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Reactions of β-sultones and carbyl sulfates with nucleophiles†,§

Bert H. Bakker, Ruud M. Schonk and Hans Cerfontain*

Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands
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Abstract. Ring opening of the octane-β-sultones **1a-c** by methanol gives the β-methoxyoctanesulfonic acids **2a-c** by S_N2 substitution at C–O with inversion of the configuration. Hydrolysis of *cis*- and *trans*-4,5-octanesultones **1a-b** under acidic conditions is stereospecific and leads to *threo*-[(*RR*,*SS*)-**4u**] and *erythro*-5-hydroxy-4-octanesulfonic acid [(*RS*,*SR*)-**4u**], respectively, by a similar S_N2 reaction on the carbon of the C–O bond. Hydrolysis of 4,5-octanesultones **1a-b** with base proceeds by attack at the sulfur atom of the β-sultone ring to provide 5-hydroxy-4-octanesulfonates (**4v**) with retention. Reaction of carbyl sulfates **5a-b** with methanol gives the methyl esters of 5-hydroxy-4-octanesulfonic acid **7a-b** in a stereospecific way with retention of configuration by attack of methanol at the sulfonate sulfur atom.

Introduction

β-Sultones are the primary reaction products of sulfonation of olefins by sulfur trioxide, and they are formed in a stereospecific manner by a *syn* cycloaddition mechanism[2-5]. They are thermally unstable compounds which rearrange easily to a mixture of β-alkenesulfonic acid and γ- and δ-sultones[6,7]. β-Sultones are strained internal sulfonate esters which are also prone to nucleophilic substitution reactions. The reaction of β-sultones with various nucleophiles, such as water, alcohols and amines, give the corresponding β-substituted sulfonic acids[8]. These substitution reactions proceed by nucleophilic attack at the oxygen-bonded carbon, leading to C–O bond cleavage (alkylation), as commonly observed for sulfonate esters. *Thaler* et al.[9] showed that *cis*- and *trans*-3,4-hexanesultone react stereospecifically with methylamine to give *threo* and *erythro* 4-(methylamino)--3-hexanesulfonates, respectively. A similar S_N2 mechanism was reported by *Mori* et al.[2] for the reaction of *cis*- or *trans*-3,4-butanesultone with aniline, although the hydrolysis of these β-sultones was not stereospecific. Halogen-substituted β-sultones are attacked by amines at the SO_2 group, yielding 2-hydroxyethanesulfonamides[10]. *Bordwell* et al.[11] examined the hydrolysis of 1,2-cyclopentanesultone under acidic conditions to give *trans*-2-hydroxycyclopentanesulfonic acid. We have recently reported that the hydrolysis of 2,3-norbornanesultone with base gave *cis*-3--hydroxy-2-norbornanesulfonate[12]. High yields of β-hydroxyalkanesulfonates were obtained by controlled hydrolysis of β-sultones derived from a mixture of internal olefins[13].

For example, for sterically congested sulfonate esters and for arenesulfonates nucleophilic attack at the sulfur atom of the sulfonate ester is observed and S–O bond cleavage occurs only in special cases. *Mori* et al.[14] reported that hydrolysis of 1,3-propanesultone in strong base proceeds with 14% S–O cleavage, whereas ethyl ethanesulfonate reacts exclusively by normal C–O scission. Recently, *King* et al.[15,16] described the hydrolysis of 2-hydroxyethanesulfonyl chloride to 2-hydroxyethanesulfonate. They proposed that the resulting unsubstituted 1,2-oxathietane 2,2-dioxide (β-sultone) is formed as an intermediate, which then hydrolyses under neutral or acidic conditions leading to C–O bond rupture, whereas under basic conditions, the S–O bond is cleaved by the nucleophile.

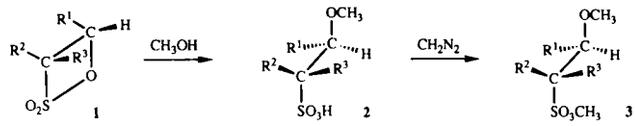
In the course of an extended study on the mechanism of the sulfonation of olefins by sulfur trioxide, we have prepared *cis*- and *trans*-substituted β-sultones and carbyl sulfates derived from 4-octene[3,17]. We have now investigated the reactions of these substituted β-sultones and carbyl sulfates with the protic nucleophiles methanol and water, the latter under basic and neutral conditions, in order to obtain information on the site of attack by these nucleophiles. Starting with pure *cis*- and *trans*-β-sultones, hydrolysis would give rise to different diastereoisomeric β-hydroxyalkanesulfonates.

Results and discussion

We have studied the reactions of the linear octane-β-sultones **1a-c** with methanol and water. Sulfonation of (*Z*)-4-octene by one equiv. of sulfur trioxide in chloroform or dichloromethane at −20°C in the presence of one equiv. of dioxane as reactivity moderator gives pure *cis*-3,4--dipropyl-1,2-oxathietane 2,2-dioxide (*cis*-4,5-octanesultone, **1a**). On adding an excess of methanol at room temperature, a substitution reaction yields (see Scheme 1) (*RR*,*SS*)-5--methoxyoctane-4-sulfonic acid (*threo* **2a**). This *threo*-5--methoxyoctane-4-sulfonic acid was isolated in 80% yield and identified as the methyl ester **3a** after reaction with diazomethane and purification with column chromatography on silica gel. Similarly, reaction of *trans*-4,5-octanesultone (**1b**), prepared by sulfonation of (*E*)-4-octene, with an excess of methanol gives (*RS*,*SR*)-5-methoxyoctane--4-sulfonic acid (*erythro* **2b**).

† Aliphatic sulfonation part 8. For part 7, see ref. 1

§ IUPAC nomenclature: β-sultone; 1,2-oxathietne 2,2-dioxide carbyl sulfate: cyclic sulfonate sulfate anhydride and 1,3,2,4--dioxadithiane 2,2,4,4-tetraoxide.



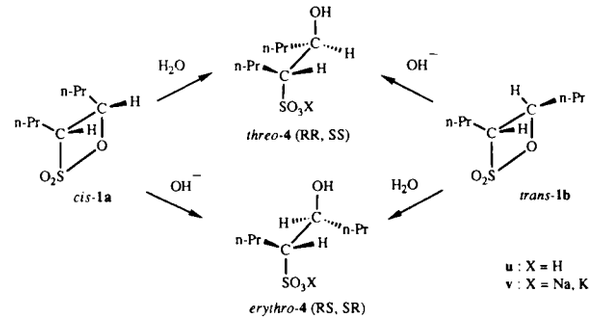
	R^1	R^2	R^3
a:	n-C_3H_7	n-C_3H_7	H
b:	n-C_3H_7	H	n-C_3H_7
c:	n-C_6H_{13}	H	H

Scheme 1

Identification of the *erythro* and *threo* isomers **3a** and **3b** is based on ^{1}H NMR data for the methine protons at the methoxy and sulfonate groups (see Table I). The difference in chemical shift of the methine protons of β-hydroxy-and β-methoxyalkanesulfonates is larger for the *erythro* than for the corresponding *threo* isomer.

Sulfonation of 1-octene gives the 1,2-octanesultone (**1c**), which reacts smoothly with methanol to the corresponding 2-methoxy-1-octanesulfonic acid (**2c**). In fact, *Canselier*[18] has used this substitution reaction by methanol as identification for the unstable 1,2-alkanesultones. Under identical conditions, the reaction rates of 1,2-octanesultone (**1c**) and *cis*-4,5-octanesultone (**1a**) are about equal, whereas the *trans*-4,5-octanesultone (**1b**) reacts at least 20 times more slowly. The main reaction of methanol is nucleophilic attack at the C–O bond of the β-sultone ring with inversion of the configuration at this carbon atom (S_N2). As a side reaction, particularly for the *trans* β-sultone **1b**, desulfonation of the β-sultones by methanol occurs with reformation of the original 4-octenes[19]. The ratio of substitution *versus* elimination increases in the series **1b** ≪ **1a** < **1c**. For the *trans*-β--sultone **1b**, we observed that the ratio of the substitution reaction over the elimination of sulfur trioxide increases with increasing methanol concentration. Furthermore, the ratio of substitution to elimination depends strongly on reaction temperature. For reaction of a 0.5 molar solution of *trans* β-sultone **1b** in $CDCl_3$ with 25 equiv. of CD_3OD, the ratio of substitution *versus* desulfonation products decreases from 3.7 at −5°C via 1.6 at 20°C to 0.5 at 60°C.

For the reaction of β-sultones with water under homogeneous conditions, we have used a water/dioxane mixture as solvent. The intermediate β-sultones **1a** and **1b** were, therefore, prepared in dioxane. Hydrolysis of *cis*-β-sultone **1a** in dioxane/water (3/4, v/v) under conditions which change gradually from neutral to acidic during the reaction gives the *threo*-β-hydroxyalkanesulfonic acid (*RR,SS*)-**4u**. Under similar reaction conditions, the *trans*-β-sultone **1b** gives rise to the *erythro*-β-hydroxyalkanesulfonic acid (*RS,SR*)-**4u** (see Scheme 2). The assignment of *erythro* and *threo* isomers of **4** is based on comparison of the spectral data of these β-hydroxyalkanesulfonates with those prepared independently by reaction of *cis*- and *trans*-4,5-epoxyoctane with sodium sulfite[11,20,21]. The stereochemistry of hydrolysis of β-sultones under neutral to acidic conditions is in agreement with nucleophilic attack of water at the carbon bonded to oxygen: the reaction proceeds stereospecifically with *inversion* of the configuration (S_N2). The *cis*- and



Scheme 2

trans-4,5-octanesultones (**1a**) and (**1b**) were also treated with an excess of KOH (2.0 M) in a water/dioxane solution. Under these basic conditions, again, the β-hydroxyoctanesulfonates **4v** are formed. However, the stereochemistry is just the opposite. The basic hydrolysis of *cis*-β-sultone **1a** in water/dioxane (4/1 v/v) yields *erythro*-β-hydroxyoctanesulfonate (*RS,SR*)-**4v**, whereas *trans*-β-sultone **1b** is converted into *threo*-β-hydroxyoctanesulfonate (*RR,SS*)-**4v**. Thus, basic hydrolysis is also stereospecific, but proceeds with *retention* of the configuration. Such stereochemistry is in agreement with attack by a hydroxyl anion at the sulfur atom, leading to cleavage of the SO_2–O bond of the β-sultone ring. The sulfur atom of the β-sultone ring has a relatively high positive charge. According to *King* et al.[15,16], the "hard" basic hydroxyl anion will attack preferentially at the sulfur atom of the sultone group. The alternative mechanism via a "sulfene" as intermediate is ruled out by the stereospecificity of the formation of the β-hydroxyoctanesulfonates **4**. When the basic hydrolysis of these β-sultones is performed in D_2O, we did not observe any D incorporation into the hydroxyoctanesulfonates **4v**, as would be expected if a "sulfene" mechanism was involved[22]. It should further be noted that both *erythro*- and *threo*-hydroxyoctane-

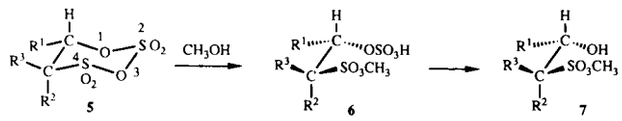
Table I ^{1}*H- and* ^{13}*C-NMR chemical shifts (ppm) of the methyl β-methoxyalkanesulfonates* **3**.

	3a (*threo*)		**3b** (*erythro*)		**3c**	
	^{1}H	^{13}C	^{1}H	^{13}C ^{1}H		^{13}C
SO_3CH_3	3.82 (s)	54.5	3.87 (s)	54.7	3.87 (s)	55.5
OCH_3	3.31 (s)	57.6	3.40 (s)	58.4	3.37 (s)	57.2
CHOMe	3.62 (m)	79.5	3.76 (m)	79.0	3.71 (m)	76.0
$CHSO_3Me$	3.30 (m)	61.4	3.08 (m)	64.2	3.30 (dd, *J* 14.7, 6.9) 3.13 (dd, *J* 14.7, 4.4)	53.7
$(CH_2)_n$	1.72 (m, 2H) 1.48 (m, 6H)	32.4, 26.8 20.6, 18.9	1.5–2.0 (8H)	34.8, 26.6 21.2, 19.1	1.57 (m, 2H) 1.26 (m, 6H)	33.6, 31.5 29.0, 24.4 22.4
CH_3	0.87 (dt, 6H)	13.6	0.93 (t, 6H, *J* 7.1)	13.7	0.85 (t, *J* 6.5)	13.9

sulfonates **4v** are stable in strongly basic D_2O (pH 13) solutions. No *erythro/threo* isomerization or D incorporation were observed with ^1H NMR and apparently do not occur. The present data clearly show that the mechanism of hydrolysis of β-sultones depends on the reaction conditions. It proceeds with *retention* of configuration under the influence of base and with *inversion* under neutral and acidic reaction conditions.

Reaction of carbyl sulfates with methanol

Sulfonation of alkenes with 2 equiv. of sulfur trioxide gives rise to 1,3,2,4-dioxadithiane 2,2,4,4-tetraoxides, also referred to as carbyl sulfates[6,7]. The formation of these mixed sulfonate sulfate anhydrides is stereospecific; (*Z*)- and (*E*)-olefins are converted into *cis*- and *trans*-carbyl sulfates, respectively[17]. Sulfonation of (*Z*)- and (*E*)-4-octene each with 2.2 equiv. of sulfur trioxide with 2.7 equiv. of nitromethane as reactivity moderator in dichloromethane at −20°C gave *cis*- and *trans*-dipropyl carbyl sulfates **5a** and **5b**, respectively. We have studied the reactions of these carbyl sulfates with methanol.



	R^1	R^2	R^3
a:	n-C_3H_7	n-C_3H_7	H
b:	n-C_3H_7	H	n-C_3H_7

Scheme 3

Hydrolysis of carbyl sulfate is known to proceed via attack by water at the SO_2 group at position 4, leading to the hydrogen sulfate of 2-hydroxyethanesulfonic acid, followed by hydrolysis to 2-hydroxyethanesulfonic acid[23]. Carbyl sulfate reacts in a similar way with phenol[24], but the reaction with pyridine proceeds differently: by nucleophilic attack at the carbon of the C–O bond[25]. From the reaction of *cis*-carbyl sulfate **5a** with methanol at room temperature for 24 h, we have obtained *erythro*-5-hydroxy-4-octanesulfonate methyl ester **7a** in 50% yield. Isomeric *trans*-carbyl sulfate **5b** yielded under similar conditions only *threo*-sulfonate ester **7b** in an isolated yield of 52%. In the reaction of methanol with the carbyl sulfates **5**, hydrogen sulfate sulfonate methyl esters **6** are the initial unstable reaction products. When the reaction of *cis*-carbyl sulfate **5a** with CD_3OD in CD_2Cl_2 at room temperature is monitored with ^1H NMR, temporary signals at δ 3.86 and δ 4.54 ppm are observed after 30 min., which can be assigned to the H atoms at carbons 4 and 5 of the hydrogen sulfate **6a**. The intensity of these signals gradually diminishes after standing for one day with the concomitant appearance of absorption peaks at δ 3.05 and δ 4.15 ppm of the *erythro*-hydroxysulfonate methyl ester **7a** as the only product, in more than 90% yield. The reaction of *trans*-carbyl sulfate **5b** with deuterated methanol shows similar transient NMR signals at δ 3.98 and δ 4.76 ppm of the hydrogen sulfate intermediate **6b**, with subsequent conversion into *threo*-hydroxysulfonate methyl ester **7b** in high yield. The low isolated yields of the methyl esters **7** are probably due to losses during the work-up procedure. These results clearly indicate that the reaction of carbyl sulfates with methanol proceeds with *retention* of the configuration. The carbyl sulfate ring is attacked by methanol at the SO_2 group in position 4 (sulfonylation), leaving the stereochemistry of the alkene skeleton unchanged.

Experimental

The ^1H- and ^{13}C-NMR spectra were recorded on Bruker WM-250 and AC-200 instruments. The IR spectra were obtained using a Perkin-Elmer 1310 spectrophotometer. The mass spectra were recorded on a Varian MAT-711 mass spectrometer at 70 eV.

Starting materials

The β-sultones **1a-c** were prepared *in situ* as 0.24 molar solutions in CH_2Cl_2 as described previously[3] by adding liquid SO_3 (12.0 mmol; 0.5 ml) to a solution of 2 ml of dry dioxane in 50 ml of dry CH_2Cl_2 under argon at −20°C, followed by addition of 12.7 mmol of the appropriate octene at −30°C. ^{13}C NMR ($CDCl_3$, δ, ppm): *cis*-4,5-octanesultone (**1a**) from (*Z*)-4-octene: 75.0 (CH), 70.0 (CH), 31.7 (CH_2), 26.3 (CH_2), 20.6 (CH_2), 18.3 (CH_2), 13.5 (CH_3) and 13.4 (CH_3); *trans*-4,5-octanesultone (**1b**) from (*E*)-4-octene: 77.7 (CH), 72.5 (CH), 36.5 (CH_2), 30.4 (CH_2), 19.9 (CH_2), 18.1 (CH_2), 13.5 (CH_3) and 13.4 (CH_3); 1,2-octanesultone (**1c**) from 1-octene: 65.6 (CHO), 64.2 (CH_2S), 34.9 (CH_2), 31.4 (CH_2), 28.5 (CH_2), 24.5 (CH_2), 22.4 (CH_2) and 14.0 (CH_3).

Solutions of the β-sultones **1a-b** (1.5 molar) in dioxane were prepared by careful dropwise addition of liquid SO_3 (24 mmol, 1.0 ml) into 10 ml of dry dioxane cooled at 10°C under argon. The 4-octene (32 mmol) was then added to the well-stirred mixture chilled in ice.

The carbyl sulfates **5a-b** were synthesized as 0.48 molar solutions in CH_2Cl_2 by the previously described procedure[17] by addition of liquid SO_3 (53 mmol, 2.2 ml) to a solution of 3.5 ml of dry CH_3NO_2 in 50 ml of dry CH_2Cl_2 at −20°C under an argon atmosphere. 4-Octene (24 mmol) was then added at −20°C and the solution was kept at 0°C for 2 h to ensure complete conversion into the carbyl sulfate. ^{13}C NMR (CD_2Cl_2, δ, ppm); *cis*-carbyl sulfate **5a**: 83.8 (CHO), 63.2 (CHS), 33.4 (CH_2), 25.9 (CH_2), 21.5 (CH_2), 18.9 (CH_2), 13.8 (CH_3) and 13.3 (CH_3); *trans*-carbyl sulfate **5b**: 83.9 (CHO), 64.2 (CHS), 32.7 (CH_2), 27.3 (CH_2), 20.1 (CH_2), 17.5 (CH_2), 13.7 (CH_3) and 13.2 (CH_3).

Sodium *erythro*-5-hydroxy-4-octanesulfonate **4v** was prepared by a procedure similar to that reported earlier[11,20,21], by refluxing *trans*-4,5-epoxyoctane[26] (5.32 mmol) and Na_2SO_3 (15.8 mmol) in 10 ml of water for 4 days. The aqueous solution was washed with ether (25 ml) and poured into 70 ml of ethanol. After filtration, the solution was concentrated by rotary evaporation and dried *in vacuo* at 60°C yielding 0.85 g (69%) of *erythro* sulfonate **4v**. ^1H NMR (D_2O, δ, ppm, relative to $Me_3SiCD_2CD_2COONa$): 4.21 (m, CHO), 2.83 (m, CHS), 1.30–1.85 (m, 8H) and 0.93 (6H, t, *J* 7.1 Hz). ^{13}C NMR (D_2O, δ, ppm, relative to Me_3Si CD_2CD_2COONa): 73.1 (CHO), 66.8 (CHS), 38.7 (CH_2), 29.4 (CH_2), 24.3 (CH_2); 21.6 (CH_2), 16.2 (CH_3) and 15.9 (CH_3).

Sodium *threo*-5-hydroxy-4-octanesulfonate **4v** was synthesized similarly in 83% yield starting with *cis*-4,5-epoxyoctane[26]. ^1H NMR (D_2O, δ, ppm, relative to $Me_3SiCD_2CD_2COONa$): 4.11 (m, CHO), 2.96 (m, CHS), 1.3–1.85 (m, 8H) and 0.93 (6H, t, *J* 7.1 Hz). ^{13}C NMR (D_2O, δ, ppm, relative to Me_3Si CD_2CD_2COONa): 73.4 (CHO), 67.7 (CHS), 36.7 (CH_2), 30.7 (CH_2), 23.7 (CH_2), 21.5 (CH_2), 16.2 (CH_3) and 16.0 (CH_3).

Reaction of β-sultones with methanol

CH_3OH (100 ml) was added to a solution of 12.0 mmol of *cis*-β-sultone **1a** in 50 ml of CH_2Cl_2 at 0°C under argon. The solution was kept for 3 days at room temperature. Most of the solvent was removed by distillation and the residue was neutralized with diazomethane in ether until pH 7. The solution was concentrated by rotary evaporation and the residue was chromatographed over silica gel with ether, yielding 2.3 g (80%) of colorless methyl *threo*-5-methoxy-4-octanesulfonate (**3a**). The NMR data are presented in Table I. IR (neat, cm^{-1}): 2965, 2875, 1465 (m), 1350 (s, SO_2), 1170 (s, SO_2), 1095 (m) and 990 (s); MS (*m/z*, %): 195 (12), 152 (3), 123 (5), 113 (8), 99 (10) and 87 (100).

A similar reaction starting with *trans*-β-sultone **1b** yielded 1.85 g (65%) of methyl *erythro*-5-methoxy-4-octanesulfonate (**3b**). IR (neat, cm^{-1}): 2960, 2870, 1465 (m), 1350 (s, SO_2), 1170 (s, SO_2),

1090 (m) and 990 (s). MS (*m/z*, %): 195 (19), 131 (5), 113 (10), 99 (21) and 87 (100).
The reaction of 1,2-octanesultone (**1c**) with methanol gave methyl 2-methoxy-1-octanesulfonate (**3c**) in 47% yield. IR (neat, cm^{-1}): 2960, 2930, 2860, 1465 (m), 1350 (s, SO_2), 1170 (s, SO_2), 1100 (m) and 995 (s). MS (*m/z*, %): 153 (100), 142 (5), 121 (11), 112 (14), 110 (9) and 96 (7).

Hydrolysis of β-sultones with base

A solution of 100 mmol of KOH in 40 ml of water was added to *cis*-β-sultone **1a** (24.0 mmol) in 10 ml of dioxane chilled in ice-water. The heterogeneous mixture was stirred vigorously for 2 h at room temperature. The aqueous solution was washed with 30 ml of ether, poured into 100 ml of ethanol and neutralized with diluted H_2SO_4 (2 N). After filtration, the solution was concentrated by rotary evaporation and the residue was dried *in vacuo*, giving 3.3 g (55%) of a potassium sulfonate with spectral data identical to *erythro*-5-hydroxy-4-octanesulfonate [(*RS,SR*)-**4v**].
A similar alkaline hydrolysis of *trans*-β-sultone **1b** (24.0 mmol) yielded 2.8 g (47%) of *threo*-5-hydroxy-4-octanesulfonate [(*RR,SS*)-**4v**].

Acidic hydrolysis of β-sultones

A solution of *cis*-β-sultone **1a** (0.22 mmol) in 0.3 ml of dioxane-d_8 and 0.4 ml of D_2O was stirred at room temperature for 24 h. ^1H NMR showed *threo*-5-hydroxy-4-octanesulfonic acid [(*RR,SS*)-**4u**] as the only product. The acidic solution was made strongly basic (pH 13) by adding 50 mg of KOH. The NMR spectra did not change after the reaction mixture was kept for 1 day at room temperature. Isomerization or D incorporation were not observed under basic conditions. Similar treatment of *trans*-β-sultone **1b** in dioxane-d_8 with D_2O gave *erythro*-5-hydroxy-4-octanesulfonic acid [(*RS,SR*)-**4u**].

Reaction of carbyl sulfates with methanol

Methanol (15 ml) was added to a solution of *cis*-carbyl sulfate **5a** (24.0 mmol) in 50 ml of CH_2Cl_2 cooled at 0°C. The solution was left for 3 days at room temperature and then washed with 50 ml of water. The water layer was washed with 30 ml of dichloromethane. The combined CH_2Cl_2 layers were washed with 20 ml of water, dried over Na_2SO_4 and concentrated by rotary evaporation, leaving 2.7 g of oil. After chromatography over silica gel with ether, 2.05 g (38%) of colorless methyl *erythro*-5-hydroxy-4-octanesulfonate [(*RS,SR*])-**7a**] was obtained. IR (neat, cm^{-1}): 3550 (OH), 2960, 2870, 1460 (m), 1340 (s, SO_2), 1165 (s, SO_2) and 985 (s). ^1H NMR ($CDCl_3$, δ, ppm): 4.17 (m, CHO), 3.89 (s, OCH_3), 3.07 (m, CHS), 2.63 (s, OH), 2.0–1.25 (m, 8H) and 0.93 (m, 6H). ^{13}C NMR ($CDCl_3$, δ, ppm): 69.3 (CHO), 65.2 (CHS), 54.9 (OCH_3), 35.8 (CH_2), 26.0 (CH_2), 21.3 (CH_2), 19.2 (CH_2), 13.7 (CH_3) and 13.6 (CH_3). MS (*m/z*, %): 195 (3), 181 (6), 163 (8), 152 (16), 123 (30), 112 (29), 110 (17), 81 (45), 69 (58) and 55 (100).
An identical reaction of *trans*-carbyl sulfate **5b** yielded after chromatographic purification 1.9 g (35%) of methyl *threo*-5-hydroxy-4-octanesulfonate [(*RR,SS*)-**7b**]. IR (neat, cm^{-1}): 3540 (OH), 2960, 2870, 1460 (m), 1345 (s, SO_2), 1165 (s, SO_2) and 990 (s). ^1H NMR ($CDCl_3$, δ, ppm): 3.97 (m, CHO), 3.86 (s, OCH_3), 3.13 (m, CHS), 1.83 (m, 2H), 1.75–1.3 (m, 6H) and 0.93 (m, 6H). ^{13}C NMR ($CDCl_3$, δ, ppm): 69.8 (CHO), 65.7 (CHS), 54.8 (OCH_3), 36.0 (CH_2), 28.5 (CH_2), 20.4 (CH_2), 19.0 (CH_2), 13.8 (CH_3) and 13.7 (CH_3). MS (*m/z*, %): 181 (23), 152 (19), 123 (81), 112 (11), 99 (10), 91 (10), 81 (21), 69 (45) and 55 (100).

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