New Oligosaccharide Esters and Xanthone *C*-Glucosides from *Polygala telephioides*

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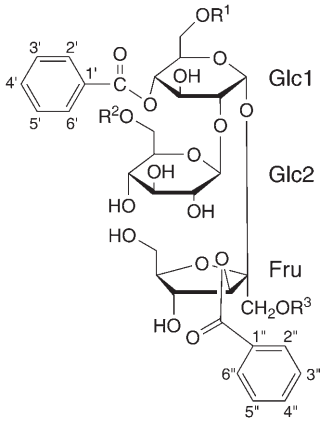
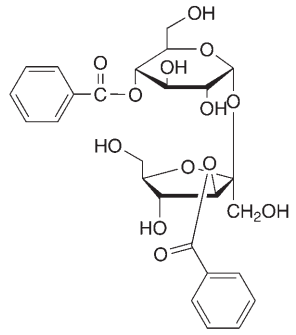
Three new oligosaccharide esters named telephioses D (**4**), E (**5**), and F (**6**), and two new xanthone *C*-glucosides, telephioxanthones A (**7**) and B (**8**), together with five known oligosaccharide esters and mangiferin, were isolated from the whole plant of *Polygala telephioides* WILLD. The structures of the new compounds were elucidated on the basis of spectral data.

Introduction. – In the course of our search for new bioactive compounds in Polygalaceae species, we have previously reported the isolation of several oligosaccharide multi-esters and xanthones from *Polygala tenuifolia* and *P. tricornis* [1–5]. Continuing our investigation of the genus *Polygala*, we have now investigated *Polygala telephioides* WILLD. This herbaceous plant of southern China, used as a detoxification agent for heroin poisoning in folk medicines, was reported to contain oligosaccharide esters, benzophenone *C*-glucosides, and the flavone *C*-glucoside telephioidin [6–8]. Our study has led to the isolation of eleven constituents, including eight oligosaccharide multi-esters and three xanthone *C*-glucosides. We describe in this paper the isolation and structural elucidation of the three new oligosaccharide multi-esters **4**–**6** and the two new xanthone *C*-glucosides (**7** and **8**) from *P. telephioides*. The known compounds were identified by extensive NMR analyses as telephiose A (**1**) [6], telephiose B (**2**) [6], telephiose C (**3**) [6], 6-*O*-benzoyl-3′-*O*-(3,4,5-trimethoxycinnamoyl)sucrose (= 3-*O*-[(2*E*)-1-oxo-3-(3,4,5-trimethoxyphenyl)prop-2-enyl]-β-D-fructofuranosyl 6-*O*-benzoyl-α-D-glucopyranoside) [9], 6-*O*-benzoyl-3′-*O*-sinapoylsucrose (= 3-*O*-[(2*E*)-3-(4-hydroxy-3,5-dimethoxyphenyl)-1-oxoprop-2-enyl]-β-D-fructofuranosyl 6-*O*-benzoyl-α-D-glucopyranoside) [9], and mangiferin (= 2-(β-D-glucopyranosyl)-1,3,6,7-tetrahydroxy-9*H*-xanthen-9-one) [10].

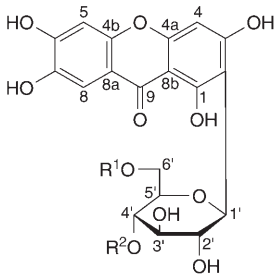
Results and Discussion. – Telephiose D (**4**) was obtained as an amorphous powder, and its positive-ion ESI-TOF-MS exhibited quasi-molecular ions $[M+NH_4]^+$, $[M+Na]^+$, and $[M+K]^+$ at *m*/*z* 856.34, 861.29, and 877.25, respectively, indicating the molecular formula $C_{38}H_{46}O_{21}$. On acid hydrolysis, **4** afforded D-glucose, D-fructose, and benzoic acid. On the basis of spectral evidence, the structure of compound **4** was established as 1-*O*-acetyl-3-*O*-benzoyl-β-D-fructofuranosyl *O*-6-*O*-acetyl-β-D-glucopyranosyl-(1 → 2)-6-*O*-acetyl-4-*O*-benzoyl-α-D-glucopyranoside, named telephiose D.



1 $R^1 = R^3 = Ac$, $R^2 = H$
2 $R^1 = H$, $R^2 = R^3 = Ac$
3 $R^1 = R^2 = R^3 = H$
4 $R^1 = R^2 = R^3 = Ac$
5 $R^1 = Ac$, $R^2 = R^3 = H$

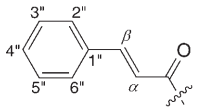


6



	R^1	R^2
9	cinnamoyl	H
10	H	cinnamoyl

cinnamoyl =



The ^{1}H-NMR spectrum of **4** (*Table 1*) suggested the presence of three acetyl groups, two benzoyl moieties, two anomeric H-atoms resonating at δ(H) 5.65 (*d*, $J = 3.5$) and 4.52 (*d*, $J = 8.0$), which indicated the α- and β-configurations of the anomeric protons of two glucose units, respectively. The ^{13}C-NMR spectrum (*Table 2*) showed three anomeric C-atom signals resonating at δ(C) 93.0, 103.4, and 106.0, respectively. Comparison of the ^{1}H- and ^{13}C-NMR data of **4** with those of telephiose A (**1**) and telephiose B (**2**) suggested that the structure of **4** is closely related to that of **1** and **2**, with the same molecular subunits, except for the presence of an additional acetyl group in **4**. All the H- and C-atoms were unambiguously assigned by ^{1}H,^{1}H-COSY, DEPT, HSQC, and HMBC experiments. In the HMBC plot, correlations from the proton signals at δ(H) 4.19 and 4.70 (Glc1 CH_2(6)) to the acetyl C=O signal at δ(C) 173.3, from the proton signals at δ(H) 4.20 and 4.53 (Glc2 CH_2(6)) to the acetyl C=O signal at δ(C) 172.4, and from the proton signals at δ(H) 4.07 and 4.50 (Fru CH_2(1)) to the acetyl C=O signal at δ(C) 172.1 permitted the determination of the position of each acetyl residue.

Telephiose E (**5**) was obtained as an amorphous powder with a molecular formula $C_{34}H_{42}O_{19}$, as deduced by data from the positive-ion ESI-TOF-MS showing the $[M + Na]^+$ ion peak at *m*/*z* 777.21. On acid hydrolysis, **5** afforded D-glucose, D-fructose, and benzoic acid. The ^{1}H- and ^{13}C-NMR spectral data (*Tables 1* and *2*) of **5** were similar to those of telephiose C (**3**) reported in [6], except for the presence of one set of

Table 1. *^{1}H-NMR Data* (500 MHz, CD_3OD) *of Compounds* **4**–**6**. δ in ppm, J in Hz. Arbitrary atom numbering.

		4	**5**	**6**
Glc1:	H–C(1)	5.65 (*d*, *J* = 3.5)	5.71 (*d*, *J* = 3.5)	5.46 (*d*, *J* = 3.5)
	H–C(2)	3.54 (*dd*, *J* = 3.5, 10.0)	3.51 (*dd*, *J* = 3.5, 10.0)	3.73–3.75 (*m*)
	H–C(3)	3.88–3.89 (*m*)	3.86–3.89 (*m*)	3.51 (*dd*, *J* = 4.0, 9.0)
	H–C(4)	5.10 (*t*, *J* = 9.5)	5.05 (*t*, *J* = 9.5)	4.98 (*dd*, *J* = 9.5)
	H–C(5)	4.38–4.39 (*m*)	4.42–4.44 (*m*)	4.11 (*ddd*, *J* = 3.5, 5.0, 9.5)
	CH_2(6)	4.19 (*dd*, *J* = 7.5, 12.5), 4.70 (*d*, *J* = 11.0)	4.17 (*dd*, *J* = 8.0, 12.0), 4.69–4.70 (*m*)	3.83 (*dd*, *J* = 6.0, 12.5), 3.78 (*dd*, *J* = 3.5, 10.0)
Glc2:	H–C(1)	4.52 (*d*, *J* = 8.0)	4.44 (*d*, *J* = 7.5)	
	H–C(2)	3.46 (*d*, *J* = 8.0)	3.48–3.49 (*m*)	
	H–C(3)	3.29–3.30 (*m*)	3.30 (overlapped)	
	H–C(4)	3.40–3.42 (*m*)	3.44–3.46 (*m*)	
	H–C(5)	3.35–3.37 (*m*)	3.30–3.32 (*m*)	
	CH_2(6)	4.20–4.23 (*m*), 4.53 (*dd*, *J* = 6.5, 12.0)	3.22–3.24 (*m*), 3.29 (overlapped)	
Fru:	CH_2(1)	4.07 (*d*, *J* = 12.0), 4.50–4.52 (*m*)	3.51 (*d*, *J* = 12.0), 3.72 (*d*, *J* = 11.5)	3.59 (*d*, *J* = 12.5), 3.69 (*d*, *J* = 12.5)
	H–C(3)	5.60 (*d*, *J* = 8.0)	5.58 (*d*, *J* = 8.0)	5.53 (*d*, *J* = 7.0)
	H–C(4)	4.42 (*t*, *J* = 8.0)	4.45–4.46 (*m*)	4.42 (*t*, *J* = 7.0)
	H–C(5)	4.02–4.04 (*m*)	3.96 (*dt*, *J* = 2.0, 10.5)	3.98 (*ddd*, *J* = 3.5, 6.5, 10.5)
	CH_2(6)	3.83 (*dd*, *J* = 3.0, 12.0), 3.91 (*d*, *J* = 10.0)	3.83–3.84 (*m*), 3.89–3.90 (*m*)	3.78 (*d*, *J* = 10.0), 3.85 (*dd*, *J* = 6.0, 12.0)
	Ac(R^1)	2.11 (*s*, 3 H)	1.96 (*s*, 3 H)	
	Ac(R^2)	2.08 (*s*, 3 H)		
	Ac(R^3)	2.02 (*s*, 3 H)		
Bz(Glc1):	H–C(2′,6′)	7.84 (*d*, *J* = 7.0)	7.82 (*d*, *J* = 7.0)	7.84 (*d*, *J* = 7.0)
	H–C(3′,5′)	7.51 (*dd*, *J* = 7.0)	7.45 (*dd*, *J* = 7.0)	7.42 (*dd*, *J* = 7.0)
	H–C(4′)	7.65 (*t*, *J* = 7.0)	7.59 (*t*, *J* = 7.0)	7.57 (*t*, *J* = 7.0)
Bz(Fru):	H–C(2″,6″)	8.15 (*d*, *J* = 7.0)	8.10 (*d*, *J* = 7.0)	8.13 (*d*, *J* = 7.0)
	H–C(3″,5″)	7.53 (*dd*, *J* = 7.0)	7.47 (*dd*, *J* = 7.0)	7.47 (*dd*, *J* = 7.0)
	H–C(4″)	7.68 (*t*, *J* = 7.0)	7.68 (*t*, *J* = 7.0)	7.61 (*t*, *J* = 7.0)

acetyl signals (δ(H) 1.96 (*s*, 3 H); δ(C) 172.5 and 20.6) in **5**. The position of the acetyl linkage was determined at C(6) of Glc1 by the HMBC experiment (cross-peak δ(H) 4.17 and 4.69 (Glc1 CH_2(6))/δ(C) 172.5 (C=O)). From the above data, the structure of **5** was determined as 3-*O*-benzoyl-β-D-fructofuranosyl *O*-β-D-glucopyranosyl-(1 → 2)-6-*O*-acetyl-4-*O*-benzoyl-α-D-glucopyranoside, and this new compound was named telephiose E.

Telephiose F (**6**) was obtained as an amorphous powder. Its positive-ion ESI-TOF-MS showed the $[M+Na]^+$ and $[M+K]^+$ ion peaks at *m*/*z* 573.09 and 589.07, respectively, in accordance with the molecular formula $C_{26}H_{30}O_{13}$, as supported by the ^{1}H- and ^{13}C-NMR data (*Tables 1* and *2*). On acid hydrolysis, **6** gave D-glucose, D-fructose, and benzoic acid. The spectral data led us to conclude that telephiose F (**6**) was 3-*O*-benzoyl-β-D-fructofuranosyl 4-*O*-benzoyl-α-D-glucopyranoside.

The IR spectrum of **6** showed the presence of OH (3405 cm^{-1}) and C=O groups (1720 cm^{-1}), double bonds (1633 cm^{-1}), and aromatic rings (1604, 1513, and 1452 cm^{-1}). The ^{1}H-NMR spectrum exhibited two groups of benzoyl-proton signals, together with a anomeric proton at δ(H) 5.46 (*d*, *J* = 3.5, Glc

Table 2. *^{13}C-NMR Data* (125 MHz, CD_3OD) *of Compounds* **4**–**6**. δ in ppm. Arbitrary atom numbering.

		4	**5**	**6**
Glc1:	C(1)	93.0	92.8	93.1
	C(2)	81.6	81.7	72.8
	C(3)	71.0	71.6	73.1
	C(4)	72.4	72.4	72.8
	C(5)	69.6	69.4	72.5
	C(6)	64.4	64.8	62.0
Glc2:	C(1)	106.0	105.9	
	C(2)	75.2	75.3	
	C(3)	77.5	77.7	
	C(4)	70.9	71.4	
	C(5)	75.0	78.1	
	C(6)	63.9	62.0	
Fru:	C(1)	66.3	63.1	65.1
	C(2)	103.4	105.5	105.4
	C(3)	79.8	79.9	80.6
	C(4)	73.9	74.1	74.6
	C(5)	84.4	84.7	85.1
	C(6)	63.9	62.8	63.1
Ac(R^1):		173.3, 20.8	172.5, 20.6	
Ac(R^2):		172.4, 20.7		
Ac(R^3):		172.1, 20.7		
Bz(Glc1):	C(1′)	130.9	131.0	131.1
	C(2′,6′)	130.8	130.8	130.8
	C(3′,5′)	129.6	129.5	129.5
	C(4′)	134.7	134.5	134.5
	C=O	167.0	167.1	167.2
Bz(Fru):	C(1″)	130.7	130.8	130.8
	C(2″,6″)	130.6	130.6	129.7
	C(3″,5″)	129.8	129.7	129.7
	C(4″)	134.6	134.5	134.4
	C=O	166.9	167.0	166.9

H−C(1)). In the ^{13}C-NMR spectrum, two anomeric C-atoms appeared at δ(C) 93.1 and 105.4, respectively. All these data inferred that **6** is a sucrose esterified with two benzoic acids. In the HMBC plot, H−C(3) of the fructose residue and H−C(4) of the glucose residue were correlated to an ester C=O at δ(C) 166.9 and 167.2, respectively.

Telephioxanthone A (**7**) was isolated as a yellow powder. The negative-ion ESI-TOF-MS of **7** showed a quasi-molecular ion peak at *m*/*z* 551.03 ($[M-H]^-$), and in conjunction with the analysis of the ^{13}C-NMR spectrum, its molecular formula was deduced to be $C_{28}H_{24}O_{12}$. Compound **7** was shown to be 6′-*O*-[(*E*)-cinnamoyl]mangiferin[1]), named telephioxanthone A.

The ^{1}H-NMR spectrum (*Table 3*) of **7** displayed three *s* (δ(H) 6.35, 6.84, and 7.35), a set of (*E*)-cinnamoyl (= 3-phenylacryloyl) proton signals (δ(H) 7.70 (*dd*, *J* = 1.5, 8.5, 2 H), 7.38 (*d*, *J* = 6.0, 2 H),

[1]) Trivial numbering; for systematic names, see *Exper. Part.*

Table 3. *^{1}H- and ^{13}C-NMR Data* (500 and 125 MHz, resp., (D_6)DMSO) *of Compounds* **7** *and* **8**. δ in ppm, J in Hz. Arbitrary atom numbering.

		7		**8**	
		δ(H)	δ (C)	δ(H)	δ(C)
Aglycone:	C(1)		162.0		161.9
	C(2)		107.3		107.1
	C(3)		163.8		164.0
	H–C(4)	6.35 (*s*)	93.0	6.39 (*s*)	93.2
	C(4a)		156.3		156.3
	C(4b)		150.7		150.7
	H–C(5)	6.84 (*s*)	102.6	6.87 (*s*)	102.6
	C(6)		154.0		154.0
	C(7)		143.7		143.7
	H–C(8)	7.35 (*s*)	108.0	7.39 (*s*)	108.0
	C(8a)		111.6		111.6
	C(8b)		101.3		101.2
	C(9)		179.0		179.0
Glucose:	H–C(1′)	4.61 (*d*, J = 10.0)	73.1	4.68 (*d*, J = 10.0)	73.1
	H–C(2′)	4.08 (*dd*, J = 7.0)	69.9	4.25 (*dd*, J = 7.0)	70.2
	H–C(3′)	3.22–3.23 (*m*)	78.7	3.51–3.52 (*m*)	76.2
	H–C(4′)	3.23–3.25 (*m*)	70.5	4.77 (*t*, J = 9.5)	72.1
	H–C(5′)	3.45 (*t*, J = 7.0)	78.1	3.46 (*t*, J = 7.0)	79.3
	CH_2(6′)	4.06 (*d*, J = 7.0), 4.48 (*dd*, J = 7.0, 12.0)	64.8	3.34–3.35 (*m*), 3.42 (*dd*, J = 7.0, 12.0)	61.2
Cinnamic acid:	C(1″)		133.9		134.0
	H–C(2″,6″)	7.70 (*dd*, J = 1.5, 8.5)	128.4	7.75 (*dd*, J = 2.5, 7.0)	128.3
	H–C(3″,5″)	7.38 (*dd*, J = 6.0)	128.8	7.44 (*dd*, J = 6.0)	128.9
	H–C(4″)	7.39 (*dd*, J = 2.0, 6.0)	130.4	7.49 (*dd*, J = 2.5, 7.0)	130.4
	H–C(α)	6.63 (*d*, J = 16.0)	117.9	6.68 (*d*, J = 16.0)	118.2
	H–C(β)	7.62 (*d*, J = 16.0)	144.7	7.69 (*d*, J = 16.0)	144.7
	C=O		166.3		165.7

7.39 (*dd*, J = 2.0, 6.0, 1 H), 6.63 (*d*, J = 16.0, 1 H), and 7.62 (*d*, J = 16.0, 1 H)) and a Glc unit, the anomeric proton resonating at δ(H) 4.61 (*d*, J = 10.0). The ^{13}C-NMR data (*Table 3*) of **7** were almost the same as those of mangiferin [10], except for the down-field-shifted C(6) of the glucosyl moiety ($\Delta\delta$ 3.2), indicating the esterification of this position by a cinnamic acid. In the HMBC plot, CH_2(6) protons of the glucosyl residue were correlated to an ester C=O at δ(C) 166.3, further supporting the structure **7**.

Telephioxanthone B (**8**) was isolated as a pale yellow powder. The positive-ion ESI-TOF-MS of **8** gave quasi-molecular ion peaks at m/z 553.14 ($[M+H]^+$) and m/z 575.12 ($[M+Na]^+$), respectively, consistent with a molecular formula $C_{28}H_{24}O_{12}$. From the spectral data, the structure of telephioxanthone B was established as 4′-*O*-[(*E*)-cinnamoyl]mangiferin[1]).

The ^{1}H-NMR spectrum (*Table 3*) of **8** showed three *s*, a set of (*E*)-cinnamoyl proton signals and a Glc unit. When the ^{1}H-NMR spectrum was compared with that of **7**, the proton signal of H–C(4) of the glucose moiety of **8** was shifted downfield to δ(H) 4.77, whereas the proton signals of CH_2(6) were shifted upfield to δ(H) 3.34 and 3.42. In the ^{13}C-NMR spectrum, C(4) of the glucose residue of **8** was also shifted downfield by 1.6 ppm. Moreover, a HMBC cross-peak was observed between δ(H) 4.77 (*t*, J = 9.5, Glc H–C(4)) and the ester C=O at δ(C) 165.7.

Among the known compounds, telephiose A – C (**1** – **3**) have been found so far only in *P. telephioides* [6]. The 6-*O*-benzoyl-3′-*O*-(3,4,5-trimethoxycinnamoyl)sucrose, 6-*O*-benzoyl-3′-*O*-sinapoylsucrose, and mangiferin have been previously reported in the genus *Polygala* [9][11] but are described here for the first time in *P. telephioides.*

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Experimental Part

General. Column chromatography (CC): silica gel (200 – 300 mesh; *Qingdao Marine Chem. Co. Ltd.*), *D101* porous polymer resin (*Tianjin Chem. Ind. Co. Ltd.*), and *Sephadex LH-20* (*Pharmacia*). TLC: $HSGF_{254}$ precoated silica gel plates (*Merck*). Semi-prep. HPLC: *Waters-600* instrument; *Waters* column *Prep. NovaPak HR* C_{18} (300 × 10 mm i.d., 6 μ), flow rate 2.5 ml/min; *Waters 2487* dual λ absorbance detector (detection wavelength 228 nm). GC: *Agilent-6890N* gas chromatograph; *HP-5* capillary column (28 m × 0.32 mm i.d.); FID detection; detector temp. 260°; column temp. 180°; carrier gas N_2; flow rate 40 ml/min. Melting points: *X-4* digital micro melting point apparatus; uncorrected. Optical rotations: *Perkin-Elmer 243B* digital polarimeter. UV Spectra: *Shimadzu* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra (KBr): *Nicolet-Avatar 360* spectrometer; in cm^{-1}. NMR Spectra: *Bruker AM-500* or *Jeol JNM-A300* spectrometers with $SiMe_4$ as internal standard. ESI-TOF-MS: *Applied-Biosystems QSTAR* mass spectrometer in both positive and negative modes; in *m*/*z*.

Plant Material. The whole plants of *Polygala telephioides* WILLD. were purchased from Guangdong Corporation of Traditional and Herbal Medicine, P. R. China, in May 2005, and identified by one of the authors (*Pengfei Tu*). A voucher specimen (A20050506) is deposited in the herbarium of the Modern Research Center for Traditional Chinese Medicine, Peking University Health Science Center, Beijing, China.

Extraction and Isolation. The dried whole plants (18 kg) of *P. telephioides* were extracted under reflux twice with 95% EtOH (2 × 180 l) for 2 h each time. After evaporation of the solvent at 60°, the residue (1.15 kg) was suspended in H_2O (2 l) and defatted with petroleum ether (4 l). The aq. layer was further extracted successively with AcOEt (6 l) and BuOH (6 l) to obtain the AcOEt extract (120 g) and BuOH extract (680 g). A portion of the BuOH extract (600 g) was subjected to CC (*D101* resin, successively 20%, 50%, and 70% aq. EtOH, after washing with H_2O). The 50% aq. EtOH eluate (140 g) was subjected to CC (silica gel (200 – 300 mesh, 1 kg), $CHCl_3$/MeOH 10 : 1 → 1 : 1): *Fractions A – I. Fr. C* (0.3 g) was subjected to CC (*Sephadex LH-20*, MeOH/H_2O 1 : 1): **4** (25 mg) and *6*-O-*benzoyl-3′*-O-*(3,4,5-trimethoxycinnamoyl)sucrose* (34 mg). *Fr. D* (12.0 g) was applied to CC (silica gel (200 – 300 mesh; 100 g), $CHCl_3$/MeOH/H_2O 20 : 1 : 0.1 → 3 : 1 : 0.1): *Fr. C.1 – C.6. Fr. C.3* was subjected to CC (*Sephadex-LH-20*, MeOH/H_2O 6 : 4): **6** (28 mg) and *6*-O-*benzoyl-3′*-O-*sinapoylsucrose* (41 mg). *Fr. C.5* was recrystallized with MeOH: **8** (55 mg). *Fr. E* (20.3 g) was first subjected to CC (silica gel, $CHCl_3$/MeOH 20 : 1 → 1 : 1), then purified by semiprep. HPLC (MeCN/H_2O 25 : 75): **1** (22 mg; t_R 12.5 min), **2** (16 mg; t_R 14.1 min), **3** (20 mg; t_R 18.7 min), and **5** (42 mg; t_R 26.9 min). *Fr. F* (16.1 g) was also first subjected to CC (silica gel, $CHCl_3$/MeOH 8 : 1 → 4 : 1): *Fr. F.1 – F.10. Fr. F.3 – F.5* were purified by CC (*Sephadex LH-20*): **7** (17 mg). *Fr. G* (18.5 g) was subjected to CC (silica gel, $CHCl_3$/MeOH 10 : 1 → 3 : 1): *Fr. G.1 – G.18. Fr. G.3 – G.7* were concentrated and kept standing overnight at r.t. After filtration, the resulting precipitate was washed with MeOH: *mangiferin* (560 mg).

Telephiose D (= *1*-O-*Acetyl-3*-O-*benzoyl-β*-D-*fructofuranosyl* O-*6*-O-*Acetyl-β*-D-*glucopyranosyl-(1 → 2)-6*-O-*acetyl-4*-O-*benzoyl-α*-D-*glucopyranoside*; **4**): Colorless, amorphous powder. M.p. 224 – 226°. $[\alpha]_D^{20} = -35.6$ ($c = 0.94$, MeOH). UV (MeOH): 323 (4.54), 241 (4.54), 205 (4.12). IR (KBr): 3410 (OH), 2937 (CH), 1698 (C=O), 1631, 1601, 1512, 1459. ^{1}H-NMR (CD_3OD, 500 MHz) and ^{13}C-NMR (CD_3OD, 125 MHz): *Tables 1* and *2*. ESI-TOF-MS (pos.): 856.34 ($[M + NH_4]^+$), 861.29 ($[M + Na]^+$), 877.25 ($[M + K]^+$).

Telephiose E (= *3*-O-*Benzoyl-β*-D-*fructofuranosyl* O-*β*-D-*Glucopyranosyl-(1 → 2)-6*-O-*acetyl-4*-O-*benzoyl-α*-D-*glucopyranoside*; **5**): Colorless, amorphous powder. M.p. 273 – 275°. $[\alpha]_D^{20} = -26.9$ ($c = 0.82$, MeOH). UV (MeOH): 320 (4.91), 235 (4.74), 205 (4.64). IR (KBr): 3415 (OH), 2930 (CH), 1710

(C=O), 1632, 1593, 1510, 1459. ^{1}H-NMR (CD_3OD, 500 MHz) and ^{13}C-NMR (CD_3OD, 125 MHz): *Tables 1* and *2*. ESI-TOF-MS (pos.): 777.21 ($[M+Na]^+$).

Telephiose F (= *3*-O-*Benzoyl-β*-D-*fructofuranosyl 4*-O-*benzoyl-α*-D-*glucopyranoside*; **6**): Colorless, amorphous powder. M.p. 259–261°. $[\alpha]_D^{20} = -53.7$ ($c = 0.91$, MeOH). UV (MeOH): 330 (4.68), 239 (4.61), 204 (4.43). IR (KBr): 3405 (OH), 2930 (CH), 1720 (C=O), 1633, 1604, 1513, 1452. ^{1}H-NMR (CD_3OD, 500 MHz) and ^{13}C-NMR (CD_3OD, 125 MHz): *Tables 1* and *2*. ESI-TOF-MS (pos.): 573.09 ($[M+Na]^+$), 589.07 ($[M+K]^+$).

Telephioxanthone A (=*1,3,6,7-Tetrahydroxy-2-{6*-O-*[(2*E*)-1-oxo-3-phenylprop-2-enyl]-β*-D-*glucopyranosyl}-9*H-*xanthen-9-one*; **7**): Yellow powder. M.p. 215–216°. $[\alpha]_D^{20} = -65.6$ ($c = 0.72$, MeOH). UV (MeOH): 361 (3.80), 309 (3.98), 256 (4.30), 237 (3.36). IR (KBr): 3407 (OH), 2931 (CH), 1653 (C=O), 1612, 1580, 1478. ^{1}H-NMR ((D$_6$)DMSO, 500 MHz) and ^{13}C-NMR ((D$_6$)DMSO, 125 MHz): *Table 3*. ESI-TOF-MS (neg.): 551.03 ($[M-H]^-$).

Telephioxanthone B (=*1,3,6,7-Tetrahydroxy-2-{4*-O-*[(2*E*)-1-oxo-3-phenylprop-2-enyl]-β*-D-*glucopyranosyl}-9*H-*xanthen-9-one*; **8**): Pale yellow powder. M.p. 228–230°. $[\alpha]_D^{20} = -82.9$ ($c = 0.77$, MeOH). UV (MeOH): 360 (3.44), 309 (3.69), 256 (3.98), 238 (3.15). IR (KBr): 3389 (OH), 2912 (CH), 1652 (C=O), 1613, 1580, 1484. ^{1}H-NMR ((D$_6$)DMSO, 500 MHz) and ^{13}C-NMR ((D$_6$)DMSO, 125 MHz): *Table 3*. ESI-TOF-MS (pos.): 553.14 ($[M+H]^+$), 575.12 ($[M+Na]^+$).

Acid Hydrolysis of **4**–**6**. Each compound (3 mg) was heated in 2N aq. CF_3COOH (5 ml) at 110° for 6 h in a sealed tube. Then, the mixture was diluted in H_2O (15 ml) and extracted with AcOEt (3 × 5 ml), the combined AcOEt extract concentrated, and the resulting residue dissolved in MeOH (0.5 ml) and analyzed by TLC comparison with standard benzoic acid. TLC (silica gel, petroleum ether/AcOEt 1:1, detection by spraying with 95% EtOH/H_2SO_4 9:1 (*v*/*v*) and heating at 120° for 5 min): R_f (benzoic acid) 0.51.

Determination of Sugar Components. The sugar components in the aq. layer left after hydrolysis of each of **4**–**6** were analyzed by GC. The aq. layer was evaporated and the residue dissolved in anh. pyridine (100 µl). Then 0.1M L-cysteine methyl ester hydrochloride (200 µl; *Sigma*) was added, and the mixture was warmed at 60° for 1 h. Trimethysilylation reagent HMDS–TMCS (hexamethyldisilazane/trimethylchlorosilane/pyridine 2:1:10; *Acros Organics*, Belgium) was added and the mixture warmed at 60° for 30 min. The supernatant was subjected to GC for sugar identification: D-glucose (t_R 12.45 min) and D-fructose (t_R 10.30 min).

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