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Sablacaurin A and B, two 19-*nor*-3,4-*seco*-lanostane-type triterpenoids from *Sabal causiarum* and *Sabal blackburniana*, respectively

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Abstract

In search for bioactive compounds from *Sabal* species, sablacaurin A [25-ethyl,23-methyl-19-*nor*-24-methylene-3,4-*seco*-4(28)-lanosten-10,3-olide] and sablacaurin B [24-ethyl,24-methyl-19-*nor*-3,4-*seco*-4(28),25(26)-lanostadiene-10,3-olide], the first 19-*nor* lanostane derivatives of the 3,4-*seco* type with a spiro element, have been isolated from the leaves of *Sabal causiarum* and *Sabal blackburniana* respectively, together with the known squalene (*S. blackburniana*) and ß-sitosterol (*S. causiarum*). From leaves of *Sabal peregrina*, the known triterpenes 3-oxo-24-methylenecycloartane and 24-methylcycloart-25(26)-en-3-one were isolated. The structures of these compounds were established from spectroscopic studies.

Keywords: *Sabal*; Arecaceae; Triterpenoids; 19-*Nor*-3,4-*seco*-lanostane type; Sablacaurins

1. Introduction

The genus *Sabal* (Arecaceae) comprises 14 species native to the United States, Central America, northern south America and the West Indies (Jones, 1996). Following the well documented medicinal use of the fruits of *Sabal serrulata* (Michaux) Nuttal et Schultes for the treatment of benign prostatic hyperplasia (Braun et al., 1998), this species has been the subject of intensive pharmacological and chemical investigations (Koch, 2001). Previous studies revealed the presence of various fatty acids and their derivatives, triglycerides, phytosterols, aliphatic alcohols, and various polyprenic compounds. By contrast, little attention has been paid to chemical constituents of other members. For example, fatty acids present in the seeds of *Sabal blackburniana* (Idiem'Opute, 1979), and flavonoids occurring in flowers of the same species (Harborne et al., 1974) have been reported, while the occurrence of some steroidal saponins and the *C*-glucosylflavone vitexin in *S. causiarum* has been recorded (Idaka et al., 1988). In search for new bioactive compounds and having in mind the hitherto limited information on metabolites of *Sabal* species, the metabolic pool of leave extracts of *S. blackburniana*, *S. causiarum* and *S. peregrina* was investigated.

This paper reports on the isolation and structure elucidation of two novel 19-*nor* lanostane derivatives of the 3,4-*seco* type from *S. blackburniana* and *S. causiarum*, respectively, and two known cycloartane analogues from *S. peregrina*.

2. Results and discussion

The aqueous methanol extract of leaves of *S. blackburniana*, *S. causiarum* and *S. peregrina* was initially successively extracted with petroleum ether, dichloromethane, ethyl acetate and *n*-butanol saturated with water in each instance. Subsequent chromatographic purification of lipophilic fractions by CC and prep. TLC afforded the novel 19-nor-3,4-secolanostane type triterpenoids **1** and **2** from *S. causiarum* and *S.*

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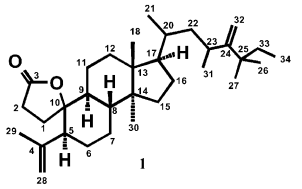
blackburniana, respectively. Initial identification of compounds **1** and **2** as triterpenoids clearly followed from their visualisation on silica plates upon treatment with $SbCl_3$, taking into account mass spectral analyses. Structural assessment of these unique lanostane derivatives of the 3,4-*seco* type was effected by analysis of ^1H and ^{13}C NMR spectroscopic data. Allocation of signals was facilitated by COSY, DEPT, NOESY, HMQC and HMBC experiments.



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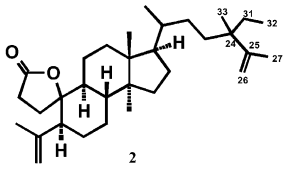

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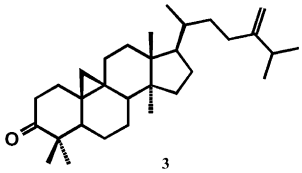

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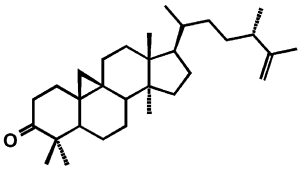

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The CH_2Cl_2 extractives of *S. causiarum* were subjected to column chromatography on silica gel using petroleum ether–ethyl acetate gradient systems followed by prep. TLC to yield chromatographically homogeneous **1**. It was obtained as a creamy white solid and established to have a molecular formula of $C_{33}H_{54}O_2$ by HR-EIMS ($M^{+\cdot}$ at m/z 482.4121; calc. 482.4124). The negative FAB-MS of **1** showed a $[M–H]^-$ peak at m/z 481, consistent with the molecular formula. IR (KBr) absorptions at 897 and 1768 cm^{-1} suggested the presence of at least one terminal methylene group and a γ-lactone element, respectively. From the ^1H and ^{13}C NMR spectra signals for a lanostane skeleton but structurally modified could be concluded. The ^{13}C NMR and DEPT spectra exhibited 33 resonances, including 7× C, 12× CH_2, 6× CH and 8× CH_3 including a primary methyl (δ_C 9.03, H_3-34), two *sec*- (δ_C 18.62, H_3-21; δ_C 18.71, H_3-31) and five *tert*-methyls (δ_C 22.70, H_3-29; δ_C 14.70, H_3-18; δ_C 26.97, H_3-26 and H_3-27; δ_C 16.74, H_3-30) as evident from their multiplicities in the ^1H NMR spectrum (Table 1). Of the ^{13}C resonances for methylene carbons, two signals appeared at conspicuously low fields [δ_C 107.54 (C-32) and 115.00 (C-28)] relative to the majority of these absorbances (δ_C 29–50). Taking into account the presence of two pairs of 'isolated' methylene protons (δ 4.76 and 4.79; δ 4.82 and 4.93; see Table 1) in the ^1H NMR spectrum of **1**, these spectral features indicated the existence of two terminal methylene groups. Consistent with the above NMR data analysis, the ^1H–^1H COSY spectrum indicated the presence of aliphatic proton signals arising from a 1-methylethenyl side chain (δ 1.77, *s*, H_3-29; δ 4.82 and 4.93, each br *s*, vinylic H-28). The position of this substituent, assigned to C-5 (δ_C 54.85), was established through long-range HMBC correlations with both H_2-28 (δ 4.82 and 4.93) and H_3-29 (δ 1.77), and couplings between C-4 (δ_C 146.73) and H-5 (δ 2.57) as well as H_3-29 (δ 1.77). The α-configuration of H-5 (δ 2.57) followed from the NOESY spectrum which showed clear NOE correlations with H_a-28 (δ 4.82), H-6a (δ 1.49) and H-9 (δ 1.92) as well as H-9 and H_3-30 (δ 0.80).

Further analysis of the observed COSY and HMBC correlations indicated that the gross structure of the side chain at C-17 was the same as that of skimmiwallin (Kostova et al., 1996) except for the presence of a methyl at C-23: one methyl group (H_3-21; δ 0.90, δ_C 18.62) with a $^3J_{H,H}$-coupling of 6.4 Hz to a methine proton (H-20; δ 1.42, δ_C 37.32), an additional methyl group forming the portion of an ethyl functionality (C-34; δ 0.70, *t*, $J = 7.5$ Hz, δ_C 9.03), two methylene groups with δ_C 30.61 (C-22) and δ_C 33.30 (C-33), a methine carbon at δ_C 27.85 (C-23), two vinylic protons at δ 4.76 and 4.79 (methylene carbon at δ_C 107.54) and a quaternary carbon at δ_C 156.70, and two methyl groups showing one singlet in the ^1H NMR spectrum at δ 1.01. Long range correlations observed in the HMBC spectrum from both vinylic protons to the quaternary carbons at δ_C 156.70 (C-24) and 39.56 (C-25) as well as from δ 1.37 (H_2-33) to the coincided methyl carbons at δ_C 26.97 (C-26 and C-27), and from δ 0.70 (C-34) to the quaternary carbon at δ_C 39.56 (C-25) established the proposed arrangement. Other significant HMBC associations were the connectivities of two broad one-proton signals (δ 4.76, 4.79), H_3-34, and H_3-26/H_3-27 (6H, δ 1.01) with the quaternary C-25 (δ_C 39.56).

The low-field carbonyl carbon (δ_C 177.23, C-3) in the 2D HMBC plot was observed to be associated with two pairs of methylene protons (δ 2.47, H_2-2; δ 2.33 and 1.74, H_2-1). In addition, the H_2-1 and H_2-2 signals showed distinct correlations to the quaternary oxygenated carbon (δ_C 91.69, C-10), consistent with a lactone substructure. The binding mode of the γ-lactone moiety was based on definite associations observed in the HETCOR and HMBC experiments between C-1 and both H-5 and H-9, and couplings between C-10 and H-5, H-2 and H_2-11, providing strong evidence for its bonding at the C-10 spiro carbon. Thus, compound **1** was identified as 25-ethyl,23-methyl-19-*nor*-24-methylene-3,4-*seco*-4(28)-lanosten-10,3-olide, a new natural triterpenoid designated as sablacaurin A.

Compound **2** was isolated as a creamy white solid from the petroleum ether extract of *S. blackburniana*, following a combination of similar chromatographic techniques as described above. Its molecular formula, $C_{32}H_{52}O_2$, was established from HR-EIMS ($M^{+\cdot}$ at m/z

Table 1
^{1}H, ^{13}C NMR data and HMBC connectivities of compounds **1** and **2** [$CDCl_3$, *J* values (Hz) are given in parentheses]

No	**1**			**2**		
	δ_C	δ_H	HMBC	δ_C	δ_H	HMBC
1	29.61	2.33 (*ddd*, 13.0, 12.7, 8.0, H_b 1) 1.74 (*m*, H_a-1)	H-5; H-9	29.61	2.33 (*ddd*, 13.0, 12.7, 8.0, H_b-1) 1.74 (*m*, H_a-1)	H-5; H-9
2	31.58	2.47 (*m*, H_2-2)		31.57	2.47 (*m*, H_2-2)	
3	177.23	–	H_a-1; H_b-1; H_a-2; H_b-2	177.26	–	H_a-1; H_b-1; H_a-2; H_b-2
4	146.73	–	H-5; H_3-29	146.72	–	H-5; H_3-29
5	54.85	2.57 (br *d*, 9.3, H-5)	H_a-28; H_b-28; H_3-29	54.84	2.56 (br *d*, 9.3, H-5)	H_a-28; H_b-28; H_3-29
6	29.71	1.75 (*m*, H $_b$- 6) 1.49 (*m*, H_a-6)	H-8	29.71	1.75 (*m*, H_b-6) 1.47 (*m*, H_a-6)	H-8
7	31.47	1.50 (*m*, H_b-7) 1.27 (*m*, H_a-7)		31.45	1.48 (*m*, H_b-7) 1.28 (*m*, H_a-7)	
8	48.48	1.43 (*m*, H-8)	H_3-30	48.46	1.45 (*m*, H-8)	H_3-30
9	31.77	1.92 (*m*, H-9)	H_a-1; H_b-1	31.75	1.90 (*m*, H-9)	H_a-1; H_b-1
10	91.69	–	H_a-1; H_b-1; H_a-2; H_b-2; H-5; H_a-11; H_b-11	91.70	–	H_a-1; H_b-1; H_a-2; H_b-2; H-5; H_a-11; H_b-11
11	49.21	1.82 (*m*, H_b-11) 1.68 (*m*, H_a-11)		49.19	1.80 (*m*, H_b-11) 1.68 (*m*, H_a-11)	
12	32.72	1.63 (*m*, H_b-12) 1.52 (*m*, H_a-12)	H_3-18	32.66	1.63 (*m*, H_b-12) 1.49 (*m*, H_a-12)	H_3-18
13	45.52	–	H_3-18; H_3-30	45.45	–	H_3-18; H_3-30
14	49.23	–	H_3-18; H_3-30	49.21	–	H_3-18; H_3-30
15	33.40	1.25 (*m*, H_2-15)	H_3-30	33.38	1.23 (*m*, H_2-15)	H_3-30
16	27.96	1.93 (*m*, H_b-16) 1.23 (*m*, H_a-16)		27.88	1.92 (*m*, H_b-16) 1.24 (*m*, H_a-16)	
17	50.88	1.53 (*m*, H-17)	H_3-18; H_3-21	50.76	1.53 (*m*, H-17)	H_3-18; H_3-21
18	14.70	0.82 (*s*, H_3-18)		14.64	0.80 (*s*, H_3-18)	
19	–	–		–	–	
20	37.32	1.42 (*m*, H-20)	H_3-21	36.70	1.32 (*m*, H-20)	H_3-21
21	18.62	0.90 (*d*, 6.40, H_3-21)		18.70	0.85 (*d*, 6.6, H_3-21)	
22	30.61	1.65 (*m*, H_b-22) 1.44 (m, H_a-22)		30.60	1.64 (*m*, H_b-22) 1.45 (*m*, H_a-22)	
23	27.85	1.58 (*m*, H-23)	H_a-32; H_b-32	36.22	1.47 (*m*, H_b-23; H_a-23[a]) 1.03 (*m*, H-23a)	H_3-33
24	156.70	–	H_3-26; H_3-27; H_a-32; H_b-32	42.06	–	H_a-26; H_b-26; H_3-27; H_3-33
25	39.56	–	H_3-26; H_3-27; H_a-32; H_b-32; H_3-34	150.20	–	H_3-27; H_3-33
26	26.97	1.01 (*s*, H_3-26)	H_2-33	111.15	4.81 (br *s*, H_b-26) 4.63 (br s, H-26a) 4.63 (br *s*, H_a-26)	H_3-27
27	26.97	1.01 (*s*, H_3-27)	H_2-33	19.32	1.63 (*s*, H_3-27)	H_a-26; H_b-26
28	115.00	4.93 (br *s*, H_b-28) 4.82 (br *s*, H_a-28)		114.98	4.93 (br *s*, H_b-28) 4.82 (br *s*, H_a-28)	H-5; H_3-29
29	22.70	1.77 (*s*, H_3-29)	H_a-28; H_b-28	22.69	1.77 (br *s*, H_3-29)	H-5; H_a-28; H_b-28
30	16.74	0.86 (*s*, H_3-30)		16.73	0.84 (*s*, H_3-30)	H-8
31	18.71	0.85 (*d*, 6.7, H_3-31)		32.27	1.46 (*m*, H_b-31) 1.24 (*m*, H-31a) 1.24 (*m*, H_a-31)	H-33
32	107.54	4.79 (br *s*, H_b-32) 4.76 (br *s*, H_a-32)		8.40	0.71 (*t*, 7.4, H_3-32)	
33	33.30	1.37 (*q*, 7.50, H_3-33)	H_3-26, H_3-27	22.21	0.94 (*s*, H_3-33)	
34	9.03	0.70 (*t*, 7.50, H_3-34)				

[a] Not clearly observed.

468.3961; calc. 468.3967), indicating that the molecular weight of this metabolite was 14 mass units less than that of **1**. Again, prominent fragment ions at *m*/*z* 355 $[C_{24}H_{35}O_2]^+$ and 327 $[C_{22}H_{31}O_2]^+$ were detected in the EI-MS of **2**. Close structural similarity of compounds **1** and **2** followed tentatively from the general congruence of ^{1}H and ^{13}C resonances. Thus, analysis of the NMR data of **2** again revealed the presence of a 1-methyl-ethenyl side chain and a lactone ring element in the lanostane skeleton. Inspection of ^{1}H–^{13}C long-range correlations established once more the location of these substituents at C-5 and C-10, respectively. The most significant difference between the spectra of compounds **1** and **2** was associated with signals for the aliphatic side chain at C-17, with the appearance of a methyl group (H_3-21; δ 0.85, δ_C 18.70) coupled to a methine carbon (H-20; δ 1.32, δ_C 36.70), two methylene functions with δ_C 30.60 and δ_C 36.22, two quaternary carbons at δ_C

42.06 and δ_C 150.20, two methyl groups with singlets in the ^1H NMR spectrum at δ 0.94 (δ_C 22.21) and 1.63 (δ_C 19.32) as well as one ethyl group [methyl triplet at δ 0.71 (δ_C 8.40), coupled to a methylene group (δ 1.24 and 1.46; δ_C 32.27)]. The sequence of these functionalities in the side chain was confirmed by HMQC and HMBC experiments. Collectively, these spectral features defined the structure of **2** as depicted in its formula. Compound **2**, 24-ethyl,24-methyl-19-*nor*-3,4-*seco*-4(28),25(26)-lanostadiene-10,3-olide and designated as sablacaurin B, was isolated for the first time from a natural source.

The identification of compounds **1** and **2** not only extends the small group of lanostane derivatives of the 3,4-*seco* type (Rösecke and König, 1999; Mulholland et al., 1994; Tai et al., 1993) but also introduces the first members of 19-*nor* analogues within this group of natural products possessing a unique spiro-type lactone element in their molecules. Unfortunately, prolonged exposure to $CDCl_3$ eventually led to decomposition of compounds **1** and **2**, which precluded the acquisition of an optical rotation. Biosynthetically, this structural subunit may be formed by lactonization between a propionic moiety resulting from opening of the ring A of the lanostane skeleton and a hydroxyl group originating from combined oxidation and reduction steps of the 19-methyl group. It should also be noted that 3,4-*seco* lanostane derivatives have predominantly been obtained from fungi (Rösecke and König, 1999).

The known cycloartane derivatives **3** and **4** were isolated from the petroleum ether fraction of *S. peregrina* and identified as 3-oxo-24-methylenecycloartane (Alves et al., 2000; Ohta et al., 1958) and 24-methyl-cycloart-25(26)-en-3-one (cyclolaudenone) (Cantillo-Ciau et al., 2001), respectively, on the basis of their spectral data.

3. Experimental

3.1. General

UV spectra were recorded on a Shimadzu UV-160 spectrophotometer and IR spectra were measured on a Perkin Elmer 1420 ratio recording infrared spectrophotometer. ^1H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were obtained using a Bruker DPX-400 and a Bruker AMX-400 instrument. HMBC experiments were optimised for $^{2-3}J_{H/C} = 8$ Hz. EIMS, HR-EIMS and FAB-MS were acquired with a Varian MAT CH_7A, a Finnigan MAT 711 and a Finnigan MAT CH_5DF spectrometer, respectively. Column chromatography was carried out on silica gel 60 (0.063–0.200 mm; Merck), Sephadex LH-20 (Fluka) and RP C-18 (5–20 μm; Merck) material, while precoated plates (silica gel 60 F_{254}, 0.25 mm) were used for prep. TLC without activation. Compounds were visualised by spraying with $SbCl_3$ reagent.

3.2. Plant material

The leaves of *S. blackburniana* (Glazebrook ex J. A. & J. H. Schultes), *S. causiarum* (O.F. Cook) Beccari and *S. peregrina* (L.H. Bailey) F. Palmae were collected in June 2000 from cultured plants grown in Al-Orman Botanical Garden, Cairo, and identified by Dr. M. Gibali, Plant Flora and Taxonomy in National Research Centre, Dokki, Cairo, Egypt. Voucher specimens numbers (Sab-1, Sab-2 and Sab-3) have been deposited at the Department of Pharmacognosy and Medicinal Plants, Helwan University, Ain-Helwan, Cairo, Egypt.

3.3. Extraction and isolation

Freshly collected leaves of *S. causiarum* *S. blackburniana* and *S. peregrina* (ca 3.6 kg each) were blended and exhaustively extracted with 70% aqueous MeOH to afford a dark brown residue (225 g, 90 g and 257 g, respectively) on evaporation of the solvent in each instance. A portion of the individual crude extracts (100 g, 75 g and 100 g, respectively) was suspended in H_2O and successively treated with petroleum ether (6×250 ml), CH_2Cl_2 (4×250 ml), EtOAc (9×250 ml), and *n*-BuOH saturated with H_2O (7×250 l).

A portion of the CH_2Cl_2 soluble extractives (5 g) of *S. causiarum* was subsequently applied to a silica gel G 60 column (3×40 cm) using an *n*-hexane–CH_2Cl_2 gradient system (1:0→0:1), followed by a CH_2Cl_2–EtOAc gradient system (19:1→0:1). The content of test tubes eluted with *n*-hexane–CH_2Cl_2 (6:4→5.5:4.5) was subjected to prep. TLC separation with hexane–CH_2Cl_2 (1:9) as developing system to yield compound **1** (7.7 mg). Elution with *n*-hexane–CH_2Cl_2 (1:1) and subsequent similar TLC purification [CH_2Cl_2–EtOAc (4:1)] afforded β-sitosterol (6.5 mg).

A portion of the petroleum ether soluble extractives of *S. blackburniana* (3 g) was similarly subjected to chromatography on silica gel 60 using a petroleum ether–EtOAc gradient system (10:0→9.5:0.5). The content of test tubes eluted with just petroleum ether (25.2–27 l) was purified by prep. TLC separation with petroleum ether–EtOAc (4:1; ×2) to yield compound **2** (8.8 mg). From eluants 6060–7500 ml squalene (12 mg) was obtained.

Similar purification steps of the petroleum ether soluble extractives of *S. peregrina* (2 g) as described above afforded compounds **3** and **4** (8 mg).

3.3.1. 25-Ethyl,23-methyl-19-nor-24-methylene-3,4-seco-4(28)-lanosten-10,3-olide (*1*)

Creamy white solid; IR (KBr) ν_{max} 3413, 2928, 2872, 1768, 1594, 1565, 1455, 1406, 1378, 1170, 897 cm $^{-1}$; UV (CH_2Cl_2) λ_{max} nm (log ϵ): 231 (2.1); HR-EIMS *m*/*z* 482.4121 ($M^{+\cdot}$, calc. for $C_{33}H_{54}O_2$: 482.4124); EI-MS *m*/*z* (rel. int.): 482 $[M]^{+\cdot}$ (21), 370 (64), 356 (15), 355

(38), 327 (100), 313 (23), 303 (26), 287 (55), 147 (38), 95 (63) 55 (41); ^{1}H and ^{13}C NMR data, see Table 1.

3.3.2. 24-Ethyl,24-methyl-19-nor-3,4-seco-4(28),25(26)-lanostadiene-10,3-olide (**2**)

Creamy white solid; IR (KBr) ν_{max} 3435, 2935, 2873, 1770, 1638, 1455, 1376, 1194, 1170, 892 cm $^{-1}$; UV (CH_2Cl_2) λ_{max} nm (log ϵ): 230 (2.6); HR-EI-MS m/z 468.3963 ($M^{+}\cdot$, calc. for $C_{32}H_{52}O_2$: 468.3967); EI-MS m/z (rel. int.): 468 $[M]^{+}\cdot$ (47), 453 (23), 370 (43), 355 (28), 327 (100), 303 (22), 287 (57), 95 (70), 55 (45); ^{1}H and ^{13}C NMR data, see Table 2.

3.3.3. 3-Oxo-24-methylenecycloartane (**3**)

Yellowish oily residue; IR (KBr) IR ν_{max}: 3435, 2927, 2861, 2359, 2340, 1713, 1655, 1638, 1458, 1376, 1364, 1262, 1113, 1092, 1028, 802 cm^{-1}; UV (CH_2Cl_2) λ_{max} nm (log ϵ): 272 (2.4), 231 (3.0); HR-EIMS m/z 438.3865 ($M^{+}\cdot$, calc. for $C_{31}H_{50}O$: 438.3862). NMR data of **3** corresponded to those in the literature (Alves et al., 2000; Ohta et al., 1958).

3.3.4. 24-Methylcycloart-25(26)-en-3-one (cyclolaudenone) (**4**)

Yellowish oily residue; IR, UV and MS spectroscopic features were identical with those of compound **3**. NMR data of **4** were consistent with those previously reported (Cantillo-Ciau et al., 2001).

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