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Diastereoselective Addition of 2-Trimethylsilyloxyfuran to (*S*)-(+)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone

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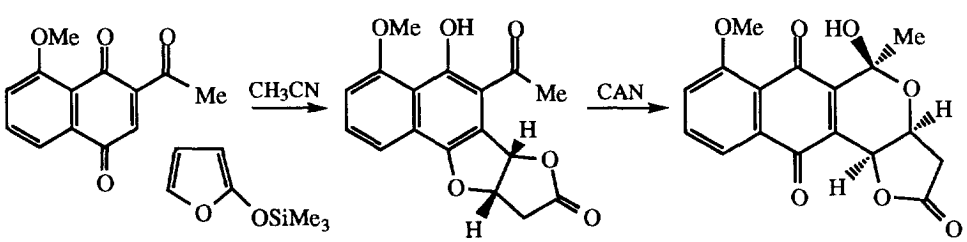
Abstract: The uncatalyzed addition of 2-trimethylsilyloxyfuran to (*S*)-(+)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone **1** afforded a 3.4:1 ratio of the diastereomeric adducts **2**:**3**. Acetonitrile was found to be the optimum solvent whilst the use of Lewis acid catalysts afforded lower overall yields.

The Michael addition of 2-trimethylsilyloxyfuran to 2-acetyl-1,4-naphthoquinones has played a key role in our synthetic effort directed towards the synthesis of members of the pyranonaphthoquinone family of antibiotics. The resulting furonaphthofuran adducts undergo oxidative rearrangement upon treatment with ceric ammonium nitrate to afford the furonaphthopyran skeleton present in these natural products (Scheme 1). Using this methodology syntheses of kalafungin[1], frenolicin[2] and the arizonins[3] have now been achieved. To date the key addition step has been carried out with no control over absolute stereochemistry of the bridgehead protons. The work reported herein is directed towards extension of the addition of 2-trimethylsilyloxyfuran to a quinone bearing a chiral auxiliary at C-2 in an attempt to develop this key reaction in an asymmetric sense.



Scheme 1

The conjugate addition of nucleophiles to electron deficient quinones has been well demonstrated in that dicarbonyl compounds,[4] furans,[4] silyl enol ethers,[5] allylsilanes,[6] allylstannanes,[6,7] electron rich dienes[8], pyridinium ylides[9], amino acid esters[10] and enamines[11] all add effectively to quinones. Given the variety of nucleophilic species that have been added to quinones and the fact that Michael addition to conjugated systems bearing a chiral auxiliary is well established[12], it is somewhat surprising that conjugate additions to quinones bearing a chiral auxiliary have not been reported.

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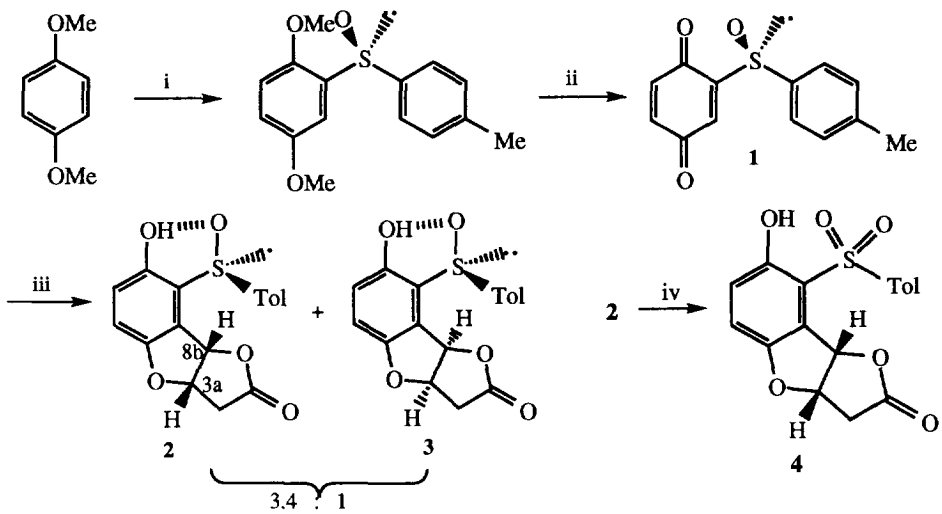
Based on strong precedent for the use of a chiral sulfoxide group as a chiral auxiliary in diastereoselective Michael reactions[13] we decided to investigate the addition of 2-trimethylsilyloxyfuran to 1,4-benzoquinone **1**. Quinone-sulfoxide **1** has previously been reported to undergo highly diastereoselective Diels-Alder reactions,[14] however, its potential use as a diastereoselective Michael acceptor had not been investigated. We were, however, encouraged by reports of diastereoselective addition of organometallic nucleophiles to related chiral 3-(*p*-tolylsulfinyl)-4-chromones[15] and chiral 3-(*p*-tolylsulfinyl)-2(5*H*)-furanones.[16]

Benzoquinone-sulfoxide **1** was prepared in 70% yield *via* lithiation of 1,4-dimethoxybenzene and subsequent reaction with (-)-menthyl (*S*)-*p*-tolylsulfinate by using the procedure reported by Carreno *et al.*[17] followed by subsequent oxidation with freshly prepared silver(II) oxide (Scheme 2). 2-Trimethylsilyloxyfuran (2 mol equiv.) was then added to a solution of quinone **1** in acetonitrile at 0°C. Careful column chromatography afforded two diastereomeric furonaphthofuran adducts. The more polar isomer **2** was isolated as a colourless crystalline solid whilst the minor adduct **3** was isolated as an oil. A major contaminant which had the same R_f as the minor adduct **3** in several different solvent mixtures was the butenolide by-product formed *via* hydrolysis of any unreacted 2-trimethylsilyloxyfuran present. Thus, in an attempt to minimize butenolide formation and optimise the overall yield only one equivalent of 2-trimethylsilyloxyfuran was used. Under these conditions adducts **2** and **3** were isolated in a 3.4:1 ratio and in 86% overall yield.



Reagents and Conditions: (i) ^{n}BuLi, room temp., THF, then (-)-menthyl p-tolylsulfinate , 70% ; (ii) AgO (8 equiv.), HNO_3 (6 molL^{-1}), dioxane, room temp., 81%; (iii) 2-trimethylsiloxyfuran (1 equiv.), CH_3CN, 0°C, 2h., 86%; (iv) m-CPBA, NaOAc, CH_2Cl_2, 86%.

Scheme 2

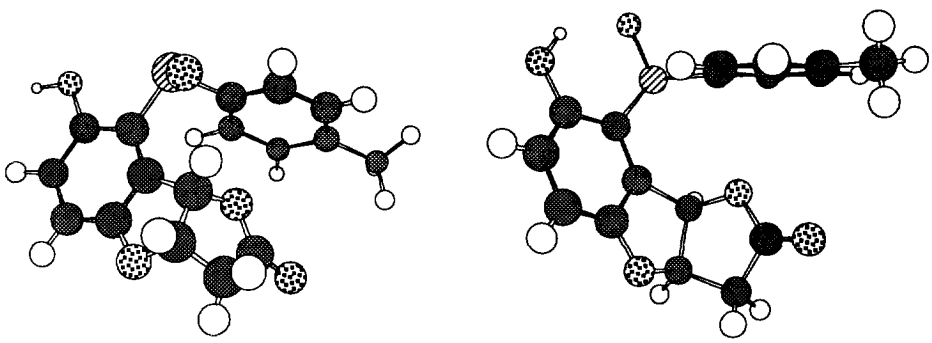
Formation of the diastereomeric adducts was confirmed upon spectroscopic analysis. Elemental analysis and high resolution mass spectroscopy established the molecular formula $C_{17}H_{14}O_5S$. The peak at *m/z* 314 in the mass spectrum corresponding to loss of oxygen is a characteristic fragmentation for a sulfoxide group and the stretch at 1789 cm^{-1} in the IR spectrum also supported the presence of the γ-lactone

functionality. The ^{1}H NMR spectrum of the major adduct **2** exhibited a characteristic double double doublet at δ5.26 and a doublet at δ5.76 assigned to the bridgehead protons H-3a and H-8b, respectively, of the furobenzofuran ring system. Similarly, the minor adduct **3** also displayed a double double doublet at δ5.43 and a doublet at δ6.17 with both resonances observed further downfield than the corresponding resonances in the major adduct. The coupling constants $J_{3a,8b}$ 6.3 and 6.1 Hz for the major and minor adducts respectively were indicative of *cis* fusion of the two five membered rings.

Having separated the diastereomeric adducts the task remained to assign the absolute stereochemistry at the bridgehead positions. Hydrogen bonding between the phenolic proton and the sulfinyl oxygen, conformationally locks the S-O bond into the same plane as the main aromatic ring. Thus, assuming this conformation for the two adducts **2** and **3**, in adduct **2** the bridgehead protons occupy the same face as the tolyl ring of the auxiliary and are shielded by the aromatic ring appearing further upfield in the ^{1}H NMR spectrum relative to the equivalent protons in the other diastereomer.

The diastereomeric sulfoxides **2** and **3** exhibited different optical rotations. Thus, the major sulfoxide **2** recorded $[\alpha]_D^{20}$ -240 (c, 0.34, CH_2Cl_2) and the minor sulfoxide **3** $[\alpha]_D^{20}$ +4.2 (c, 0.24, CH_2Cl_2). Oxidation of the major sulfoxide **2** to a sulfone **4** with *m*-CPBA in dichloromethane at room temperature removed the chirality associated with the sulfur atom. Sulfone **4** was also optically active with $[\alpha]_D^{20}$ -134 (c, 0.32, $CHCl_3$) thus establishing the chirality at the bridgehead protons. The enantiomeric excess of sulfone **4** was determined by using ^{1}H NMR spectroscopy with the chiral solvent (*R*)-(-)-2,2,2-trifluoro-1-(9-anthryl)ethanol. Upon mixing sulfone with three equivalents of the chiral solvent no shifts due to differing enantiomers were observed, thereby indicating an enantiomeric excess of >95%. Use of racemic sulfone **4** which was prepared from racemic quinone-sulfoxide, however, resulted in separation of the resonances assigned to the bridgehead protons for the individual enantiomers.

Molecular modelling of the two diastereomeric adducts **2, 3** was carried out by using MacroModel 4.5 (Figure). The conditions used for both searches were MM2*, GB/SA chloroform, 500 steps MCMM with usage-directed searching. For each diastereomer there were eight conformers within 3 kcal/mol of the global minimum. At 300K the Boltzmann average energies are very close: 48.16 kJ/mol for adduct **2** and 48.40 KJ/mol for adduct **3** corresponding to 52:48%.

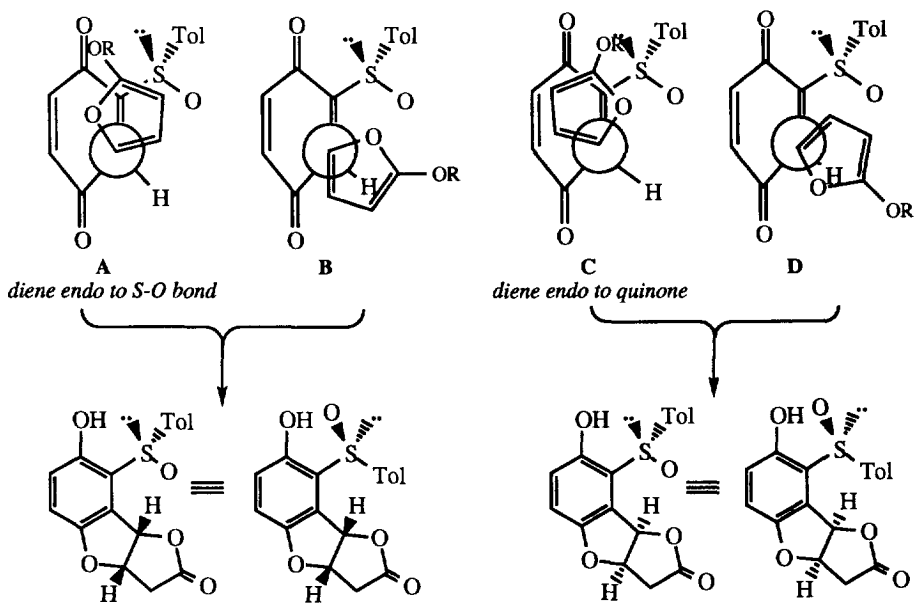


major adduct **2** 48.16 kJ/mol (300K) ***minor adduct*** **3** 48.40 kJ/mol (300K)

Figure

The closeness in energy observed for these two isomers suggests that the diastereoselectivity in this furofuran annulation reaction is attributable to differences in transition state energies leading to the products rather than the formation of a more stable adduct. The explanation for predominant formation of the major adduct **2** is complicated by the fact that the precise mechanism for formation of these adducts is unclear with either a Diels-Alder[18] or a Michael addition pathway[1] being available.

Given that quinone-sulfoxide **1** prefers to adopt a conformation in which the S-O bond is *anti* to the quinone carbonyl group analogous to that postulated for α-sulfinyl-α,β-unsaturated ketones[13] and lactones,[16] formation of the major adduct **2** can arise from either transition state A (Diels-Alder) or B (Michael addition) (Scheme 3). The minor adduct **3** on the other hand would be produced *via* transition states C (Diels-Alder) or D (Michael addition). "Diels-Alder like" transition state A in which the diene is endo to the sulfoxide group allows favourable frontier orbital overlap of the HOMO of the diene with the LUMO of the α,β-unsaturated sulfoxide. Such interactions have already been shown to be important in determining the stereochemical outcome of Diels-Alder reactions of dienes with vinyl sulfoxide esters.[19] Considering the reaction as a Michael addition process, the antiperiplanar transition state B is also considered favourably in that a similar rationale has been proposed in Lewis acid catalyzed additions to aldehydes and imines.[20] The exact nature of the origin of the stereoselectivity observed in the present work, however awaits clarification of the exact mechanism by which this annulation proceeds.



Scheme 3

In an attempt to improve or invert the observed diastereoselectivity several different solvents and Lewis acid catalysts were investigated. Use of dichloromethane, tetrahydrofuran and methanol at both 0°C and -78°C in the uncatalyzed reaction led to similar levels of diastereoselectivity in favour of adduct **2**. However, only inferior yields of the order of 40% were obtained. Use of zinc bromide in dichloromethane, methanol,

and tetrahydrofuran at 0°C and-78°C also afforded little change in the ratio of **2**:**3**. However, once again lower yields were obtained. Other Lewis acids, namely, titanium tetrachloride, boron trifluoride and tin tetrachloride afforded only small quantities of the desired adducts **2** and **3**. Decomposition of the 2-trimethylsilyloxyfuran may well be a complication in this case. Thus, it appears that the optimum conditions for this furofuran annulation reaction require use of acetonitrile as solvent and the absence of any Lewis acid catalyst. These latter observations may well favour a conjugate addition mechanism in that acetonitrile is known to be an excellent solvent for the addition of silyl enol ethers to Michael acceptors.

Given the level of diastereoselectivity observed in the uncatalyzed addition of 2-trimethylsilyloxyfuran to quinone-sulfoxide **1** we then proceeded to remove the sulfoxide auxiliary. Unfortunately, treatment of the major adduct **2** with Raney nickel, Al/Hg amalgam, magnesium/methanol led to fragmentation of the furofuran ring system whilst Bu_3SnH/AIBN and samarium iodide were also unsuccessful. Removal of the sulfoxide is complicated in this case by the presence of a benzylic C-O bond and the steric hindrance associated with removal of a diaryl sulfoxide.

In summary, the uncatalyzed addition of 2-trimethylsilyloxyfuran to quinone-sulfoxide **1** affords a 3.4:1 ratio of the adducts **2**:**3**. This represents the first example of a diastereoselective Michael addition to a quinone system bearing a chiral auxiliary. Rationalisation of this inherent diastereoselectivity awaits a detailed understanding of the precise mechanism by which the addition occurs which is finely balanced between a Diels-Alder like addition and a Michael addition process.

EXPERIMENTAL

General Details

Melting points were determined using a Reichert Kofler block and are uncorrected. Optical rotations were measured using a Perkin Elmer 241 polarimeter in either CH_2Cl_2 or $CHCl_3$ at the indicated concentrations. Infrared Absorption Spectra were recorded using Perkin Elmer 1600 Series FTIR spectrometer as Nujol Mulls or thin films between sodium chloride plates. ^1H NMR spectra were obtained using either a Bruker AM 400 or Bruker AC 200 Spectrometer. ^{13}C NMR data were recorded using a Bruker AM 400 or Bruker AC 200 Spectrometer. ^{13}C spectra were interpreted with the aid of DEPT 135 and DEPT 90 experiments. Low resolution mass spectra were recorded using a VG 70-SE Spectrometer operating at a normal accelerating voltage of 70 eV. High resolution mass spectra were recorded at a nominal resolution of 5000 or 10000 as appropriate. Elemental analyses were performed at the Microanalytical Laboratory, University of Otago, Dunedin, New Zealand. Flash chromatography was performed using Merck Kieselgel 60 (230-400 Mesh) with the indicated solvents.

(S)-(-)-1,4-Dimethoxy-2-(p-tolylsulfinyl)benzene

(*S*)-(-)-1,4-Dimethoxy-2-(*p*-tolylsulfinyl)benzene was prepared according to the method of Carreno *et al*.[17] as pale yellow crystals, m.p. 85-86°C (lit.,[17] m.p. 83-85°C); $[\alpha]_D^{20}$ -23 (c, 1.15, $CHCl_3$) (lit.,[17] $[\alpha]_D^{20}$ -20 (c, 1.00, $CHCl_3$) .

(S)-(+)-2-(p-tolylsulfinyl)-1,4-benzoquinone ***1***

(*S*)-(+)-1,4-Dimethoxy-2-(*p*-tolylsulfinyl)benzene (111 mg, 0.4 mmol) and freshly prepared AgO (200 mg, 1.6 mmol) were mixed in dioxane (4 cm^3). To this was added HNO_3 (6 mol dm^{-3}, 0.4 cm^3) and the mixture stirred for 5 min in air, after which time further AgO (200 mg, 1.6 mmol) and HNO_3 (6 mol dm^3) were added. After stirring an additional 5 min. the reaction mixture was quenched with water (6 cm^3) and chloroform (20 cm^3) was added. The organic layer was washed with water (2 x 7 cm^3), dried ($MgSO_4$) and the solvent removed under reduced pressure to give the title compound **1** (80 mg, 81%) as red crystals, m.p. 125-126°C (lit.,[17] m.p. 129°C); $[\alpha]_D^{20}$ +1083 (c, 1.21, $CHCl_3$) (lit.,[17] $[\alpha]_D^{20}$ +1099 (c, 1.00. $CHCl_3$).

*(S_S, 3aS, 8bS)-(-)-3a,8b-Dihydro-7-hydroxy-8-(p-*tolyl*sulfinyl)furo[3,2-b]benzofuran-2(3H)-one* ***2*** *and (S_S, 3aR, 8bR)-(+)-3a,8b-Dihydro-7-hydroxy-8-(p-*tolyl*sulfinyl)furo[3,2-b]benzofuran-2(3H)-one* ***3***.

To a solution of the quinone **1** (60 mg, 0.24 mmol) in acetonitrile (5 cm^3) was added 2-trimethylsilyloxyfuran (38 mg, 0.24 mmol) under nitrogen at 0°C. The mixture was left stirring for 2 h. before removing the solvent under reduced pressure to give a yellow oil. Flash chromatography of this oil using hexane-ethyl acetate (1:1) as eluent gave the *major adduct* **2** (52 mg, 66%) as a white solid, m.p. 143-144°C; R_f=0.17 (1:1 hexane-ethyl acetate); $[\alpha]_D^{20}$ -240 (c, 0.34, CH_2Cl_2); (Found : C, 61.2; H, 4.5. $C_{17}H_{14}O_5S$ requires C, 61.8; H, 4.3%); ν_{max} (nujol)/cm^{-1} 1789m (C=O); δ_H (200 MHz; $CDCl_3$) 2.38 (3H, s, ArMe), 2.95-2.98 (2H, m, 3-H_a and 3-H_b), 5.26 (1H, ddd, $J_{3a,8b}$ 6.3, $J_{3a,3\text{-}Hb}$ 6.3 and $J_{3a,3\text{-}Ha}$ 3.3, 3a-H), 5.76 (1H, d, $J_{8b,3a}$ 6.3, 8b-H), 6.85 (1H, d, $J_{5,6}$ 8.9, 5-H or 6-H), 6.92 (1H, d, $J_{6,5}$ 8.9, 6-H or 5-H), 7.34 (2H, d, $J_{3',2'}$ 8.0, 3'-H), 7.73 (2H, d, $J_{2',3'}$ 8.0, 2'-H), and 10.32 (1H, br.s, OH); δ_C (100 MHz; d_6-acetone) 21.3 (ArMe), 35.6 (CH_2, C-3), 81.7 (CH, C-3a), 83.3 (CH, C-8a), 114.6 (CH, C-5), 121.3 (CH, C-6), 122.2 (quat, C-8a), 126.6 (CH, C-3'), 127.1 (quat, C-4'), 130.6 (CH, C-2'), 142.6 (quat, C-1'), 142.8 (quat, C-8), 151.0 (quat, C-4a), 156.4 (quat, C-7) and 175.1 (quat, C-2); *m/z* 330 (M^+, 100%), 314 (*M*-O, 28), 267 (38) and 139 (*M*-$SOC_6H_4CH_3$, 25) and the *minor adduct* **3** (16 mg, 20%) as a pale yellow oil that darkens on standing; R_f = 0.36 (1:1 hexane - ethyl acetate); $[\alpha]_D^{20}$ +4.2 (c, 0.24, CH_2Cl_2); (Found: M^+ 330.05622. $C_{17}H_{14}O_5S$ requires 330.05620); ν_{max} (nujol)/cm^{-1} 1789m (C=O); δH (200 MHz; $CDCl_3$) 2.37 (3H, s, ArMe), 2.99-3.04 (2H, m, 3-Ha and 3-Hb), 5.43 (1H, ddd, $J_{3a,8b}$ 6.1, $J_{3a,3\text{-}Hb}$ 6.1 and $J_{3a,3\text{-}Ha}$ 2.4, 3a-H), 6.17 (1H, d, $J_{8b,3a}$ 6.1, 8b-H), 6.88 (2H, s, 5-H and 6-H), 7.32 (2H, d, $J_{3',2'}$ 8.1, 3'-H), 7.72 (2H, d, $J_{2',3'}$ 8.1, 2'-H) and 9.77 (1H, br.s, OH); δ_C (50 MHz; $CDCl_3$) 21.4 (ArMe), 35.1 (CH_2, C-3), 81.7 (CH, C-3a and C-8b), 115.3 (CH, C-5), 120.0 (quat, C-4'), 123.4 (CH, C-6), 125.0 (quat, C-8a), 125.4 (CH, C-3'), 130.2 (CH, C-2'), 138.3 (quat, C-8)), 142.5 (quat, C-1'), 154.1 (quat, C-4a and C-7) and 173.7 (quat, C-2); *m/z* 330 (M^+, 100%), 314 (*M*-O, 14), 267 (33) and 139 (*M*-$SOC_6H_4CH_3$, 10).

*(3aS,8bS)-(-)-3a,8b-Dihydro-7-hydroxy-8-(p-*tolyl*sulfonyl)furo[3,2-b]benzofuran-2(3H)-one* ***4***

To a solution of the sulfoxide adduct **2** (30 mg, 0.10 mmol) in dichloromethane (30 cm^3) was added anhydrous sodium acetate (60 mg, 0.73 mmol) and *m*-CPBA (45 mg, 0.18 mmol). After stirring for 20 h. the reaction mixture was filtered and the filtrate extracted with dichloromethane (20 cm^3). The extract was washed with saturated sodium bicarbonate (10 cm^3) and water (2 x 10 cm^3) before drying ($MgSO_4$) and concentration under reduced pressure to give a yellow oil. Flash chromatography using hexane-ethyl acetate (1:2) gave the *title compound* **4** (27 mg, 86%) as a pale yellow solid, m.p. 78-79°C; $[\alpha]_D^{20}$ -134 (c, 0.320, $CHCl_3$); (Found: M^+, 346.0520. $C_{17}H_{14}O_6S$ requires 346.0511); ν_{max} (nujol)/cm^{-1} 3338br (OH), 1320m (SO_2) and 1126 (SO_2); δ_H (200MHz; $CDCl_3$) 2.94 (1H, dd, J_{gem} 17.7 and $J_{3\text{-}Ha,3a}$ 1.8, 3-H_a), 3.04 (1H, dd,

J_{gem} 17.7 and $J_{3\text{-}Hb,3a}$ 5.9, 3-H_b), 5.36 (1H, ddd, $J_{3a,8b}$ 5.9, $J_{3a,3\text{-}Hb}$ 5.9 and $J_{3a,3\text{-}Ha}$ 1.8, 3a-H), 7.01, 7.02 (1H, s, 5-H and 6-H), 7.36 (2H, d, $J_{3',2'}$ 8.2, 3'-H), 7.97 (2H, d, $J_{2',3'}$ 8.2, 2'-H) and 8.93 (1H, s, OH); δ_C (100 MHz; $CDCl_3$) 21.6 (ArMe), 35.0 (CH_2, C-3), 82.1, 82.4 (CH, C-3a, C-8b), 118.5, 123.5 (CH, C-5, C-6), 120.4, 121.1 (quat, C-8, C-8a), 127.5 (CH, C-3'), 129.9 (CH, C-2'), 137.6 (quat, C-4'), 145.6 (CH, C-1'), 150.6 (quat, C-4a), 155.2 (quat, C-7) and 173.8 (quat, C-2); *m/z* 346 (M^+, 100%), 301 (M -CO_2H, 31), 237 (M -CO_2H-SO_2, 8) and 223 (M -CH_2CO_2H-SO_2, 28).

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