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Two new aromatic compounds from the resin of *Styrax tonkinensis* (Pier.) Craib

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Two new aromatic compounds, *trans*-(tetrahydro-2-(4-hydroxy-3-methoxyphenyl)-5-oxofuran-3-yl)-methyl benzoate (**1**), 3-(4-hydroxy-3-methoxyphenyl)-2-oxopropyl benzoate (**2**) and one new natural product, 4-((E)-3-ethoxyprop-1-enyl)-2-methoxyphenol (**3**) together with five known aromatic compounds have been isolated from the resin of *Styrax tonkinensis* (Pier.) Craib. Their structures were determined by physical and spectroscopic methods.

Keywords: *Styrax tonkinensis* (Pier.) Craib; Styracaceae; Resin; *trans*-(Tetrahydro-2-(4-hydroxyl-3-methoxyphenyl)-5-oxofuran-3-yl)methyl benzoate; 3-(4-Hydroxyl-3-methoxyphenyl)-2-oxopropyl benzoate; 4-((E)-3-Ethoxyprop-1-enyl)-2-methoxyphenol

1. Introduction

Styrax tonkinensis (Pier.) Craib is an arbor distributed in several regions of South-East Asia and its resin has been used as a traditional medicine for expelling phlegm, waking up the patient from unconsciousness, promoting flow of Qi and blood, and alleviating pain in China. One triterpenoid, siaresinolic acid, and some aromatics series, benzoic acid, vanillin, coniferyl benzoate, cinnamyl benzoate have been isolated from the resin of the plant before [1]. In order to search the active ingredients of the resin, we do further isolation through ethanol extraction. Two new aromatic compounds **1**, **2** and one new natural product **3** were obtained together with five known aromatic compounds. The known compounds were identified as benzoic acid [2,3], vanillin [4,5], dehydrodivanillin, vanillic acid [6,7] and coniferyl aldehyde [8] (figure 1).

2. Results and discussion

Compound **1** was obtained as a colorless cube. Its molecular formula was determined as C₁₉H₁₈O₆ on the basis of its HREIMS spectrum (*m/z* 342.1101 [M]⁺). The ¹H-NMR spectrum gave five aromatic proton signals at δ 7.93 (2H, dd, *J* = 8.4, 1.8 Hz), 7.59

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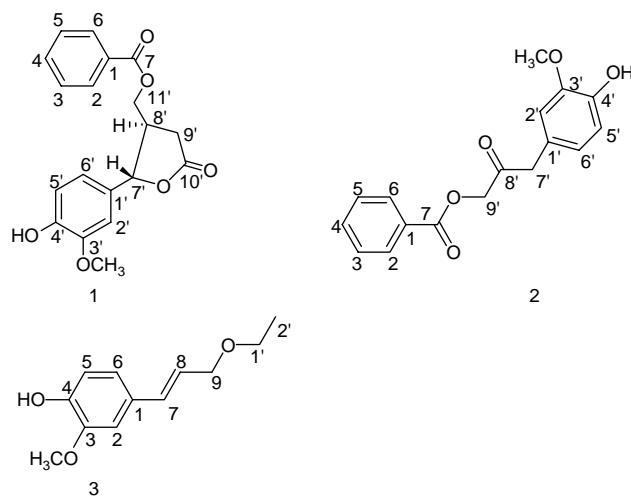


Figure 1. The structures of compounds **1**, **2** and **3**.

(1H, tt, $J = 8.4$, 1.8 Hz) and 7.44 (2H, t, $J = 8.4$ Hz) indicating a benzoxy group. The presence of 4-hydroxy-3-methoxyphenyl group was confirmed based on the $^1\text{H-NMR}$ signals of methoxy- and hydroxyl groups (δ 3.87 and 5.68) and three aromatic proton signals between δ 6.84 to 6.93. There were also six protons assigned to CH at δ 5.28 (1H, d, $J = 7.2$ Hz), CH_2 at δ 4.45 (2H, m), CH at δ 2.96 (1H, m) and CH_2 at δ 2.90 (1H, dd, $J = 16.8$, 8.7 Hz), 2.68 (1H, dd, $J = 16.8$, 8.4 Hz) in the $^1\text{H-NMR}$ spectrum. The $^1\text{H}-^1\text{H}$ COSY spectrum showed correlations between CH (δ 2.96) and CH (δ 5.28), CH_2 (δ 4.45) and CH_2 (δ 2.90, 2.68), respectively. The $^{13}\text{C-NMR}$ spectrum showed a carbonyl group signal which was correlated with the proton signal at δ 2.68 in the HMBC spectrum. The above findings suggested the presence of a five-membered lactone.

4-Hydroxy-3-methoxyphenyl group was located at C-7' based on the HMBC spectrum which showed correlations between CH at δ 5.28 and aromatic carbons C-2' at δ 119.4 and C-6' at δ 108.2, respectively. Evidently, the benzoxy group was located at C-11'. The NOESY spectrum showed correlation between the methoxy signal at δ 3.87 and the proton signal at δ 6.84 indicating the methoxy group was located at C-3'. The *trans*-configuration of H-7' and H-8' was determined based on the presence of the correlation between H-8' and H-6' or H-2' and between H-7' and H-11'. Thus, compound **1** was identified to be *trans*-(tetrahydro-2-(4-hydroxy-3-methoxyphenyl)-5-oxofuran-3-yl)methyl benzoate.

Compound **2** was obtained as pale yellow oil. Its EIMS showed the molecular ion peak at m/z 300. Its aromatic proton signals were similar to **1** in the $^1\text{H-NMR}$ spectrum and resonated at δ 8.08 (2H, dd, $J = 7.8$, 1.5 Hz), 7.59 (1H, tt, $J = 7.8$, 1.5 Hz), 7.46 (2H, t, $J = 7.8$ Hz), 6.87 (1H, d, $J = 8.4$ Hz), 6.74 (1H, d, $J = 1.8$ Hz) and 6.72 (1H, dd, $J = 8.4$, 1.8 Hz), indicating that compound **2** also has 4-hydroxy-3-methoxyphenyl and benzoxy groups. Signals of two CH_2 at δ 4.93 (2H, s), 3.74 (2H, s) and one CH_3O at δ 3.85 (3H, s) were shown in the $^1\text{H-NMR}$ spectrum (table 1). The $^{13}\text{C-NMR}$ spectrum showed seventeen carbon signals including two carbonyl groups resonating at δ 201.8, 165.8, twelve aromatic carbons, two methylenes and one methoxy group (table 1). The ketone carbonyl signal at δ 201.8 in the $^{13}\text{C-NMR}$ spectrum correlated with the two CH_2 signals shown in the HMBC spectrum. Thus, the carbonyl group was located between two CH_2 . Furthermore, the HMBC spectrum showed the correlations between CH_2 at δ 4.93 and the carbonyl at δ 165.8 and between CH_2

Table 1. The ^1H -NMR and ^{13}C -NMR data of **1**, **2** and **3** in CDCl_3 ^a.

	1		2		3	
	δ_{H} (J_{Hz})	δ_{C}	δ_{H} (J_{Hz})	δ_{C}	δ_{H} (J_{Hz})	δ_{C}
1	–	129.2	–	129.1	–	128.2
2	7.93(1H,dd, 8.4,1.8)	129.6	8.08(1H,dd,7.8,1.5)	129.8	6.80(1H,brs)	113.5
3	7.44(1H,t,8.4)	128.5	7.46(1H,t,7.8)	128.4	–	144.7
4	7.59(1H,tt,8.4,1.8)	133.5	7.59(1H,tt,7.8,1.5)	133.4	–	144.6
5	7.44(1H,t,8.4)	128.5	7.46(1H,t,7.8)	128.4	6.74(1H,brs)	113.5
6	7.93(1H,dd,8.4,1.8)	129.6	8.08(1H,dd,7.8,1.5)	129.8	6.74(1H,brs)	119.2
7	–	166.1	–	165.8	6.40(1H,d,15.6)	131.4
8	–	–	–	–	6.01(1H,m)	122.7
9	–	–	–	–	4.02(2H,d,6.2)	70.4
1'	–	129.6	–	124.4	3.43(2H,q,6.9)	64.5
2'	6.84(1H,d,1.8)	119.4	6.74(1H,d,1.8)	122.3	1.14(3H,t,6.9)	14.1
3'	–	146.9	–	146.7	–	–
4'	–	146.2	–	145.0	–	–
5'	6.92(1H,d,8.4)	114.5	6.87(1H,d,8.4)	114.6	–	–
6'	6.86(1H,dd,8.4,1.8)	108.2	6.72(1H,dd,8.4,1.8)	111.7	–	–
7'	5.28(1H,d,7.2)	83.7	3.74(2H,s)	46.1	–	–
8'	2.96(1H,m)	43.7	–	201.8	–	–
9'	2.68(1H,dd,16.8,8.4) 2.90(1H,dd,16.8,8.7)	32.1	4.93(2H,s)	67.8	–	–
10'	–	175.1	–	–	–	–
11'	4.45(2H,m)	63.6	–	–	–	–
OCH_3	3.87(3H,s)	56.0	3.88(3H,s)	55.9	3.72(3H,s)	54.7

^a Assignment were made by ^1H - ^1H COSY, HMQC, HMBC and NOESY spectrum.

at δ 3.74 and the aromatic carbons at δ 111.7, 122.3 and 124.4. These correlations suggested a fragment CH_2COCH_2 linked to 4-hydroxy-3-methoxyphenyl at one side and formed an ester with the benzoxy group at another side. Thus, compound **2** was identified to be 3-(4-hydroxy-3-methoxyphenyl)-2-oxopropyl benzoate.

Compound **3** was obtained as a brown oil. An ethoxyl group at δ 1.14 (3H, t, $J = 6.9$ Hz) and 3.43 (2H, q, $J = 6.9$ Hz), a disubstituted olefin at δ 6.40 (1H, d, $J = 15.6$ Hz) and 6.01 (1H, m), a methylene group at δ 4.01 (2H, d, $J = 6.2$ Hz), a methoxy at 3.72 (3H, s), a hydroxy at 6.07 (1H, s) and three aromatic protons between δ 6.74 to 6.80 which indicated the presence of 4-hydroxy-3-methoxyphenyl group were shown in the $^1\text{H-NMR}$ spectrum. The correlations between δ 3.43 (H-1') and 14.1 (C-2'), between δ 4.02 (H-9) and 64.5 (C-1'), 122.7 (C-8), between δ 6.01 (H-8) and 70.4 (C-9), 131.4 (C-7) indicating the presence of a $-\text{CH}=\text{CHCH}_2\text{OCH}_2\text{CH}_3$ moiety were shown in the HMBC spectrum. Moreover, the HMBC spectrum also showed a correlation between hydroxyl group at δ 6.07 and C-5 resonating at δ 113.5, which indicated that a hydroxyl group was located at C-4. Thus, compound **3** was identified to be 4-((E)-3-ethoxyprop-1-enyl)-2-methoxyphenol, which has been synthesized by A. Zanarotti [9].

3. Experimental

3.1 General experimental procedures

Melting points were measured on a Yanaco MP-S3 micro-melting point apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 241MC polarimeter. UV was recorded with Shimadzu UV-2201. NMR were recorded on a Bruker ARX 300 NMR spectrometer and a Bruker ARX 600 NMR spectrometer. The chemical shifts were quoted relative to TMS and coupling constants are in Hz. DEPT, HMBC, HMQC and COSY experiments were measured on a Bruker ARX 300 NMR spectrometer. EIMS spectra (70 eV) were conducted on a Shimadzu GCMS-QP5050A spectrometer. HREIMS was recorded on an Autospec-UltimaETOF instrument. IR was conducted on a Perkin IFS-55 spectrometer. The chromatographical silica gel (200–300 mesh) was produced by Qindao Ocean Chemical Factory and ODS (50 μm) was produced by YMC, CO., LTD.

3.2 Plant material

The resin of *Styrax tonkinensis* (Pier.) Craib was bought from Liaoning Medicinal Material Corporation, Shenyang, China and identified by Prof. Qishi Sun of Shenyang Pharmaceutical University.

3.3 Extraction and isolation

The resin of *Styrax tonkinensis* (Pier.) Craib (900 g) was extracted with 95% ethanol. After evaporation of ethanol, a portion (150 g) of the residue was chromatographed on a column of silica gel with a gradient elution using petroleum with increasing proportions of EtOAc and sequentially solvent gradient from EtOAc to MeOH to give ten fractions: fractions I ~ X. Fraction II [petroleum:EtOAc (100: 5)] was subsequently chromatographed over a column of silica gel to furnish compound **3** (8 mg). Repeated chromatography of fraction III

[petroleum:EtOAc (100:7)] on a column of silica gel followed by open ODS column chromatograph (70% MeOH in water) afforded compound **2** (4 mg). Fraction VI was chromatographed on a column of silica gel with gradient elution using CHCl_3 with increasing proportions of MeOH and was subsequently chromatographed over a column of silica gel with gradient elution using petroleum with increasing proportions of acetone to afford compound **1** (12 mg).

3.3.1 trans-(Tetrahydro-2-(4-hydroxy-3-methoxy-phenyl)-5-oxofuran-3-yl)methyl benzoate (1). Mp 136–138°C; colorless cube, $[\alpha]_{\text{D}} + 7.5$ (CHCl_3 ; c 0.75). UV (MeOH) λ_{max} 215, 246 nm. IR (KBr) ν_{max} cm^{-1} : 3358 (OH), 1753 (C=O), 1720 (C=O), 1599, 1519, 1446, 1437, 1315, 1276, 716. EIMS m/z (rel. int): 342 $[\text{M}]^+$ (23), 220 (69), 192 (48), 151 (79). HREIMS m/z : 342.1101 $[\text{M}]^+$ (calcd. for $\text{C}_{19}\text{H}_{18}\text{O}_6$, 342.1103). $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$: see table 1.

3.3.2 3-(4-Hydroxy-3-methoxyphenyl)-2-oxopropyl benzoate (2). Pale yellow oil. EIMS m/z (rel. int): 300 $[\text{M}]^+$ (23), 151 (71), 137 (56), 105 (100). $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$: see table 1.

3.3.3 4-((E)-3-Ethoxyprop-1-enyl)-2-methoxyphenol (3). Pale yellow oil. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$: see table 1.

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