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# A General Procedure to Enantiopure Conduritols: Sulfur-Mediated Synthesis of (+)-Conduritol B and (−)-Conduritol F Derivatives and of (−)-Conduritol E and F

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**Abstract**—We have demonstrated the generality of a simple procedure, synthesizing enantiomerically pure (+)-conduritol B and (−)-conduritol F derivatives, starting from D-mannitol and D-sorbitol, respectively. This method, slightly modified, can also be applied to the synthesis of unprotected conduritols: (−)-conduritol E and (−)-conduritol F were obtained. 

## Introduction

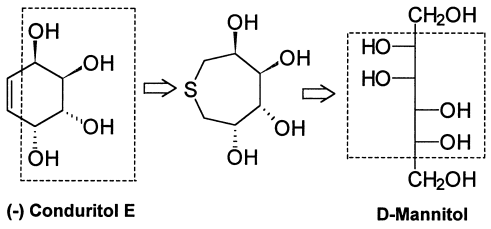
The stereocontrolled synthesis of conduritols, 5-cyclohexen-1,2,3,4-tetrols, is receiving increasing attention as these compounds are useful intermediates for the preparation of conduritol epoxides, cyclitols, aminoconduritols and cyclophellitols. All these compounds possess interesting biological properties: epoxyconduritols and aminoconduritols act as inhibitors of D-glycosidases,[1] cyclitols have been recognized as cell mediators[2] and cyclophellitols have proved to be potent inhibitors of infection by human immunodeficiency virus (HIV).[3]

As outlined in the recent review by Balci[4] difficulties can be encountered in the synthesis of the ten possible stereoisomers, two *meso* forms (conduritols A and D) and four couples of enantiomers (conduritols B, C, E, and F). In fact, due to the presence of four stereogenic centers in the cyclohexene system, many of these syntheses result in racemic mixtures, mainly because of the unavailability of optically pure starting materials. The importance of the synthetic targets has stimulated several groups and recently a few stereocontrolled syntheses have been found.[4] Good results have been achieved starting from enantiopure unsaturated cyclic *cis*-diols, obtained by microbial oxidation of halobenzenes.[5] Other approaches worth noting start from the 'naked sugar' of Vogel,[6] from D-mannitol using a samarium diiodide-mediated carbocyclization[7] and from meso-symmetric cyclic dienes.[8] Nevertheless, other synthetic approaches, even if they proceed with good enantiomeric excess, require a chemical or enzymatic resolution step to obtain enantiomerically pure compounds.

We have recently described a new synthetic method,[9] to produce the enantiopure (−)-1,4-dimethoxy conduritol E, starting from D-mannitol, maintaining the chirality of the four asymmetric carbons and using all the carbons of the starting alcohol sugar. Considering the great interest in the stereocontrolled synthesis of different conduritols, we have engaged a study in order to extend this simple strategy to other alcohol sugars, with the aim of obtaining a range of enantiomerically pure conduritols. In particular we were interested in the synthesis of the enantiomerically pure (+)-1,4-dimethoxy conduritol B and (−)-1,4-dimethoxy conduritol F as well as in the synthesis of conduritols with four unprotected hydroxyl groups.

## Results and Discussion

Our synthetic strategy[9] requires the use, as starting material, of an alcohol sugar which has the same configuration at the four chiral carbon atoms of those of the desired conduritol. The cyclization of the sugar can be achieved (Scheme 1) by means of an intramolecular thiacyclization to the corresponding thiepane. After oxidation to the related sulfone it is possible, by means of a Ramberg–Bäcklund reaction, to generate the double bond.




**Scheme 1.**

*Keywords*: biologically active compounds; cyclitols; enantiomeric purity; thiosugars.

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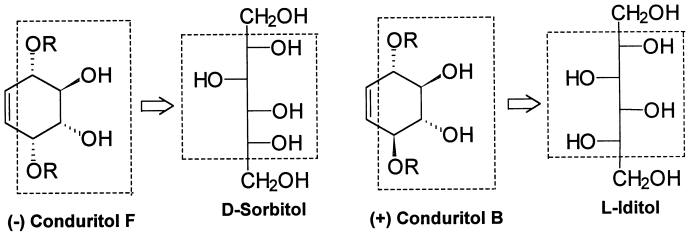
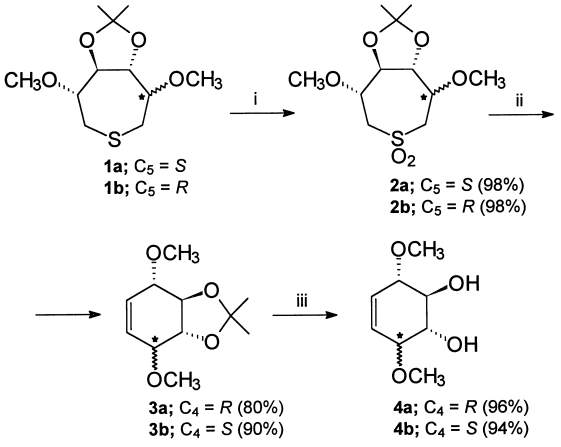



**Scheme 2.**

Since this methodology, described for the synthesis of the enantiomerically pure (−)-1,4-dimethoxy conduritol E[9] proved to be simple and inexpensive, we wondered if this approach, mediated by sulfur, could have a general character and could be applied as such to the synthesis of 1,4-dimethoxy (−)-conduritol F and (+)-conduritol B derivatives (Scheme 2) starting from D-sorbitol and L-iditol, respectively.

With this in mind, we synthesized (Scheme 3) the intermediate **1a**[10] from D-sorbitol, applying to this alcohol sugar the same methodology already described in the literature for D-mannitol.[11] In the case of **1b** the high cost of L-iditol prompted us to use a procedure[11,12] which starts from D-mannitol and through an inversion at $C_2$ and $C_5$ leads to the stereochemically suitable thiepane derivative **1b**, whose stereochemistry at the chiral centers corresponds to that of the skeleton of the L-iditol. These thiepane derivatives **1a**,**b** (Scheme 3) were oxidized using MCPBA to give the sulfones **2a**,**b** which were subjected to a Ramberg–Bäcklund reaction. Both the substrates gave, in excellent yields, the expected cyclohexene derivatives **3a**,**b**. Finally, under acidic conditions, the expected conduritol derivatives **4a** and **4b** were obtained, from **1a** and **1b**, respectively, in 75 and 83% overall yield.

The good results obtained for the Ramberg–Bäcklund reaction make our methodology particularly attractive, especially with regard to the average yields reported for this kind of reaction[13] and clearly outline the general character of our procedure which can be successfully applied to the synthesis of conduritols with different stereochemistry, with or without $C_2$ symmetry.

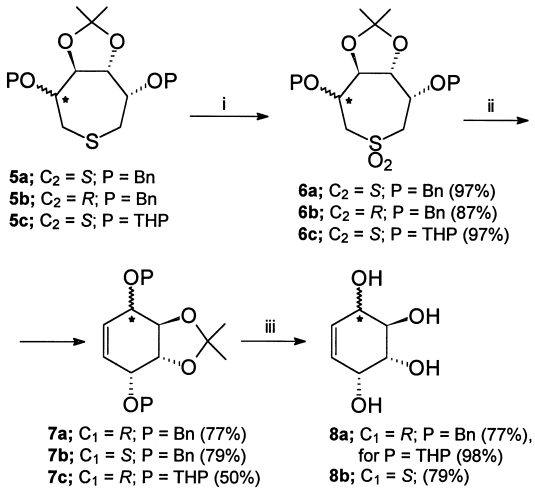



**Scheme 3.** (i) MCPBA; (ii) $CCl_4$, KOH, *t*-BuOH, $H_2O$; (iii) $H_2SO_4$ 0.1N.

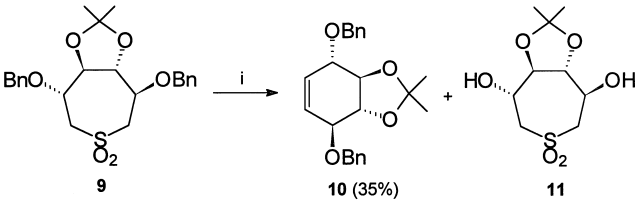
The strong protection of two hydroxyl groups as methyl ethers in the thiepane derivatives **1a** and **1b** allows further selective transformations on the remaining OH moieties and in this regard a thorough study is currently underway.

We were interested as well in the synthesis of conduritols with four unprotected OH groups. Unfortunately, following usual deprotection conditions, we have experienced some difficulties in the removal of the methyl groups. Previous attempts of subjecting directly the 1,6-dideoxy-3,4-*O*-isopropylidene-1,6-thio-D-mannitol-*S*,*S*-dioxide, not protected at the hydroxyl groups on $C_2$ and $C_5$, to the Ramberg–Bäcklund reaction, using the Meyers[14] and the Chan[15] conditions, were completely unsuccessful because we recovered, in both cases, only unreacted starting material. The above mentioned compound was converted to the corresponding *bis*-acetonide but the substrate decomposed during the Ramberg–Bäcklund reaction and, presumably due to the constricted conformation, was not able to produce the desired double bond. In light of these results we looked for a different protective group which could stand the Ramberg–Bäcklund conditions and be removed together with the acetonide. A good result was finally obtained using the benzyl derivative as depicted in Scheme 4.

The 1,6-dideoxy-3,4-*O*-isopropylidene-1,6-thio-D-mannitol was protected as benzyl ethers at the hydroxyl groups on $C_2$ and $C_5$ giving **5a**. This compound was oxidized to the sulfone **6a** and subjected to a Ramberg–Bäcklund reaction. The benzyl group withstood the basic conditions, allowing the formation of the double bond giving **7a**. By treatment of




**Scheme 4.** (i) MCPBA; (ii) KOH, $CCl_4$, *t*-BuOH, $H_2O$; (iii) for P=Bn: $SnCl_4$, $CH_2Cl_2$; (iii) for P=THP: $CF_3COOH$.




**Scheme 5.** (i) KOH, $CCl_4$, *t*-BuOH, $H_2O$.

**7a** with $SnCl_4$ both protecting groups could be easily removed to produce the (−)-conduritol E (**8a**).

Similarly, starting from 1,6-dideoxy-2,5-*O*-dibenzyl-3,4-*O*-isopropylidene-1,6-thio-D-sorbitol **5b**, we synthesized **6b** and following the same procedure (Scheme 4) applied to the D-mannitol derivative **6a** we obtained the (−)-conduritol F (**8b**), in an analogous yield.

In order to complete our generalisation we subjected 1,6-dideoxy-2,5-*O*-dibenzyl-3,4-*O*-isopropylidene-1,6-thio-L-iditol-S,S-dioxide **9** to the Ramberg–Bäcklund reaction (Scheme 5). The (+)-conduritol B derivative **10** was obtained but in lower yield compared to the D-mannitol and D-sorbitol derivatives **7a** and **7b**.

In fact in the aqueous phase we recovered **11** which clearly derives from the undesired deprotection of the benzyl groups of the starting material **9**. This disappointing result was not experienced on the D-mannitol or on the D-sorbitol derivatives which differ from compound **9** simply in the configuration of one stereocenter. Furthermore, treating the (+)-conduritol B derivative **10** with $SnCl_4$ we did not observe the expected debenzylation but only the loss of the acetonide.

We then examined another protecting group, tetrahydropyran-2-yl (THP) group. This group proved to be effective on D-mannitol leading, after acidic hydrolysis, to the (−)-conduritol E, indicated in Scheme 4, even if the Ramberg–Bäcklund reaction gives a slightly lower yield compared to the benzyl. Introducing the THP on the 1,6-dideoxy-4,5-*O*-isopropylidene-1,6-thio-L-iditol and subjecting the corresponding sulfone to Ramberg–Bäcklund reaction we observed complete decomposition of the substrate. Considering these experimental results we believe that a further and thorough study should be necessary for the synthesis of (+)-conduritol B.

On the other hand, our approach provides a simple and efficient access to 1,4-dimethoxy conduritols and to the (−)-conduritols E and F, starting from inexpensive materials from natural sources. Furthermore, the conduritols are obtained enantiomerically pure, in good yields, and without restrictions on the symmetry of the final products since the stereochemistry of the chiral centers of the starting alcohol sugar remains untouched.

## Experimental

**General.** All moisture-sensitive reactions were performed in flame-dried glassware equipped with rubber septa under positive pressure of dry nitrogen. Organic extracts were dried over $CaSO_4$. Melting points are uncorrected. Preparative flash chromatographic experiments were performed using ICN Silica gel 230–400 mesh. For TLC precoated glass plates were used (Stratochrom $SIF_{254}$, 0.25 mm thick) and the spots were developed at 110°C with an aqueous solution of $(NH_4)_6Mo_7O_{24}$ (2.5%) and $(NH_4)_4Ce(SO_4)_4$ (1%) in 10% $H_2SO_4$ or $KMnO_4$ 0.1 M/$H_2SO_4$ 1 M 1/1. Yields are for isolated compounds. Unless specified otherwise $^1H$ and $^{13}C$ NMR spectra were recorded at 300 and 75 MHz, respectively, in $CDCl_3$ as solvent. Chemical shifts are in ppm downfield of TMS; signal multiplicities were established by DEPT experiments. Signal assignments, if necessary, were elucidated by decoupling $^1H$ NMR and by 2D $^1H$–$^1H$ and $^1H$–$^{13}C$ NMR experiments. Optical rotations were measured at 589 nm. Solvents and reagents were obtained dry as follows: DMSO was distilled under *vacuum* from $CaH_2$ and $CH_2Cl_2$ was refluxed over and distilled from $CaH_2$.

**(−)-1,6-Dideoxy-3,4-*O*-isopropylidene-2,5-di-*O*-methyl-1,6-thio-D-sorbitol-*S*,*S*-dioxide (2a).** To 0.50 g (2.01 mmol) of 1,6-dideoxy-3,4-*O*-isopropylidene-2,5-di-*O*-methyl-1,6-thio-D-sorbitol (**1a**),[12] dissolved in 7 mL of $CH_2Cl_2$ and cooled at 0°C, 0.79 g (4.58 mmol) of 50% *m*-chloroperbenzoic acid were added. After 4 h at room temperature, $Na_2S_2O_5$ was added to destroy the unreacted peracid. The reaction mixture, washed with saturated solution of $NaHCO_3$, was extracted with $CH_2Cl_2$. The extracts washed with brine and dried gave, after evaporation of the solvent, 0.68 g (98%) of an only product as a white solid which could be used as such for the following reaction without purification. Nevertheless the title compound was purified by flash chromatography ($SiO_2$; $Et_2O/CH_3OH$; 95:5), to give a white crystalline product, mp 145–147°C. $^1H$ NMR $\delta$: 4.40–4.28 (m, 1H, CHO), 4.19–4.10 (m, 1H, CHO), 4.07–4.00 (m, 1H, CHO), 3.82–3.68 (m, 1H, CHO), 3.50 (s, 3H, $OCH_3$), 3.48 (s, 3H, $OCH_3$), 3.45–3.40 (m, 2H, 2C*H*HS), 3.36–3.29 (m, 2H, 2CH*H*S), 1.42 (s, 3H, $CH_3$), 1.39 (s, 3H, $CH_3$). $^{13}C$ NMR $\delta$: 109.5 (C), 77.9 (CHO), 77.5 (CHO), 77.2 (CHO), 73.5 (CHO), 60.2 ($CH_3O$), 59.7 ($CH_2S$), 58.5 ($CH_3O$), 55.0 ($CH_2S$), 27.4 ($CH_3$), 27.0 ($CH_3$). $[\alpha]_D^{25}=-27.41$ ($c$=1.12, $CHCl_3$). Anal. Calcd for $C_{11}H_{20}O_6S$: C, 47.13; H, 7.19. Found: C, 47.15; H, 7.15. *m/z* (EI): 280 (12), 265 (70), 222 (10), 126 (60), 109 (95), 100 (100), 85 (97), 71 (85), 59 (63), 43 (78). IR (Nujol) $\nu_{max}/cm^{-1}$=3000, 1329, 1131, 1096.

**(1*S*,2*R*,3*R*,4*R*)-(−)-2,3-Isopropylidene-1,4-dimethoxycyclohex-5-ene-2,3-diol (3a).** To 0.21 g (0.75 mmol) of 1,6-dideoxy-3,4-*O*-isopropylidene-2,5-di-*O*-methyl-1,6-thio-D-sorbitol-*S*,*S*-dioxide (**2a**) 2.0 mL of *t*-BuOH, 3.0 mL of $CCl_4$ and 0.3 mL of $H_2O$ were added.[11] The mixture was stirred to complete solution of the reagent, then, under $N_2$, 1.98 g of KOH finely powdered, were added. After stirring for 70 min at room temperature, the mixture was diluted with $H_2O$ and extracted with $CH_2Cl_2$. The organic layers washed with $H_2O$, dried and evaporated gave the title compound **3a** which could be purified by flash chromatography ($SiO_2$; light-petroleum/$Et_2O$, 3:1) to give 0.13 g (80%) of a pale yellow oil. $^1H$ NMR $\delta$: 5.85 (ddd, 1H, CH=, $J$=10.8, 4.9, 1.8 Hz), 5.75 (dd, 1H, CH=, $J$=10.1, 1.7 Hz), 4.05–3.99 (m, 1H, CHO), 3.98–3.90 (m, 1H, CHO), 3.88–3.82 (m,

1H, CHO), 3.48 (s, 3H, $CH_3O$), 3.44 (s, 3H, $CH_3O$), 3.45–3.38 (m, 1H, CHO), 1.43 (s, 3H, $CH_3$), 1.40 (s, 3H, $CH_3$). $^{13}$C NMR $\delta$: 131.3 (CH=), 126.7 (CH=), 110.4 (C), 80.2 (CHO), 77.7 (CHO), 75.7 (CHO), 73.0 (CHO), 58.9 ($CH_3O$), 57.1 ($CH_3O$), 27.2 ($CH_3$), 26.7 ($CH_3$). $[\alpha]_D^{25}=-133.48$ ($c$=1.13, $CHCl_3$). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.60; H, 8.45. $m/z$ (EI): 199 (1), 139 (39), 127 (100), 114 (65), 73 (34). IR (neat) $\nu_{max}/cm^{-1}$=2990, 2840, 1385, 1230, 1100.

**(1*S*,2*R*,3*R*,4*R*)-(−)-2,3-Dihydroxy-1,4-dimethoxycyclohex-5-ene (4a).** The suspension constituted by 0.47 g (2.20 mmol) of (1*S*,2*R*,3*R*,4*R*)-(−)-2,3-isopropylidene-1,4-dimethoxy cyclohex-5-ene-2,3-diol (**3a**) and 5.6 mL of 0.1 N $H_2SO_4$ was warmed at 90°C for 4 h. The mixture was neutralized with 10% $Na_2CO_3$ aqueous solution and, after evaporation of the aqueous phase a solid residue was obtained. The solid was extracted with $CH_2Cl_2$, dried, and after evaporation of the solvent 0.36 g (96%) of **4a** were obtained as a colorless oil. A sample was purified by flash chromatography ($SiO_2$; $Et_2O/CH_3OH$, 19:1). $^1$H NMR $\delta$: 6.04–5.84 (m, 2H, CH=), 3.90–3.65 (m, 4H, 4CHO), 3.46 (s, 3H, $CH_3$), 3.41 (s, 3H, $CH_3$), 3.05 (br s, 2H, 2OH). $^{13}$C NMR $\delta$: 131.4 (CH=), 125.2 (CH=), 81.3 (CHO), 75.0 (CHO), 72.1 (CHO), 71.6 (CHO), 57.5 ($CH_3$), 57.2 ($CH_3$). $[\alpha]_D^{25}=-64.4$ ($c$=1.40, $CH_3OH$). Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.18; H, 8.09. $m/z$ (EI): 114 (100), 99 (29), 71 (24) 45 (16). IR (neat) $\nu_{max}/cm^{-1}$=3520, 3000, 1085, 720.

**(−)-1,6-Dideoxy-3,4-*O*-isopropylidene-2,5-di-*O*-methyl-1,6-thio-L-iditol-*S*,*S*-dioxide (2b).** The title compound was obtained starting from **1b**[12] and using the procedure adopted for the synthesis of **2a**. The crude product was obtained in 98% yield as a white solid which could be used as such for the following reaction without purification. A sample was purified by flash chromatography ($SiO_2$; $Et_2O/CH_3OH$, 95:5) giving a white crystalline product, mp 141–142°C. $^1$H NMR $\delta$: 4.14–4.05 (m, 2H, 2CHO), 3.73–3.64 (m, 2H, 2CHO), 3.49 (s, 6H, $2OCH_3$), 3.52–3.39 (m, 2H, 2C*H*HS), 3.27–3.17 (m, 2H, 2CH*H*S), 1.43 (s, 6H, $2CH_3$). $^{13}$C NMR $\delta$: 109.9 (C), 79.5 (2CHO), 77.7 (2CHO), 58.7 ($2OCH_3$), 56.0 ($2CH_2S$), 27.0 ($2CH_3$). $[\alpha]_D^{27}=-58.07$ ($c$=1.61, $CHCl_3$). Anal. Calcd for $C_{11}H_{20}O_6S$: C, 47.13; H, 7.19. Found: C, 47.15; H, 7.15. $m/z$ (EI): 280 (8), 265 (75), 248, (20), 222 (16), 126 (50), 100 (100), 85 (90). IR (Nujol) $\nu_{max}/cm^{-1}$=3020, 1307, 1111, 1081.

**(1*S*,2*R*,3*R*,4*S*)-(+)-2,3-Isopropylidene-1,4-dimethoxycyclohex-5-ene-2,3-diol (3b).** The synthesis was carried out in 2 h using the same procedure used for the synthesis of **3a**, starting from **2b**. After purification by flash chromatography ($SiO_2$; light-petroleum/$Et_2O$, 3:1) the title compound was obtained as a colorless oil in 90% yield. $^1$H NMR $\delta$: 5.70 (br s, 2H, 2CH=), 4.04–3.95 (m, 2H, 2CHO), 3.58–3.47 (m, 2H, 2CHO), 3.47 (s, 6H, $2OCH_3$), 1.42 (s, 6H, $2CH_3$). $^{13}$C NMR $\delta$: 128.4 (2CH=), 111.2 (C), 79.9 (2CHO), 79.3 (2CHO), 57.6 ($2OCH_3$), 27.2 ($2CH_3$). $[\alpha]_D^{25}=+32.8$ ($c$=1.20, $CHCl_3$). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.65; H, 8.40. $m/z$ (EI): 214 (2), 199 (15), 184 (23), 139 (30), 127 (100), 124 (50), 114 (60), 97 (30), 73 (35). IR (neat) $\nu_{max}/cm^{-1}$=3005, 2830, 1379, 1227.

**(1*S*,2*R*,3*R*,4*S*)-(+)-2,3-Dihydroxy-1,4-dimethoxycyclohex-5-ene (4b).** The title compound was prepared using the same methodology employed in the preparation of **4a** starting from **3b**. After 6 h **4b** was obtained and purified by flash chromatography ($SiO_2$; $Et_2O/CH_3OH$, 95:5), giving a white crystalline product in 90% yield, mp 48–49°C. $^1$H NMR ($CD_3OD$) $\delta$: 5.79 (br s, 2H, 2CH=), 3.88–3.75 (m, 2H, 2CHO), 3.67–3.56 (m, 2H, 2CHO), 3.49 (s, 6H, $2OCH_3$). $^{13}$C NMR ($CD_3OD$) $\delta$: 128.6 (2CH=), 83.1 (2CHO), 76.0 (2CHO), 57.9 ($2CH_3$). $[\alpha]_D^{25}=+106.87$ ($c$=1.50, $CH_3OH$). Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.18; H, 8.08. $m/z$ (EI): 174 (2), 114 (100), 99 (32), 71 (20) 41 (17). IR (Nujol) $\nu_{max}/cm^{-1}$=3503, 3018, 1050, 730.

**(−)-1,6-Dideoxy-2,5-di-*O*-benzyl-3,4-*O*-isopropylidene-1,6-thio-D-mannitol (5a).** To 150 mg (3.12 mmol) of 50% (w/w) NaH, washed under nitrogen with light-petroleum, were added 7.0 mL of dry THF and, under stirring, 568 mg (2.58 mmol) of 1,6-dideoxy-3,4-*O*-isopropylidene-1,6-thio-D-mannitol,[12] previously dried for 3 h at 35°C and 0.3 mm Hg. After 30 min 0.3 mL (2.71 mmol) of benzyl bromide dissolved in 1.8 mL of THF and 2 mg (0.012 mmol) of KI were added. The reaction mixture was stirred for 7 h, then 150 mg (3.12 mmol) of NaH and 0.3 mL (2.71 mmol) of benzyl bromide were added, as previously described. After 12 h the crude mixture was quenched with water and extracted with $Et_2O$. The organic layer dried on $MgSO_4$, was filtered and by evaporation of the solvent gave 0.96 g (2.39 mmol, 93%) of **5a**, as a yellow oil which could be used as such for the following reaction. Nevertheless the title compound, purified by flash chromatography ($SiO_2$; $CH_2Cl_2$/light-petroleum, 3/1) gave a yellow solid (mp 55–57°C). $^1$H NMR $\delta$: 7.50–7.25 (m, 10H, 10CHAr), 4.90 (d, 2H, 2CH*H*Ph, $J$=12.1 Hz), 4.75–4.68 (m, 2H, 2CHO, irradiating at 4.18 ppm a singlet was obtained), 4.69 (d, 2H, 2C*H*HPh, $J$=12.1 Hz), 4.25–4.10 (m, 2H, 2CHOBn), 2.97–2.80 (m, 2H, 2CH*H*S, irradiating at 4.18 ppm a doublet was obtained, $J$=15.0 Hz), 2.70–2.55 (m, 2H, 2C*H*HS, irradiating at 4.18 ppm a doublet was obtained $J$=15.3 Hz), 1.50 (s, 6H, $2CH_3$). $^{13}$C NMR $\delta$: 138.8 (2CAr), 128.4 (4CHAr), 127.7 (4CHAr), 127.6 (2CHAr), 109.4 ($C(CH_3)_2$), 77.8 (2CHO), 74.2 (2CHO), 73.5 ($2CH_2O$), 36.9 ($2CH_2S$), 27.0 ($2CH_3$). $[\alpha]_D^{25}=-47.2$ ($c$=1.19, $CHCl_3$). Anal. Calcd for $C_{23}H_{28}O_4S$: C, 68.97; H, 7.99. Found: C, 68.92; H, 7.92. $m/z$ (EI): 400 (1), 385 (3), 340 (2), 293 (1), 251 (4), 91 (100). IR (Nujol) $\nu_{max}/cm^{-1}$=2940, 1250, 1080, 700.

**(−)-1,6-Dideoxy-2,5-di-*O*-benzyl-3,4-*O*-isopropylidene-1,6-thio-D-mannitol-*S*,*S*-dioxide (6a).** Starting from the (−)-1,6-dideoxy-2,5-di-*O*-benzyl-3,4-*O*-isopropylidene-1,6-thio-D-mannitol (**5a**) and using the procedure adopted for the synthesis of **2a**, the title compound was obtained in 97% yield as a solid product which could be used as such for the following reaction. Nevertheless the title compound, purified by flash chromatography ($SiO_2$; $Et_2O$/light-petroleum, 3:2), gave a white solid at mp 125–127°C. $^1$H NMR $\delta$: 7.45–7.25 (m, 10H, 10CHAr), 4.84–4.50 (m, 6H, 2CHO and $2CH_2Ph$), 4.29–4.19 (m, 2H, 2CHO), 3.40–3.30 (m, 4H, $2CH_2S$), 1.50 (s, 6H, $2CH_3$). $^{13}$C NMR $\delta$: 137.7 (2CAr), 128.6 (4CHAr), 128.1 (4CHAr), 127.9 (2CHAr), 109.9 ($C(CH_3)_2$), 76.8 (2CHO), 73.8 ($2CH_2Ph$), 69.9 (2CHO), 57.8 ($2CH_2S$), 26.9 ($2CH_3$). $[\alpha]_D^{25}=-34.5$

($c$=1.58, $CHCl_3$). Anal. Calcd for $C_{23}H_{28}O_6S$: C, 63.87; H, 6.53. Found: C, 63.84; H, 6.57. *m/z* (EI): 432 (<1), 417 (2), 341 (12), 91 (100). IR ($CCl_4$) $\nu_{max}/cm^{-1}$=2926, 1312, 1124.

**(−)-(1*R*,2*R*.3*R*,4*R*)-1,4-di-*O*-Benzyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol (7a).** The same methodology described for **3a** was followed starting from the (−)-1,6-dideoxy-2,5-di-*O*-benzyl-3,4-*O*-isopropylidene-1,6-thio-D-mannitol-*S*,*S*-dioxide (**6a**). The reaction was carried out in 1.45 h and after the usual work-up the title compound was obtained, in 77% yield, as a solid which could be used as such for the following reaction. Nevertheless the title compound, purified by flash chromatography ($SiO_2$; $Et_2O$/light-petroleum, 7:1), gave a white solid at mp 66–68°C. $^1$H NMR $\delta$: 7.35–7.15 (m, 10H, 10CHAr), 5.81 (dd, 2H, 2CH=, $J$=1.4, 3.2 Hz), 4.89 (d, 2H, 2C*H*HPh, $J$=11.7 Hz), 4.55 (d, 2H, 2CH*H*Ph, $J$=11.7 Hz), 4.30–4.20 (m, 2H, 2CHO), 4.15–4.05 (m, 2H, 2CHO), 1.45 (s, 6H, $2CH_3$). $^{13}$C NMR $\delta$: 138.8 (2CAr), 129.6 (4CHAr), 128.5 (4CHAr), 127.8 (2CHAr), 127.7 (2CH=), 110.2 ($C(CH_3)_2$), 75.0 (2CHO), 73.6 ($2CH_2$), 72.1 (2CHO), 27.1 ($2CH_3$). $[\alpha]_D^{25}$=−192.3 ($c$=0.87, $CHCl_3$). Anal. Calcd for $C_{23}H_{26}O_4$: C, 75.37; H, 7.16. Found: C, 75.40; H, 7.20. *m/z* (EI): 366 (<1), 351 (1), 308 (4), 91 (100). IR ($CCl_4$) $\nu_{max}/cm^{-1}$=2986, 1234, 1000.

**(−)-Conduritol E (8a).** To 168 mg (0.46 mmol) of (−)-(1*R*,2*R*,3*R*,4*R*)-1,4-di-*O*-benzyl-2,3-*O*-isopropylidene-cyclohex-5-ene-1,2,3,4-tetrol (**7a**) dissolved in 4 mL of $CH_2Cl_2$ 0.2 mL of $SnCl_4$ were added. After 1 h the reaction mixture was neutralized with a saturated solution of $NaHCO_3$ and extracted with $CH_2Cl_2$. By evaporation of the aqueous layer was recovered a residue which was extracted with 10 mL of $CH_3OH$. The organic layer was dried on $MgSO_4$, filtered on celite and by evaporation of the solvent gave 54 mg (0.354 mmol, 77%) of the expected (−)-conduritol E[16] as a white solid at mp 191–193°C. $^1$H NMR ($D_2O$) $\delta$: 5.72 (m, 2H, 2CH=), 4.15 (m, 2H, 2CHO), 3.76 (m, 2H, 2CHO). $^{13}$C NMR ($D_2O$) $\delta$: 127.3 (2CH=), 66.7 (2CHO), 64.2 (2CHO). $[\alpha]_D^{25}$=−330.0 ($c$=1.90, $H_2O$). Anal. Calcd for $C_6H_{10}O_4$: C, 49.30; H, 6.90. Found: C, 49.25; H, 6.97. *m/z* (EI): 146 (<1), 110 (100), 82 (8). IR (Nujol) $\nu_{max}/cm^{-1}$=3520, 3000, 1092, 1030.

**(−)-1,6-Dideoxy-2,5-di-*O*-benzyl-3,4-*O*-isopropylidene-1,6-thio-D-sorbitol (5b).** The reaction was carried out using the same methodology described for the synthesis of **5a** starting from the 3,4-*O*-isopropylidene-1,6-thio-D-sorbitol.[12] The reaction was quantitative and the product, obtained as yellow oil, could be used for the following reaction as such. Nevertheless the title compound, purified by flash chromatography ($SiO_2$; light-petroleum/$Et_2O$, 5:1) gave a yellow solid (mp=55–58°C). $^1$H NMR $\delta$: 7.50–7.15 (m, 10H, 10CHAr), 4.90–4.73 (m, 4H, $2CH_2Ph$), 4.67 (dd, 1H, CHO, $J$=12.2, 2.3 Hz), 4.17–4.08 (m, 1H, CHOBn), 3.97 (dd, 1H, CHO, $J$=9.1, 2.2 Hz), 3.78–3.67 (m, 1H, CHOBn), 2.84 (dd, 1H, C*H*HS, $J$=15.5, 4.3 Hz), 2.73–2.54 (m, 3H, 2CH*H*S and C*H*HS), 1.49 (s, 3H, $CH_3$), 1.42 (s, 3H, $CH_3$). $^{13}$C NMR $\delta$: 138.7 (CAr), 138.6 (CAr), 128.4 (2CHAr), 128.3 (2CHAr), 128.2 (2CHAr), 127.7 (2CHAr), 127.6 (2CHAr), 109.1 ($C(CH_3)_2$), 79.8 (2CHO), 79.0 (CHO), 74.5 (CHO), 73.0 ($CH_2Ph$), 71.5 ($CH_2Ph$), 36.8 ($CH_2S$), 36.6 ($CH_2S$), 27.2 ($CH_3$), 26.7 ($CH_3$). $[\alpha]_D^{25}$=−26.9 ($c$=1.14, $CHCl_3$). Anal. Calcd for $C_{23}H_{28}O_4S$: C, 68.97; H, 7.99. Found: C, 69.04; H, 7.93. *m/z*: 400 (<1), 385 (1), 292 (13), 126 (23), 91 (100). IR ($CCl_4$) $\nu_{max}/cm^{-1}$=3060, 2900, 1450, 1370, 1220, 1080, 700.

**(−)-1,6-Dideoxy-2,5-di-*O*-benzyl-3,4-*O*-isopropylidene-1,6-thio-D-sorbitol-*S*,*S*-dioxide (6b).** The reaction was carried out using the same methodology described for the synthesis of **6a** starting from the (−)-1,6-dideoxy-2,5-di-*O*-benzyl-3,4-*O*-isopropylidene-1,6-thio-D-sorbitol (**5b**). The title compound was obtained in 87% yield as a white solid (mp 120–122°C). $^1$H NMR $\delta$: 7.40–7.25 (m, 10H, 10CHAr), 4.85 (d, 1H; CH*H*Ph, $J$=11.9 Hz), 4.75 (d, 1H; CH*H*Ph, $J$=11.8 Hz), 4.67 (d, 1H, C*H*HPh, $J$=12.0 Hz), 4.66 (d, 1H; C*H*HPh, $J$=11.8 Hz), 4.54 (t, 1H, CHO, $J$=9.0 Hz), 4.27–4.22 (m, 1H, CHOBn), 4.20 (dd, 1H, CHO, $J$=9.1, 1.4 Hz), 4.00 (ddd, 1H, CHOBn, $J$=9.1, 9.1, 3.9 Hz), 3.47–3.24 (m, 4H, $2CH_2S$), 1.51 (s, 3H, $CH_3$), 1.46 (s, 3H, $CH_3$). $^{13}$C NMR $\delta$: 137.6 (CAr), 137.1 (CAr), 128.6 (2CHAr), 128.5 (2CHAr), 128.2 (2CHAr), 127.9 (2CHAr), 127.8 (2CHAr), 109.1 ($C(CH_3)_2$), 78.3 (CHO), 76.9 (CHO), 74.9 (CHO), 73.7 ($CH_2Ph$), 72.9 ($CH_2Ph$), 70.4 (CHO), 59.5 ($CH_2S$), 56.1 ($CH_2S$), 27.1 ($CH_3$), 26.8 ($CH_3$). $[\alpha]_D^{25}$=−35.5 ($c$=1.16, $CHCl_3$). Anal. Calcd for $C_{23}H_{28}O_6S$: C, 63.87; H, 6.53. Found: C, 63.81; H, 6.57. *m/z*: 432 (<1), 417(2), 341 (8), 91 (100). IR (Nujol) $\nu_{max}/cm^{-1}$=2900, 1320, 1130.

**(1*S*,2*R*,3*R*,4*R*)-(−)-1,4-di-*O*-Benzyl-2,3-*O*-isopropylidene-cyclohex-5-ene-1,2,3,4-tetrol (7b).** The reaction was carried out using the same methodology described for the synthesis of **7a** starting from the (−)-1,6-dideoxy-2,5-di-*O*-benzyl-3,4-*O*-isopropylidene-1,6-thio-D-sorbitol-*S*,*S*-dioxide (**6a**). The reaction was carried in 2 h and, after usual workup **7b** was obtained as a yellow oil in 79% yield. The title compound was purified by flash chromatography ($SiO_2$; light-petroleum/$Et_2O$, 8:1). $^1$H NMR $\delta$: 7.75–7.50 (m, 10H, 10CHAr), 6.18–6.04 (m, 2H, 2CH=), 5.24 (d, 1H, C*H*HPh, $J$=12.0 Hz), 5.15 (d, 1H, CH*H*Ph, $J$=12.0 Hz), 4.99 (d, 1H, C*H*HPh, $J$=11.9 Hz), 4.96 (d, 1H, CH*H*Ph, $J$=11.9 Hz), 4.60–4.38 (m, 3H, 3CHO), 3.81 (dd, 1H, CHO, $J$=3.4, 9.8 Hz), 1.80 (s, 6H, $2CH_3$). $^{13}$C NMR $\delta$: 138.9 (CAr), 138.6 (CAr), 131.9 (CH=), 128.4 (2CHAr), 128.3 (2CHAr), 127.9 (2CHAr), 127.8 (2CHAr), 127.7 (2CHAr), 127.0 (CH=), 110.6 ($C(CH_3)_2$) 78.3 (CHO), 78.0 (CHO), 76.6 (CHO), 73.2 ($CH_2Ph$), 71.5 ($CH_2Ph$), 71.1 (CHO), 27.4 ($CH_3$), 26.9 ($CH_3$). $[\alpha]_D^{25}$=−88.6 ($c$=1.46, $CHCl_3$). Anal. Calcd for $C_{23}H_{26}O_4$: C, 75.37; H, 7.16. Found: C, 75.41; H, 7.12. *m/z*: 366 (<1), 351 (1), 202 (8), 149 (16), 91 (100). IR ($CCl_4$) $\nu_{max}/cm^{-1}$=2987, 1371, 1089.

**(−)-Conduritol F (8b).** The title compound was synthesized analogously to **8a** starting from the (1*S*,2*R*,3*R*,4*R*)-(−)-1,4-di-*O*-benzyl-2,3-*O*-isopropylidene-cyclohex-5-ene-1,2,3,4-tetrol (**7b**). After 70 min, by usual workup, the title compound[16] was obtained in 79% yield as a pale yellow solid at mp 128–130°C. $^1$H NMR $\delta$: 5.79 (ddd, 1H, CH=, $J$=10.0, 4.7, 1.9 Hz), 5.71 (dd, 1H, CH=, $J$=10.0, 1.9 Hz), 4.15 (t, 1H, CHO, $J$=4.3 Hz), 3.92 (dt, 1H, CHO, $J$=7.5, 1.6 Hz), 3.61 (dd, 1H, CHO, $J$=10.4, 7.7 Hz), 3.41 (dd, 1H, CHO, $J$=10.4, 4.2 Hz). $^{13}$C NMR

δ: 133.8 (CH=), 128.1 (CH=), 74.1 (CHO), 73.8 (CHO), 72.7 (CHO), 68.0 (CHO). $[\alpha]_D^{25}=-84.0$ (*c*=0.71, $CH_3OH$). Anal. Calcd for $C_6H_{10}O_4$: C, 49.30; H, 6.90. Found: C, 49.35; H, 6.87. *m*/*z*: 110 (2), 99 (15), 86 (100), 82 (8), 81 (9), 71 (7), 57 (76). IR (Nujol) $\nu_{max}/cm^{-1}$=3400, 2900, 1620, 1110, 950.

**(−)-1,6-Dideoxy-2,5-di-*O*-benzyl-3,4-*O*-isopropylidene-1,6-thio-L-iditol-*S*,*S*-dioxide (9).** The reaction was carried out using the same methodology described for the synthesis of **5a** starting from the 3,4-*O*-isopropylidene-1,6-thio-L-iditol.[12] The reaction was quantitative and the product, obtained as yellow oil, could be used as such for the following reaction. Nevertheless after purification with flash chromatography ($SiO_2$; $CH_2Cl_2$/light-petroleum, 2:1) the (−)-1,6-dideoxy-2,5-di-*O*-benzyl-3,4-*O*-isopropylidene-1,6-thio-L-iditol was obtained, as yellow solid (mp 53–55°C). $^1$H NMR δ: 7.45–7.20 (m, 10H, 10CHAr), 4.81 (d, 2H, 2CH*H*Ph, *J*=12.3 Hz), 4.66 (d, 2H, 2C*H*HPh, *J*=12.3 Hz), 4.18–4.03 (m, 2H, 2CHO), 3.77–3.62 (m, 2H, 2CHOBn), 2.72 (d, 4H, $2CH_2S$, *J*=5.5 Hz), 1.45 (s, 6H, $2CH_3$). $^{13}$C NMR δ: 138.5 (2CAr), 128.4 (4CHAr), 127.9 (4CHAr), 127.8 (2CHAr), 109.1 ($C(CH_3)_2$), 81.5 (2CHO), 79.9 (2CHO), 72.2 ($2CH_2Ph$), 36.6 ($2CH_2S$), 27.1 ($2CH_3$). $[\alpha]_D^{25}=+10.9$ (*c*=1.12, $CHCl_3$). Anal. Calcd for $C_{23}H_{28}O_4S$: C, 68.97; H, 7.99. Found: C, 69.03; H, 7.91. *m*/*z*: 400 (<1), 385 (1), 342 (1), 292 (17), 184 (7), 126 (52), 91 (100). IR ($CCl_4$) $\nu_{max}/cm^{-1}$=2980, 1370, 1200, 1050, 700.

Application to the (−)-1,6-dideoxy-2,5-di-*O*-benzyl-3,4-*O*-isopropylidene-1,6-thio-L-iditol of the same procedure adopted for the synthesis of **2a**, gave the title compound **9** in 90% yield as a white solid at mp 128–130°C. $^1$H NMR δ: 7.50–7.25 (m, 10H, 10CHAr), 4.83 (d, 2H, 2CH*H*Ph, *J*=12.2 Hz), 4.65 (d, 2H, 2C*H*HPh, *J*=12.2 Hz), 4.25–4.10 (m, 2H, 2CHO), 3.95–3.80 (m, 2H, 2CHOBn), 3.33 (dd, 2H, 2CH*H*S, *J*=15.7, 6.2 Hz), 3.18 (dd, 2H, 2CH*H*S, *J*=15.7, 6.2 Hz), 1.45 (s, 6H, $CH_3$). $^{13}$C NMR δ: 137.6 (2CAr), 128.7 (4CHAr), 128.2 (4CHAr), 128.1 (2CHAr), 109.8 ($C(CH_3)_2$), 80.2 (2CHO), 74.9 (2CHO), 73.1 ($2CH_2Ph$), 57.2 ($2CH_2S$), 27.1 ($2CH_3$). $[\alpha]_D^{25}=-36.5$ (*c*=0.88, $CHCl_3$). Anal. Calcd for $C_{23}H_{28}O_6S$: C, 63.87; H, 6.53. Found: C, 63.90; H, 6.49. *m*/*z*: 432 (1), 417 (3), 374 (<1), 341 (4), 262 (4), 163 (10), 107 (16), 91 (100). IR ($CHCl_3$) $\nu_{max}/cm^{-1}$=2987, 1324, 1068, 851.

**(1*S*,2*R*,3*R*,4*S*)-(+)-1,4-di-*O*-Benzyl-2,3-*O*-isopropylidene-cyclohex-5-ene-1,2,3,4-tetrol (10).** For the synthesis of the title compound was used the same procedure followed for **7a**, starting from the 1,6-dideoxy-3,4-*O*-isopropylidene-2,5-di-*O*-benzyl-1,6-thio-L-iditol-*S*,*S*-dioxide (**9**). After 1 h, the reaction mixture, extracted with $CH_2Cl_2$, gave a residue which was purified by flash chromatography ($SiO_2$; light-petroleum/$Et_2O$, 3:1) obtaining the title compound (35%) as a yellow oil. $^1$H NMR δ: 7.45–7.20 (m, 10H, 10CHAr), 5.70–5.66 (m, 2H, 2CH=), 4.82 (d, 2H, 2C*H*HPh, *J*=12.0 Hz), 4.66 (d, 2H, 2CH*H*Ph, *J*=12.0 Hz), 4.30–4.18 (m, 2H, 2CHO), 3.68–3.57 (m, 2H, 2CHO), 1.48 (s, 6H, $2CH_3$). $^{13}$C NMR δ: 138.5 (2CAr), 129.2 (4CHAr), 128.5 (4CHAr), 128.0 (2CHAr), 127.8 (2CH=), 111.1 ($C(CH_3)_2$), 80.5 (2CHO), 77.4 (2CHO), 71.9 ($2CH_2Ph$), 27.3 ($2CH_3$). $[\alpha]_D^{25}=6.1$ (*c*=1.46, $CHCl_3$). Anal. Calcd for $C_{23}H_{26}O_4$: C, 75.37; H, 7.16. Found: C, 75.31; H, 7.21. *m*/*z*: 366 (<1), 351 (<1), 308 (<1), 266 (13), 91(100). 65 (6). IR ($CHCl_3$) $\nu_{max}/cm^{-1}$=2987, 1324, 1068.

**1,6-Dideoxy-3,4-*O*-isopropylidene-2,5-di-*O*-tetrahydropiranyl-1,6-thio-D-mannitol (5c).** To 0.30 g (1.38 mmol) of 1,6-dideoxy-3,4-*O*-isopropylidene-1,6-thio-D-mannitol,[12] dissolved in 13 mL of $CH_2Cl_2$, 1.26 mL (13.8 mmol) of dihydropyran were added. To the reaction mixture, cooled at 0°C, 6 mg (0.014 mmol) of *p*-toluensulfonic acid were added. After 10 min at 0°C, the mixture was stirred for 1.5 h at room temperature, then diluted with $H_2O$ and extracted with $CH_2Cl_2$. The organic layers, were washed with brine and dried, then evaporated to give a white crude product which was purified by flash chromatography ($SiO_2$; $CH_2Cl_2$/AcOEt, 10:1) to give 0.49 g (93%) of **5c** as a diastereomeric 4:1 mixture. The major isomer was obtained pure by crystallization from *n*-pentane; mp 101–102°C. The data of the major isomer are reported. $^1$H NMR δ: 4.85–4.76 (m, 2H, 2OCHO), 4.51–4.50 (m, 2H, 2CHO), 4.35–4.25 (m, 2H, 2CHO), 3.93–3.78 (m, 2H, 2C*H*HO), 3.53–3.39 (m, 2H, 2CH*H*O), 2.97 (dd, 2H, 2C*H*HS, *J*=15.7, 5.3 Hz), 2.68 (dd, 2H, 2CH*H*S, *J*=15.6, 6.2 Hz), 1.88–1.40 (m, 12H, $6CH_2$), 1.36 (s, 6H, $2CH_3$). $^{13}$C NMR (in brackets are reported the chemical shifts of the minor isomer) δ: 108.8 [109.0] (C), 100.8 [100.7] (2OCHO), 77.0 [76.6] (2CHO), 72.8 [72.4] (2CHO), 62.6 [60.7] ($2CH_2O$), 38.1 [37.4] ($2CH_2S$), 30.5 [30.3] ($2CH_2$), 27.1 [27.1] ($2CH_3$), 25.4 [25.4] ($2CH_2$), 19.7 [18.4] ($2CH_2$). For the major isomer $[\alpha]_D^{25}=-12.71$ (c=1.40, $CHCl_3$). Anal. Calcd for $C_{19}H_{32}O_6S$: C, 58.73; H, 8.31. Found: C, 58.70; H, 8.28. *m*/*z*: 388 (<1), 245 (<1), 85 (74), 84 (57), 55 (100) 43 (60). IR ($CCl_4$) $\nu_{max}/cm^{-1}$=2960, 1388, 1210, 1130, 990.

**1,6-Dideoxy-3,4-*O*-isopropylidene-2,5-di-*O*-tetrahydropiranyl-1,6-thio-D-mannitol-*S*,*S*-dioxide (6c).** The same methodology described for **2a** was followed using **5c** as diastereoisomeric mixture, obtaining **6c** as a white viscous oil (97%), constituted by a 4:1 mixture of diastereoisomers, which was used as such for the following reaction without further purification. The purification of a sample was performed by flash chromatography ($SiO_2$; $Et_2O$/light-petroleum, 3:1). $^1$H NMR δ: 4.88–4.75 (m, 2H, 2OCHO), 4.63–4.52 (m, 2H, 2CHO), 4.47–4.32 (m, 2H, 2CHO), 4.00–3.80 (m, 2H, 2C*H*HO), 3.59–3.27 (m, 6H, $2CH_2S$ and 2CH*H*O), 1.90–1.40 (m, 12H, $6CH_2$), 1.35 (s, 6H, $2CH_3$). $^{13}$C NMR (in brackets are reported the chemical shifts of the minor isomer) δ: 110.2 [110.0] (C), 101.7 [101.3] (2OCHO), 76.2 [74.5] (2CHO), 69.2 [68.5] (2CHO), 62.9 [62.8] ($2CH_2O$), 58.9 [58.8] ($2CH_2S$), 30.6 [30.1] ($2CH_2$), 27.4 [27.3] ($2CH_3$), 25.8 [25.8] ($2CH_2$), 19.6 [18.6] ($2CH_2$). Anal. Calcd for $C_{19}H_{32}O_8S$: C, 54.26; H, 7.68. Found: C, 54.30; H, 7.62. *m*/*z*: 420 (<1), 126(1), 85 (55), 55 (100), 40 (98). IR (neat) $\nu_{max}/cm^{-1}$=2980, 1320, 1105.

**(1*R*,2*R*,3*R*,4*R*)-1,4-Tetrahydropiranyl-2,3-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol (7c).** The title compound was synthesized using the same procedure described for **3a**, using the diastereoisomeric mixture of **6c**. After 3 h **7c** was obtained (50%) as a diastereoisomeric 4:1 mixture which was used as such for the following reaction. The purification of a sample was performed by

flash chromatography ($SiO_2$; light-petroleum/$Et_2O$, 3:1) obtaining a yellow pale oil. $^1$H NMR $\delta$: 6.01–5.85 (m, 2H, 2CH=), 4.92–4.82 (m, 2H, 2OCHO), 4.62–4.48 (m, 2H, 2CHO), 4.20–3.98 (m, 2H, 2CHO), 3.96–3.82 (m, 2H, 2C*H*HO), 3.60–3.48 (m, 2H, 2CH*H*O), 1.90–1.43 (m, 12H, 6$CH_2$), 1.40 (s, 6H, 2$CH_3$). $^{13}$C NMR (in brackets are reported the chemical shifts of the minor isomer) $\delta$: 129.8 [130.3] (2CH=), 109.9 [109.7] (C), 74.2 [74.0] (2CHO), 69.4 [69.5] (2CHO), 62.8 [62.9] (2$CH_2$O), 30.7 [30.5] (2$CH_2$), 26.8 [26.8] (2$CH_3$), 25.5 [25.6] (2$CH_2$), 19.8 [18.6] (2$CH_2$). Anal. Calcd for $C_{19}H_{30}O_6$: C, 64.37; H, 8.54. Found: C, 64.33; H, 8.60. *m*/*z*: 339 (<1), 171 (2), 85 (84), 84 (65), 55 (100). IR (neat) $\nu_{max}$/cm$^{-1}$=2980, 1320, 1105.

**(−)-Conduritol E (8a).** To 0.10 g of the diastereoisomeric mixture of **7c** 2 mL of $CF_3COOH$ were added. After 10 min at room temperature the mixture was evaporated to give 40 mg (98%) of **8a** whose spectral data and properties are identical to those reported in the literature.[16]

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