources were obtained exclusively *via* a mechanochemical process. As a result, these sulfated derivatives of 2H-HBO were formed quantitatively and isolated in 69-79% overall yields. Critical micellar concentration (CMC) was evaluated for some of them and revealed an interesting anionic surfactant properties.

Introduction

Nowadays, more and more chemists are engaged in concepts such as sustainable chemistry and bioeconomy, in particular in biomass valorisation, which remains one of the major resources to reach environment-friendly processes and overcome petrol scarcity. However, there are still many challenges to tackle in the valorisation of biomass to produce valuable and versatile chemicals with high selectivity and yields while limiting waste production. In this context, many synthetic strategies have been developed in particular in solventless conditions combining adequate technologies, such as ball milling. Initially developed in material sciences,¹ mechanical milling became more and more attractive in organic synthesis for these three past decades.² Designated by IUPAC as “a chemical reaction that is induced by mechanical energy”,³ this tool presents many advantages, such as reduced time reaction and solventless conditions, which present serious environmental and economic issues. Also, mechano-synthesis can afford higher yields and, for some examples, higher selectivity or reactivity never reached in conventional solvent-based reactions.⁴ As an example, the one-pot synthesis of *N*-sulfonylguanidines from aryl sulfonamides was successfully achieved in higher concentration in the presence of copper chloride as catalyst through mechanochemical coupling procedure while resulting in poor conversions or failure when conducted in solution.⁵ Another example is the Diels-Alder reaction between diphenylfulvene and maleimide which was investigated either under solution conditions and under grinding conditions. Many advantages were observed for the mechanochemical process: better selectivity, shorter reaction time and full conversion.⁶

In a context of development of petroleum-derived surfactants alternatives, we have previously synthesized and described different families of glycolipids.⁷ Sugar-based amphiphiles were prepared by condensation of a lipidic chain to the anomeric position of an aldose *via* an amide function. We have shown that solubility of these compounds in water decreased with alkyl chain with more than eight carbons.^{7b} In order to expand the series of sugar-based surfactants, an anionic moiety (sulfate group) was added on the primary position of the monosaccharide.^{7c,d} The surface properties of these anionic sugar-based surfactants were similar to those of commercial anionic surfactants such as sodium dodecyl sulfate (SDS) and sodium lauryl ether sulfate (SLES) with good ability to reduce surface tension.

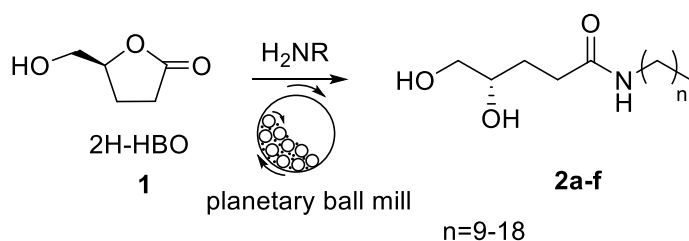
Recently, cellulose-derived levoglucosenone (LGO)⁸ has been proven a very promising bio-based starting material for the synthesis of value-added chiral building blocks, namely (S)- γ -hydroxymethyl- γ -butenolide (HBO) and (S)- γ -hydroxymethyl- γ -butyrolactone (2H-HBO, **1**),⁹ that allow the production of a wide variety of molecules of interest¹⁰ such as flavor,¹¹ drugs intermediates,¹² monomers and polymers.¹³

In our continuous interest in the synthesis of higher added value bio-based compounds, herein we describe a green one-pot two-step mechanochemical synthesis of new high value derivatives of 2H-HBO (**1**), (4S)-*N*-alkyl-4,5-bis-sulfooxypentanamides, as potential anionic surfactants. To the best of our knowledge, it is the first report of sulfation reaction by mechano-synthesis in solventless conditions.

Results and discussion

A recent work of Browne *et al.*¹⁴ described a direct mechanochemical-assisted amidation of esters applicable to a large series of primary and secondary amines, aryl and alkyl esters substrates. In their procedure, *t*-BuOK (85 mol%) or a slight excess of ester (1.2 eq.) were required to obtain full conversion. Herein, our optimized conditions resulted in stoichiometric proportions without any base. First, we started by conducting mechano-aminolysis of 2H-HBO (**1**) with different primary alkylamines to evaluate the reaction time to convert quantitatively **1** into the corresponding amide compounds (Table 1). The mechano-synthesis was carried out in a planetary mill (Fritsch Pulverisette 7 Premium Line), in a zirconia jar in inverse mode (Table 1). The lactone **1** was grinded with 1 equivalent of alkylamine at 400 rpm. The reaction was monitored by TLC and stopped when complete conversion was observed. The crude powder was then analysed by NMR spectroscopy. *N*-alkyl-amides compounds **2a-f** were formed with excellent conversion in reaction time corresponding to 8 cycles of 5 min (with 1 min of pause between each cycle). A total time of 47 min, whatever the alkylamine, was necessary to convert **1** into amide derivatives with good to excellent conversions. Noteworthy, additional cycles did not change the conversion of the starting material. All new (4*S*)-*N*-alkyl-4,5-dihydroxy-pentanamides **2a-c** were then purified by flash chromatography or recrystallized from EtOH for **2d-f** for full characterization (see SI). For compounds **2a-c**, the NMR analyses were recorded in deuterated methanol. The hydrosolubility of the *N*-alkyl-4,5-dihydroxypentanamides **2d-f** being limited, spectra were recorded either in deuterated pyridine or in deuterated dimethyl sulfoxide.

Table 1 Mechano-aminolysis of 2H-HBO (**1**) with primary amines

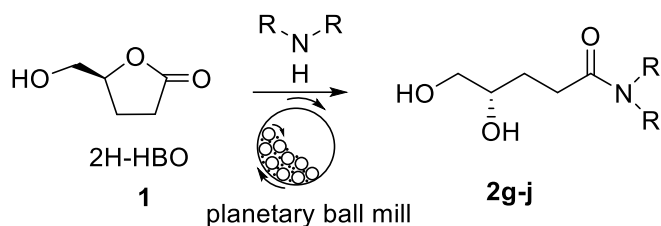


Entry	Alkylamine ^a	rpm/ Time (min)	Product	Conversion [%] ^b	Yield [%]
1	C ₁₀ H ₂₁ NH ₂	400 / 47	2a	90	75 ^c
2	C ₁₂ H ₂₅ NH ₂	400 / 47	2b	93	76 ^c
3	C ₁₄ H ₂₉ NH ₂	400 / 47	2c	>97	66 ^c
4	C ₁₆ H ₃₃ NH ₂	400 / 47	2d	90	72 ^d
5	C ₁₈ H ₃₇ NH ₂	400 / 47	2e	88	71 ^d
6	C ₁₉ H ₃₉ NH ₂	400 / 47	2f	ND	62 ^d

^a 2H-HBO (1 eq.) and alkylamine (1 eq.) in a zirconia jar (20 mL) equipped with 80 zirconia balls of 5 mm diameter were grinded during 8 cycles of 5 min (each cycle is followed by a pause time of 1 min), in inverse mode in a planetary ball mill. ^b Estimated by ¹H NMR (H-4 ratio between **1** and **2**). ^c Isolated yield after flash chromatography. ^d Isolated yield after recrystallization from EtOH. ND: Not Determined

We also studied the reactivity of **1** with secondary alkylamines. For dimethylamine, commercially available in water (40 wt.% in H₂O), a stoichiometric addition of dimethylamine did not give a total conversion and no amide was isolated (Entry 1, Table 2). Full conversion was reached with an excess of reagent (4 eq.) and a longer time reaction than with primary alkylamines (Entry 3, Table 2). This optimized condition gave full conversion and the corresponding amide **2g** was isolated with a yield of 77%.

Table 2 Mechano-aminolysis of 2H-HBO (**1**) with secondary amines

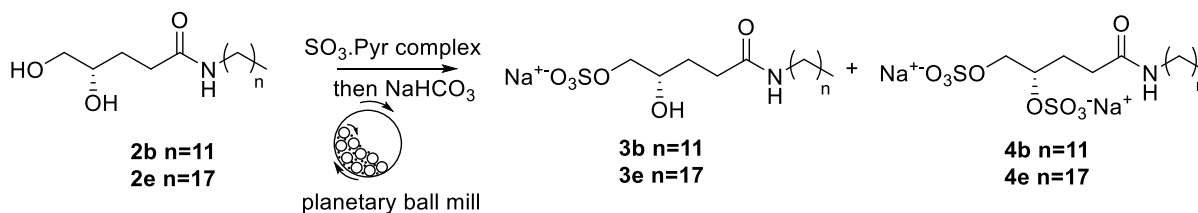


Entry	Alkylamine ^a /eq.	rpm / Time(min) ^b	Product	Conversion [%] ^c	Yield [%] ^d
1	(CH ₃) ₂ NH /1	400 / 71	2g	68	NI
2	(CH ₃) ₂ NH /1.5	400 / 71	2g	79	NI
3	(CH ₃) ₂ NH /4	400 / 71	2g	>97	77
4	(C ₂ H ₅) ₂ NH /1	400 / 71 then 500 / 23	2h	0	-
5	pyrrolidine /1	400 / 71	2i	88	70
6	piperidine/1400 / 143		2j	73	38
7	piperidine/2	400 / 71	2j	91	52

^a 2H-HBO (1 eq.) and alkylamine (1-4 eq.) in a zirconia jar (20 mL) equipped with 80 zirconia balls of 5 mm diameter were grinded during x cycles in inverse mode in a planetary ball mill. ^b Corresponding to 4, 12 or 24 cycles of 5 min, each cycle is followed by a pause time of 1 min. ^c Estimated by ¹H NMR (H-4 ratio between **1** and **2**). ^d Isolated by flash chromatography. NI: Not Isolated.

At the first attempt, the aminolysis of **1** with diethylamine also failed with 1 eq. of amine, even with a longer reaction time and a higher frequency. Excess of this amine (4 eq.) resulted in the very poor conversion of starting material with traces of the expected amide. This is probably due to the flexibility of the ethyl chains that prevents the nucleophilic attack of the nitrogen atom on the lactone carbonyl. As a confirmation, this effect was not observed with constrained secondary amine like pyrrolidine which resulted in the formation of the corresponding amide **2i** with a conversion of 88% and 70% isolated yield after 12 cycles (Entry 5, Table 2). A similar result was observed with piperidine with a conversion of 91% when an excess of amine was used (2 eq.) and an average isolated yield (52%) (Entry 7, Table 2).

In a second step, sulfated derivatives were synthesized from aforementioned alkylamides. Sulfation is a well-known reaction usually using SO₃. amino complex in pyridine or DMF as solvent in conventional conditions, which are toxic. Another drawback is that those reactions are not easy to handle in solution due to the modification of the physico-chemical properties of the as-obtained sulfated molecule.¹⁵ Furthermore, high temperature can be required (up to 80-100 °C),¹⁶ leading sometimes to degradation of thermosensitive compounds. In a previous work, we have developed a microwave-assisted sulfation of oligoglucuronans,¹⁷ and compared the results between reaction in solvent media and solventless conditions. While sulfation conventionally conducted in DMF or pyridine required longer heating in an oil bath, we observed that MW short reaction times prevented decomposition of carbohydrates. Oligoglucuronans with low degree of polymerization (DP) were directly sulfated in solvent-less conditions whereas higher DP (superior to 10) needed to be transformed into their ammonium salt and treated with the sulfating reagent in DMF to obtain satisfactory yields. Therefore, mechanochemistry appears to be an inspiring alternative eliminating any solubility problem, tedious reaction work-up and the use of toxic solvents.

Table 3 Optimization of sulfation reaction in solventless conditions with compound **2b-e**

Entry	Alkylamide ^a	$\text{SO}_3 \cdot \text{Pyr}$ (eq./OH)	rpm/Time(min) ^b	Auxiliary ^c	Conversion [%] ^f (3/4)
1	2b	4	400 / 59	-	78 (5:95)
2	2b	4	400 / 59	NaCl	>97 4b
3	2b	4	400 / 59	EtOAc ^d	>97 (3:97)
4	2b	2	400 / 95	NaCl	>97 4b
5	2b	1.5	400 / 95	NaCl	83 (7:93)
6	2e	2	400 / 95	AcOEt ^e	71 (27:73)
7	2e	2	500 / 95	AcOEt ^e	>97 4e
8	2e	2	400 / 95	NaCl	>97 4e
9	2e	2	200 / 95	-	47 (28:72)
10	2e	1	200 / 95	-	41 (29 :71)
11	2e	0.5	200 / 95	-	23 (83 :17)

^a *N*-Alkyl-amide (1 eq.) and $\text{SO}_3 \cdot \text{Pyr}$ complex were grinded in a zirconia jar (20 mL) equipped with 80 zirconia balls of 5 mm diameter in a P7PL Fritsch ball mill. ^b Corresponding to 7, 10 or 16 cycles of 5 min, each cycle is followed by a pause time of 1 min. ^c The amount of NaCl (120%) is calculated comparatively to the total amount of powder. LAG is defined by $\eta = \text{liquid quantity } (\mu\text{L}) / \text{solid reactants mass (mg)}$. ^d $\eta = 2$. ^e $\eta = 0.6$. ^f Estimated by $^1\text{H NMR}$.

No example of sulfation under ball-milling having been described in the literature, our first attempt was carried out with an excess of $\text{SO}_3 \cdot \text{pyridine}$ complex reagent (4 equivalents per OH) for 10 cycles (400 rpm) of 5 min in a zirconia jar to ensure the formation of the disulfated compound **4b** (Entry 1, Table 3). With a conversion of 78% of **2b**, the expected disulfated derivative **4b** was successfully obtained. Unfortunately, the presence of the side product **3b** corresponding to a monosulfation of **2b** was observed. To push forward the reaction and reach complete conversion, the addition of NaCl as grinding auxiliary or EtOAc as Liquid-Assisted Grinding (LAG) agent was then considered.¹⁸ LAG generally improves reaction kinetics, allows optimization of reactivity to quantitative yields and reduces the problems of product amorphization which can be observed with neat grinding. The parameter η is defined as the ratio of the added liquid (in μL) to the total weight of the solid reactants (in mg), found to be in the η range of ca. 0–2 $\mu\text{L} \cdot \text{mg}^{-1}$. Both strategies led to a complete conversion of **2b** into **4b**. With NaCl, no trace of **3b** was observed (Entry 2, Table 3), but with EtOAc as LAG ($\eta=2$), disulfated **4b** was obtained accompanied with traces of **3b**, as observed in $^1\text{H NMR}$ (Entry 3, Table 3). The mechano-sulfation of disulfated **4b** was then optimized with 2 equivalents of $\text{SO}_3 \cdot \text{pyridine}$ complex per alcohol function and NaCl as grinding agent in 16 cycles of 5 min (Entry 4, Table 3).

Lowering sulfating agent to 1.5 eq./OH resulted in an incomplete conversion (83%) and the formation of the monosulfated **3b** (Entry 5, Table 3). In the case of *N*-dodecyl-amide **2e**, same results were observed. A conversion of only 71% was observed in the presence of 2 eq./OH of $\text{SO}_3 \cdot \text{pyridine}$ and EtOAc as LAG ($\eta=2$), with the formation of disulfated derivative **4e** and monosulfated **3e** in a 73:23 ratio respectively (Entry 6, Table 3). The mechano-sulfation of **2e** in presence of EtOAc was optimized at 500 rpm with a total conversion and selectivity in 16 cycles of 5 min (Entry 7, Table 3), compound **4e** was formed quantitatively with an excellent selectivity. Finally, replacing EtOAc by NaCl resulted in total conversion and total selectivity into **4e** without increasing frequency (Entry 8, Table 3).

In order to selectively synthesize one or the other of these sulfated compounds, some parameters of the mechano-synthesis were modified. Reducing the rpm (200 rpm) and the amount of sulfating reagent, decreased not surprisingly the yield of the sulfation reaction (Entries 9–10, Table 3). With 0.5 equivalent per OH of sulfating agent, monosulfated compound **3e** was obtained in higher amount but in a low yield (Entry 11, Table 3)

As a benchmark, and to be objective, we also synthesised compounds **4b-e** from **1** following conventional procedures. This implied repeating the reaction with solvents for amidation and sulfation.¹⁸ These experiments resulted in the formation of **2b-e** derivatives at 50 °C for 24–48 h in 71–83% yield. Sulfation was also successful by using 2 eq. per OH group in average 48 h and afford **4b-e** in 59–73% yield (see SI). With the same range of yields but with longer reaction time and using solvent conditions, these

benchmarks confirm unambiguously that mechano-synthesis is a well-founded approach and presents many advantages for such transformation.

The aminolysis and sulfation reactions being optimized separately, we tried to push further our eco-friendly cursor and ambioned a one-pot two-step procedure. To transform directly **1** into *N*-alkyl-disulfated compounds **4b-e**, without isolation of the intermediate *N*-alkyl-amide. The addition of grinding agent (NaCl) at the first step (Entries 1-2, Table 4), or at the second stage (Entries 3-4, Table 4) was also studied. In these conditions, the addition of grinding agent on the crude amide **2b** gave incomplete conversion but the selectivity in favour of the corresponding disulfated compound was still observed. Since the addition of ethyl acetate as LAG has previously shown same efficiency as NaCl during the sulfation step, we decided to study it in this one-pot procedure.

The use of ethyl acetate as LAG ($\eta=0.6$), only added with the sulfating reagent at the second step, gave better results with quantitative conversion of the amide intermediate **2** formed from **1**.

Interestingly, disulfated amides **4b-d** could be formed quantitatively from **1** in a one-pot two step procedure. All new disulfated compound were isolated by reverse chromatography in good yields (Entries 5, 6, 7, 9, Table 4). As already observed for the synthesis of octadecyl derivative **2e**, 500 rpm was optimal to achieve a total conversion of the amide **2e** into disulfated **4e** (Entry 9, Table 4).

Table 4 One-pot sequential mechano-synthesis of compounds **4b-e**

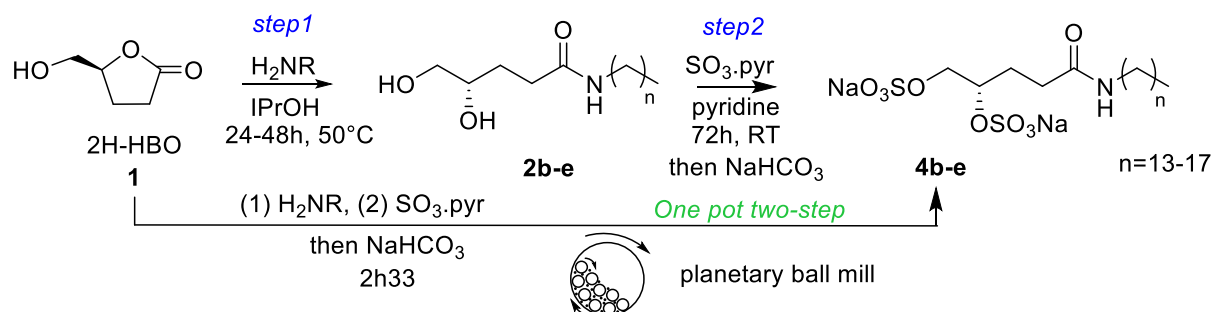


Entry	Alkylamine ^a	rpm/Time 1 ^b (min)	Auxiliary 1 ^c	SO ₃ .Pyr (eq./OH)	Auxiliary 2 ^c	rpm/Time 2 ^e (min)	Product	Conversion [%] ^f	Yield [%] ^g 4b-e
1	dodecylamine	400 /47	NaCl	3	-	400/95	4b	89 (3:97)	NI
2	dodecylamine	400 /47	NaCl	2	-	400/95	4b	73(15:85)	NI
3	dodecylamine	400 /65	-	3	NaCl	400/95	4b	89 (2:98)	NI
4	dodecylamine	400 /65	-	2	NaCl	400/95	4b	87(2:98)	NI
5	dodecylamine	400 /47	-	2	EtOAc ^d	400/95	4b	>97 4b	77
6	tetradecylamine	400 /47	-	2	EtOAc ^d	400/95	4c	>97 4c	62
7	hexadecylamine	400 /47	-	2	EtOAc ^d	400/95	4d	>97 4d	79
8	octadecylamine	400 /47	-	2	EtOAc ^d	400/95	4e	71 (27:73)	40
9	octadecylamine	400 /47	-	2	EtOAc ^d	500/95	4e	>97 4e	79

^a 2H-HBO (1 eq.) and alkylamine (1 eq.) in a zirconia jar (20 mL) equipped with 80 zirconia balls of 5 mm diameter were grinded during x cycles in inverse mode in a planetary ball mill. After a TLC control, SO₃.Pyr complex with or without auxiliary agent was added and the crude powder was milled for x cycles of 5 min in inverse mode. ^b Time for **2b-e** synthesis. Corresponding to 8 or 11 cycles of 5 min, each cycle is followed by a pause time of 1 min. ^c The amount of NaCl (120%) is calculated comparatively to the total amount of powder. LAG is defined by η = liquid quantity (μ L) / solid reactants mass (mg). ^d η = 0.6. ^e Time for **4b-e** synthesis. Corresponding to 16 cycles of 5 min, each cycle is followed by a pause time of 1 min. ^f Estimated by ¹H NMR. ^g Isolated yield after reverse column chromatography, NI: not isolated.

Finally, we determined the green chemistry metrics to compare the optimized one-pot two-step procedure to the classical solvent route (Table 5, see SI for details calculations). As expected, E-factor decreases considerably for the mechano-synthesis procedure. Process mass intensity (PMI), reaction mass efficiency (RME), atom economy (AE) proved to be better as well. Another advantage is the decrease of the reaction time obtained for the one-pot two-step synthesis with a quantitative conversion of **1** into sulfated derivatives **4b-e** in 2.5 h only.

Table 5 Comparison of green metrics of **4b-e** between conventional and mechano-synthesis conditions



Entry	Green metrics	Ideal value ^a	step 1 (solvent)	step 2 (solvent)	One-pot two-step (planetary ball mill)
1	E-factor	0	6-7	18-25	1.6-1.7
2	PMI	1	7-8	19-26	2.6-3
3	RME	100%	12-14%	4-5%	33-38%
4	AE	100%	100%	81-83%	79-82%

^a These metric values have been calculated without considering the work-up step

Due to the interesting structure of compounds **4c-e** the determination of critical micellar concentration (CMC) was secondly evaluated. Surface tension measurements for these compounds were determined with a TC1 tensiometer using the Du Noüy ring method. These anionic potential bio-based surfactants showed promising active surface properties: their CMC values, between 0.6 and 4.0 mM, are lower than that of SDS (8-8.5 mM) (see SI).²⁰

Conclusions

In summary, we reported for the first time a one-pot two-step mechano-synthesis of sulfated compounds in solventless conditions. The bio-sourced platform 2H-HBO was transformed into amide derivatives with different alkyl chains lengths, which were then bis-sulfated. Notably, a one-pot two step strategy was established which showed that quantitative conversion of 2H-HBO toward aminolysis followed by a sequential sulfation of the crude amide formed in the ball mill can be effective without pyridine, usually used as solvent for the second step. Ethyl acetate was used as Liquid-Assisted Grinding (LAG) agent with a $\eta = 0.6 \text{ mL/mg}$. (4S)-N-Alkyl-4,5-bis-sulfooxypentanamide compounds displayed interesting interfacial properties suggesting their potential as substitute of petroleum-based surfactants.

Conflicts of interest

There are no conflicts to declare.

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