Benzofuran Derivatives from *Gerbera saxatilis*

by **Yan-Jun Chen**, **Ya Li**, **Jian-Jun Chen**, and **Kun Gao***

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China
(phone: +86-931-8912592; fax: +86-931-8912582; e-mail: npchem@lzu.edu.cn)

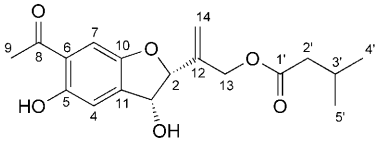
Three new substituted 2,3-dihydro-1-benzofuran derivatives, compounds **1**–**3**, were isolated from two extracts of *Gerbera saxatilis*, together with twelve known constituents. The structures of the new compounds were established by means of detailed spectroscopic analysis and by comparison of analytical data with those reported for structurally related compounds.

Introduction. – A large number of sesquiterpenoids, triterpenoids, coumarins, and glycosides have been isolated and identified from the plants of the family Compositae. In the past, we have conducted several phytochemical investigations of selected *Ligularia*, *Eupatorium,* and *Erigeron* species [1–3], all belonging to the Compositae.

The genus *Gerbera* (Compositae) consists of *ca*. 80 species all over the world, with 20 species being distributed in China, mainly in the southwest [4]. Several *Gerbera* species have long been used as folk remedies, especially as detoxifying and diuretic agents, and for relieving cough and inner heat [5]. Some *Gerbera* species have been reported to contain acetylenes and *para*-hydroxyacetophenone derivatives [6][7], coumarins [6–10], sesquiterpenoids [11], triterpenoids [12], and cyanogenic glycosides [13], some of which were found to exhibit antibacterial properties [12][14].

In continuation of our search for biologically active compounds from Compositae, we studied the whole plant of *Gerbera saxatilis*. Herein, we report the isolation and identification of three new benzofuran derivatives, **1**–**3**, and of a known benzofuran derivative, **4**. In addition, eleven other constituents, including five triterpenoids, **5**–**9**, two coumarins, **10** and **11**, two sesquiterpenoids, **12** and **13**, a hydroxylated acetophenone derivative, **14**, and one glycoside, **15**, were isolated and identified.

Results and Discussion. – The known constituents of *G. saxatilis* were identified by comparing their physical, spectroscopic (IR, NMR), and mass-spectrometric (MS) data with those reported in the literature. Thus, the following compounds were identified: 2-[(2*S**)-6-acetyl-2,3-dihydro-5-hydroxybenzofuran-2-yl]prop-2-enyl 3-methylbutanoate (**4**) [11], (3*S**)-*D*:*C*-friedo-*B*:*A*-neogrammer-9(11)-en-3-ol (**5**) [15], (3*S**)-*D*:*C*-friedo-*B*:*A*-neogrammer-9(11)-en-3-yl acetate (**6**) [16][17], (3*S**)-*B*′:*A*′-neogrammacer-13(18)-en-3-yl acetate (**7**) [18], (3*S**)-*D*-friedoolean-14-en-3-yl acetate (**8**) [19], *D*:*A*-friedooleanan-3-one (**9**) [15], 2,2,10-trimethyl-2*H*,5*H*-pyrano[3,2-*c*] [1]benzopyran-5-one (**10**) [20], 2,3-dihydro-2-(1-hydroxy-1-methylethyl)-7*H*-furo[3,2-*g*] [1]benzopyran-7-one (**11**) [21][22], (1*R**,2*S**,5*R**,8*S**)-4,4,8-trimethyltricyclo[6.3.1.$0^{2,5}$]do-



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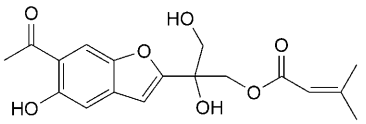

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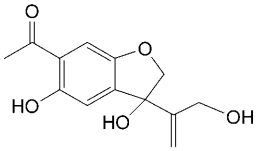

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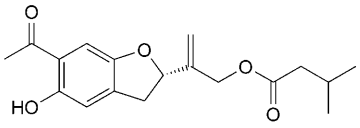

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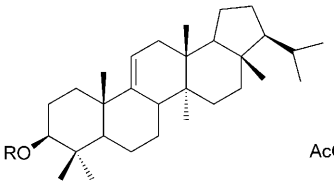

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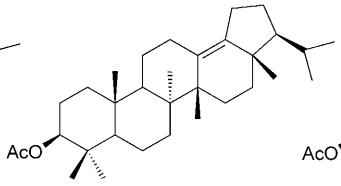

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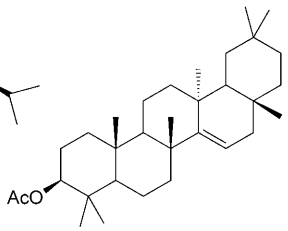

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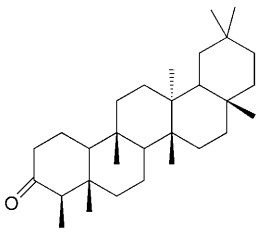

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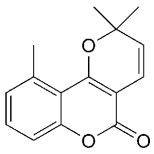

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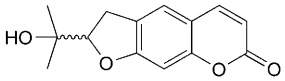

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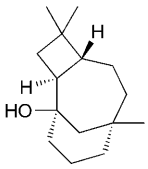

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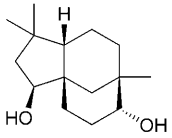

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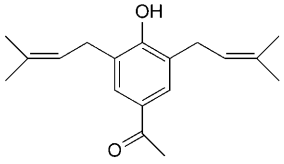

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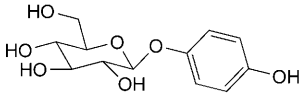

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decan-1-ol (**12**) [23], (3*S**,3a*S**,6*R**,7*R**,9a*S**)-decahydro-1,1,7-trimethyl-3a,7-methano-3a*H*-cyclopentacyclooctene-3,6-diol (**13**) [24], 1-[4-hydroxy-3,5-bis(3-methylbut-2-enyl)phenyl]ethanone (**14**) [6], and 4-hydroxyphenyl β-D-glucopyranoside (**15**) [25][26].

The new compound **1** was obtained as a yellow oil. HR-ESI-MS showed the $[M-H]^-$ peak at *m/z* 333.1347 ($C_{18}H_{21}O_6^+$; calc.333.1338), and EI-MS showed the M^+ signal at *m/z* 334, corresponding to the molecular formula $C_{18}H_{22}O_6$. The IR spectrum of **1** showed absorption bands for OH (3447), ester C=O (1735), and C=C (1636 cm^{-1}) groups, as well as a substituted benzene moiety (1606, 1500, 1426 cm^{-1}). The signals of two Me groups (δ(H) 0.95 (*d*, *J* = 6.6 Hz, 6 H)), one CH_2 group (δ(H) 2.24 (*d*, *J* = 6.9 Hz)), and one CH moiety (δ(H) 2.13 (*m*)) in the ^{1}H-NMR spectrum of **1** (*Table 1*), together with a quaternary C-atom at δ(C) 173.0 in the ^{13}C-NMR spectrum, and a fragment-ion peak at *m/z* 232 ($[M - C_5H_{10}O_2]^+$) in the EI mass spectrum, indicated that **1** contained a (3-methylbutanoyl)oxy group [11].

Table 1. *^{1}H-NMR Data of* **1**–**4**. At 300 MHz (**1**, **2**) or 400 MHz (**3**, **4**) in $CDCl_3$; δ in ppm, *J* in Hz. Arbitrary atom numbering.

Position	**1**	**2**	**3**	**4**
2	5.16 (br. *d*, *J* = 2.4)	–	5.19 (*d*, *J* = 7.2) 5.29 (*d*, *J* = 7.2)	5.26 (*dd*, *J* = 8.8, 8.4)
3	6.17 (*d*, *J* = 2.4)	6.76 (*s*)	–	3.17 (br. *dd*, *J* = 16, 8.4) 3.42 (br. *dd*, *J* = 16, 8.8)
4	7.01 (*s*)	7.06 (*s*)	7.09 (*s*)	6.82 (br. *s*)
7	7.24 (*s*)	7.83 (*s*)	7.21 (*s*)	7.06 (*s*)
9	2.62 (*s*)	2.68 (*s*)	2.62 (*s*)	2.57 (*s*)
13	4.26 (br. *d*, *J* = 11.2) 4.28 (br. *d*, *J* = 11.2)	4.45 (*d*, *J* = 9.6) 4.56 (*d*, *J* = 9.6)	4.24 (br. *d*, *J* = 12.0) 4.38 (br. *d*, *J* = 12.0)	4.65 (br. *d*, *J* = 13.6) 4.70 (br. *d*, *J* = 13.6)
14	5.20 (br. *s*) 5.23 (br. *s*)	3.90 (*d*, *J* = 9.9) 3.93 (*d*, *J* = 9.9)	5.45 (br. *s*) 5.49 (br. *s*)	5.26 (br. *s*) 5.34 (br. *s*)
2′	2.24 (*d*, *J* = 6.9)	5.66 (*s*)	–	2.18 (*d*, *J* = 6.0)
3′	2.13 (*m*)	–	–	2.09 (*m*)
4′	0.95 (*d*, *J* = 6.6)	1.91 (*s*)	–	0.93 (*d*, *J* = 6.0)
5′	0.95 (*d*, *J* = 6.6)	2.15 (*s*)	–	0.93 (*d*, *J* = 6.0)
5-OH	12.00 (*s*)	12.13 (*s*)	12.06 (*s*)	12.21 (*s*)

The ^{1}H-NMR spectrum of **1** further showed the presence of four CH groups (δ(H) 5.16 (br. *d*, *J* = 2.4 Hz); 6.17 (*d*, *J* = 2.4 Hz); 7.01 (*s*); 7.24 (*s*)), an oxygenated CH_2 group (δ(H) 4.26, 4.28 (2 br. *d*, *J* = 11.2 Hz each)), a terminal C=C bond (δ(H) 5.20, 5.23 (2 br. *s*, 1 H each)), an Ac group (δ(H) 2.62 (*s*, 3 H)), and an aromatic OH group (δ(H) 12.00 (*s*)). The corresponding C-atom signals in the ^{13}C-NMR spectrum appeared at δ(C) 87.8 (H–C(2)), 77.2 (H–C(3)), 116.4 (H–C(4)), 109.5 (H–C(7)), 63.3 (CH_2(13)), 144.1 (H–C(12)), 113.9 (H–C(14)), and 203.9 (C(8))[1]). Besides, four aromatic quaternary C-atoms were observed at δ(C) 157.7 (C(5)), 120.5 (C(6)), 152.6 (C(10)), and 133.2 (C(11)). By analyzing the above data and comparing it to related literature data [11][27][28], the structure of **1** was deduced as a 2,3-dihydrobenzofuran derivative with an Ac group, two OH functions, and a 3-[(3-methylbutanoyl)oxy]prop-2-enyl moiety. The positions of the substituents were determined by the following HMBC correlations: H–C(4)/C(5), H–C(7)/C(10), H–C(7)/C(6), OH/C(5), Me(9)/C(6), H–C(2)/

[1]) Arbitrary atom numbering.

C(12), H–C(2)/C(3), CH_2(13)/C(12), and CH_2(13)/C(14). Also, the ^{1}H- and ^{13}C-NMR spectra of **1** were very similar to those of the known compound **4** [11], except that the CH_2(3) resonances (δ(H) 3.42, 3.17 (*2dd*)) of **4** were not present in **1**, which, instead, showed an oxygenated CH group (δ(H) 6.17; δ(C) 77.2). Thus, compound **1** was the 3-hydroxy derivative of **4**.

The relative configuration of **1** was determined on the basis of the small observed NMR coupling constant between H–C(2) and H–C(3) ($J(2,3) = 2.4$ Hz), in combination with an NOE experiment: irradiation of H–C(3) at δ(H) 6.17 enhanced the signal at δ(H) 5.16 (H–C(2)). Thus, H–C(2) and H–C(3) were on the same side of the ring. So, the structure of **1** was determined as 2-[(2*S**,3*S**)-6-acetyl-2,3-dihydro-3,5-dihydroxy-1-benzofuran-2-yl]prop-2-enyl 3-methylbutanoate.

Table 2. *^{13}C-NMR Data of* **1**–**4**. At 75 MHz (**1**, **2**) or 100 MHz (**3**, **4**) in $CDCl_3$; δ in ppm, *J* in Hz. Arbitrary atom numbering.

Atom	**1**	**2**	**3**	**4**
C(2)	87.8 (*d*)	162.6 (*s*)	73.0 (*t*)	82.9 (*d*)
C(3)	77.2 (*d*)	109.8 (*d*)	87.9 (*s*)	35.9 (*t*)
C(4)	116.4 (*d*)	114.8 (*d*)	117.3 (*d*)	114.6 (*d*)
C(5)	157.7 (*s*)	158.4 (*s*)	157.4 (*s*)	158.1 (*s*)
C(6)	120.5 (*s*)	104.8 (*s*)	121.8 (*s*)	117.9 (*s*)
C(7)	109.5 (*d*)	108.1 (*d*)	109.6 (*d*)	108.1 (*d*)
C(8)	203.9 (*s*)	203.8 (*s*)	203.8 (*s*)	203.6 (*s*)
C(9)	26.9 (*q*)	26.7 (*q*)	29.7 (*q*)	26.7 (*q*)
C(10)	152.6 (*s*)	146.8 (*s*)	151.2 (*s*)	151.7 (*s*)
C(11)	133.2 (*s*)	135.8 (*s*)	137.8 (*s*)	137.2 (*s*)
C(12)	144.1 (*s*)	74.4 (*s*)	144.7 (*s*)	142.7 (*s*)
C(13)	63.3 (*t*)	65.6 (*t*)	64.1 (*t*)	63.4 (*t*)
C(14)	113.9 (*t*)	65.3 (*t*)	115.7 (*t*)	114.7 (*t*)
C(1′)	173.0 (*s*)	168.8 (*s*)	–	172.6 (*s*)
C(2′)	43.2 (*t*)	112.3 (*d*)	–	43.2 (*t*)
C(3′)	25.7 (*d*)	159.3 (*s*)	–	25.6 (*d*)
Me(4′)	22.3 (*q*)	27.6 (*q*)	–	22.4 (*q*)
Me(5′)	22.3 (*q*)	20.5 (*q*)	–	22.4 (*q*)

Compound **2** was obtained as a yellow oil. HR-ESI-MS showed the $[M+Na]^+$ signal at *m*/*z* 371.1102 ($C_{18}H_{20}NaO_7^+$; calc. 371.1107), and EI-MS revealed the M^+ peak at *m*/*z* 348, with fragment-ions at *m*/*z* 248 ($[M-C_5H_8O_2]^+$), 174 ($[M-C_5H_8O_2-C_3H_6O_2]^+$), and 83 ($C_5H_7O^+$), in accord with the molecular formula $C_{18}H_{20}O_7$. The IR spectrum of **2** suggested the presence of OH groups (3425), an α,β-unsaturated ester function (1710, 1638), and a substituted benzene moiety (1600, 1520, 1460 cm^{-1}). The ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*, resp.) displayed an Ac group (δ(H) 2.68 (*s*); δ(C) 26.7)), three CH groups (δ(H) 6.76 (*s*), 7.06 (*s*), 7.83 (*s*); δ(C) 109.8, 114.8, 108.1), an OH group (δ(H) 12.13 (*s*)), and six quaternary C-atoms (δ(C) 203.8, 162.6, 158.4, 104.8, 146.8, 135.8). Thus, compound **2** was also a 6-acetyl-5-hydroxybenzofuran derivative, with a substituent at C(2) [11].

The NMR signals at δ(H) 1.91 (*s*, 3 H), 2.15 (*s*, 3 H), and 5.66 (*s*, 1 H), and at δ(C) 168.8 (C_q), 159.3 (C_q), 112.3 (CH), 27.6 (Me), and 20.5 (Me) indicated the presence of a

3-methylbutenoate, as confirmed by the EI-MS signals at *m/z* 248 ($[M-C_5H_8O_2]^+$), 100 ($C_5H_8O_2^+$), and 83 ($C_5H_7O^+$). In addition, the signals of two OCH_2 groups at δ(C) 65.6 (C(13)) and 65.3 (C(14)), and of an oxygenated quaternary C-atom at δ(C) 74.4 (C(12)) were observed. These moieties could be connected easily by HMBC correlations of H–C(13) to C(1′), C(12), and C(14), respectively.

From the above data, the structure of compound **2** was deduced as 2-(6-acetyl-5-hydroxy-1-benzofuran-2-yl)-2,3-dihydroxypropyl 3-methylbut-2-enoate. Unfortunately, the quantity of **2** isolated was too small to determine its absolute configuration, especially since no effective chemical transformation could be made.

Compound **3** was obtained as an amorphous, optically active yellow powder ($[\alpha]_D^{29}=+10$ ($c=0.2$, $CHCl_3$)). HR-ESI-MS showed the $[M-H]^-$ signal at *m/z* 249.0771 ($C_{13}H_{13}O_5^-$, calc. 249.0763), and EI-MS showed the M^+ peak at *m/z* 250, in accord with the molecular formula $C_{13}H_{14}O_5$. The IR spectrum of **3** suggested the presence of OH groups (3443), a C=C bond (1635), and a substituted benzene moiety (1603, 1501, 1452 cm^{-1}). By comparing the IR and NMR spectra of **1**–**3**, compound **3** was deduced to be another 6-acetyl-5-hydroxybenzofuran derivative.

A comparison of the ^{1}H- and ^{13}C-NMR spectra of **3** and **1** revealed that the signals of the 3-methylbutanoate moiety of **1** were absent in **3**; instead, a 3-hydroxyprop-2-enyl residue was observed for **3**, with signals of an oxygenated CH_2 group (δ(H) 4.24, 4.38 (2*d*, $J=12$ Hz, 1 H each); δ(C) 64.1) and a terminal C=C bond (δ(H) 5.45, 5.49 (br. *s*, 1 H each); δ(C) 115.7 (CH_2), 144.7 (C)). The oxygenated CH_2(3) group of **1** was replaced with an oxygenated quaternary C-atom (δ(C) 87.9) in **3**. This suggested a 3-hydroxyprop-2-enyl moiety at C(3) in **3**. The structure of **3** could be further deduced by the HMBC correlations between CH_2(14) and both C(13) and C(3). Again, the absolute configuration of **3** could not be determined due to only minute amounts of material isolated. So, the structure of **3** was deduced as 1-{2,3-dihydro-3,5-dihydroxy-3-[1-(hydroxymethyl)ethenyl]-1-benzofuran-6-yl}ethanone.

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Experiment Part

General. Column chromatography (CC): silica gel (200–300 mesh; *Qingdao Marine Chemical Factory*). TLC: silica gel GF_{254} plates (10–40 μm; *Qingdao*). Optical rotations: *Perkin-Elmer-341* polarimeter. IR Spectra: *Nicolet NEXUS-670 FT-IR* spectrometer. ^{1}H- and ^{13}C-NMR Spectra: *Varian Mercury-300BB* (300/75 MHZ) and *Varian Inova-400* spectrometers (400/100 MHz), in $CDCl_3$, δ in ppm rel. to Me_4Si, *J* in Hz. EI-MS: *VG ZAB-HS* instrument, at 70 eV; in *m/z*. HR-ESI-MS: *Bruker APEX-II* instrument, with glycerol as matrix.

Plant Material. *Gerbera saxatilis* plants were collected from Huili County, Sichuan Province, P. R. China, in 2004, and identified by Prof. *Guoliang Zhang*, School of Life Science, Lanzhou University, P. R. China.

Extraction and Isolation. The air-dried whole-plant material was separated into two parts: *1*) roots and stems, and *2*) leaves. The dried powder of the roots and stems (1.955 kg) was extracted at r.t. with MeOH (4×7 d). The combined extract was evaporated, and the residue (253.5 g) was subjected to CC (SiO_2; petroleum ether (PE)/AcOEt 1:0, 60:1, 30:1, 15:1, 5:1, 3:1, 1:1, 0:1, then MeOH): nine fractions (*Fr. A*–*Fr. I*). *Fr. C* afforded a mixture of **7** and **8** (11 mg), which was not fully separable by CC. The crystalline material from *Fr. D* was recrystallized from PE/acetone 20:1 to afford pure **14** (11 mg). From

Fr. E, stigmasterol was obtained. The residue of *Fr. E* was subjected to CC (SiO_2; PE/AcOEt 15:1, 10:1, 5:1, 3:1) and further purified by prep. TLC (SiO_2; $CHCl_3$/AcOEt 20:1) to afford **4** (2 mg). *Fr. F* was subjected to CC (SiO_2; PE/AcOEt 10:1, 5:1, 3:1) to provide two subfractions: *Fr. F.1* and *Fr. F.2.* The former, *Fr. F.1*, was separated by repeated CC (SiO_2; PE/acetone 20:1, 15:1, 10:1, 5:1, 1:1) to afford five further subfractions: *Fr. F.1.1–Fr. F.1.5. Fr. F.1.4* was further purified by CC (SiO_2; PE/AcOEt 10:1, 5:1, 3:1) to afford **12** (4 mg). *Fr. F.1.5* was also purified by CC (SiO_2; PE/acetone 5:1, 3:1) to provide **3** (2 mg). *Fr. F.2* was further separated by CC (SiO_2; PE/acetone 10:1, 5:1, 3:1) and prep. TLC (SiO_2; $CHCl_3$/acetone 20:1) to give **1** (3 mg). Recrystallization of the residue of *Fr. H* from MeOH afforded **11** (8 mg); the remaining mother liquor of *Fr. H* was subjected to CC to afford eight subfractions: *Fr. H.1–Fr. H.8. Fr. H.5* was further separated by repeated CC (SiO_2; $CHCl_3$/AcOEt 10:1, 5:1, 3:1, then $CHCl_3$/MeOH 50:1 and 40:1) to afford **13** (2 mg).

The dried powder of the *leaves* (915 g) was extracted at r.t. with acetone (4×7 d). The combined extracts were evaporated, and the residue (70.5 g) was subjected to CC (SiO_2; PE/AcOEt 1:0, 60:1, 30:1, 15:1, 5:1, 3:1, 1:1, 0:1, then MeOH) to afford nine fractions (*Fr. a–Fr. i*). From *Fr. b*, crude **6** was obtained, which was recrystallized from PE/acetone 30:1 to afford pure **6** (15 mg). From *Fr. c*, crude **9** was obtained and recrystallized from PE/acetone 30:1 to afford pure **9** (8 mg). From *Fr. d*, crude **10** was obtained and recrystallized from acetone to afford pure **10** (16 mg). The mother liquor of *Fr. d* was separated into two subfractions, *Fr. d.1* and *Fr. d.2*, according to TLC. *Fr. d.1* was further purified by CC (SiO_2, PE/$CHCl_3$ 5:1, 3:1, 1:1) to provide **5** (11 mg). *Fr. g* was separated by CC (SiO_2; PE/AcOEt 4:1, 2:1, 1:1) to afford three subfractions: *Fr. g.1–Fr. g.3. Fr. g.1* was further purified by prep. TLC (SiO_2; PE/AcOEt 1:1) to give **2** (1 mg). *Fr. h* was subjected to CC (SiO_2; $CHCl_3$/AcOEt 10:1, 5:1, 2:1, 1:1) to afford crude **15**, which was recrystallized from MeOH to afford the pure compound (5 mg).

2-[(2S,3S*)-6-Acetyl-2,3-dihydro-3,5-dihydroxy-1-benzofuran-2-yl]prop-2-enyl 3-Methylbutanoate* (**1**). Yellow oil. $[\alpha]_D^{29} = -45$ ($c = 0.3$, $CHCl_3$). IR (KBr): 3447, 1735, 1636, 1606, 1500, 1426. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS (70 eV): 334 (8, M^+), 271 (7), 250 (2), 232 (41, $[M - C_5H_{10}O_2]^+$), 217 (40), 203 (2), 102 (3, $C_5H_{10}O_2^+$), 85 (40, $C_5H_9O^+$), 57 (80), 43 (100). HR-ESI-MS: 333.1347 ($[M-H]^-$, $C_{18}H_{21}O_6^-$; calc. 333.1338).

2-(6-Acetyl-5-hydroxy-1-benzofuran-2-yl)-2,3-dihydroxypropyl 3-Methylbut-2-enoate (**2**). Yellow oil. $[\alpha]_D^{29} = +47$ ($c = 0.1$, $CHCl_3$). IR (KBr): 3425, 1710, 1638, 1600, 1520, 1460. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS (70 eV): 348 (0.4, M^+), 248 (0.8, $[M - C_5H_8O_2]^+$), 218 (9), 203 (7), 189 (6), 174 (2, $[M - C_5H_8O_2 - C_3H_6O_2]^+$), 146 (4), 100 (1, $C_5H_8O_2^+$), 83 (100, $C_5H_7O^+$), 55 (23), 43 (32). HR-ESI-MS: 371.1102 ($[M+Na]^+$, $C_{18}H_{20}NaO_7^+$; calc. 371.1107).

1-{2,3-Dihydro-3,5-dihydroxy-3-[1-(hydroxymethyl)ethenyl]-1-benzofuran-6-yl}ethanone (**3**). Yellow powder. $[\alpha]_D^{29} = +10$ ($c = 0.2$, $CHCl_3$). IR (KBr): 3443, 1635, 1603, 1501, 1452. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS (70 eV): 250 (6, M^+), 232 (2, $[M - H_2O]^+$), 219 (13), 206 (3), 179 (14), 175 (2, $[M - H_2O - C_3H_5O]^+$), 161 (9), 152 (10), 123 (12), 109 (16), 107 (16), 85 (59), 55 (41), 43 (100). HR-ESI-MS: 249.0771 ($[M-H]^-$, $C_{13}H_{13}O_4^-$; calc. 249.0763).

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