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Steroidal saponins and homoisoflavanone from the aerial parts of *Sansevieria cylindrica* Bojer ex Hook.

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ABSTRACT

Phytochemical study on the methanolic extract of *Sansevieria cylindrica* aerial parts lead to the isolation, characterization and structure elucidation of a new steroidal saponin, 1β-hydroxy-kryptogenin-1-*O*-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranoside (**1**), a new homoisoflavanone, (3S)-3,7-dihydroxy-8-methoxy-3-(3′,4′-methylenedioxybenzyl) chroman-4-one (**2**) and the known saponin alliospiroside A (**3**). To the best of our knowledge, the genin 1β-hydroxy-kryptogenin is reported here for the first time. The structures of the new compounds were determined by UV, IR, EIMS, HRESIMS together with 1D (^{1}H and ^{13}C) and 2D (HSQC and HMBC) NMR spectral analysis. The isolated compounds 1–3 were tested for their radical scavenging activity (DPPH). Compound 2 exhibited activity compared to that of ascorbic acid as a standard. The cytotoxicity of the isolated compounds and the standard doxorubicin was tested against the three human tumor cell lines HT116, MCF-7 and PC-3. The results showed that the isolated compounds were inactive.

1. Introduction

Q3 *Sansevieria* belongs to family Dracaenaceae (Patil and Pai, 2011), is a genus of xerophytic perennial herbs growing in dry tropical and subtropical parts of the world. The genus consists of about 70 species with a distribution ranging from Africa through Asia to Burma and the islands of the Indian Ocean (Takawira and Nordal, 2003). Some species have an ethnopharmacological background, in particular *S. trifasciata* which in tropical America and South Africa, is used for the treatment of inflammatory conditions and marketing as a crude drug for snakebite treatment (Morton, 1981). Literature survey revealed that phytochemical studies carried out on some *Sansevieria* species, led to the isolation of several steroidal sapogenins and saponins. 25 S-ruscogenin and new steroidal saponin with pregnane-type, were reported from *S. hyacinthoides* (Gamboa-Angulo et al., 1996). Four new pregnane glycosides and ten new steroidal saponins were isolated from *S. trifasciata* (Mimaki et al., 1996a,b, 1997). Sansevistatins 1 and 2 isolated from the African *S. ehrenbergii* were shown to possess anticancer activity against the P388 lymphocytic leukemia cell line and a panel of human cancer cell lines. Sansevistatin 2 and other saponins isolated from the same source, exhibited antifungal activity against *Candida albicans* and *Cryptococcus neoformans* (Pettit et al., 2005). From the leaves of *S. cylindrica*, a new steroidal saponin was isolated and showed inhibition of the capillary permeability activity (Da Silva Antunes et al., 2003).

Sansevieria cylindrica Bojer ex Hook. native to the subtropical regions of the African continent, is cultivated in Egypt for ornamental purposes. As a part of our interest in investigating plants cultivated in Egypt, we describe in this report the isolation and characterization of two steroidal saponins **1** and **3** including a new one **1** together with one new homoisoflavonoid **2**. The structures of the new compounds were determined by the combined use of EIMS, HRESIMS, UV and IR together with 1D and 2D NMR. The isolated compounds were tested for their antioxidant activity and cytotoxicity against human cancer cell lines.

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2. Results and discussion

2.1. Isolation, characterization and structure elucidation of compounds

The 70% aqueous methanolic extract of *Sansevieria cylindrica* unflowering aerial parts was subjected to repeated column chromatography to afford two new compounds **1** and **2** as well as the known compound alliospiroside A **3** (Huang et al., 2013).

Compound **1** was isolated as colorless amorphous solid. It showed pseudo-molecular ion peaks $[M+Na]^+$ at *m/z* 747.3926 and $[M+K]^+$ at *m/z* 763.3666 in the positive HRESIMS corresponding to the molecular formula $C_{38}H_{60}O_{13}$. A prominent fragment ion $[M-H_2O+H]^+$ at 707.4001 was also observed. IR spectrum of **1** displayed absorption bands at 3406 and 1047 cm^{-1}, suggesting its glycosidic nature, in addition to a characteristic strong absorption band at 1725 cm^{-1} (C=O). The combined analysis of ^1H and ^{13}C NMR resonances of **1** in CD_3OD (Table 1), showed the presence of four methyl groups [(δ_C/δ_H 15.8/0.93) (3H, d, *J* = 6.8 Hz), 14.0/1.07 (3H, d, *J* = 6.8 Hz), 14.7/1.12 (3H, s) and 12.3/0.85 (3H, s)], two carbonyl functions (δ_C 219.2 and 215.6), an olefinic group [(δ_C/δ_H 124.3/5.58) (d, *J* = 5.2 Hz) and δ_C 138.4] and a hydroxymethylene group [δ_C/δ_H 66.8/3.43, 3.36], suggesting a steroidal moiety. The glycosidic nature of **1** was confirmed by acid hydrolysis which afforded sugar components identified as L-arabinose and L-rhamnose. The two anomeric proton resonances [δ_C/δ_H 99.6/4.31

Table 1
^1H and ^{13}C-NMR data of compound **1**, its acetate derivative **1a** and selected ^{13}C-NMR data of alliospiroside A **3**.

C	**1**		3	**1a**	
	δ_C (CD_3OD)	δ_H (CD_3OD)	δ_C (C_5D_5N)	δ_C (C_5D_5N)	δ_C (CD_3OD)	δ_H (CD_3OD)
1	83.2	3.42	83.6	83.4	83.3	3.60 (dd, 12.0, 4.0)
2	37.1	2.18, 1.70	37.2	37.2	36.9	
3	69.4	3.77	67.7	68.0	70.1	
4	41.3	2.22, 2.20	43.6	43.4	41.4	
5	138.4	–	139.4	139.3	136.5	
6	124.3	5.58 (brd, 5.2)	125.0	124.5	125.9	
7	31.1	1.93, 1.59	31.4		30.9	
8	32.1	1.54	32.1		31.9	
9	49.8	1.43	49.8	50.2	49.6	
10	42.0	–	42.6	42.7	41.9	
11	23.2	2.68, 1.50	23.5		23.4	
12	39.0	1.98, 1.60	37.4		38.8	
13	42.0	–	41.3		41.9	
14	51.4	1.62	51.2		51.4	
15	37.1	2.12, 1.72	38.9		37.9	
16	215.6	–	213.2		215.0	
17	66.5	2.57 (d, 12.0)	66.3		66.2	
18	12.3	0.85 (s)	15.4		12.4	
19	14.7	1.12 (s)	14.8		14.7	
20	43.4	2.70	43.5		43.3	
21	14.0	1.07 (d, 6.8)	12.9		13.7	
22	219.2	–	217.9		219.0	
23	39.4	2.72, 1.70	37.2		39.0	
24	26.5	1.75, 1.37	27.4		26.5	
25	34.9	1.63	35.9		31.8	
26	66.8	3.43, 3.36	67.2		69.0	
27	15.8	0.93 (d, 6.8)	17.1		15.8	
1-O-sugars						
Ara						
1′	99.6	4.31 (d, 6.8)	100.4	100.2	99.2	4.63 (d, 7.6)
2′	74.3	3.72	75.0	74.9	74.2	3.86 (dd, 8.0,8.0)
3′	74.7	3.48	75.8	75.7	74.2	5.10 (dd, 8.0,3.8)
4′	67.7	3.88	69.9	69.9	68.5	5.03 (brs)
5′	66.8	3.84, 3.54 (d, 12.0)	67.2	68.0	63.7	3.78 (d, 2.0)
						3.59 (dd, 12.0,3.0)
Rha						
1′	100.2	5.31 (brs)	101.5	101.5	96.6	5.14 (brs)
2′	70.9	3.92	72.3	72.4	71.3	5.26 (brs)
3′	70.7	3.67	72.3	72.3	70.2	5.30 (dd, 8.0,3.0)
4′	72.7	3.40	74.0	74.0	72.1	5.03 (dd, 9.0,9.0)
5′	68.3	4.12	69.2	69.2	66.5	4.44 (dq, 9.0,6.0)
6′	17.1	1.28 (d, 6.9)	18.9	18.8	16.9	1.23 (d, 6.0)
AC					170.2	2.00, 2.05, 2.05,
					170.4	2.07, 2.11, 2.11, 2.16
					170.5	
					170.6	
					170.7	
					171.2	
					172.0	

Ara = α-L-arabinosyl.
Rha = α-L-rhamnopyranosyl.
Overlapped signals are represented without designated multiplicity.
Values in parentheses represent ^1H–^1H splitting.

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(d, J = 6.8 Hz), 100.2/5.31 (brs)] indicated the presence of one arabinose and one rhamnose units in the molecule. The structure of the steroid moiety with 27 carbons was determined by the use of 1D and 2D (HSQC and HMBC) NMR analysis which allowed proton and carbon assignments. The assigned carbon resonances due to the steroid part of **1** were in agreement with the reported data of kryptogenin (Agrawal et al., 1985) except the significant lowfield position of C-1 resonance at δ_C 83.2, as well as the relatively deshielded positions observed for C-2 (δ_C 37.1) and C-10 (δ_C 42.0) and the shielded location of Me-19 (δ_C 14.7); indicating attachment of the disaccharide unit at C-1 position and recognizing β-orientation of an oxygen function at this position (Mimaki et al., 1996a,b). The presence of an axial oxymethine proton resonance assigned to H-1 at δ_H 3.60 (dd, J = 12.0, 4.0 Hz) in the ^{1}H NMR spectrum of the acetate derivative **1a** (Table 1), confirmed the deduced stereochemistry at C-1. The HMBC correlations between the resonances due to C-19 (δ_C 14.7) and H-1 (δ_H 3.42) and between the resonances of C-1 (δ_C 83.2) and H-1′ (δ_H 4.31) confirmed glycosylation at C-1 position. Therefore, the steroid part of **1** was assigned the structure of 1β-hydroxy kryptogenin. To the best of our knowledge, this is the first reported occurrence of this genin. The full structure of the disaccharide unit was defined by ^{1}H NMR spectrum of the heptaacetate derivative **1a**. The spectrum showed better resolution of the oxymethine and oxymethylene sugar resonances and revealed that H-2″ (δ_H 5.26, brs), H-3″ (δ_H 5.30, dd, J = 8.0, 3.0 Hz) and H-4″ (δ_H 5.03, dd, J = 9.0, 9.0 Hz) of the rhamnose unit, were linked to acetylated carbon atoms as indicated by their lowfield positions; suggesting the terminal position of this unit. The relatively highfield chemical shift of arabinose H-2′ at δ_H 3.86 (dd, J = 8.0, 8.0 Hz) clearly proved position 2′ to be a glycosidic linkage site. The ^{13}C NMR spectrum of **1** measured in C_5D_5N (Table 1) provided definitive evidence for the structure of the disaccharide unit. The resonances at δ_C 101.5, 72.3, 72.3, 74.0, 69.2 and 18.9 assigned to a terminal rhamnose unit and 100.4, 75.0, 75.8, 69.9 and 67.2 attributed to a C-2′ glycosylated arabinose, were very close to the corresponding data (C_5D_5N) reported for the co-existed metabolite alliospiroside A **3** (Huang et al., 2013) and other steroidal saponins bearing identical 1β, 3β oxygenation pattern for A ring of the steroid moiety as well as disaccharide unit at C-1 position (Mimaki et al., 1996a,b, 1997, 1999). The pyranose form of the two sugar units was derived from their ^{13}C chemical shift values and the α-anomeric configuration of the arabinose unit was deduced from $^3J_{H1\text{-}H2}$ value (6.8 Hz). The broad singlet of the anomeric proton and the chemical shift values of the resonances due to C-3 and C-5 as well as the presence of three-bond strong HMBC correlations between the resonance of the anomeric proton and those due to C-3 and C-5 of the rhamnose unit, indicated an α-orientation. Therefore compound **1** was assigned the structure of 1β-hydroxy-kryptogenin-1-*O*-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranoside. This is the first reported occurrence of **1** (Fig. 1).

Compound **2** was isolated as yellow amorphous solid. It had the molecular formula $C_{18}H_{16}O_7$ as determined by the HRESIMS which exhibited a pseudo-molecular ion peak $[M+1]^+$ at m/z 345.0969. Compound **2** also showed in its EIMS a molecular ion peak at m/z 344. The IR spectrum exhibited absorption bands at 3443 and 1646 cm^{-1}, indicating the presence of hydroxyl and conjugated carbonyl groups. The ^{1}H NMR spectrum of **2** displayed the typical splitting pattern of homoisoflavonoid (Table 2) with two pairs of geminal coupled proton resonances at δ_H 4.41 and 4.14 (each a doublet, J = 11.2 Hz, H-2) and δ_H 2.94 and 2.91 (each a doublet, J = 10.5 Hz, H-9) (Böhler and Tamm, 1967). The observation of resonances due to 12 aromatic carbons, a flavones carbonyl carbon at δ_C 194.4 (C-4), an oxygenated quaternary carbon at δ_C 72.6 (C-3) and methylene carbon at δ_C 40.9 (C-9) in the ^{13}C NMR of **2** (Table 2), confirmed the eucomol type homoisoflavonoid structure (Böhler and Tamm, 1967; Heller et al., 1976; Saitoh et al., 1986). The basic skeleton of 3-hydroxy-3-benzyl-4-chromanone was corroborated by the HMBC correlations (Fig. 2) between H_2-2 and C-3, H_2-9 and C-2, H_2-2 and C-4, H_2-9 and C-4 and H_2-9 and C-1′. The ^{1}H NMR spectrum of **2** ($CDCl_3$) exhibited resonances for three aromatic protons of the B-ring [(δ_H 6.74 (1H, brs, H-2′); δ_C 110.9), (δ_H 6.75 (1H, d, J = 8.5 Hz, H-5′); δ_C 108.1), (δ_H 6.63 (1H, d, J = 8.5 Hz, H-6′); δ_C 123.6)], characteristic of homoisoflavonoids having 3′,4′ dioxygenation. The spectrum also showed two proton singlets at δ_H 5.95 suggesting a methylene dioxy group (OCH_2O). In the HSQC spectrum of **2** the OCH_2O group was recognized at δ_C 100.9 and its location was confirmed by the observed HMBC correlations between the methylene proton resonances at δ_H 5.95 and the carbon resonances at δ_C 147.5 and δ_C 146.7 assignable to C-3′ and C-4′, respectively. In the EIMS spectrum of **2**, the base peak at m/z 135 ($C_8H_7O_2$) due to B-ring tropylium fragment, lent further support to the structure of B-ring. The oxygenation pattern of A ring in **2** was established by the combined use of UV and NMR spectra. The absorption at 287 nm in the UV spectrum of **2** experienced bathochromic shift upon addition of sodium methoxide (6 nm) and sodium acetate (2 nm), indicating the presence of a hydroxyl group at C-7 position. This UV absorption remained unaffected upon addition of aluminum chloride revealing that **2** was devoid of a hydroxyl function at C-5 position. This information together with the observation of further two doublets in the ^{1}H NMR spectrum of **2** at δ_H 7.61 (1H, d, J = 8.5 Hz; δ_C 123.9) and 6.75 (1H, d, J = 8.5 Hz; δ_C 110.4) demonstrated the presence of two *o*-coupled protons located at C-5 and C-6 positions. Furthermore, a three proton singlet located at δ_H 4.0 in the ^{1}H NMR spectrum of **2**, corresponding to aromatic carbon resonance at δ_C 61.4 in the HSQC, indicated the presence of sterically hindered methoxyl group. The methoxyl group was then placed at the only available C-8 position. This conclusion was confirmed by the HMBC correlation between the resonances of OCH_3 protons and the oxygenated carbon at δ_C 134.4 assigned to C-8. Further evidence for the oxygenation pattern of A ring was allowed from the very similar ^{13}C NMR data for A ring of **2** and the corresponding values for other homoisoflavonoids bearing identical A ring oxygenation pattern (Chen and Yang, 2007). The HMBC correlations between the resonances of H-5 (δ_H 7.61) and C-4 (δ_C 194.4), C-7 (δ_C 156.0) and C-8a (δ_C 154.5) and between H-6 (δ_H 6.75) and C-5 (δ_C 123.9), C-8 (δ_C 134.4) and C-4a (δ_C 113.0) provided definitive evidence for A ring structure. The stereochemistry at C-3 was determined by comparison of its electronic circular dichorism (ECD) spectrum with these of previously reported homoisoflavonoids (Adinolfi et al., 1988). The negative $\pi \rightarrow \pi^*$-p*Cotton effect at 288 nm and the positive n-π^*Cotton effect at 318 nm indicated S configuration. Thus, the structure of compound **2** was concluded to be (3S)-3,7-dihydroxy-8-methoxy-3-(3′,4′-methylenedioxybenzyl) chroman-4-one. This is the first reported occurrence of **2**.

2.2. Evaluation of antioxidant and cytotoxic activities

2.2.1. Antioxidant

The isolated compounds **1**, **2**, **3** were tested for their radical scavenging activity using DPPH assay with ascorbic acid as standard. The IC_{50} values were 67.7, 35.2, 254 μg/ml, respectively. The IC_{50} value of ascorbic acid was 33.3 μg/ml. The results showed that compound **2** exhibited activity compared to that of ascorbic acid.

2.2.2. Cytotoxicity

The cytotoxicity of the isolates **1**–**3** was performed against the three human tumor cell lines HCT116, MCF-7 and PC-3, using doxorubicin as a standard drug. The IC_{50} values were 38, 318 and 90 μM against HCT116 cell line, 153, 131 and 69 μM against

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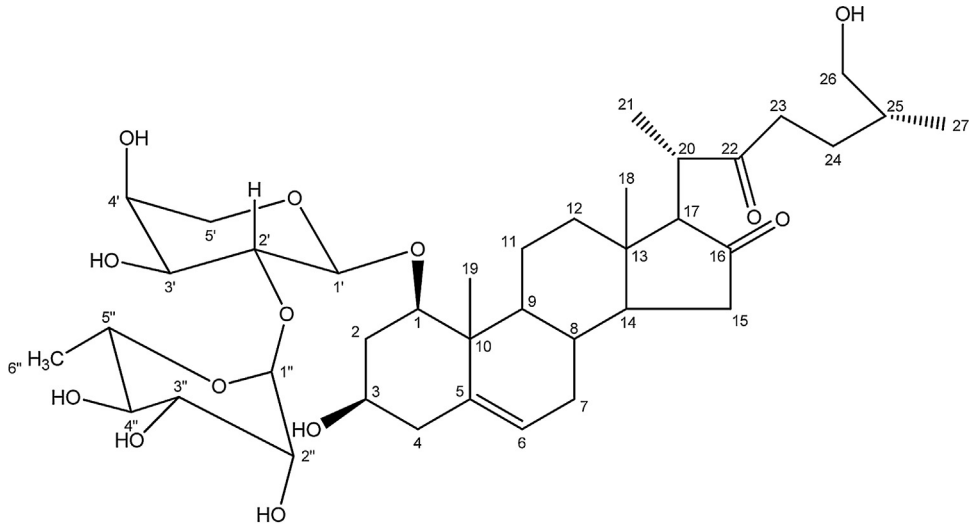
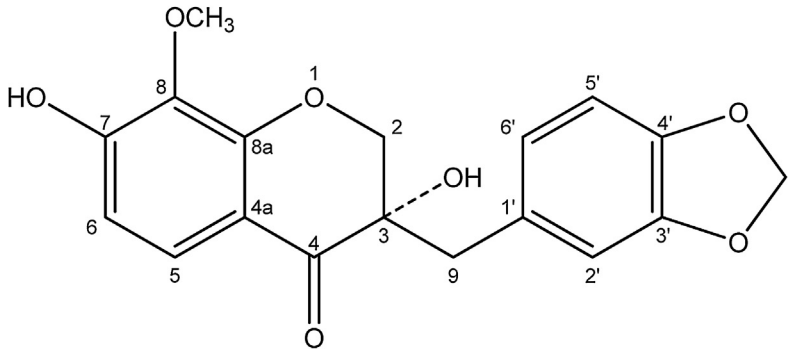


Compound **1**



Compound **2**

Fig. 1. Chemical structures of compound **1** and **2**.

MCF-7 cell line, 175, 366 and 99 μM against PC-3 cell line, respectively. The IC_{50} values of doxorubicin were 10, 6 and 4 μM against the used cell lines, respectively. The results showed that the isolated compounds were inactive.

Table 2
^{1}H and ^{13}C-NMR data of compound **2** in $CDCl_3$.

Position	^{13}C	^{1}H
2	72.7	4.41 (d, 11.2), 4.14 (d, 11.2)
3	72.6	–
4	194.4	–
4a	113.0	–
5	123.9	7.61 (d, 8.5)
6	110.4	6.75 (d, 8.5)
7	156.0	–
8	134.4	–
8a	154.5	–
9	40.9	2.94 (d, 10.5), 2.91 (d, 10.5)
1′	128.0	–
2′	110.9	6.74 (brs)
3′	147.5	–
4′	146.7	–
5′	108.1	6.75 (d, 8.5)
6′	123.6	6.63 (d, 8.5)
OCH_2O	100.9	5.95 (s)
8-OMe	61.4	4.00 (s)

Values in parentheses represent ^{1}H–^{1}H splitting.

3. Experimental

3.1. General

Optical rotations were measured in MeOH or $CHCl_3$ with Kruss polarimeter P8000. FT-IR was measured on FT-IR/FT Roman spectrometer. Circular dichroism was performed on Jasco J-805 spectrometer. UV measurements were obtained using UV-Visible Jasco V-670 spectrophotometer. EI-MS and HRESI-MS data were measured using Jeol JMS-Ax500 spectrometer and Bruker micro-TOF-QII MS (Amherst, MA), respectively. NMR spectra were measured using Bruker High Performance Digital FT-NMR Spectrometer Avance III operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C nuclei. Polyamide 6S (50–160 μ) (Fluka Chemie GmbH, Germany), Silica gel 60 (Merck) and Sephadex LH-20 (Pharmacia, Uppsala, Sweden) were used for column chromatography. Silica gel aluminum sheets G 60 (F_{254}-Merck) were used for TLC. TLC plates were observed under UV (254 and 366 nm) then visualized by heating after spraying with vanillin-H_2SO_4.

3.2. Plant material

The unflowering aerial parts of *Sansevieria cylindrica* fam. Dracaenaceae were collected from Orman botanical garden, Giza,

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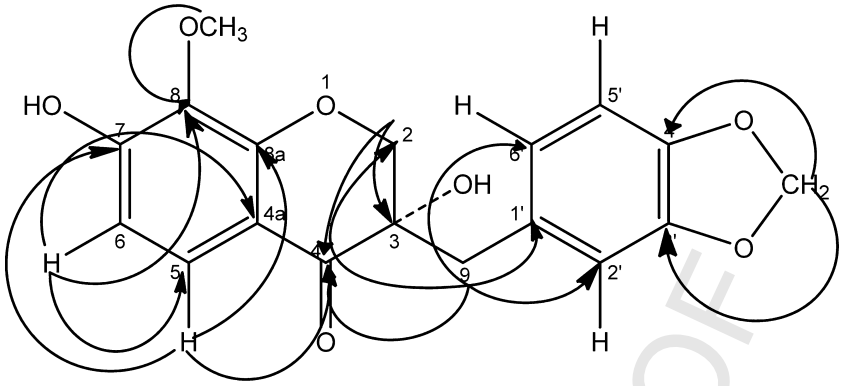

Fig. 2. Key HMBC correlation of compound **2**.

Egypt in June 2009, kindly authenticated by Dr. Mohammed El-Gebaly, Department of Botany, National Research Centre and confirmed by Dr. Abd El-Magali, Flora & Phytotaxonomy Research – Horticultural Research Institute, Agricultural Research Centre, Ministry of Agriculture. A voucher specimen is deposited in the Herbarium, Pharmacognosy Department, Faculty of Pharmacy, Cairo University (2014-12).

3.3. Extraction and isolation

The air-dried powdered unflowering aerial parts (1 kg) of *S. cylindrica* were extracted by maceration with 70% aqueous methanol until exhaustion. The combined methanolic extract was evaporated under vacuum to dryness. The dark brown residue (350 g) was applied on a chromatographic column packed with polyamide gel (1 kg) and eluted with gradient solvent system H_2O–MeOH (1:0–0:1) then MeOH–CH_2Cl_2 (7:3) to give 109 fractions (1 L) each. Fractions were detected by silica TLC using two different solvent systems MeOH-CH_2CL_2 (2:8) and EtOAc-*n*-hexane (4:6). The TLC was visualized by spraying with vanillin-H_2SO_4 reagent and heating at 100 °C. Similar fractions were pooled to give 12 main fractions. Fraction 4 (10 g) eluted with H_2O-MeOH (9:1) was chromatographed on silica gel CC (300 g) eluted with gradient CH_2Cl_2–EtOAc (9:1–1:9) to give 104 fractions 50 ml each. Fractions (48–64) eluted with CH_2Cl_2–EtOAc (88:12) were combined (2 g) and rechromatographed on silica gel CC (10 g) eluted with *n*-C_6H_{14}–CH_2Cl_2–MeOH–isoPrOH (8:1:2:2) to afford 30 fractions 10 ml each. The material from fractions (11–20) that showed one major spot on silica gel TLC (CH_2Cl_2–MeOH, 8:2) was purified using sephadex LH-20 CC (10 g) using MeOH–CH_2Cl_2 (8:2) to afford compound **1** (25 mg). Fraction 8 (27 g) eluted from the main column with H_2O–MeOH (7:3), was subjected to silica gel CC (300 g) eluted with gradient *n*-hexane-EtOAc (9:1–1:9) followed by MeOH to give 87 fractions 50 ml each. Fractions 6–8 (40 mg) eluted with *n*-hexane-EtOAc (7:3) exhibiting one major spot on silica gel TLC (CH_2Cl_2–MeOH, 97:3), were purified using silica gel CC (10 g) eluted with *n*-hexane–EtOAc (7:3) to afford compound **2** (15 mg). Fraction 83 (42 mg) eluted with MeOH was rechromatographed on silica gel CC (10 g) eluted with CH_2Cl_2–MeOH (95:5) to afford 15 fraction 10 ml each. The material from fractions 2 and 3 (20 mg) exhibiting one major spot on silica TLC (CH_2Cl_2–MeOH, 8:2), were combined and purified using sephadex LH-20 CC eluted with MeOH–CH_2Cl_2 (8:2) to afford compound **3** (11 mg).

3.3.1. 1β-hydroxy-kryptogenin-1-O-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranoside (**1**)

Colorless amorphous solid; $[\alpha]_D^{20}$ −6.97 (*c* 0.1,MeOH); IR (KBr) ν_{max} (cm^{-1}): 3406, 2929, 1725, 1646, 1452, 1375, 1257, 1047; HRESIMS (positive ion mode) *m/z*: 763.3666 $[M+K]^+$ (calcd for $C_{38}H_{60}O_{13}K$ 763.3671), 747.3926 $[M+Na]^+$ (calcd for $C_{38}H_{60}O_{13}Na$ 747.3932), 707.4001 $[M-H_2O+H]^+$(calcd for $C_{38}H_{59}O_{12}$ 707.4007); ^1H NMR (400 MHz, CD_3OD) and ^{13}C NMR (100 MHz) see Table 1.

3.3.2. (3S)-3,7-dihydroxy-8-methoxy-3-(3′,4′-methylenedioxybenzyl) chroman-4-one (**2**)

Yellow amorphous solid; $[\alpha]_D^{20}$ +16.62 (*c* 0.1, CH_2Cl_2); UV λ_{max} (log ε): (MeOH) 235 (4.9), 287 (4.9) nm, (NaOMe) 257 (4.9), 293 (5)sh., 339 (5.1) nm, ($AlCl_3$) 235 (4.9), 287 (5), 364 (5.1) nm, ($AlCl_3$/HCl) 235 (4.9), 287 (5), 365 (5.1) nm, (NaOAc) 257 (4.9), 289 (5) nm, 339 (5.1) nm, (NaOAc/H_3BO_3) 288(5) nm; ECD: $[\Theta]_{288}$-11 074, $[\Theta]_{318}$ + 7 669; IR ν_{max} (cm^{-1}): 3443, 2924, 1646,1501, 1455, 1384, 1034; EIMS *m/z*: 344 (M^+), 209, 152, 149, 135, 105, 95, 77; HRESIMS (positive ion mode) *m/z*: 345.0969 $[M+H]^+$ (calcd for $C_{18}H_{17}O_7$ 345.0974); ^1H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) see Table 2.

3.4. Acid hydrolysis of compound **1**

Compound **1** (2 mg) in 1.5 N HCl (2 ml) was heated at 100 °C for 4 h. The solvent was evaporated and the residue was dissolved in H_2O then extracted four times with CH_2Cl_2. The remaining aqueous layer was repeatedly evaporated to dryness with MeOH until neutral, and the sugars were then analyzed by paper chromatography (*n*-BuOH–CH_3COOH–H_2O, 4:1:5, upper layer) by comparison against authentic samples. The chromatogram was visualized by spraying with aniline hydrogen phthalate reagent and heating at 110 °C till the color of the spots appeared. L-Rhamnose and L-arabinose were detected.

3.5. Acetylation of 1

Compound **1** (10 mg) was acetylated with acetic anhydride (2 ml) in pyridine (2 ml) and the crude acetate was purified by sephadex LH-20 CC using MeOH to yield the corresponding peracetate **1a** (7 mg).

3.6. Antioxidant activity

A stock solution (1 mg ml^{-1}) of each test compound was prepared in methanol. Sample concentrations of 20, 50, 100, 150, 200 and 250 μg/ml were prepared in methanol. The free radical scavenging activity of compounds (**1**–**3**) was evaluated according to the method described by Braca et al. (2001). Test sample (0.1 ml) was added to 3 ml of a 0.004% methanol solution of DPPH (1,1-diphenyl-2-picrylhydrazyl). Absorbance at 517 nm was determined after 30 min, and the percentage inhibition activity was calculated from $[(A_0 - A_1)/A_0] \times 100$, where A_0 is the absorbance of the control, and A_1 is the absorbance of the test sample or standard (ascorbic acid).

3.7. Cytotoxicity assay

The cytotoxicity of isolated compounds, **1**, **2** and **3** were tested against HCT116 (Colon Cancer), MCF-7 (Breast Cancer) and PC-3 (prostate Cancer) cell lines using SulphoRhodamine-B (SRB) method as previously described by Skehan et al. (1990), with doxrubcine as a standard drug. The cells were obtained from American Type Culture Collection (ATTC) (University Boulevard, Manassas, Virginia, USA). The absorbance at 490 nm (reference wavelength) was measured with an ELISA microplate reader. The IC_{50} values were calculated using sigmoidal concentration–response curve fitting models (SigmaPlot software).

Q5 Uncited reference

Haraguchi et al. (1994).

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