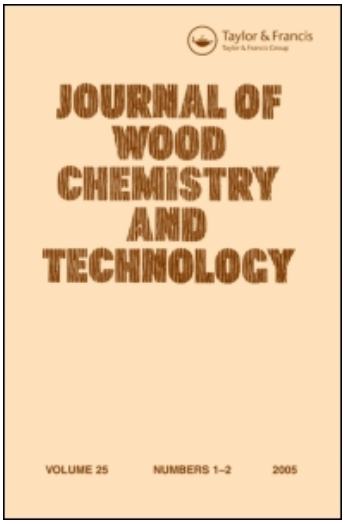

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REACTIONS OF PINOSYLVIN AND PINOSYLVIN DIMETHYL ETHER WITH CHLORINE DIOXIDE

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ABSTRACT

Products from the reaction of pinosylvin **1a** and pinosylvin dimethyl ether **1b** with chlorine dioxide were characterized. Pinosylvin was more extensively degraded and gave benzoic acid, traces of other monomeric carboxylic acids, 2,6-dichloro- and 2,4,6-trichloropinosylvin **2**, (n = 2 and 3), the benzilic acid rearrangement product **3** and the maleic acids **4a** and **4b**. Pinosylvin dimethyl ether gave similar monomeric products, the dichloroderivative **5**, the dichloroepoxide **6** and a small amount of the dichlorohydroxyketone **7**.

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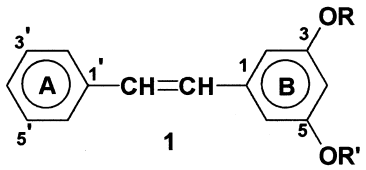
INTRODUCTION

Pinosylvins **1** are wood extractives that occur in the heartwood of pine and other woody plants.[1,2] They are present in tall oil recovered from the kraft pulping of pine,[3,4] and pinosylvin dimethyl ether **1b** is also present in distilled tall oil.[3] Pinosylvins have a range of physiological activities, including fungicidal, feeding deterrent and nematocidal properties.[1,5,6]



1

1a R, R' = H

1b R, R' = CH_3

Since small amounts of wood extractives, such as resin acids and sterols, remain in pulp entering the bleach plant, detectable amounts of these compounds or products resulting from their reaction with bleaching agents are often found in bleaching liquors. However, no reports on the occurrence of pinosylvins or their reaction products in bleaching liquors have appeared in the literature, nor has the nature of the reactions between pinosylvins and chlorine dioxide been reported. The present work describes the reactions of pinosylvin **1a** and pinosylvin dimethyl ether **1b** with chlorine dioxide.

RESULTS AND DISCUSSION

Since the compounds studied contained both free and etherified phenolic, and olefinic functional groups, reactions characteristic of all three groups were anticipated. The types of reactions displayed by these groups have been reported in several publications and have been reviewed both for individual compounds,[7] and in relation to pulp bleaching.[8] Phenolic compounds are oxidized to a variety of products, including quinones and unsaturated carboxylic acids, whereas phenolic ethers are less reactive. Olefinic compounds are oxidized to mixtures of unsaturated ketones and other products. It was more difficult to predict how compounds

such as the pinosylvins, which contain these functional groups together in the same molecule, would react.

Reactions of Pinosylvin 1a and Pinosylvin Dimethyl Ether 1b with Chlorine Dioxide

Both pinosylvin and pinosylvin dimethyl ether reacted with a 3-mole ratio of chlorine dioxide to produce mixtures of monomeric and dimeric products. Since ring B (see **1)** of pinosylvin contains free phenolic groups which are more reactive in free radical and electrophilic reactions, extensive oxidative degradation of this ring occurred, whereas the major products from pinosylvin dimethyl ether were derived from the intact dimer. In both cases, the reaction products were complicated mixtures and it was only possible to characterize the major products. Yields of monomeric reaction products were obtained by gas chromatography (GC) of aliquots of the reaction products, whereas both GC and isolation were used to determine yields of dimeric products. GC analyses indicated all of the reaction products reported were present in the crude reaction mixtures.

Reactions of Pinosylvin 1a

The monomeric products identified from the reaction of pinosylvin with chlorine dioxide all originated from ring A and the two carbon atoms between the rings. The products are shown on the left side of Figure 1 with the yields of each product in brackets. Benzoic acid was the major monomeric product, formed in 8% yield, the combined yield of monomeric products amounting to approximately 15%.

Dimeric products identified from the reaction of pinosylvin are shown in the center of Figure 1 with the yield ranges in brackets. Yields were difficult to estimate accurately because of the complexity of the reaction mixture and variations which occurred in the amounts of the products upon repetition of the reaction. Chlorination of pinosylvin with hypochlorous acid resulting from the reduction of chlorine dioxide, and further reactions of the chlorinated products accounted for most of the dimeric compounds identified. 2,6-Dichloro- and 2,4,6-trichloropinosylvin (**2**, $n = 2$ and 3) were identified by comparison with standards prepared by the chlorination of pinosylvin. The trichlorocyclopentene-1,3-dione **3**, a yellow crystalline compound, was identified by X-ray crystallography. The dione probably forms via a benzilic acid rearrangement and decarboxylation as shown in Figure 2, analogous to mechanisms reported for the formation

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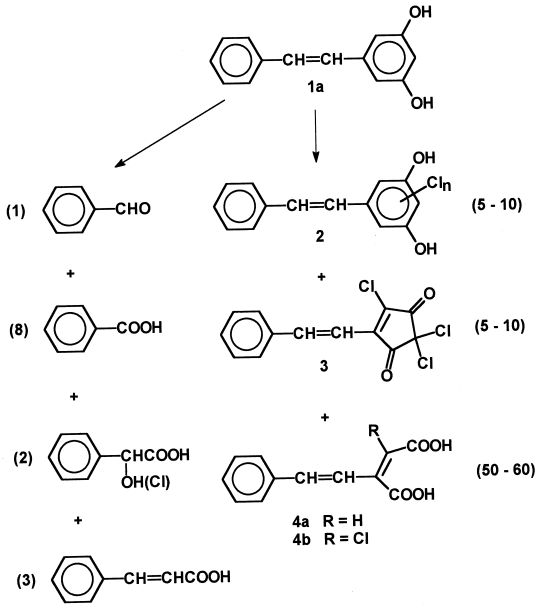

Figure 1. Reaction of pinosylvin with chlorine dioxide.

of simpler chlorocyclopentenediones from resorcinol and other compounds.[9–11] The facile rearrangement of chlorinated 1,2-diketones probably occurs in acid solution because the carbonyl group adjacent the carbon atom bearing the chlorine substitutents is hydrated.[12]

The major products were the maleic acids **4a** and **4b**. Although these compounds could not be purified satisfactorily, mass spectrometric and other evidence from the literature strongly supported their assigned chemical structures. When the underivatized reaction product was analysed by gas chromatography/mass spectrometry (GCMS), the molecular ions of these compounds appeared as m/z 200 and 234 respectively, corresponding to the anhydrides of the acids. Fragmentation in each case resulted from a loss of 44 followed by 28 amu, a pattern characteristic of cyclic anhydrides of dicarboxylic acids[13] and shown by chloro-[14] and dichloromaleic[15] anhydride. In the case of the chloroproduct **4b**, a further loss of 35 amu occurred as is the case with dichloromaleic anhydride.[15] After methylation, the molecular ions appeared 28 amu higher than those of the corresponding acids, and high resolution mass spectrometry of the chlorodimethyl ester product indicated the correct molecular formula, $C_{14}H_{13}ClO_4$. This infor-

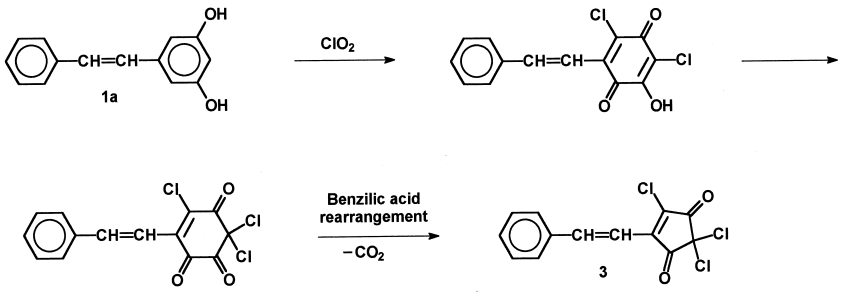

Figure 2. Suggested mechanism for formation of the trichlorocyclopentenedione **3**.

mation, combined with the fact that maleic acids are formed by the reaction of a variety of polyphenolic compounds with chlorine dioxide[7,16,17] strongly supports the structures proposed for the maleic acids **4a** and **4b**.

Reactions of Pinosylvin Dimethyl Ether 1b with Chlorine Dioxide

Pinosylvin dimethyl ether also reacted with a three mole ratio of chlorine dioxide to yield monomeric and dimeric products. Again, the major monomeric products identified were derived from ring A (see left side of Figure 3, yields in brackets), benzoic acid being the main product. Although ring B is less susceptible to degradation in the case of the dimethyl ether, traces of 2-chloro- and 2,6-dichloro-3,5-dimethoxybenzoic acid, shown on the right side of Figure 3, were the only detectable monomeric products found which were derived from this ring.

The major products of the reaction were the dimeric dichloroderivative **5** and the dichloroepoxide **6**. The positions of the chlorine atoms in **5** were clearly evident from the NMR and mass spectral data of the same compound prepared by the chlorination of pinosylvin dimethyl ether with chlorine in acetic acid/chloroform. Signals for the two olefinic protons of **5** were present at 7.09 ppm in the ^{1}H NMR, whereas those for the two aromatic protons at the 2- and 6-positions of the starting compound were absent. The molecular weight from mass spectrometry was 308 which corresponds to the substitution of two chlorine atoms for hydrogen atoms rather than the addition of two chlorine atoms which would be the case if addition to the double bond occurred. Previous work has shown pinosylvin dimethyl ether also brominates in the 2- and 6-positions on the aromatic ring.[18] The structure of the epoxide **6** was determined by X-ray crystallo-

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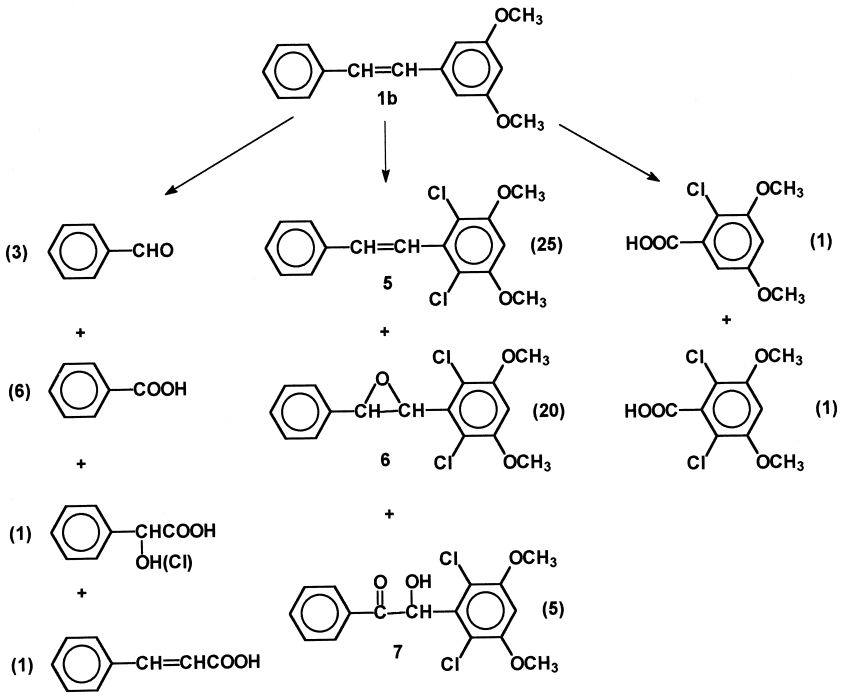

Figure 3. Reaction of pinosylvin dimethyl ether with chlorine dioxide.

graphy. A minor product of the reaction was tentatively identified as the dichlorohydroxyketone **7** on the basis of NMR and mass spectrometry, and the fact it could be reduced with sodium borohydride. The ^{1}H NMR of **7** had two doublets at 4.78 and 6.44 ppm corresponding to the hydroxyl proton and the proton on the adjacent benzylic carbon atom respectively. Upon addition of D_2O, the doublet at 6.44 ppm collapsed to a singlet. A weak molecular ion appeared at m/z 340, corresponding to the molecular weight of 7 and the base peak was m/z 105, arising from the benzyloxy fragment. A number of minor products were not identified, however as several peaks in the gas chromatogram of the reaction product disappeared on treatment with sodium borohydride, evidently ketones or possibly quinones, resulting from demethylation of ether groups in the starting material, were present.

The results obtained in this work clearly show that pinosylvin is much more reactive than the dimethyl ether with chlorine dioxide. This was expected as there are numerous reports in the literature which show

that phenolic compounds are much more reactive than phenyl ethers with chlorine dioxide, and in the case of pulp bleaching, chlorine dioxide has, at best, a limited capability of generating new phenolic hydroxyl groups.[8] In the case of the present work with pinosylvin dimethyl ether, some unidentified minor products may have resulted from demethylation, but the main site of oxidative reactions was the double bond. Chlorination, however, occurred only on the methoxy-substituted aromatic ring, as is the case with bromination[18] as mentioned earlier. If the ring-activating effects of the electron-donating hydroxyl and methoxyl groups are removed, for instance by conversion of pinosylvin to the diacetate, chlorine addition to the double bond then occurs,[19] as is the case with stilbene itself.

EXPERIMENTAL

General

Melting points were determined on a Fisher Johns apparatus and are uncorrected. Column chromatography was performed on silica gel, 80–200 mesh. Gas chromatography (GC) was done on a HP 5890 Gas Chromatograph equipped with a 25 m HP-1 capillary column, and gas chromatography/mass spectrometry (GCMS) on a HP 5890II Gas Chromatograph equipped with a 30 m DB-1 capillary column coupled to a VG Trio 1000 quadrupole mass spectrometer. The temperature was programmed from 50 to 300° C at 10°/min for GC and GCMS. High resolution mass spectrometry (HRMS) was done using a Micromass 70–250S mass spectrometer. ^{1}H NMR spectra were recorded on a Varian UNITY plus 500 MHz NMR spectrometer in $CDCl_3$ unless otherwise indicated. Chemical shifts are given in ppm (δ) relative to Me_4Si. X-ray crystallography was done on a Nonius Kappa-CCD Diffractometer at 200°K. Pinosylvin dimethyl ether was prepared as reported in the literature[20] and demethylated to pinosylvin in one step by adding a 20% excess of 1 M boron tribromide in dichloromethane to a solution of the ether in 1,2-dichloroethane and refluxing the mixture for 30 min. 3,5-Dimethoxybenzoic acid was purchased from a chemical supplier.

Preparation of 2,6-Dichloro- and 2,4,6-Trichloropinosylvin 2, n = 2 and 3

Chlorine (215 mg, 3 mmoles) in acetic acid (2 mL) was added to a stirred solution of pinosylvin **1a** (424 mg, 2 mmoles) in acetic acid (5 mL)

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at room temperature. The solution was stirred for 1 h, poured into water and extracted with ether. The extracts were washed with water, dried and evaporated to give a yellow product (600 mg). Fractionation on silica gel and elution with hexane : ethyl acetate : acetic acid, 9 : 1 : 0.5, gave fractions containing 2,4,6-trichloropinosylvin **2**, (n = 3), (200 mg). Crystallization from toluene gave colorless needles, m.p. 134–135°C. ^{1}H NMR: 7.01 (d, J = 17 Hz, 1H, olefinic), 7.10 (d, J = 17 Hz, 1H, olefinic), 7.32 (tt, J = 7, 2 Hz, 1H, H4′), 7.38 (t, J = 7 Hz, 2H, H3′,5′), 7.53 (m, 2H, H2′6′). MS (%): 318 ($M^+ + 4$, 5), 316 ($M^+ + 2$, 12), 314 (M^+, 12), 281 (10), 279 (15), 246 (30), 244 (100), 215 (15), 152 (20), 151 (20).

Elution with hexane : ethyl acetate : acetic acid, 4 : 1 : 0.25, gave fractions containing 2,6-dichloropinosylvin **2**, (n = 2), (120 mg). Refractionation and crystallization from toluene gave colorless crystals, m.p. 98–100°C. ^{1}H NMR: 6.69 (s, 1H, H4), 7.02 (d, J = 17 Hz, 1H, olefinic), 7.09 (d, J = 17 Hz, 1H, olefinic), 7.31 (tt, J = 7,1 Hz, 1H, H4′), 7.38 (t, J = 7 Hz, 2H, H3′5′). 7.53 (m, 2H, H2′6′). MS (%): 282 ($M^+ + 2$, 20), 280 (M^+, 28), 245 (36), 210 (100), 181 (50), 152 (25).

Preparation of 2-Chloro- and 2,6-Dichloropinosylvin Dimethyl Ether

Chlorine (250 mg, 3.5 mmoles) in acetic acid (4 mL) was added to a stirred solution of pinosylvin dimethyl ether **1b** (480 mg, 2 mmoles) in chloroform (5 mL) at 0°C. The solution was stirred at room temperature for 1 h then poured into water and extracted with chloroform. The extracts were washed with water, dried and evaporated to give a yellow solid (600 mg). Crystallization from methanol gave pink needles of 2,6-dichloropinosylvin dimethyl ether **5** (165 mg), m.p. 142–143°C. ^{1}H NMR: 3.93 (s, 6H, 2 × OCH_3), 6.52 (s, 1H, H4), 7.09 (2s, 2H, olefinic), 7.30 (tt, J = 7,1 Hz, 1H, H4′), 7.38 (t, J = 7 Hz, 2H, H3′,5′), 7.55 (m, 2H, H2′, 6′). MS (%): 310 ($M^+ + 2$, 37), 308 (M^+, 51), 275 (25), 273 (59), 238 (100), 223 (24), 152 (28).

Fractionation of the mother liquor on silica gel and elution with hexane : ether, 9 : 1, gave fractions containing a mixture of pinosylvin dimethyl ether and 2-chloropinosylvin dimethyl ether. Trituration with cold methanol followed by crystallization from methanol gave colorless prisms of 2-chloropinosylvin dimethyl ether, m.p. 112–114°C. ^{1}H NMR: 3.86, 3.89 (2s, 6H, 2 × OCH_3), 6.46 (d, J = 3 Hz, 1H, H4), 6.81 (d, J = 3 Hz, 1H, H2), 7.06, (d. J = 16 Hz, 1H, olefinic), 7.29 (t, J = 7 Hz, 1H, H4′), 7.37, (t, J = 7 Hz, 2H, H3′,5′), 7.55 (d, J = 16 Hz, 1H, olefinic), 7.56 (d, J = 7 Hz, 2H, H2′,6′). MS (%): 276 ($M^+ + 2$, 15), 274 (M^+, 42), 239 (100), 224 (47), 208 (38), 165 (25), 152 (35).

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Preparation of 2-Chloro- and 2,6-Dichloro-3,5-dimethoxybenzoic Acid

Sulfuryl chloride (1.35 g, 0.80 mL, 0.01 mole) was added to a stirred solution of 3,5-dimethoxybenzoic acid (1.82 g, 0.01 mole) in acetic acid (15 mL) at 35°C. The mixture was stirred 2 h then cooled to room temperature and filtered to give 2-chloro-3,5-dimethoxybenzoic acid (0.7 g), m.p. 187–188°C (Lit.[21] 184–185°C), after crystallization from acetone/hexane. ^{1}H NMR: (CD_3COCD_3): 3.87 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 6.82 (d, J = 3 Hz, 1H, aromatic), 6.90 (d, J = 3 Hz, 1H, aromatic). MS (%): 218 ($M^+ + 2$, 34), 216 (M^+, 100), 199 (6), 173 (20), 145 (11).

The same reaction using a two mole ratio of sulfuryl chloride to 3,5-dimethoxybenzoic acid at 50°C gave 2,6-dichloro-3,5-dimethoxybenzoic acid (1.7 g), m.p. 216–217°C (Lit.[22] 209°C) directly by filtration of the reaction product. MS (%): 254 ($M^+ + 4$, 11), 252 ($M^+ + 2$, 66), 250 (M^+, 100), 209 (24), 207 (37), 171 (9).

Reaction of Pinosylvin 1a with Chlorine Dioxide

Pinosylvin (636 mg, 3 mmoles) was added to a stirred solution of chlorine dioxide (607 mg, 9 mmoles) in water (50 mL) at room temperature. The flask was stoppered with a pressure-release stopper and heated with stirring at 65°C (bath) protected from light for 30 min. After cooling, sodium chloride (5 g) was added and the product extracted with ethyl acetate (5 × 15 mL). The combined extracts were washed with water (3 × 5 mL), dried and made up to 100 mL in a volumetric flask. Tetracosane internal standard was added to a 5-mL aliquot, and after concentration to 1 mL, the aliquot was analysed by GC and GCMS before and after methylation with diazomethane. The remainder of the product was concentrated to give a dark brown gum (750 mg). Fractionation on silica gel (50 g) and elution with hexane : ethyl acetate : acetic acid, 9 : 1 : 0.5, gave fractions containing mixtures of benzoic acid, chlorinated pinosylvins and the trichlorocyclopentenedione **3** in various proportions (250 mg). Refractionation gave **3** (35 mg), after crystallization from ethyl acetate, as yellow prisms, m.p. 141–142°C. MS (%): 304 ($M^+ + 4$, 33), 302 ($M^+ + 2$, 74), 300 (M^+, 75), 267 (75), 265 (100), 209 (63), 173 (59), 139 (50), 127 (70). HRMS calcd for $C_{13}H_7Cl_3O_2$: 299.9512; found: 299.9502. Structure determined by X-ray crystallography. Elution with hexane : ethyl acetate : acetic acid, 1 : 1 : 0.5, and ethyl acetate gave fractions containing the maleic acids **4a** and **4b**, (500 mg). Refractionation gave 300 mg of a mixture of **4a** and **4b** and a small amount of **4b**, about 90% pure. Methylation gave the dimethyl ester of **4b**. MS(%): 282 ($M^+ + 2$, 9),

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280 (M^+, 26), 249 (11), 213 (100), 127 (24). HRMS: calcd for $C_{14}H_{13}ClO_4$: 280.0502; found: 280.0489.

Reaction of Pinosylvin Dimethyl Ether 1b with Chlorine Dioxide

Pinosylvin dimethyl ether (1.2 g, 5 mmoles) was reacted with chlorine dioxide (1 g, 15 mmoles) as described for pinosylvin. After cooling, sodium chloride (10 g) was added and the product was extracted with ether (5×20 mL). The combined extracts were washed with water (3×5 mL), dried and made up to 100 mL in a volumetric flask. Tetracosane internal standard was added to an aliquot which was analysed as described for the product from the reaction of pinosylvin. The remainder of the product was extracted with 5% sodium bicarbonate (3×10 mL) to give, after reacidification and extraction with ether, an acidic fraction (180 mg), containing benzoic acid and other acids. The ether solution containing the non-acidic products was washed with water, dried and evaporated to give an orange oil (1.2 g). Treatment with cold methanol (3 mL) gave an orange solid (240 mg) containing about 85% 2,6-dichloropinosylvin dimethyl ether **5**. Crystallization from methanol gave pure 2,6-dichloropinosylvin dimethyl ether, identical to material prepared by the chlorination of pinosylvin dimethyl ether described earlier. The methanol-soluble material from two reactions processed in the above manner (2 g) was fractionated on silica gel (100 g). Elution with hexane : ethyl acetate, 9 : 1, gave fractions containing mainly the dichloropinosylvin dimethyl ether **5** (380 mg). Elution with hexane : ethyl acetate, 4 : 1, gave a mixture containing **5** and the epoxide **6** (570 mg). Treatment of this mixture with sodium borohydride to convert carbonyl-containing contaminants to more polar alcohols and refractionation gave the epoxide as colorless prisms, m.p. 129–131°C, after crystallization from acetone/hexane. ^{1}H NMR: 3.94 (s, 6H, $2 \times OCH_3$), 3.96 (d, J = 2 Hz, 1H, Hepox), 4.07 (d, J = 2 Hz, 1H, Hepox), 6.58 (s, 1H, H4), 7.36 (tt, J = 7, 1 Hz, H4′), 7.40 (t, J = 7 Hz, 2H, H3′5′), 7.49 (m, 2H, H2′6′). MS (%): 326 ($M^+ + 2$, 5), 324 (M^+, 8), 291 (43), 289 (100), 253 (42). Structure determined by X-ray crystallography. Elution with hexane : ethyl acetate, 1 : 1, gave a small amount of 7, m.p. 213–215°C, after crystallization from acetone. ^{1}H NMR: 3.88 (s, 6H, $2 \times OCH_3$), 4.78 (d, 4 Hz, 1H, OH, D_2O-exchangeable), 6.44 (d, J = 4 Hz, 1H, -CHOH, s with D_2O exchange), 6.51 (s, 1H, H4), 7.35 (t, J = 7 Hz, 2H, H3′5′), 7.45 (t, J = 7 Hz, 1H, H4′), 7.80 (m, 2H, H2′6′). MS (%): 340 (M^+, < 5), 305 (18), 237 (25), 235 (41), 172 (24), 105 (100), 77 (56).

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