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Benzofurans and another constituent from seeds of *Styrax officinalis*

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Abstract

The benzofuran constituents of the seeds of *Styrax officinalis* were investigated. From the hexane extract, two new constituents named 5-(3″benzoyloxypropyl)-7-methoxy-2-(3′,4′-methylenedioxyphenyl)-benzofuran (**5**) and 4-[3″-(1c-methylbutanoyloxy)propyl]-2-methoxy-(3′,4′-methylenedioxyphenyl)-1a, 5b-dihydrobenzo-[3,4]-cyclobutaoxirene (**6**) were isolated together with four known compounds, 5-[3″-(1c-methylbutanoyloxy)propyl]-7-methoxy-2-(3′,4′-dimethoxyphenyl)-benzofuran (**4**), 5-[3″-(1c-methylbutanoyloxy)propyl]-7-methoxy-2-(3′,4′-methylenedioxyphenyl)-benzofuran (**3**), 5-(3″-acetoxypropyl)-7-methoxy2-(3′,4′-methylenedioxphenyl)-benzofuran (**2**) and 5-(3″-hydroxypropyl)-7-methoxy-2-(3′,4′-met hylenedioxyphenyl)-benzofuran (**1**). Although the compounds **1**, **2**, and **3** have been isolated previously from the seeds of *Styrax obassia*, this is the first record of their isolation from seeds of *Styrax officinalis*. The structures of the isolated compounds were established by 1D- and 2D-NMR (HMBC, HMQC, COSY), FABMS and high-resolution ESI FTMS.

Keywords: *Styrax officinalis*; Styracaceae; Egonol; Benzofuran ester; Oxirene

1. Introduction

Styrax officinalis L. is a member of the Styracaceae family. It is a shrub found in Central America, Mexico, and the Mediterranean region including West and South Anatolia (Davis, 1972). Its resin was used by Romans, Egyptians, Phoenicians and Ionians as incense and in therapeutics (Vardar and Oflas, 1973). *Styrax* species contain egonol, a natural benzofuran, which is known to be an effective pyrethrum synergist (Takanashi and Takizawa, 1988; Paluetti et al., 2000). Earlier studies of the seeds of *Styrax* species have been reported; the isolation of egonol from *Styrax japonica* and its identification as 5(3″hydroxypropyl)-7-methoxy-2-(3′,4′-methylenedioxyphenyl)-benzofuran, homoegonol from *S. officinalis* (Segal et al., 1967), demethoxy egonol from *Styrax obassia* (Takanashi et al., 1974) benzofuran glycosides from *S. officinalis* (Anil, 1980), and esterbenzofuran from *S. obassia* (Takanashi and Takizawa, 1988). This paper describes the isolation and structural elucidation of two new compounds along with four known benzofuran compounds by using various NMR experiments including COSY, DEPT, HMQC, HMBC, and HR-ESIFTMS and FABMS.

2. Results and discussion

The seeds of *S. officinalis* were extracted with *n*-hexane. After chromatographic separation two new compounds were isolated together with four known compounds. From this mixture, compound **5**, was isolated as a viscous yellow oil and was one of the minor compounds of *S. officinalis*. Compound **5** exhibited UV absorptions at 205 (*s*), 230 (*s*), 300 (*m*), and 316 (*m*) nm which suggested the egonol skeleton. The IR (1740 cm^{-1}) and NMR spectra of the compound then suggested the presence of an ester of egonol (**1**). Positive ion mode FABMS revealed a molecular ion peak at *m*/*z* 431 $[M+H]^+$ consistent with a molecular formula of $C_{26}H_{22}O_6$. The ^{13}C NMR spectra of **5** showed the signals for 26 carbons and the DEPT 135 spectra distinguished four methylene carbons, one methoxy carbon, twenty aromatic carbons (11 CH, and nine quaternary carbons), and one carbonyl carbon (Table 1, Fig. 1). Comparison of the ^1H and ^{13}C NMR spectra of

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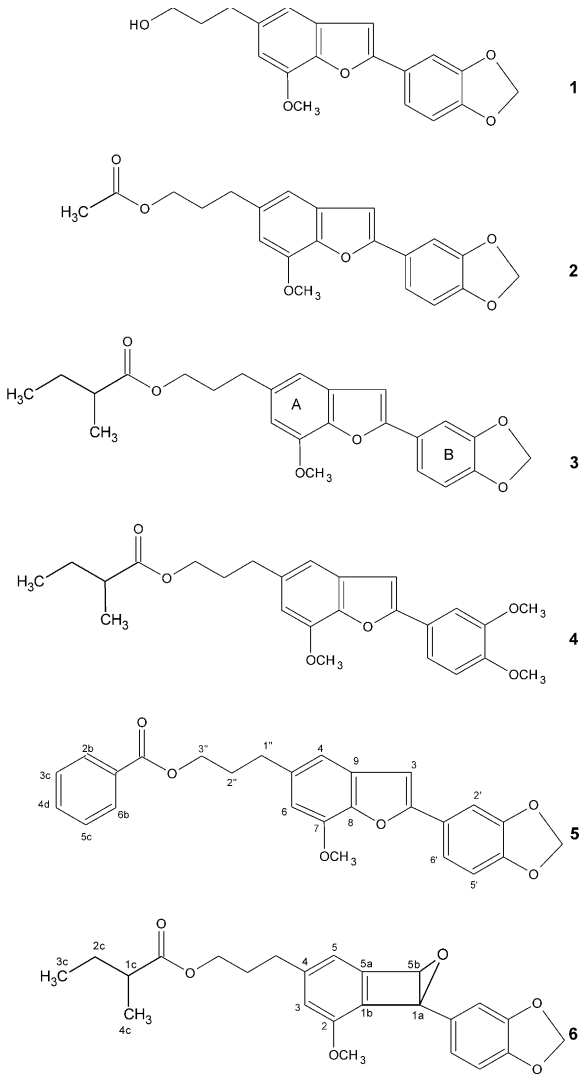

Fig. 1. Chemical structure of the isolated compounds (**1–6**).

1 with those described for **5** indicated that **5** is a benzoyl derivative of compound **1**. The NMR spectrum of **5** displayed two doublets at δ 7.35 (1H, *d*, $J=1.41$ Hz), 6.89 (1H, *d*, $J=8.13$), and two singlets at δ 7.02 (1H, *s*), 6.66 (1H, *s*) and a double doublet at δ 7.43 (1H, *dd*, $J=1.49$, 8.13) attributable to aromatic protons. In addition also observed was a singlet at δ 6.81 (1H, *s*) corresponding to H-3, a singlet due to a methylenedioxy group at δ 5.88 (2H, *s*), a singlet due to a methoxyl group at δ 4.04 (3H, *s*), two triplets due to methylene protons at δ 2.89 (2H, *t*, $J=7.46$, 7.68) and 4.4 (2H, *t*, $J=6.44$, 6.45 Hz) as well as a quintet due to a methylene group at δ 2.20. This spectroscopic pattern accommodated the characteristics of compound **1**. The ^{1}H NMR data revealed a doublet at δ 8.07 (2H, $J=7.2$ Hz) as well as two separate triplets at δ 7.58 (1H, $J=7.4$, 7.4 Hz) and δ 7.46 (2H, $J=7.8$, 7.6 Hz), resulting from benzoyl group. The difference observed in the ^{13}C NMR spectrum of **5** was seen in the presence of signals at δ 130.8 (C), 129.9 (CH), 128.7 (CH), 133.3 (CH), and 167.1 (C=O), therefore, confirming a benzoyl moiety (Kanchanapoom et al., 2001). The position of the benzoyl unit was confirmed by an HMBC spectrum. The HMBC spectrum showed $^3J_{C\text{-}H}$ correlations between the carbonyl carbon signal at δ 167.1 and the proton signals at δ 4.4 (C3″) and 8.07 (C-2b, 6b). Also informative cross peaks due to long range ^{13}C–^{1}H coupling were observed for C4d/2bH (6bH), C2b (C6b)/4dH, 3cH (5cH), C1a/3cH (5cH) in the HMBC spectrum. These data led us to assigning the structure of **5** as 5-(3″benzoyloxypropyl)-7-methoxy-2-(3′, 4′-methylenedioxyphenyl)-benzofuran.

Compound **6** was isolated as a viscous yellow oil which is another minor compound from *S. officinalis*. Its UV spectrum showed λ_{max} values at 206 (*s*), 289 (*w*) and 316 (*w*) nm, quite different from the UV spectrum of egonol. The differences between the two UV spectra indicated the disappearance of the conjugated system in compound **6**. High-resolution ESIFTMS and FABMS of compound **6** revealed a molecular ion peak at *m*/*z* 411.1862 $[M+H]^+$ and 411 $[M+H]^+$, respectively, consistent with a molecular formula of $C_{24}H_{26}O_6$ like compound **3**. The ^{13}C NMR spectrum of the title compound displayed the presence of 24 carbons and the DEPT 135 spectra could distinguish two methyl carbons (δ 11.7 and 16.7), four methylene carbons (δ 26.8, 30.4, 31.7, and 62.8), two methyne carbons (δ 41.1 and 60.8), one methylenedioxy carbon (δ 100.9), one quarternary carbon (94.2), 12 aromatic carbons (seven quarternary δ 147.3, 147.2, 146.9, 143.7, 134.7, 131.6, 126.4; five CH: δ 119.9, 118.3, 112.5, 107.4, 106.8), and one carbonyl carbon (δ 176.6 ppm, Table 1). Upon integration, the ^{1}H NMR spectrum showed 26 protons comprising methyne (δ 2.38 and 4.80), methylene (δ 1.50–3.90), methyl (δ 0.94–1.68), a methoxy (δ 3.88), a methylenedioxy (δ 5.87) and aromatic protons (δ 6.18–6.94). The ^{1}H NMR spectrum exhibited a triplet at δ 0.94 (3H, $J=7.42$–7.44 Hz) and a doublet at δ 1.18 (3H, $J=6.97$ Hz) resulting from the methyl group which is adjacent to the methylene and methyne groups. These observations suggest the possible presence of an *sec*-butyl group. Further evidence for this came from the HMBC spectrum which showed $^3J_{C-H}$ correlations between the methyl carbon signal at δ 11.7 and the proton signals of methyne at δ 2.38 (1H, *m*); $^2J_{C-H}$ correlations between the methyl carbon signal at δ 16.7 and the proton signals of methyne at δ 2.38 (1H, *m*); and the other methyl carbon signal at δ 11.7 as well as the proton signal of methylene δ 1.50–1.68 (2H, *m*). This observation was supported by the ^{1}H–^{1}H COSY spectrum and identified compound **6** as having the 2-methylbutanoyl group. The comparison of ^{1}H NMR and FABMS spectra of compounds **6** and **3** suggested that both compounds possess the same B-ring structure of 3′,4′-methylenedioxyphenyl and the side chain 2-methylbutanoyl group. Also, the ^{1}H and ^{13}C

Table 1
^{13}C and ^{1}H NMR data of compounds **5** and **6** (125 and 500 MHz, $CDCl_3$)

Compound **5**						Compound **6**					
C/H	*DEPT*	δ_C	δ_H	*J (Hz)*	*HMBC (C→H)*	*C/H*	*DEPT*	δ_C	δ_H	*J (Hz)*	*HMBC (C→H)*
2	C	156.5			H-3, H-2′, H-6′	1a	C	94.2			H-5b, H-2′, H-6′
3	CH	100.8	6.81, *s*		H-4	5b	CH	60.8	4.80, *s*		H-5
4	CH	112.8	7.02, *s*		H-6, H-1″	5	CH	118.3	6.19, *s*		H-5b, H-3
5	C	137.3			H-1″, H2″	4	C	134.7			H-1″, H-2″
6	CH	107.9	6.66, *s*		H-4, H-1″	3	CH	112.5	6.48, *s*		H-5
7	C	145.3			OMe	2	C	143.7			H-5, H-3, OMe
8	C	142.9			H-3, H-4, H-6	1b	C	146.9			H-5b, H-5, H-3
9	C	131.5			H-3, H-6	5a	C	126.5			H-5, H-5b
1′	C	125.1			H-5′	1′	C	131.6			H-5′, H-5b
2′	CH	105.9	7.35, *d*	(1.41)	H-6′	2′	CH	106.8	6.94, *d*	(1.41)	H-6′
3′	C	148.5			H-5′, OCH_2O	3′	C	147.3			H-5′, OCH_2O
4′	C	148.4			H-2,H-6′, OCH_2O	4′	C	147.2			H-2′, H-6, OCH_2O
5′	CH	109.0	6.89, *d*	(8.13)		5′	CH	107.4	6.61, *d*	(8.08)	
6′	CH	119.6	7.43, *dd*	(1.49, 8.13)	H-2′	6′	C	119.9	6.81, *dd*	(1.47, 8.09)	H-2′
OCH_2O	CH_2	101.7	6.03, *s*			OCH_2O	C	100.9	5.88, *s*		
1″	CH_2	33.1	2.89, *t*	(7.46, 7.68)	H-4, H-6, H-3	1″	CH_2	31.6	2.47, *m*		H-5, H-3, H-3″
2″	CH_2	31.2	2.20, *q*		H-1″	2″	CH_2	30.4	1.71, *m*		H-1″
3″	CH_2	64.7	4.4, *t*	(6.44, 6.45)	H-2″, H-1″	3″	CH_2	62.8	3.93, *t*	(6.4, 6.5)	H-1″
OMe	CH_3	56.6	4.04, *s*			OMe	CH_3	56.1	3.90, *s*		
1a	C	130.8			H-3c (5c)	1c	CH	41.1	2.38, *m*		H-4c, H-3c
2b,6b	CH	129.9	8.07, *d*	(7.24)	H-4d, H-3c (5c)	2c	CH_2	26.8	1.50–1.68, *m*		H-4c, H-3c
3c,5c	CH	128.7	7.46, *t*	(7.81, 7.64)		3c	CH_3	11.7	0.94, *t*	(7.42, 7.44)	H-2c
4d	CH	133.3	7.58, *t*	(7.41, 7.40)	H-2b (6b)	4c	CH_3	16.7	1.18, *d*	(6.97)	
C=O	C	167.1			H-2b (6b), H-3″	C=O	C	176.6			H-3″, H-4c

NMR signal patterns were similar, except for the signal at δ 94.2 (*q*) and 60.8 (*d*, δ 4.80) ppm instead of two carbon signals at δ 156.1 (*q*) and 100.8 (*d*, 6.80) in the ^{13}C NMR spectrum of compound **3**. Based on these NMR and MS data, this compound has an epoxy group in the A ring. ^{1}H–^{13}C one bond (HMQC) data were used to assessing carbon resonances. The location of an epoxy group and the assignment of the NMR signals were achieved by analysis of the direct and long-range ^{1}H–^{13}C correlation. HMBC correlations of compound **6** showed a $^{3}J_{C-H}$ correlation between the methyne carbon signal at δ 60.8 and the proton signal at δ 6.19 (1H, *s*, C5-H). The HMBC spectrum also showed a $^{2}J_{C-H}$ correlation between the quarternary carbon signal at δ 94.2 and the proton signal at δ 4.80 (1H, *s*; C5b) and also there was a $^{3}J_{C-H}$ correlation between the quarternary carbon signal δ 94.2 and the proton signal at 6.94 (1H, *d*, J= 1.41, C2′) and 6.81 (1H, *dd*, J=1.47, 8.09 Hz, C6′) as shown in Table 1. Also informative cross peaks due to long-range ^{13}C–^{1}H couplings were observed for C5/H5b, H3; C3/H5; C4/H1″, H2″; C2/H3, OMe, H5; C1b/H3, H5b, H5 in the HMBC spectrum. The ^{1}H–^{1}H COSY spectrum of the title compound showed a correlation between proton signals at δ 6.81 ppm (1H, *dd*, J=1.47, 8.09 Hz, C6′) and the proton signal at δ 6.61ppm (1H, *d*, J=8.08 Hz, C5′). All of these data suggested that an epoxy ring is on the 1a and 5b carbons. Thus spectroscopic data led to the structure of 4-[3″-(1cmethylbutanoyloxy)propyl]-2-methoxy-1a-(3′,4′-methylenedioxyphenyl) 1a-5b-dihydrobenzo-[3,4])-cyclobutaoxirene for compound **6**.

Compound **4** was isolated as a solid constituent and identified in our previous research (Yayla Akgul and Anil, 2003) Although compound **3** and compound **2** have been isolated previously from *S. obassia* (Takanashi and Takizawa, 1988; Takanashi et al., 1974), this is the first record of its isolation from *S. officinalis*. Compound **1** (egonol) was also isolated and identified by using NMR and HR-ESIFTMS spectra as a naturally occuring minor constituent of *S. officinalis*.

3. Experimental

3.1. General experimental procedure

NMR spectra were recorded at 500 MHz for H and 125 MHz for ^{13}C in $CDCl_3$ on a Bruker Avance DRX500FT spectrometer. Proton-detected heteronuclear correlations were measured using HMQC and HMBC. Mass spectra were obtained with a Bruker BioApex High Resolution Fourier Transform Mass Spectrometer with electrospray ionisation (HR-ESIFTMS) and ZapSpec Fast Atom Bombardment Mass Spectrometer (FABMS) operated in positive ion mode. The IR spectra were recorded using on an ATI

Mattson Genesis Series Fourier Transform Infrared (FTIR) spectrometer. TLC was performed on Alugram (Sil G/UV 254, Merck) 0.2 mm layer thick plates with spots visualized with anisaladehyde 20% in H_2SO_4 after heating. Column Chromatography (CC) was carried out on a Baker Sigel 40 μm and Centrifugal Preparative Thin Layer Chromatography (CPTLC) was performed on a Harrison Research Model 8924 CPTLC apparatus using 2 and 4 mm thick silica gel plates.

3.2. Plant material

Fruits of *S. officinalis* were collected in August 1996 from Ephesus (Aydin, Turkey) and were identified by Prof. Dr. Özcan Secmen, Department of Botany, Faculty of Science, Ege University. A voucher specimen (EGE:HERB.22936) is preserved in the herbarium of Ege University.

3.3. Extraction and isolation

The shade dried seeds of *S. officinalis* (600 g) were extracted three times with *n*-hexane at room temperature over 3 days. After filtration, the combined extract (8 l) was evaporated under vacuum to give 122 g of a yellow oily material. Twenty grams of this oily residue was subjected to a Sigel column (1 kg, 12×190 cm) eluted with CH_2Cl_2/*n*-hexane (6/3), followed by increasing concentrations of CH_2Cl_2 to give eight 2.5 l fractions, labelled as fractions A–H. Column chromatographic separation was repeated four times in the same way. The individual fractions were combined and then each combined fraction was then evaporated under reduced pressure. Further purification for each fraction was carried out by using silica gel column chromatography (*n*-hexane/ethylacetate: 9/1, 9/2, 9/3 and $CHCl_3$, CH_2CH_2), CPTLC (*n*-hexane/ethylacetate: 10/0.5, 10/1), and PTLC with different solvent polarity. The six compounds of this paper were then isolated as follows: compound **6** (6.2 mg), **5** (7.8 mg), **4** (26.5 mg), **3** (92.6 mg), **2** (59.1 mg), **1** (6.5 mg).

3.3.1. 4-[3″-(1c-Methylbutanoyloxy)propyl]-2-methoxy-1a-(3′,4′-methylenedioxyphenyl)-1a, 5b-dihydrobenzo-[3,4]-cyclobutaoxirene (**6**, 6.2 mg)

IR bands (film): 2927, 1725, 1615, 1523, 1436, 1268, 1099, 1053, 951 cm^{-1}, UV_{max} (EtOH): 206 (*s*), 289 (*w*), 316 (*w*) nm; FABMS: *m/z*: 411 $[M+H]^+$, HRESIFTMS: 411.1862 $[M+H]^+$; ^1H–^{13}C NMR (see Table 1).

3.3.2. 5(3″Benzoyloxypropyl)-7-methoxy-2(3′,4′methylenedioxyphenyl)benzofuran (**5**, 7.8 mg)

IR bands (film): 2956, 1740, 1620, 1490, 1260, 1090, 1040, 970, 790, 740 cm^{-1} ; UV_{max} (EtOH): 205 (*s*), 230 (*s*), 300 (*m*), 316 (*m*) nm, FABMS: *m/z*: 431 $[M+H]^+$; ^1H–^{13}C NMR (see Table 1).

3.3.3. 5-[3″-(1c-Methylbutanoyloxy)propyl]-7-methoxy-2-(3′,4′-dimethoxyphenyl)-benzofuran (**4**, 26.5 mg)

Mp 62–65 °C; IR bands (film): 2959, 1728, 1599, 1482, 1463, 1251, 1142, 1025 cm^{-1}; UV_{max} (EtOH): 215 (*s*), 304 (*m*), 313 (*m*) nm; HR-ESIFTMS *m/z* 427.2112 $[M+H]^+$; ^{13}C NMR δ_{ppm}: 177.2 *q*, 156.8 *q*, 100.7 *d*, 131.3 *q*, 112.8 *d*, 137.4 *q*, 107.8 *d*, 145.2 *q*, 143.0 *q*, 123.9 *q*, 108.7 *d*, 150.0 *q*, 149.6 *q*, 111.8 *d*, 118.5 *d*, 32.9 *t*, 31.3 *t*, 63.9 *t*, 41.9 *d*, 27.2 *t*, 12.1 *s*, 17.1 *s*, 56.4 *s*, 56.5 *s*, 56.6 *s*; ^1H NMR: 6.80 (1H, *s*), 6.93 (1H, *s*), 6.58 (1H, *s*), 7.34 (1H, *d*, $J=1.88$ Hz), 6.91 (1H, *d*, $J=8.14$ Hz), 7.73 (1H, *dd*, $J=8.34$ and 1.92 Hz), 2.74 (2H, *t*, $J=7.62$ and 7.72 Hz), 1.19 (2H, *p*), 4.11 (2H, *m*), 2.37 (1H, *m*), 1.46 and 1.66 (2H, *m*), 0.90 (3H, *t*, $J=7.43$ and 7.44 Hz), 1.16 (3H, *d*, $J=6.99$ Hz), 4.01 (3H, *s*), 3.95 (3H, *s*), 3.96 (3H, *s*).

3.3.4. 5-[3″-(1c-Methylbutanoyloxy)propyl]-7-methoxy-2-(3′,4′-methylenedixyphenyl)-benzofuran (**3**, 92.6 mg)

Mp 40–41 °C; IR bands (film): 2959, 1728, 1599,1482, 1463, 1271, 1251,1142, 1025, 937 cm^{-1}; UV_{max} (EtOH): 216 (*s*), 300 (*m*), 317 (*m*) nm, HR-ESIFTMS *m/z* 411.1797 $[M+H]^+$; ^{13}C NMR δ_{ppm} 177.1 *q*, 156.5 *q*, 148.5 *q*, 148.4 *q*, 145.2 *q*, 142.9 *q*, 137.4 *q*, 131.5 *q*, 125.1 *q*, 119.6 *d*, 112.8 *d*, 109.0 *q*, 107.9 *d*, 105.9 *d*, 101.7 *t*, 100.7 *d*, 63.9 *t*, 56.6 *s*, 41.6 *d*, 32.9 *t*, 31.2 *t*, 27.2 *m*, 17.1 *s*, 12.1 *s* ; ^1H NMR δ_{ppm} 7.30 (1H, *dd*, $J=8.12$–1.50), 7.21 (1H, *s*), 6.84 (1H, *s*), 6.76 (1H, *d*, $J=8.12$ Hz), 6.67 (1H, *s*), 6.49 (1H, *s*), 5.88 (2H, *s*), 4.05 (3H, *s*), 4.11 (2H, *m*), 2.77 (2H, *t*, $J=7.43$–7.87 Hz), 2.41 (1H, *m*), 2.02 (2H, *p*) 1.51–1.70 (2H, *m*), 1.20 (3H, *d*, $J=6.97$ Hz), 0.96 (3H, *t*, $J=7.44$–7.45 Hz).

3.3.5. 5-(3″-Acetoxypropyl)-7-methoxy-2-(3′,4′-methylenedioxyphenyl)-benzofuran (**2**, 59.1 mg)

Mp 94–95 °C; IR bands(film): 2959, 1728, 1599, 1483, 1463,1271, 1251, 1142, 1025, 937cm^{-1}; UV_{max} (EtOH): 216 (*s*), 300 (*m*), 317 (*m*) nm; HR-ESIFTMS *m/z* 369.1300 $[M+H]^+$, 391.2640 $[M+Na]^+$; ^{13}C NMR δ_{ppm} 171.5 *q*, 156.6 *q*, 148.5 *q*, 148.4 *q*, 145.2 *q*, 142.9 *q*, 137.3 *q*, 131.5 *q*, 125.1 *q*, 119.6 *d*, 112.7 *d*, 109.0 *d*, 105.9 *d*, 107.9 *d*, 101.7 *t*, 100.7 *d*, 64.3 *t*, 56.6 *s*, 32.9 *t*, 31.1 *t*, 21.4 *s*; ^1H NMR δ_{ppm} 7.40 (1H, *dd*, $J=8.11$–0.88), 7.28 (1H, *d*, $J=0.40$), 6.98 (1H, *s*), 6.89 (1H, *d*, $J=8.12$), 6.81 (1H, *s*), 6.63 (1H, *s*), 6.02 (2H, *s*), 4.14 (2H, *m*), 4.06 (3H, *s*), 2.77 (2H, *t*, $J=7.48$–7.84), 2.03 (2H, *p*), 2.09 (3H, *s*).

3.3.6. 5-(3″-Hydroxypropyl)-7-methoxy-2-(3′,4′-methylenedioxyphenyl)-benzofuran (**1**, 6.5 mg)

IR bands (film) 3463, 2956, 1633, 1473, 1240, 1124, 1039, 935 cm^{-1}; UV_{max} (EtOH): 216 (*s*), 300 (*m*), 317 (*m*) nm; HR-ESIFTMS *m/z* 326.2300; ^{13}C-NMR δ_{ppm} 156.5 *q*, 100.8 *d*, 131.5 *q*, 112.7 *d*, 137.9 *q*, 107.9 *d*, 142.9 *q*, 145.2 *q*, 125.1 *q*, 105.9 *d*, 148.5 *q*, 148.3 *q*, 109.0 *d*, 119.6 *d*, 101.7 *d*, 56.6 *s*, 32.8 *t*, 35.1 *t*, 62.7 *t*; ^1H NMR δ_{ppm} 6.81(1H, *s*), 6.99

(1H, *s*), 6.66 (1H, *s*), 7.34 (1H, *d*, $J=1.47$ Hz), 6.90 (1H, *d*, $J=8.13$ Hz), 7.43 (1H, *dd*, $J=6.56$, 1.53 Hz), 6.02 (1H, *s*), 4.05 (3H, *s*), 1.97 (2H, *t*, $J=7.52$, 7.78 Hz), 2.81 (2H, *p*), 3.74 (2H, *t*, $J=6.37$, 6.37 Hz).

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