Three New Sucrose Fatty Acid Esters from Equisetum hiemale L.

by Jin-Tang Cheng<sup>a</sup>)<sup>b</sup>), Juan He<sup>a</sup>), Xing-Yao Li<sup>a</sup>)<sup>b</sup>), Xing-De Wu<sup>a</sup>)<sup>b</sup>), Li-Dong Shao<sup>a</sup>)<sup>b</sup>), Liao-Bin Dong<sup>a</sup>)<sup>b</sup>), Xu Deng<sup>a</sup>)<sup>b</sup>), Xiu Gao<sup>a</sup>)<sup>b</sup>), Li-Yan Peng<sup>a</sup>), Xiao Cheng<sup>a</sup>), Yan Li<sup>a</sup>), and Qin-Shi Zhao<sup>\*a</sup>)

<sup>a</sup>) State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204, P. R. China

(phone: +86-871-5223058; fax: +86-871-5215783; e-mail: qinshizhao@mail.kib.ac.cn)

b) Graduate University of Chinese Academy of Sciences, Beijing 100039, P. R. China

Three new monosubstituted sucrose fatty acid esters, 1-3, were isolated from *Equisetum hiemale* L., together with nine known compounds, 4-12. Their structures were elucidated by spectroscopic analyses. Compounds 5, 6, and 10-12 were isolated from the title plant for the first time. All these compounds were evaluated for their cytotoxic activity. However, none of them was cytotoxic.

Introduction. - The family Equisetaceae, comprised of two genera (Equisetum and Hippochaete) and about 25 species, is widely distributed in temperate regions [1]. Members of this family are known to contain several types of compounds such as flavonoids, steroids, megastigmanes, and fatty acids [2-7]. Equisetum hiemale L. (Equisetaceae) was used as a Traditional Chinese Medicine called as 'Muzei' in Chinese for the treatment of eye diseases [8]. Previous chemical investigations on this plant have led to the isolation of a series of flavonoids and phenolic compounds [9]. In the course of our search for structurally unique and potentially bioactive natural products, three new monosubstituted sucrose fatty acid esters, 6-O-[(9Z,12Z,15Z)octadeca-9,12,15-trienoyl]- $\beta$ -D-fructofuranosyl  $\alpha$ -D-glucopyranoside (1), 6-O-[(7Z, 10Z,13Z)-hexadeca-7,10,13-trienoyl]- $\beta$ -D-fructofuranosyl  $\alpha$ -D-glucopyranoside (2), and  $6 - O - [(7Z, 10Z) - hexadeca - 7, 10 - dienoyl] - \beta - D - fructofuranosyl \alpha - D - glucopyranoside$ (3), together with nine known compounds,  $\beta$ -sitosterol (4) [10],  $\alpha$ -tocopherolquinone (5) [11], 3,3'-[propane-2,2-diylbis(benzene-4,1-diyloxy)]bis(propane-1,2-diol) (6) [12], *trans*-feruloyl-4- $\beta$ -glucoside (7) [13], *trans*-ferulic acid (8) [14], vanillic acid (9) [14], (6R,7aS)-5,6,7,7a-tetrahydro-6-hydroxy-4,4,7a-trimethylbenzofuran-2(4H)-one (10) $3\beta$ -hydroxy- $5\alpha$ , $6\alpha$ -epoxy-7-megastigmen-9-one (=(3E)-4-[(1S,4R,6R)-4-hy-[15], droxy-2,2,6-trimethyl-7-oxabicyclo[4.1.0]hept-1-yl]but-3-en-2-one; 11) [16], 4-hydroxy-2,3-dimethylnon-2-en-4-olide (= 5-hydroxy-3,4-dimethyl-5-pentylfuran-2(5H)one; 12) [17], were isolated from the aerial parts of *E. hiemale* L. Herein, we describe the isolation and structure elucidation of the isolates.

**Results and Discussion.** – The AcOEt extract of the aerial parts of *E. hiemale* L. was subjected to various column chromatographic separation columns, as well as preparative HPLC, to afford three new compounds, 1-3.

Compound **1** was isolated as a colorless oil. The molecular formula was established as  $C_{30}H_{50}O_{12}$  by HR-ESI-MS (m/z 625.3186 ( $[M + Na]^+$ ); calc. 625.3200), correspond-

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ing to six degrees of unsaturation. The IR absorption bands at 3428 and 1726  $cm^{-1}$ implied the presence of ester and OH groups. The <sup>1</sup>H-NMR data (*Table 1*) revealed the occurrence of six olefinic H-atoms ( $\delta(H)$  5.31–5.39), four CH<sub>2</sub> groups ( $\delta(H)$  1.25– 1.33), and one terminal Me group ( $\delta$ (H) 0.98, t, J=7.5, Me(18)). Correspondingly, the <sup>13</sup>C-NMR spectrum (*Table 2*) exhibited the signals of six olefinic C-atoms ( $\delta(C)$ ) 132.7, 131.1, 129.2, 129.1, 128.9, 128.3), ten CH<sub>2</sub> groups ( $\delta$ (C) 21.5–34.9), a Me group  $(\delta(C) 14.7 (q, C(18)))$ , and a CO group  $(\delta(C) 175.5 (s, C(1)))$ . These data suggested that 1 possessed a linolenic acid residue, which was confirmed by comparison of the spectroscopic data with those reported in the literature [18]. The other twelve C-atom resonances were displayed in the region of  $\delta(C)$  62.5 – 105.5, suggesting the existence of a disaccharide moiety, which was determined as sucrose and confirmed by alkaline hydrolysis of compound 1. Alkaline hydrolysis of 1 with 0.5% NaOH yielded linolenic acid and sucrose (see *Exper. Part*). The fatty acid residue is attached to HO-C(6'') of sucrose, as deduced by HMBCs of the signals of  $CH_2(6'')$  ( $\delta(H)$  4.39 and 4.33) with the one of  $C(1)(\delta(C) 175.5(s))$  of **1**. Based on these data, compound **1** was characterized as 6-O-[(9Z,12Z,15Z)-octadeca-9,12,15-trienoyl]- $\beta$ -D-fructofuranosyl  $\alpha$ -D-glucopyranoside.

H-Atom	1	2	3	
CH <sub>2</sub> (2)	2.35 $(t, J = 7.4)$	2.35 $(t, J = 7.5)$	2.35 $(t, J = 7.4)$	
$CH_2(3)$	1.60 - 1.61 (m)	1.61 - 1.65 (m)	1.61 - 1.65 (m)	
$CH_2(4)$	1.25 - 1.33 (m)	1.29 - 1.38 (m)	1.30 - 1.40 (m)	
CH <sub>2</sub> (5)	1.25 - 1.33 (m)	1.29 - 1.38 (m)	1.30 - 1.40 (m)	
CH <sub>2</sub> (6)	1.25 - 1.33 (m)	2.07 - 2.11 (m)	2.06 - 2.09(m)	
$CH_2(7)$ or $H-C(7)$	1.25 - 1.33 (m)	5.31 - 5.40 (m)	5.31 - 5.38(m)	
$CH_2(8)$ or $H-C(8)$	2.05 - 2.10 (m)	5.31 - 5.40 (m)	5.31 - 5.38(m)	
$H-C(9)$ or $CH_2(9)$	5.31 - 5.39(m)	2.80 - 2.83 (m)	2.78 (dd, J = 6.2, 6.2)	
H-C(10)	5.31 - 5.39(m)	5.31 - 5.40 (m)	5.31 - 5.38(m)	
CH <sub>2</sub> (11) or H–C(11)	2.80 - 2.83 (m)	5.31 - 5.40 (m)	5.31 - 5.38(m)	
$H-C(12)$ or $CH_2(12)$	5.31 - 5.39(m)	2.80 - 2.83(m)	2.06 - 2.09(m)	
$H-C(13)$ or $CH_2(13)$	5.31 - 5.39(m)	5.31 - 5.40 (m)	1.30 - 1.40 (m)	
CH <sub>2</sub> (14) or H–C(14)	2.05 - 2.10 (m)	5.31 - 5.40 (m)	1.30 - 1.40 (m)	
$H-C(15)$ or $CH_2(15)$	5.31 - 5.39(m)	2.07 - 2.11 (m)	1.30 - 1.40 (m)	
H–C(16) or Me(16)	5.31–5.39 ( <i>m</i> )	0.98(t, J = 7.5)	0.91 (t, J = 6.6)	
CH <sub>2</sub> (17)	2.05 - 2.10 (m)	-	-	
Me(18)	0.98(t, J = 7.5)	_	-	
H–C(1')	5.34 (overlap)	5.34 (overlap)	5.34 (overlap)	
H–C(2')	3.42 (dd, J = 9.7, 3.6)	3.41 (dd, J = 9.8, 3.8)	3.41 (dd, J = 9.8, 3.8)	
H–C(3')	3.72 (overlap)	3.72 (overlap)	3.71 (overlap)	
H–C(4')	3.34 (dd, J = 9.5, 9.5)	3.32 (dd, J = 9.5, 9.5)	3.33 (dd, J = 9.5, 9.5)	
H–C(5')	3.83 (overlap)	3.83 (overlap)	3.83 (overlap)	
CH <sub>2</sub> (6')	3.72 (overlap),	3.72 (overlap),	3.71 (overlap),	
	3.83 (overlap)	3.83 (overlap)	3.83 (overlap)	
CH <sub>2</sub> (1")	3.62 (br. <i>s</i> )	3.62 (br. <i>s</i> )	3.62 (br. s)	
H–C(3")	4.10 (d, J = 8.2)	4.09 (d, J = 8.2)	4.09(d, J = 8.2)	
H–C(4")	4.01 ( <i>t</i> -like, $J = 8.1$ )	$4.00 \ (t-like, J=8.1)$	$4.01 \ (t-like, J=8.1)$	
H–C(5")	3.92 (td, J = 7.8, 3.0)	3.92 (td, J = 7.8, 3.3)	3.92 (td, J = 7.8, 3.1)	
CH <sub>2</sub> (6")	4.39 (dd, J = 11.5, 7.9), 4.33 (dd, J = 11.6, 3.0)	4.39 ( <i>dd</i> , <i>J</i> = 11.7, 7.8), 4.32 ( <i>dd</i> , <i>J</i> = 11.7, 3.3)	4.39 (dd, J = 11.7, 7.8), 4.32 (dd, J = 11.6, 3.1)	

Table 1. <sup>1</sup>*H*-*NMR Data of Compounds* **1**–**3**. Recorded in CD<sub>3</sub>OD;  $\delta$  in ppm, *J* in Hz.

Compound 2, a colorless oil, showed a molecular-ion peak at m/z 597 ([M + Na]<sup>+</sup>) in the ESI-MS, corresponding to the molecular formula C<sub>28</sub>H<sub>46</sub>O<sub>12</sub>. The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra (*Tables 1* and 2, resp.) revealed that compound 2 was quite similar to compound 1. The most striking difference was the absence of two non-O-bearing CH<sub>2</sub> groups. Detailed analysis of the <sup>1</sup>H,<sup>1</sup>H-COSY and HMBC spectra revealed the occurrence of a partial structure,  $-CH_2-(CH=CH-CH_2)_3$ -Me with the following chemical shifts:  $\delta(C)$  28.0 (t), 128.1 (d), 128.9 (d), 26.3 (t), 129.1 (d), 129.2 (d), 26.5 (t), 130.8 (d), 132.7 (d), 21.4 (t), and 14.6 (q). The two CH<sub>2</sub> groups absent in 2 were part of the CH<sub>2</sub> chain between the olefinic and ester groups in compound 1, which suggested that compound 2 possessed a hexadeca-7,10,13-trienoic acid residue. In the <sup>13</sup>C-NMR spectrum, the three allylic CH<sub>2</sub> C-atoms (C(6), C(9), and C(12)) were shifted upfield to  $\delta(C)$  28.0, 26.3, and 26.5, which indicated that the geometry of C=C bonds is most probably (Z) [19–21]. The HMBCs of the signals of CH<sub>2</sub>(6'') ( $\delta(H)$  4.39 and 4.32) with the one of C(1) ( $\delta(C)$  175.4 (s)) indicated that the hexadeca-7,10,13-trienoic acid residue was attached to HO–C(6'') of sucrose. Accordingly, the structure of compound

C-Atom	1	2	3	C-Atom	1	2	3
C(1)	175.5 (s)	175.4 (s)	175.6 (s)	C(16)	132.7(d)	14.6(q)	14.6(q)
C(2)	34.9(t)	34.8(t)	35.0(t)	C(17)	21.5(t)		
C(3)	26.0(t)	25.8(t)	26.0(t)	C(18)	14.7(q)		
C(4)	$30.2(t)^{a}$	29.8 (t)	30.0(t)	C(1')	93.5 (d)	93.4 (d)	93.6 (d)
C(5)	$30.2(t)^{a}$	30.4 (t)	$30.6 (t)^{b}$	C(2')	73.3 (d)	73.2(d)	73.3 (d)
C(6)	$30.4(t)^{a}$	28.0(t)	$28.1 (t)^{c}$	C(2')	74.7(d)	74.6(d)	74.7(d)
C(7)	30.7 (t)	$128.1 (d)^{d}$	$129.2 (d)^{e}$	C(4')	71.5(d)	71.4(d)	71.6(d)
C(8)	28.2(t)	$128.9 (d)^{d}$	$129.4 (d)^{e}$	C(5')	74.2(d)	74.2(d)	74.4(d)
C(9)	$128.3 (d)^{f}$	$26.3 (t)^{g}$	26.7(t)	C(6')	62.5(t)	62.4(t)	62.6 ( <i>t</i> )
C(10)	$128.9 (d)^{f}$	$129.1 (d)^{d}$	$130.8 (d)^{e}$	C(1'')	63.8 ( <i>t</i> )	63.7 ( <i>t</i> )	63.8 ( <i>t</i> )
C(11)	$26.4 (t)^{\rm h}$	$129.2 (d)^{d}$	$131.1 (d)^{e}$	C(2'')	105.5(s)	105.4 (s)	105.6(s)
C(12)	$129.1 (d)^{f}$	$26.5 (t)^{g}$	$28.3 (t)^{c}$	C(3'')	78.9(d)	78.8(d)	78.9(d)
C(13)	$129.2 (d)^{f}$	$130.8 (d)^{d}$	$30.7 (t)^{b}$	C(4'')	76.9(d)	76.8(d)	77.0(d)
C(14)	$26.6 (t)^{h}$	132.7(d)	32.8(t)	C(5'')	80.6 ( <i>d</i> )	80.6 ( <i>d</i> )	80.8(d)
C(15)	$131.1 (d)^{f}$	21.4(t)	23.8(t)	C(6'')	67.0(t)	66.9(t)	67.1 ( <i>t</i> )

Table 2. <sup>13</sup>C-NMR Data of Compounds 1 (100 MHz), 2 (100 MHz), and 3 (150 MHz). Recorded in CD<sub>3</sub>OD;  $\delta$  in ppm.

**2** was determined as 6-*O*-[(7*Z*,10*Z*,13*Z*)-hexadeca-7,10,13-trienoyl]- $\beta$ -D-fructofuranosyl  $\alpha$ -D-glucopyranoside.

Compound **3** was obtained as a colorless oil. The molecular formula was established as  $C_{28}H_{48}O_{12}$  by the HR-ESI-MS (m/z 599.3036 ( $[M + Na]^+$ ); calc. 599.3043), indicating five degrees of unsaturation. The <sup>13</sup>C-NMR spectrum (*Table 2*) indicated the presence of two C=C bonds ( $\delta$ (C) 131.1 (d), 130.8 (d), 129.4 (d), 129.2 (d)), ten non-O-bearing CH<sub>2</sub> groups, as well as one Me group ( $\delta$ (C) 14.6 (q, C(16)). Comparison of the spectroscopic data with those of **2** revealed an overall similarity, except for the absence of one C=C bond. The upfield shift of the signal of CH<sub>2</sub>(15) ( $\delta$ (H) 1.30–1.40 (overlap)) suggested that the C=C bond between C(13) and C(14) of compound **2** was saturated in compound **3**, which was confirmed by HMBC and <sup>1</sup>H,<sup>1</sup>H-COSY correlations (*Fig.*). On the basis of the fact that signals of the allylic C-atoms were shifted upfield ( $\delta$ (C) 28.1 and  $\delta$ (C) 28.3), the geometry of C=C bonds in compound **3** was determined as (Z) [19–21]. The fatty acid residue was attached to HO–C(6'') of sucrose, as deduced by HMBCs of the signals of CH<sub>2</sub>(6'') ( $\delta$ (H) 4.39 and 4.32) with the



Figure. Key <sup>1</sup>H,<sup>1</sup>H-COSY correlations (-) and HMBCs ( $H \rightarrow C$ ) of 3

one of C(1) ( $\delta$ (C) 175.6 (*s*)). Consequently, the chemical structure of compound **3** was determined to be 6-*O*-[(7*Z*,10*Z*)-hexadeca-7,10-dienoyl]- $\beta$ -D-fructofuranosyl  $\alpha$ -D-glucopyranoside.

The structures of the known compounds were identified by comparison of their spectroscopic data with those reported in the literature.

Compounds **1**–**12** were tested for cytotoxicity against HL-60, A-549, SMMC-7721, MCF-7, and SW480 cell lines *in vitro*. However, all of them were inactive.

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## **Experimental Part**

General. Solvents were distilled before use. Column chromatography (CC): silica gel (SiO<sub>2</sub>; 200–300 mesh, 10–40 µm; Qingdao Marine Chemical Inc., Qingdao, P. R. China), MCI gel (75–150 µm; Mitsubishi Chemical Corporation, Japan), and Sephadex LH–20 (Amersham Pharmacia Biotech, Sweden). Fractions were monitored by TLC, and spots were visualized by heating SiO<sub>2</sub> plates sprayed with 10% H<sub>2</sub>SO<sub>4</sub> in EtOH. Semi-prep. HPLC: Zorbax SB-C-18 column (i.d.  $9.4 \times 250$  mm; Agilent Co., Ltd.). Prep. HPLC: Shimadzu PRC-ODS (K) column, Shimadzu LC-8A prep. liquid chromotography. Optical rotations: JASCO P-1020. UV Spectra: Shimadzu UV-2401PC. IR Spectra: Tensor 27; KBr pellets. 1D- and 2D-NMR spectra: Bruker AM-400 and Advance III 600 spectrometers with TMS as internal standard; unless specified, chemical shifts ( $\delta$ ) in ppm with reference to the solvent signals, J in Hz. MS: API QSTAR Pulsar-1 mass spectrometer.

*Plant Material.* The aerial parts of *E. hiemale* were collected from the area of Changbaishan, Jilin Province, P. R. China, in July 2010. The sample was identified by *X. C.*, and a voucher specimen (KIB 100701) has been deposited with the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation. The air-dried and powdered aerial parts of the plant (5 kg) were extracted with EtOH 95% ( $3 \times 15$  l, 24 h each) at r.t. and filtered. The filtrate was evaporated to give a residue (420 g), which was suspended in H<sub>2</sub>O and then extracted with AcOEt. The AcOEt extract (160 g) was decolorized over MCI gel (eluted with 90% MeOH) and then was subjected to CC (SiO<sub>2</sub>; petroleum ether (PE)/Me<sub>2</sub>CO, gradient system) to afford Frs. 1-5. Repeated crystallization from a mixture of Me<sub>2</sub>CO/MeOH from Fr. 1 gave compound 4 (5 g). Fr. 2 was subjected to CC (SiO<sub>2</sub>; PE/Me<sub>2</sub>CO 99:1, and Sephadex LH-20; CHCl<sub>3</sub>/MeOH, 1:1) to yield compound 5 (46 mg). Fr. 3 was subjected to CC (SiO<sub>2</sub>; PE/ Me<sub>2</sub>CO, increasing polarity) to provide Frs. 3.1-3.8. Fr. 3.2 was purified by using semi-prep. HPLC (20% MeOH in  $H_2O$  to yield compounds 10 (88 mg) and 11 (9 mg). After the purification of Fr. 3.7 with Sephadex LH-20 (CHCl<sub>3</sub>/MeOH 1:1) and prep. HPLC (65% MeOH in H<sub>2</sub>O) compound 12 (60 mg) was isolated. Fr. 3.8 was subjected to prep. HPLC (35% MeOH in H<sub>2</sub>O), compounds 8 (16 mg) and 9 (23 mg) were obtained. Fr. 5 was subjected to CC (SiO<sub>2</sub>; CHCl<sub>3</sub>/MeOH 95:5 $\rightarrow$ 1:1) to provide Frs. 5.1-5.10. Repeated chromatography of Fr. 5.3 with a gradient system of CHCl<sub>3</sub>/MeOH 95:5 $\rightarrow$ 7:3 yielded compound 6 (25 mg). From Fr. 5.7, compound 7 (30 mg) was obtained after prep. HPLC (60% MeOH in H<sub>2</sub>O). Fr. 5.8 was first subjected to CC (SiO<sub>2</sub>; CHCl<sub>3</sub>/MeOH 93:7), then to prep. HPLC (78% MeOH in  $H_2O$ ) to yield compounds 1 (60 mg), 2 (6 mg), and 3 (3 mg).

6-O-[(9Z,12Z,15Z)-Octadeca-9,12,15-trienoyl]-β-D-fructofuranosyl α-D-Glucopyranoside (1). Colorless oil. [a]<sup>25.8</sup> = +35.9 (c = 0.50, MeOH). UV (MeOH): 268 (3.35), 232 (3.60), 202 (3.69). IR (KBr): 3428, 2931, 1726, 1063. <sup>1</sup>H- and <sup>13</sup>C-NMR: see *Tables 1* and 2, resp. ESI-MS (pos.): 625 ([M + Na]<sup>+</sup>). HR-ESI-MS: 625.3186 ([M + Na]<sup>+</sup>, C<sub>30</sub>H<sub>50</sub>NaO<sup>+</sup><sub>12</sub>; calc. 625.3200).

6-O-[(7Z,10Z,13Z)-Hexadeca-7,10,13-trienoyl]-β-D-fructofuranosyl α-D-Glucopyranoside (2). Colorless oil.  $[a]_{25}^{25.7} = +30.7$  (c = 0.30, MeOH). UV (MeOH): 268 (3.33), 231 (3.42), 203 (3.96). IR (KBr):

3425, 2930, 1726, 1065. <sup>1</sup>H- and <sup>13</sup>C-NMR: see *Tables 1* and 2, resp. ESI-MS (pos.): 597 ( $[M + Na]^+$ ). HR-ESI-MS (pos.): 597.2872 ( $[M + Na]^+$ ,  $C_{28}H_{46}NaO_{12}^+$ ; calc. 597.2887).

6-O-[(7Z,10Z)-Hexadeca-7,10-dienoyl]-β-D-fructofuranosyl α-D-Glucopyranoside (**3**). Colorless oil. [α]<sub>D</sub><sup>25.8</sup> = +44.6 (c = 0.20, MeOH). UV (MeOH): 229 (3.43), 202 (3.97). IR (KBr): 3422, 2928, 1736, 1064. <sup>1</sup>H- and <sup>13</sup>C-NMR: see *Tables 1* and 2, resp. ESI-MS (pos.): 599 ([M + Na]<sup>+</sup>). HR-ESI-MS (pos.): 599.3036 ([M + Na]<sup>+</sup>, C<sub>28</sub>H<sub>48</sub>NaO<sub>12</sub>; calc. 599.3043).

Alkaline Hydrolysis of **1**. Compound **1** was treated with 0.5% NaOH (0.5 ml) in MeOH (3 ml) at r.t. for 18 h. The mixture was neutralized with 1N HCl and extracted with CHCl<sub>3</sub>. The org. layer and the H<sub>2</sub>O layer were concentrated under reduced pressure. From the org. layer of compound **1**, linolenic acid was identified with authentic samples and by TLC. Sucrose was obtained from the H<sub>2</sub>O layer, and identified as sucrose by comparison with authentic samples and by TLC behavior, solvent: CHCl<sub>3</sub>/MeOH/H<sub>2</sub>O 45:30:1.

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