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Unusual stilbenoids and a stilbenolignan from seeds of *Syagrus romanzoffiana*

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ABSTRACT

Stilbenoids, syagrusins A–B (**1**–**2**), and a stilbenolignan, 5-hydroxyaiphanol (**3**), along with three known phenylpropanoids (**4**–**6**), were isolated from seeds of *Syagrus romanzoffiana*. Compounds **1** and **2** possess unusual 1,4,4a,9a-tetrahydrofluoren-9-one and bicyclo[3.3.0]octanedione skeletons, respectively, whereas compound **3** is a stilbenolignan belonging to a very rare structural class of plant secondary metabolites. Their structures were elucidated by spectroscopic analyses. Compounds **1**–**3** exhibited moderate inhibitory activity against α-glucosidase with IC_{50} values of 16.9 μM (**1**), 23.7 μM (**2**) and 12.8 μM (**3**), respectively.

1. Introduction

Stilbenoids have been reported to possess many interesting biological activities such as anti-oxidant (Murias et al., 2005), anti-inflammatory (Murias et al., 2004), and anti-cancer (Iliya et al., 2006) properties. Thus, stilbenoids are important lead compounds for new drug development (Saiko et al., 2008). Recently, we reported seven stilbenoids isolated from seeds of *Syagrus romanzoffiana* (Cham.) Glassman (Arecaceae) (Lam et al., 2008), where their hypoglycemic activities were examined by an *in vitro* α-glucosidase activity assay and by an *in vivo* sucrose challenge study using normal Wistar rats (Lam et al., 2008), respectively. Continuation of this study through a more extensive investigation of the active fraction of the *n*-BuOH soluble fraction of the same plant extract (Lam et al., 2008), identified in the last report, via Sephadex LH-20 and Lobar RP-18 column chromatography led to isolation of six additional constituents. Of these, compounds **1–2** are new stilbenoid derivatives possessing unusual skeletons, and compound **3** is a new stilbenolignan (Fig. 1). The other three compounds were characterized as known 4-*O*-(6-*O*-*p*-coumaroyl-β-glucopyranosyl)-*p*-coumaric acid (**4**) (Sashida et al., 1991), *p*-coumaric acid (**5**) (Chaudhuri and Thakur, 1986) and *cis*-3,4-dihydroxycinnamaldehyde (**6**) (Demin et al., 2004). The following describes the structural characterization of compounds **1**–**3** and the α-glucosidase inhibitory activities of these compounds.

2. Results and discussion

Compound **1**, obtained as an amorphous solid, had the molecular formula $C_{27}H_{22}O_9$, as deduced from its HR-FAB-MS. The ^1H NMR spectrum (Pyr-d_5, Table 1) exhibited signals for two *trans*-coupled olefinic protons (δ_H 6.72 and 6.58, $J = 16.2$ Hz, H-8 and H-7); the former (δ_H 6.72) was long-range coupled to an olefinic proton at δ_H 6.12 (*br s*, H-10), whereas the latter was further coupled to a two-proton doublet at δ_H 6.92 (2H, *d*, $J = 1.7$ Hz, H-2/H-6) via benzylic-like coupling. These were all deduced from analysis of the COSY spectrum (Fig. 2) even though the couplings were non-resolvable. The 2D-spectrum also established vicinal coupling between δ_H 6.12 (H-10) and δ_H 3.91 (*d*, $J = 2.6$ Hz, H-11), with the latter being benzylically coupled to a two-proton singlet at δ_H 7.26 (H-2′/H-6′), whereas the two-proton doublet at δ_H 6.92 was *meta*-coupled to a triplet proton at δ_H 6.93 (H-4). The spin–spin coupling data thus constituted a 1-phenyl-1,3-diene structural moiety **1-A** (Fig. 3). The remainder of the ^1H NMR spectrum of **1** included signals for a D_2O exchangeable proton at δ_H 12.71 (12″-OH), an AB system (δ_H 6.62 and 6.66, $J = 2.1$ Hz, H-5″ and H-3″), and three aliphatic protons at δ_H 3.63 (*m*, H-13), 2.73 (*br dd*, $J = 3.5$, 17.2 Hz, H-14β) and 2.37 (*br d*, $J = 17.2$ Hz, H-14α), with the latter two belonging to a methylene group (δ_C 28.6) as evidenced from the HMQC analysis (Pyr-d_5). The resonance at δ_H 12.71 was typical for the hydroxyl proton with an intra-molecular H-bond to a carbonyl function, similar to that of a 5-O*H* group in a 5-hydroxyflavone (Amaral et al., 2001). The COSY spectrum established a benzylic relationship between H-5″ and H-13, the latter being vicinally coupled to both methylene protons (Fig. 2). These coupling

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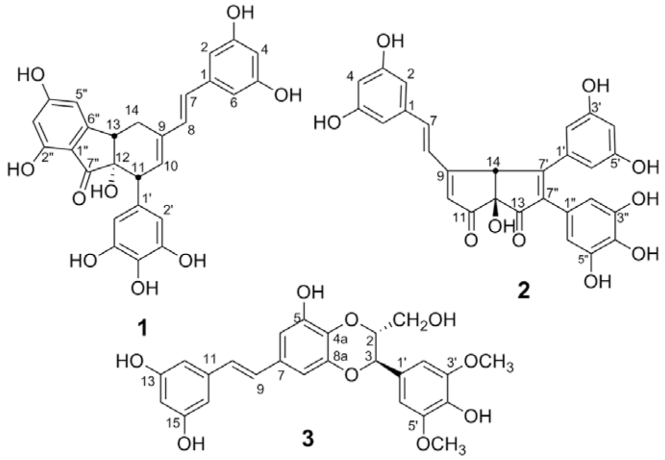

Fig. 1. Structures of syagrusins A (**1**) and B (**2**), and 5-hydroxyaiphanol (**3**).

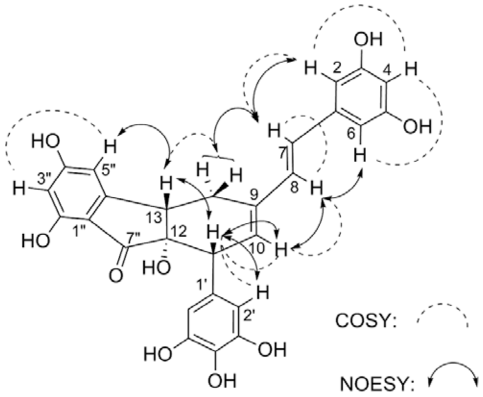

Fig. 2. COSY and NOESY correlations of **1**.

relationships when considered together thus constituted a structural moiety **1-B** (Fig. 3). Subtraction of the molecular formula from the structural moieties **1-A** and **1-B** left a –COH unit, which was a hydroxylated quaternary carbon with a chemical shift assignable at δ_C 77.1 (*s*, C-12). This carbon was coupled to H-13 (δ 3.63) and H-11 (δ 3.91) in the HMBC spectrum (Pyr-d$_5$, Table 1). This 2D-spectrum also established the correlations of H-11/C-7″ (δ_C 203.3, a carbonyl), C-13 (δ_C 44.4, *d*, a methine carbon), C-2′/C-6′ (δ 109.2, *d*) and C-10 (δ 132.4, *d*). To meet these requirements, the hydroxylated quaternary carbon should link to the carbons belonging to the carbonyl and the two methines (δ_{C-13} 44.4 and δ_{C-11} 50.9). In the HMBC spectrum, the signals of both β- and δ- protons (δ_{H-8} 6.72 and δ_{H-10} 6.12) in structure **1-A** were observed to correlate with that of the methylene carbon (δ_{C-14} 28.6) (Table 1), establishing its linkage to the γ-carbon (C-9). These structural units taken together thus established the structure of **1** as shown, leaving the stereochemistry to be determined.

The NOESY spectrum established the NOE relationships of H-11 to H-10, H-13 and H-2′/H-6′; H-10 to H-11, H-8 and H-2′/H-6′; H-7 to H-14α and H-2/H-6 (Fig. 2). Therefore, both methine protons (H-11 and H-13) were *cis*-oriented and the **1-A** structure unit contained an extended zig–zag conjugation as shown. A chemical

Table 1
^{1}H (400 MHz) spectroscopic data for **1** and **2**, ^{13}C (100 MHz) data for **1–3**, and HMBC data for **1** and **2**.

Position	1[a]			2[b]			3[b]
	δ_H	δ_C	HMBC	δ_H	δ_C	HMBC	δ_C
1		139.9 *s*			138.6 *s*		
2	6.92 *d* (1.7)	106.2 *d*	3, 4, 5, 7	6.24 *brs*	107.4 *d*	3, 5, 4, 7	78.2 *d*
3		160.5 *s*			159.6 *s*		79.9 *d*
3a							62.3 *t*
4	6.93 *t* (1.7)	104.0 *d*	2, 3, 5, 6	6.24 *brs*	105.5 *d*	2, 3, 5, 6	
4a							132.9 s
5		160.5 *s*			159.6 *s*		147.3 *s*
6	6.92 *d* (1.7)	106.2 *d*	3, 4, 5, 7	6.24 *brs*	107.4 *d*	3, 5, 4, 7	107.5 *d*
7	6.58 *d* (16.2)	129.3 *d*	1, 2, 6, 8, 9	6.92 *d* (16.2)	142.2 *d*	2, 6, 9	140.9 *s*
8	6.72 *d* (16.2)	130.3 *d*	1, 7, 9, 10, 14	6.60 *d* (16.2)	122.9 *d*	1, 9, 10, 13	107.6 *d*
8a							145.9 *s*
9		137.8 *s*			174.9 *s*		129.4 *d*
10	6.12 *brs*	132.4 *d*	8, 11, 14	6.15 *s*	124.5 *d*	8, 9, 11, 12, 13	128.4 *d*
11	3.91 *d-like* (2.6)	50.9 *d*	1′, 2′, 6′, 7″, 12, 13, 14		202.4 *s*		131.8 *s*
12		77.1 *s*			83.6 *s*		105.9 *d*
13	3.63 *m*	44.4 *d*	6″, 9, 12		201.8 *s*		159.6 *s*
14	2.37 *brd* (17.2, α) 2.73 *brdd* (3.5,17.2, β)	28.6 *t*	6″, 9, 10, 11, 13 6″, 9	4.50 *s*	59.8 *d*	7′, 8′, 9, 10, 12	102.9 *d*
15							159.6 *s*
16							105.9 *d*
1′		131.5 *s*			139.1 *s*		128.4 *s*
2′, 6′	7.26 *s*	109.2 *d*	1′, 3′, 4′, 5′, 11	6.30 *d* (2.0)	107.7 *d*	1′, 3′, 4′, 5′, 7′	105.9 *d*
3′, 5′		147.7 *s*			160.0 *s*		149.5 *s*
4′		134.2 *s*		6.26 *t* (2.0)	104.9 *d*		137.3 *s*
7′					169.2 *s*		
1″		108.1 *s*			134.7 *s*		
2″		166.2 *s*		6.19 *s*	109.9 *d*	8′, 11′, 12′, 13′	
3″	6.66 *d* (2.1)	102.2 *d*	1″, 2″, 4″		146.4 *s*		
4″		166.7 *s*			122.2 *s*		
5″	6.62 *d* (2.1)	108.7 *d*	1″, 3″, 4″, 13		146.4 *s*		
6″		152.7 *s*		6.19 *s*	109.9 *d*	8′, 11′, 12′, 13′	
7″		203.3 *s*			137.9 *s*		
OMe							58.3 *q*

[a] Recorded in Pyr-d$_5$.

[b] Recorded in CD$_3$OD.