Constituents from Leaves of *Scolopia chinensis*

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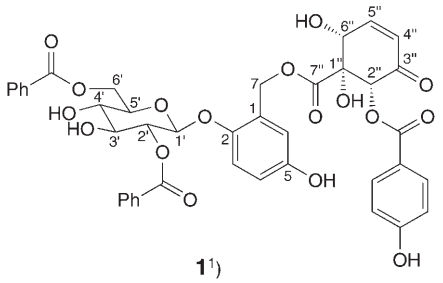
Two new phenolic glycosides, scolochinenosides A and B (**1** and **2**), and a new flavonoid glycoside, scoloside A (**3**), were isolated from the leaves of *Scolopia chinensis* (LOUR.) CLOS, together with eight known compounds. The structures of the new compounds were established on the basis of chemical and spectroscopic evidences.

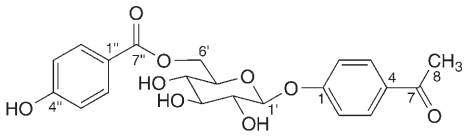
Introduction. – *Scolopia chinensis* (LOUR.) CLOS (Flacourtiaceae), is an evergreen shrub or tree, mainly distributed in Fujian, Guangdong, and Guangxi province of P. R. China. It is used as folk medicine for the treatment of diarrhea and rheumatoid arthritis in China [1]. Up to date, there are no studies on the chemical constituents of this plant.

Herein, we report the isolation and characterization of two new phenolic glycosides, **1** and **2**, and a new flavonoid glycoside, **3**, from *S. chinensis*, together with eight known compounds, populin (=2-(hydroxymethyl)phenyl β-D-glucopyranoside 6-benzoate) [2], eximine (=(7a*S*)-6,7,7a,8-tetrahydro-10,11-dimethoxy-7-methyl-5*H*-benzo[*g*]-1,3-benzodioxolo[6,5,4-*de*]quinoline) [3], lanceoloside A (=4-hydroxyphenyl β-D-glucopyranoside 6-(4-hydroxybenzoate) [4], apigenin 7-[3″-*O*-acetyl-6″-*O*-(*p*-coumaroyl)-β-D-glucopyranoside] [5] (apigenin = 5,7-dihydroxy-2-(4-hydroxyphenyl)-4*H*-1-benzopyran-4-one; *p*-coumaric acid (=(2*E*)-3-(4-hydroxyphenyl)prop-2-enoic acid), apigenin 7-[6″-*O*-(*p*-coumaroyl)-β-D-glucopyranoside] [6], gallic acid (= 3,4,5-trihydroxybenzoic acid), β-amyrin, and hexacosanoic acid, which were identified by comparison of their spectroscopic data with literature data and/or by co-elution on TLC with authentic samples.

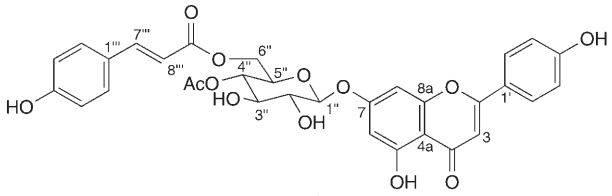


1[1])

[1]) Arbitrary name and atom numbering; for systematic names, see *Exper. Part.*



2[1])



3[1])

Results and Discussion. – Compound **1** was obtained as an amorphous, light yellowish powder. The HR-ESI-MS showed a pseudomolecular ion at *m*/*z* 801.2030 ($[M+H]^+$), in accord with the molecular formula $C_{41}H_{36}O_{17}$ which was also supported by the ^{1}H- and ^{13}C-NMR data (*Table 1*). The IR spectrum showed OH (br., 3404 cm^{-1}) and C=O (unsaturated ester, 1707 cm^{-1}) absorption bands. From further data, including HMBC data (*Fig.*), the structure of **1** was elucidated as *rel*-2-[(2,6-di-*O*-

Table 1. *^{1}H- and ^{13}C-NMR Data of* **1**[1]). At 500 (^{1}H) and 125 MHz (^{13}C), resp.; in CD_3OD; δ in ppm, *J* in Hz.

	δ(H)	δ(C)		δ(H)	δ(C)
C(1)	–	127.5	C(7″)	–	171.1
C(2)	–	149.6	6′-(*O*-benzoyl):		
H–C(3)	6.75 (*d*, *J* = 9.0)	119.8	C=O	–	167.7
H–C(4)	6.21 (*dd*, *J* = 3.0, 9.0)	116.7	C(1)	–	131.1
C(5)	–	153.9	H–C(2,6)	7.99 (*t*, *J* = 7.5, 2 H)	130.6
H–C(6)	6.56 (*d*, *J* = 3.0)	117.2	H–C(3,5)	7.44 (*t*, *J* = 7.5, 2 H)	129.6
CH_2(7)	4.83–4.87 (*m*, 2 H)	64.3	H–C(4)	7.57 (*t*, *J* = 7.5)	134.4
H–C(1′)	4.94 (*d*, *J* = 7.5)	102.2	2′-*O*-benzoyl:		
H–C(2′)	5.24 (*t*, *J* = 8.0)	76.0	C=O	–	167.3
H–C(3′)	3.74–3.79 (*m*)	75.6	C(1)	–	131.2
H–C(4′)	3.56 (*t*, *J* = 9.5)	72.2	H–C(2,6)	7.99 (*t*, *J* = 7.5, 2 H)	130.8
H–C(5′)	3.74–3.79 (*m*)	75.6	H–C(3,5)	7.37 (*t*, *J* = 7.5, 2 H)	129.6
CH_2(6′)	4.72 (*dd*, *J* = 2.0, 12.0), 4.43 (*dd*, *J* = 7.5, 12.0)	65.3	H–C(4)	7.50 (*t*, *J* = 7.5)	134.4
C(1″)	–	84.2	2″-*O*-(4-hydroxybenzoyl):		
H–C(2″)	5.78 (*s*)	78.3	C=O	–	166.3
C(3″)	–	192.8	C(1)	–	121.2
H–C(4″)	5.99 (*dd*, *J* = 2.5, 10.5)	127.4	H–C(2,6)	7.72 (*d*, *J* = 8.5, 2 H)	133.4
H–C(5″)	6.71 (*dd*, *J* = 2.0, 10.5)	150.8	H–C(3,5)	6.66 (*d*, *J* = 8.5, 2 H)	116.0
H–C(6″)	4.95 (br. *s*)	72.0	C(4)	–	163.5

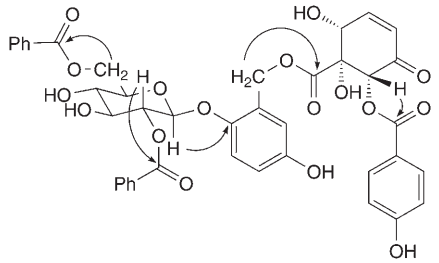


Figure. *Selected HMBC data of scolochinenoside A* (**1**)

benzoyl-β-D-glucopyranosyl)oxy]-7-*O*-{{(1*R*,2*R*,6*R*)-1,6-dihydroxy-2-[(4-hydroxybenzoyl)oxy]-3-oxocyclohex-4-en-1-yl}carbonyl}-5-hydroxybenzyl alcohol[1]), and the compound was named scolochinenoside A.

The ^{1}H- and ^{13}C-NMR spectra of **1** (*Table 1*) showed signals that were unambiguously attributed to two benzoyl residues, a 4-hydroxybenzoyl group, a di-*O*-substituted 2,5-dihydroxybenzyl alcohol moiety, and a glucose unit. The anomeric H-atom of the latter resonated at δ(H) 4.94 (*d*, $J = 7.5$ Hz) and the anomeric C-atom at δ(C) 102.2, the large coupling constant ($J = 7.5$ Hz) suggesting the presence of a β-D-glucopyranose. In addition, the NMR spectra also revealed resonances of an α,β-unsaturated ketone (δ(H) 5.99 (*dd*, $J = 10.5$, 2.5 Hz) and 6.71 (*dd*, $J = 10.5$, 2.0 Hz); δ(C) 127.4, 150.8, and 192.8), an ester C=O group (δ(C) 171.1), and two secondary and one tertiary O-bearing C-atoms (δ(C) 72.0, 78.3, and 84.2), which suggested the existence of a 1,2,6-trihydroxy-5-oxocyclohex-3-ene-1-carboxylic acid unit, a structural element frequently encountered in compounds isolated from plants of the family Flacourtiaceae [7][8]. The location of the two benzoyloxy residues at C(2′) and C(6′) of the glucose unit and the O-linkage between C(1′) of the sugar and C(2) of the benzyl alcohol were unambiguously established by the correlations between δ(H) 5.24 (H–C(2′)) and δ(C) 167.3 (C=O of one benzoyl), δ(H) 4.72 and 4.43 (CH_2(6′)) and δ(C) 167.7 (C=O of the other benzoyl), and δ(H) 4.94 (H–C(1′)) and δ(C) 149.6 (C(2)) in the HMBC plot (*Fig.*[1]). In addition, a cross-peak between δ(H) 4.83–4.87 (*m*, CH_2(7) of the benzyl alcohol moiety) and the C-atom signal at δ(C) 171.1 suggested the placement of the cyclohexenecarbonyl residue at O–C(7) of the benzyl alcohol unit. This substructure was identical to xylosmin (=4-hydroxy-2-{{{[(1*R*,2*R*,6*R*)-1,2,6-trihydroxy-5-oxocyclohex-3-en-1-yl]carbonyl}oxy}methyl}phenyl β-D-glucopyranoside 2,6-dibenzoate), a known compound previously found in *Xylosma flexuosum*, a species belonging to the same plant family [7]. Comparison of the NMR data of **1** with those of xylosmin showed differences due to an additional 4-hydroxybenzoyl group in **1**. The chemical shift of H–C(2″) (δ(H) 5.78) of the cyclohexenecarboxylic acid residue indicated deshielding of this proton and thus suggested the placement of this 4-hydroxybenzoyloxy group at C(2″). Confirmation was provided by the HMBC experiment which revealed the correlation of δ(H) 5.78 (*s*, H–C(2″)) with δ(C) 166.3 (C=O of the 4-hydroxybenzoyl group). The orientation of the OH groups at C(1″) and C(6″) was established as α and that of H–C(2″) as β by comparing the spectral data with those of xylosmin whose relative configuration has been determined by X-ray diffraction [7]. The chemical shifts of the corresponding C-atoms and the multiplicity of the H–C(2″) and H–C(6″) signals of **1** were in agreement with those of the known compound.

Compound **2** was obtained as a white, amorphous powder. The HR-ESI-MS showed a pseudomolecular ion at *m*/*z* 419.1333 ($[M+H]^+$), in accord with the molecular formula $C_{21}H_{22}O_9$ which was also supported by the ^{1}H- and ^{13}C-NMR data (*Exper. Part*). Compound **2** was elucidated as 4-acetylphenyl 6′-*O*-(4-hydroxybenzoyl)-β-D-glucopyranoside[1]), and was given the trivial name scolochinenoside B.

The ^{1}H- and ^{13}C-NMR spectra of **2** showed the signals of a 4-hydroxybenzoyl moiety (δ(H) 7.84 (*d*, *J* = 9.0 Hz, 2 H) and 6.79 (*d*, *J* = 9.0 Hz, 2 H); δ(C) 122.0 (C(1″)), 132.9 (C(2″,6″)), 116.1 (C(3″,5″)), 163.7 (C(4″)), and 167.2 (C=O)), and of a 4-acetylphenyl residue, with signals at δ(H) 7.71 (*d*, *J* = 9.0 Hz, 2 H), 7.02 (*d*, *J* = 9.0 Hz, 2 H), and 2.44 (*s*, Me), and at δ(C) 162.6 (C(1)), 117.1 (C(2,6)), 131.4 (C(3,5)), 132.5 (C(4)), 199.2 (C=O), and 26.5 (Me). In addition, the NMR spectra also revealed a β-glucose unit, the anomeric H-atom thereof resonating at δ(H) 4.97 (*d*, *J* = 7.5 Hz, 1 H) and the anomeric C-atom at δ(C) 101.2. All resonances of the H- and C-atoms were unambiguously assigned by HSQC and HMBC experiments. The HMBC cross-peak H–C(1′) (δ(H) 4.97)/C(1) (δ(C) 162.6) confirmed that the 4-acetylphenoxy moiety was attached to the anomeric C-atom of the glucose unit. The linkage of the 4-hydroxybenzoyloxy moiety at C(6′) of the glucose unit was readily confirmed by the cross-peak between the 2 H–C(6′) (δ(H) 4.59 (*dd*, *J* = 2.0, 12.0 Hz) and 4.36 (*dd*, *J* = 8.0, 12.0 Hz)) and the C=O of the 4-hydroxybenzoyl group (δ(C) 167.2).

Compound **3** was obtained as yellowish powder. The HR-ESI-MS exhibited a pseudomolecular ion at *m*/*z* 621.1614 ($[M+H]^+$) compatible with the molecular formula $C_{32}H_{28}O_{13}$. The IR spectrum indicated absorption bands typical of OH groups (3342 cm^{-1}) and of an α,β-unsaturated ester (1682 and 1655 cm^{-1}). From the ^{1}H- and ^{13}C-NMR (*Table 2*) and HMBC data, the structure of compound **3** was determined as apigenin 7-[6″-*O*-(*p*-coumaroyl)-4″-*O*-acetyl-β-D-glucopyranoside] and named as scoloside A.

Table 2. *^{1}H- and ^{13}C-NMR Data of* **3**^{1}). At 500 (^{1}H) and 125 MHz (^{13}C), resp.; in (D_6)DMSO; δ in ppm, *J* in Hz.

	δ(H)	δ(C)		δ(H)	δ(C)
C(2)	–	163.7	H–C(3″)	4.13–4.18 (*m*)	73.0
H–C(3)	6.83 (*s*)	102.5	H–C(4″)	4.73 (*t*, *J* = 9.5)	70.7
C(4)	–	181.4	H–C(5″)	3.42 (*m*)	70.3
C(4a)	–	104.9	CH_2(6″)	4.13–4.18 (*m*)	63.9
C(5)	–	160.8	6″-*O*-(*p*-coumaroyl):		
H–C(6)	6.49 (*d*, *J* = 2.0)	98.6	C=O	–	165.6
C(7)	–	161.9	C(1‴)	–	124.3
H–C(8)	6.81 (*d*, *J* = 2.0)	94.2	H–C(2‴,6‴)	7.39 (*d*, *J* = 8.5, 2 H)	129.6
C(8a)	–	156.3	H–C(3‴,5‴)	6.68 (*d*, *J* = 8.5, 2 H)	115.1
C(1′)	–	120.4	C(4‴)	–	160.6
H–C(2′,6′)	7.93 (*d*, *J* = 8.5, 2 H)	128.0	H–C(7‴)	7.48 (*d*, *J* = 16.0)	144.6
H–C(3′,5′)	6.92 (*d*, *J* = 8.5, 2 H)	115.4	H–C(8‴)	6.30 (*d*, *J* = 16.0)	112.9
C(4′)	–	159.3	4″-*O*-acetyl:		
H–C(1″)	5.28 (*d*, *J* = 8.0)	98.8	C=O	–	168.0
H–C(2″)	3.56–3.61 (*m*)	72.3	Me	2.04 (*s*)	20.4

The ^{1}H-NMR spectrum of **3** showed the presence of a 1,4-disubstituted benzene unit (δ(H) 7.93 (*d*, *J* = 8.5 Hz, 2 H) and 6.92 (*d*, *J* = 8.5 Hz, 2 H)), of a 1,2,3,5-substituted benzene moiety (δ(H) 6.49 (*d*, *J* = 2.0 Hz, 1 H) and 6.81 (*d*, *J* = 2.0 Hz, 1 H)), and of the typical H–C(3) signal of flavone (δ(H) 6.83 (*s*, 1 H)), which suggested the existence of an apigenin unit. Another 1,4-substituted benzene unit (δ(H) 7.39 (*d*, *J* = 8.5 Hz, 2 H) and 6.68 (*d*, *J* = 8.5 Hz, 2 H)) and a *trans*-disubstituted ethene moiety (δ(H) 6.30 (*d*, *J* = 16.0 Hz, 1 H) and 7.48 (*d*, *J* = 16.0 Hz, 1 H)) indicated the presence of a *p*-coumaroyl unit. In addition, the NMR spectra showed signals of a β-glucose unit, with the anomeric H-atom resonating at δ(H) 5.28 (*d*, *J* = 8.0 Hz, 1 H) and the anomeric C-atom at δ(C) 98.8. In addition, signals at δ(H) 2.04 (*s*, 3 H) and δ(C) 20.4 and 168.0 were typical of an acetyl unit. The O-linkage between C(7) of the apigenin

unit and the anomeric C-atom and the position of the *p*-coumaroyloxy unit at C(6″) of the sugar moiety were easily determined by analysis of the correlations in the HMBC plot (δ(H) 5.28 (H–C(1″))/δ(C) 161.9 (C(7)); δ(H) 4.13–4.18 (*m*, CH_2(6″))/δ(C) 165.6 (C=O of *p*-coumaroyl)), and also confirmed by comparison with the data of the similar known compound apigenin 7-[3″-*O*-acetyl-6″-*O*-(*p*-coumaroyl)-β-D-glucopyranoside] [5]. A downfield shift of the C(4″) signal and the upfield shifts of the C(3″) and C(5″) signals of the glucose moiety suggested that the acetyloxy group was attached at C(4″). A correlation between the H-atom at δ(H) 4.73 (*d*, J = 9.5 Hz, H–C(4″)) and the C-atom at δ(C) 168.0 (Me*C*=O) in the HMBC plot also confirmed this assignment.

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Experimental Part

General. Column chromatography (CC): silica gel *H* (200–300 mesh; *Qingdao Marine Chemical Industry*), *Sephadex-LH-20* gel (*Pharmacia*). Prep. HPLC: *ODS* column (250 × 10 mm, 5 μm; *Inertsil*), *Dionex-P680-UVD-170U* UV detector (280 nm), *Dionex-P680* pump; flow rate 2.5 ml/min. UV Spectra: *TU-1901* spectrometer; λ_{max} (log ε) in nm. IR Spectra: *Nicolet-Nexus-470* FT-IR spectrometer; KBr samples; in cm^{-1}. Optical rotations: *Perkin-Elmer-243B* digital polarimeter. NMR Spectra: *Varian-Unity-500* apparatus; at 500 (^{1}H) or 125 MHz (^{13}C), resp.; δ in ppm rel. to $SiMe_4$, J in Hz. HR-ESI-MS (pos.): *Bruker-APEX-IV-FTMS* spectrometer; in *m*/*z*.

Plant Material. The leaves of *Scolopia chinensis* (LOUR.) CLOS were collected in December 2004 from Guangxi province, P. R. China. The plant was identified by Mr. *Chao-Liang Zhang* (Medical Material Company of Guangxi Province). A voucher specimen (SC20041205) was deposited at the Herbarium of the Peking University Modern Research Center for Traditional Chinese Medicine.

Extraction and Isolation. The leaves (9.5 kg) of *S. chinensis* were extracted with 80% EtOH (2 × 35 l; each 2 h at 80°). After evaporation of the solvent at 60°, the residue (1.3 kg) was suspended in H_2O (4 l) and extracted with petroleum ether (60–90°; 3 × 3 l), AcOEt (3 × 3 l), and BuOH (3 × 2 l), resp. The petroleum ether and AcOEt extracts were combined (70 g) and subjected to CC (SiO_2, petroleum ether/AcOEt 8:1 → 1:1). *Fr. 1–3*. *Fr. 1* was crystallized from MeOH: β-amyrin (2.1 g). *Fr. 2* was subjected to CC (SiO_2, $CHCl_3$/MeOH 25:1 → 1:1): *Fr. 2.1* and *2.2*. *Fr. 2.2* was subjected to CC (SiO_2, $CHCl_3$/MeOH 25:1 → 1:1): *Fr. 2.2.1–2.2.3*. *Fr. 2.2.1* crystallized from MeOH: hexacosanoic acid ($Me(CH_2)_{24}COOH$; 14 mg). *Fr. 2.2.2* was purified by prep. HPLC (MeOH/H_2O (0.5‰ CF_3COOH) 40:60): **1** (21 mg; t_R 71 min) and **3** (9 mg; t_R 80 min). *Fr. 2.2.3* was purified by CC (*Sephadex LH-20*, MeOH/H_2O 1:1): apigenin 7-[3″-*O*-acetyl-6″-*O*-(*p*-coumaroyl)-β-D-glucopyranoside] (9 mg). *Fr. 3* was subjected to CC (SiO_2, $CHCl_3$/MeOH 15:1 → 1:1): *Fr. 3.1–3.5*. *Fr. 3.1* was purified by CC (SiO_2, petroleum ether/Me_2CO 1:1): gallic acid (11 mg). *Fr. 3.2* was subjected to CC (SiO_2, petroleum ether/Me_2CO 1:1): populin (20 mg). *Fr. 3.3* was purified by CC (*Sephadex LH-20*, $CHCl_3$/MeOH 1:1) and prep. HPLC (MeOH/H_2O 36:64): eximine (18 mg; t_R 42 min) and **2** (22 mg; t_R 46 min). *Fr. 3.4* was subjected to CC (SiO_2, $CHCl_3$/Me_2CO 2:1 → 1:1): lanceoloside A (38 mg). *Fr. 3.5* was purified by CC (SiO_2, $CHCl_3$/Me_2CO 2:1 → 1:1): apigenin 7-[6″-*O*-(*p*-coumaroyl)-β-D-glucopyranoside] (2.2 g).

Scolochinenoside A (= rel-*2-{{{{(1*R,*2*R,*6*R*)*-1,2-Dihydroxy-6-[(4-hydroxybenzoyl)oxy]-5-oxocyclohex-3-en-1-yl}carbonyl}oxy}methyl}-4-hydroxyphenyl β-D-Glucopyranoside 2,6-Dibenzoate* = *4-Hydroxybenzoic Acid* rel-*(1*R,*5*R,*6*R*)*-6-{{[2-[(2,6-di*-O-*benzoyl-β-D-glucopyranosyl)oxy]-5-hydroxyphenyl}methoxy}carbonyl}-5,6-dihydroxy-2-oxocyclohex-3-en-1-yl Ester*; **1**): Amorphous, light yellowish powder. $[\alpha]_D^{25} = -10.0$ (c = 1.0, MeOH). UV (MeOH): 260 (4.17), 228 (4.50). IR: 3404, 2924, 1707, 1606, 1275, 1072, 715. ^{1}H- and ^{13}C-NMR (CD_3OD): *Table 1*. HR-ESI-MS: 801.2030 ($[M+H]^+$, $C_{41}H_{37}O_{17}^+$; calc. 801.2031).

Scolochinenoside B (=*4-Acetylphenyl β-D-Glucopyranoside 6-(4-Hydroxybenzoate)* = *1-{4-{[6-O-(4-Hydroxybenzoyl)-β-D-glucopyranosyl]oxy}phenyl}ethanone*; **2**): White, amorphous powder. $[\alpha]_D^{25} = +28.0$ (c = 2.5, DMSO). UV (DMSO): 262 (5.34). IR: 3325, 2925, 1689, 1604, 1562, 1540, 939, 860. ^{1}H-NMR (500 MHz, CD_3OD): 7.84 (*d*, J = 9.0, H–C(2″), H–C(6″)); 7.71 (*d*, J = 9.0, H–C(3), H–C(5)); 7.02 (*d*, J = 9.0, H–C(2), H–C(6)); 6.79 (*d*, J = 9.0, H–C(3″), H–C(5″)); 4.97 (*d*, J = 7.5, H–C(1′)); 4.59

(*dd*, J = 2.0, 12.0, H_a–C(6′)); 4.36 (*dd*, J = 8.0, 12.0, H_b–C(6′)); 3.77–3.81 (*m*, H–C(5′)); 3.46–3.48 (*m*, H–C(2′), H–C(3′)); 3.37–3.39 (*m*, H–C(4′)); 2.44 (*s*, Me). ^{13}C-NMR (125 MHz, CD_3OD): 162.6 (C(1)); 117.1 (C(2), C(6)); 131.4 (C(3), C(5)); 132.5 (C(4)); 199.2 (C(7)); 26.5 (Me(8)); 101.2 (C(1′)); 74.7 (C(2′)); 77.9 (C(3′)); 72.0 (C(4′)); 75.6 (C(5′)); 64.8 (C(6′)); 122.0 (C(1″)); 132.9 (C(2″), C(6″)); 116.1 (C(3″), C(5″)); 163.7 (C(4″)); 167.2 (C(7″)). HR-ESI-MS: 419.1333 ($[M+H]^+$, $C_{21}H_{23}O_9^+$; calc. 419.1342).

Scoloside A (= *7-{[4-*O*-Acetyl-6-*O*-[(2*E*)-3-(4-hydroxyphenyl)-1-oxoprop-2-en-1-yl]-β-*D*-glucopyranosyl}oxy}-5-hydroxy-2-(4-hydroxyphenyl)-4*H*-1-benzopyran-4-one*; **3**): Yellowish powder. $[\alpha]_D^{25}$ = −120.0 (c = 2.2, DMSO). UV (DMSO): 322 (4.56), 270 (4.34). IR: 3342, 2925, 1734, 1682, 1655, 1604, 1174, 1081, 832. ^{1}H- and ^{13}C-NMR ((D_6)DMSO): *Table 2*. HR-ESI-MS: 621.1614 ($[M+H]^+$, $C_{32}H_{29}O_{13}^+$; calc. 621.1608).

Acid Hydrolysis of Compounds **1**–**3**. Each compound **1**–**3** (5 mg each) was heated in 10% HCl soln./dioxane 1:1 (5 ml) at 80° for 4 h. After evaporation of the dioxane, the soln. was extracted with AcOEt (3 × 3 ml) to yield the sugar and the aglycone, resp. The sugar components in the aq. layer were analyzed by TLC (silica gel $CHCl_3$/MeOH/H_2O 8:5:1) by comparison with the standard sugars. The spots were visualized by spraying with 95% EtOH/H_2SO_4/anisaldehyde 9:0.5:0.5 (*v*/*v*), followed by heating at 120° for 10 min; glucose was detected from **1**–**3** (R_f 0.30). The results were confirmed by GC analyses of methyl sugar peracetates. For this, the aq. layer was evaporated, the residue dissolved in anh. pyridine (100 µl), and the soln. mixed with 0.1M L-cysteine methyl ester hydrochloride (200 µl). After warming at 60° for 1 h, the trimethysilylation reagent HMDS/Me_3SiCl (hexamethyldisilazane/trimethylchlorosilane/pyridine 2:1:10; *Acros Organics*; Geel, Belgium) was added, and the temp. was maintained at 60° for another 30 min. The thiazolidine derivatives were analyzed by GC for sugar identification; D-glucose (t_R 12.45 min) was detected from **1**–**3**.

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