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NOVEL RINGS B,D-SECOLIMONOIDS FROM THE STEM BARK OF *KHAYA SENEGALENSIS*

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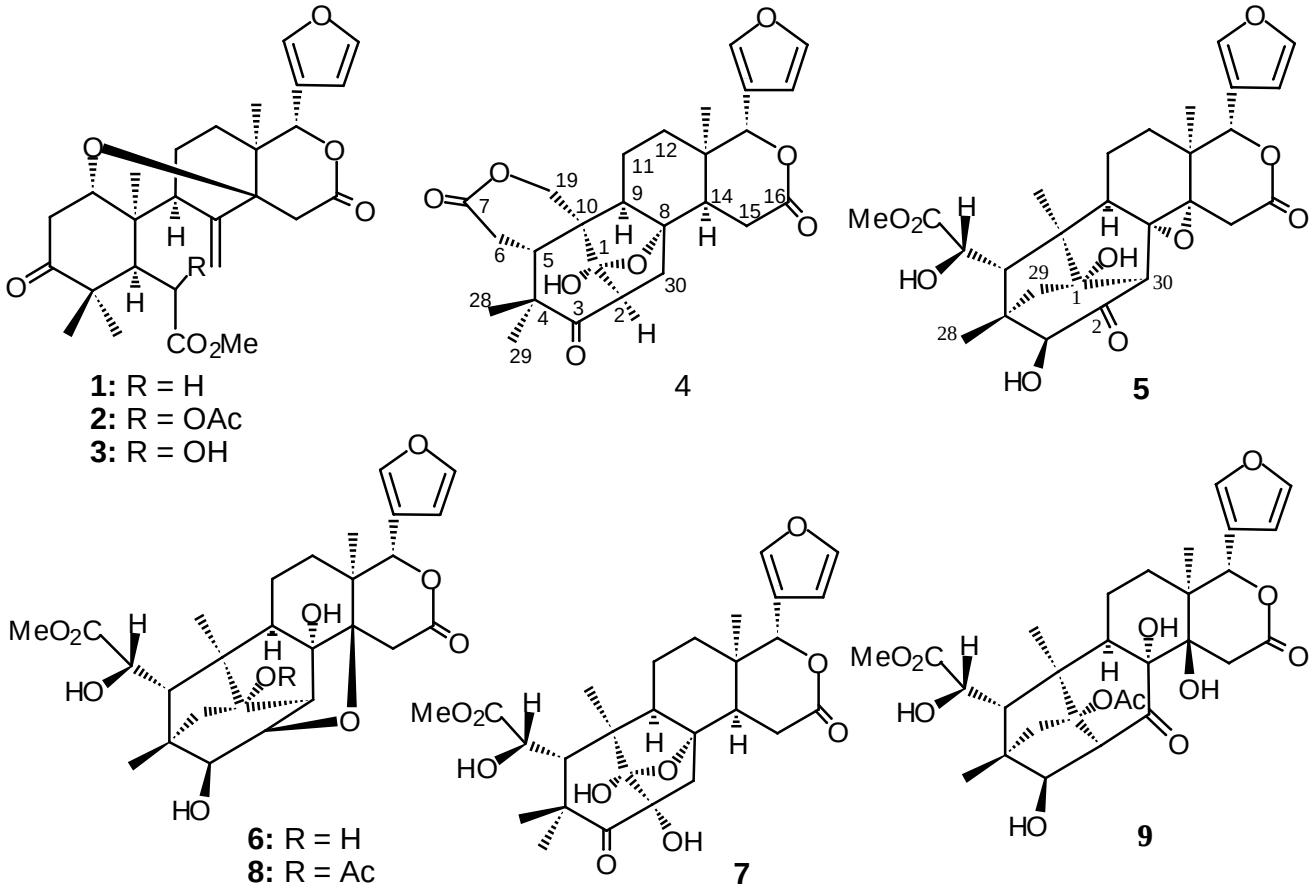
Abstract—Two new rings B,D-secolimonoids, named khayalactol and 1-*O*-acetylkhayanolide B, were isolated together with three known rings B,D-seco-limonoids, methyl angolensate and its 6-hydroxy and 6-acetoxy derivatives, from the ether extract of the stem bark of a meliaceous plant *Khaya senegalensis*. The structure of these new compounds was elucidated by spectrospcopic means. The antifeedant property of the isolated compounds is also described.

In a series of our experiments on limonoid constituents from Meliaceae plants, several types of compounds have been isolated as insect antifeedant from *Trichilia roka*,[1] *Melia azedarach*[2] and *Melia toosendan*.[3] *Khaya senegalensis* is a large tree native to the sub-Sahara savannah area from Senegal to Uganda[4] and one of the most popular medicinal meliaceous plants in the African traditional remedies. The decoction of the bark is extensively used as febrifuge which could be associated with its use as an antimalarial drug.[5] This genus is the main source of African mahogany and is also one of the main source of rings B,D-secolimonoids,[6-9] methyl angolensates, mexicanolides and phragmalin limonoids.
In view of our interest in the antifeedant activity of members of the family Meliaceae, we have studied the ether extract of the stem bark of *K. senegalensis*. Droplet countercurrent chromatography (DCCC) with descending mode of the extract, followed by reversed phase HPLC purification, resulted in the isolation of several novel limonoids together with three known rings B,D-secocompounds, methyl angolensate (**1**),[10] 6-hydroxyangolensate (**3**) and 6-acetoxyangolensate (**2**).[11] Recently, we have reported the structure of three compounds, named seneganolide (**4**)[12] and khayanolides A (**5**)and B (**6**),[13] from the extract. In this paper, we report the structure of two new compounds, one mexicanolide named khayalactol (**7**) and a rearranged phragmalin limonoid 1-*O*-acetylkhayanolide B (**8**), and the antifeedant activity of the isolated compounds against the larvae of a Japanese insect pest *Spodoptera littoralis* by a



spect conventional leaf disk method.[14]

The structures of the angolensates (**1**-**3**) were identified in comparison of their NMR data with those reported and their stereochemistry was also confirmed by NOE studies (Figure 1).

Khayalactol (**7**) was obtained as an amorphous powder of mp 179-181˚C. Its molecular formula $C_{27}H_{34}O_{10}$ (11 unsaturations) was shown by accurate MS measurement (HRFAB-MS: m/z 541.2107 $[M+Na]^+$; Δ +5.7 mmu). The UV maximum at 210 nm and the IR absorption at 3600-3300, 1730, 1700, 1640 and 875 cm^{-1} showed the presence of carbon-carbon double bonds, hydroxyl group and carbonyl (ester) moiety. The CD spectrum showed absorption due to keto group at 327 nm (Δε –1.0). From the ^1H and ^{13}C NMR spectra (Table 1), it was evident that five of the elements of unsaturation were present as double bonds: two carbon-carbon and three CO (one ketone and two esters). Thus, the molecule is hexacyclic. The NMR data also revealed that **7** contained 5 CH_3 (four tertiary and one methoxy), 4 CH_2, 8 CH (three olefinic), 10 carbons (one olefinic, one acetal, one carbonyl and two alkoxycarbonyl) not bonded to hydrogen, and three protons due to OH group. The presence of a β-furyl moiety and one methoxycarbonyl

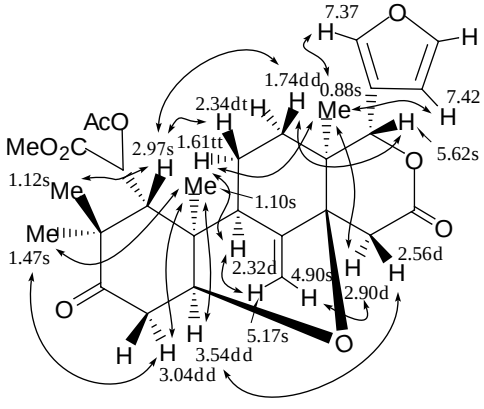


Figure 1. Selected NOE correlations in **2**.

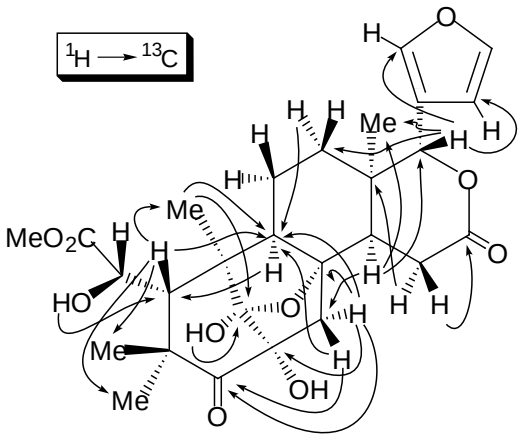


Figure 2. Selected HMBC correlations in **7**.

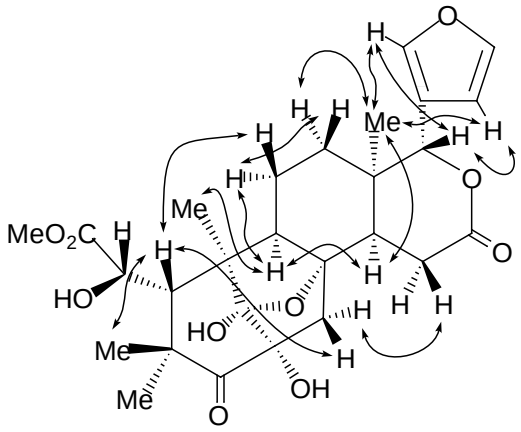


Figure 3. Significant NOE correlations in **7**.

group was also apparent from the spectra.

After assignment of all protons directly bonded with carbon atoms by the ^{1}H-^{13}C shift-correlated measurement (HMQC spectrum), it was possible to assume from the ^{1}H-^{1}H COSY spectrum, decouplings and the HMBC spectrum (Figure 2) that **7** was a mexicanolide. A singlet at δ 5.15 and a doublet at δ 2.19 (J= 8.5 Hz) coupling with a signal at δ 4.31 (dd, J= 9.8 and 8.5 Hz, 6-H) which coalesced to a doublet by the addition of D_2O, were easily assigned to 17- and 5-H, respectively. A methine proton at δ 1.70 (dd, J= 12.5 and 3.8 Hz; 9-H) was coupled to methylene protons at δ 2.08 (dddd, J= 13.8, 5.2, 4.0 and 3.8 Hz,11β-H) and 1.59 (m, 11α-H) coupling with the protons of the adjacent methylene at δ 1.37 (ddd, J= 14.5, 10.7 and 5.2 Hz, 12α-H) and 1.79 (dt, J= 19.2 and 3.1 Hz, 12β-H), from which the structure of the C-9—C-12 fragment was established. The C-14—C-15 linkage was also elucidated from the chemical shifts and couplings of the protons of a methylene attached to a lactone carbonyl function and the adjacent methine; 15α-H: δ 2.85, dd, J= 19.2 and 8.0 Hz; 15β-H: δ 2.69, dd, J= 19.2 and 3.1 Hz; 14-H: δ 2.13, dd, J= 8.0 and 3.1 Hz. These assignments were confirmed by HMBC correlations (Figure 3). The remaining isolated methylene signals at δ 2.67 (br d, J= 17.2 Hz) and 2.86 (d, J= 17.2 Hz) were assigned to 30-H_2 from the HMBC correlations with C-2, 3, 8 and 9 and a NOE observation of the δ 2.67 signal with the 15β-H signal.

Especially, the presence of an acetal linkage of C-1 to C-8 in **7** was confirmed from the chemical shifts of C-1 (δ 111.0 s) and C-8 (δ 89.2 s) and a W-type long range coupling between the 9 and 30α-H signals. A similar acetal linkage of C-1 to C-8 has been observed in some mexicanolides,[12,15] in which the ring C is present in a skew boat form. The NOE correlations (Figure 3) of 5β–H with 11β-H, 14–H with 9-H and 18-H (13α-Me) at δ 1.01, and 15β–H with 30α-H also elucidated the relative configuration of four chiral centers at C-8, 9, 13 and 14.

The presence of four tertiary methyls at 4α (29), 4β (28), 10α and 13α (18) in the basic mexicanolide skeleton was confirmed in **7** from the HMBC spectrum. Then, the relative stereochemical assignment of all of the protons was established from the NOESY experiment (Figure 3). Although the stereochemistry at C-6 could not be clarified from any spectra, it was assumed to be the same *S* with that in khayanolide A isolated by us from the same specimen, the configuration of which was determined by

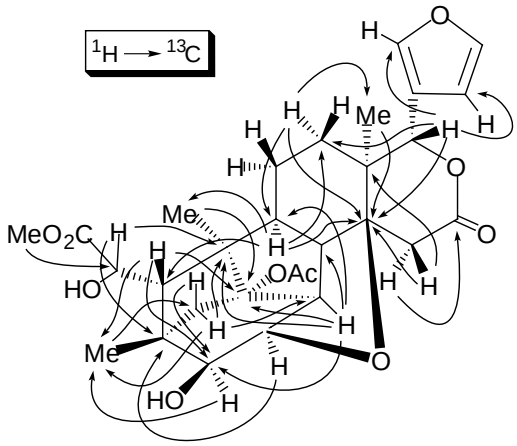


Figure 4. Selected HMBC correlations in **8**.

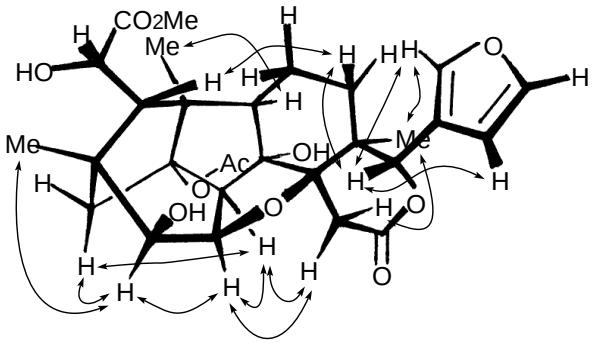


Figure 5. Significant NOE correlations in **8**.

X-Ray analysis and CD study.[16]

The second compound (**8)**, $C_{29}H_{36}O_{11}$; HRFABMS m/z 561.2335 $[C_{29}H_{37}O_{11}]^+$, Δ -0.1 mmu, showed the presence of hydroxyl (3650-3200 cm^{-1}) and ester (1750-1725 cm^{-1}) groups and furan ring (1650 and 875 cm^{-1}) in the IR spectrum. The ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ containing a small amount of CD_3OD owing to the poor solubility of **8** in $CDCl_3$. The NMR data (Table 1) showed that **8** contained 5 CH_3 (three tertiary, one methoxy and one acetyl), 4 CH_2, 10 CH (three olefinic), 10 quarternary carbons (one olefinic and three ester carbonyl), which were also confirmed by the HMQC spectrum. From the subsequent NMR studies of the ^{1}H-^{1}H COSY and HMBC (Figure 4) and NOE measurements (Figure 5), **8** was expected to be a phragmalin-type limonoid biogenatically derived *via* the mexicanolide. Particularly, the presence of three tertiary methyl signals at δ 1.10 (18-H), 1.29 (19-H) and 1.11 (28-H) and two isolated AB-type signals due to the C-29 / C-1 methylene bridge at δ 1.83 (d, J= 12.2 Hz, 29-$H_{pro\text{-}S}$) and 2.30 (d, J= 12.2 Hz, 29-$H_{pro\text{-}R}$) and the 15-methylene at δ 3.05 (d, 18.8 Hz, 15α–H) and 2.75 (d, J= 18.8 Hz, 15β–H) adjacent to a lactone carbonyl (δ 170.9) strongly suggested **8** to be a phragmalin like **9** or to be the acetate of a rearranged phragmalin such as khayanolide B (**6**).[13] The NMR data was very similar to those of khayanolide B (**6**) except for the addition of an acetyl group and the large chemical shift change of some signals; 29-$H_{Pro\text{-}R}$: δ 2.30 in **8** and δ 1.37 in **6**, C-29: δ 41.2 in **8** and δ 44.6 in **6** and C-30: δ 58.8 in **8** and δ 63.3 in **6** (Table 1). On the other hand, although phragmalins so far isolated have been reported to be almost present as the 1,8,9-orthoacetates, the structure of **9** appeared to fully explain the NMR data for **8**. To resolve these subjects, further studies by decouplings and NOE measurements were done using a model for the molecule, and elucidated **8** to be the 1-acetate of khayanolide B (**6**).

Antifeedant activity of the isolated compounds was tested by a conventional leaf disk method against the third instar larvae of Japanese insect pest *Spodoptera littoralis* (Boisduval).[11] Compounds (**4**, **5**, **7** and **8)** were active at 300 ppm, corresponding to a concentration of *ca.* 6 μg / leaf-cm^2. The activity is weaker than that of the well known limonoid antifeedants azadirachtins from *Melia azadirachta indica*,[17] but comparable to that of the second trichilins[1] and azedarachins[2] from *Trichilia roka* and *M. azedarach*. Compounds (**1-3)** also showed a moderate activity at 500 ppm, but **6** was active at 1000 ppm.

Table 1. NMR spectral data of khayalactol (**7**), 1-*O*-acetylkhayanolide B (**8**) and khayanolide (**6**).

no.	**7**		**8***		**6***	
C	H	C	H	C	H	C
1		111.0 s		91.4 s		84.3 s
2		78.3 s	4.52 dd (9.7, 6.7)	72.0 d	4.50 dd (9.5, 6.8)	72.2 d
3		205.8 s	3.48 d (6.7)	78.1 d	3.41 d (6.8)	78.5 d
4		43.1 s		44.1 s		42.7 s
5	2.19 d (8.5)	52.9 d	3.02 d (7.4)	39.4 d	3.05 d (7.3)	40.9 d
6	4.31 dd (9.8, 8.5)	70.1 d	4.22 d (7.4)	71.6 d	4.21 d (7.3)	71.6 d
7		175.0 s		175.2 s		175.4 s
8		89.2 s		86.3 s		87.0 s
9	1.70 br dd (12.5, 3.8)	60.3 d	2.22 d (7.6)	55.8 d	2.09 d (8.1)	56.1 d
10		50.9 s		61.2 s		59.4 s
11α	2.08 dddd(13.8, 5.2, 4.0, 3.8)	20.2 t	1.85 m	16.4 t	1.86 m	16.5 t
β	1.59 m		1.77 m		1.74 m	
12α	1.37 ddd (14.5, 10.7, 5.2)	34.7 t	0.99 m	26.1 t	0.97 m	26.0 t
β	1.79 dt (14.5, 4.0)		1.84 m		1.85 m	
13		36.4 s		37.7 s		37.7 s
14	2.13 dd (8.0, 3.1)	49.9 d		81.6 s		81.5 s
15α	2.80 dd (19.2, 8.0)	27.8 t	3.05 d (18.8)	31.9 t	3.14 d (18.8)	32.0 t
β	2.69 dd (19.2, 3.1)		2.75 d (18.8)		2.78 d (18.8)	
16		169.3 s		170.9 s		171.4 s
17	5.15 s	78.2 d	5.60 s	80.9 d	5.61 s	81.0 d
18	1.01 s	23.3 q	1.10 s	14.4 q	1.10 s	14.4 q
19	1.43 s	19.3 q	1.29 s	18.0 q	1.21 s	17.7 q
20		121.1 s		120.6 s		120.7 s
21	7.45 m	141.0 d	7.45 br d (0.7)	141.0 d	7.45 br t (0.7)	140.9 d
22	6.38 m	110.1 d	6.40 br d (1.7)	110.0 d	6.41 br dd (1.7, 0.7)	110.0 d
23	7.42 t (1.7)	143,1 d	7.40 t (1.7)	142.7 d	7.40 t (1.7)	142.6 d
28	0.64 s	24.0 q	1.11 s	19.2 q	1.09 s	19.2 q
29	1.11 s	17.3 q	1.83 d (12.2)	41.2 t	1.88 d (12.2)	44.6 t
			2.30 d (12.2)		1.37 d (12.2)	
30α	2.67 br d (17.2)	40.9 t	3.18 d (9.7)	58.8 d	2.60 d (9.5)	63.3 d
β	2.86 d (17.2)					
OMe	3.81 s	52.5 q	3.77 s	52.5 q	3.77 s	52.1 q
OH	4.45 s, 3.75 s, 2.20 d (9.8)					
OAc			2.03 s	21.7 q		
				170.7 s		

Measured in $CDCl_3$ and *$CDCl_3$ containing a small amount of CD_3OD.
Chemical shift values are in ppm from TMS, and J values (in Hz) are presented in parentheses.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were measured at 500 and 125 MHz at 40˚ C in $CDCl_3$ (compounds **1**-**3** and **7**) and $CDCl_3$ containing a small amount of CD_3OD (compounds **4**-**6** and **8**) on a JEOL FX-500 spectrometer. IR (KBr) and UV (MeOH) spectra were recorded on JASCO FT/IR 5300 and Shimadzu UV-210A spectrophotometers. Optical rotations and CD spectra were measured at 22˚ C in MeOH using JASCO DIP-370S and JASCO J-720 spectropolarimeters. HPLC was performed on Waters

μBondapak C_{18} column by using 30-60% H_2O-MeOH as solvent.

Plant material. The stem bark was collected in January 1999 at Alexandria in Egypt.

Extraction and isolation. After defatting with hexane, the dried stem bark (910 g) was extracted with Et_2O (3 L) at 20° C for 1 week to yield 3.9 g of material, which was fractionated by DCCC using CH_2Cl_2-MeOH-H_2O (5:5:3 v/v) in descending mode to give 200 fractions (weight of each fraction; Fr no. 1~100: 5 g and Fr no. 101~200: 10 g). Using TLC, these fractions were rearranged to six limonoid fractions; fr 1 (Fr no. 40: 1.13 g), fr 2 (Fr no. 52-58: 45 mg), fr 3 (Fr no. 54-70: 74 mg), fr 4 (Fr no. 80-94; 21 mg), fr 5 (Fr no. 104-138; 38 mg) and fr 6 (Fr no. 140-174; 12 mg). The first fr (1.1 g) was purified through HPLC with 35-45% H_2O/MeOH as the solvent to give **1** (2.5 mg), **2** (33 mg) and **3** (9 mg). The second fr (45 mg) was purified by HPLC using 50-55% H_2O/MeOH solvent system to give **4** (5 mg). A similar purification of the third fr (74 mg) by using 50-55% H_2O-MeOH gave **7** (3.5 mg) and **8** (6 mg), and from the sixth and the seventh frs, compounds (**5**) (17 mg) and (**6**) (4.5 mg) were purified with 50-60% H_2O-MeOH, respectively.

Khayalactol (7). A white amorphous powder, mp 179-181° C; $C_{27}H_{34}O_{10}$; HRFABMS m/z: 541.2107 $[M+Na]^+$, Δ +5.7 mmu; $[\alpha]_D$ –30° (c 0.54); IR ν_{max} cm^{-1}: 3640-3200, 1740-1710, 1635, 875 cm^{-1}; UV λ_{max} nm (ε): 211 (5000); CD: $\Delta\varepsilon_{255}$ –1.8 and $\Delta\varepsilon_{327}$ –1.0 (π–π* of C=O).

1-*O*-Acetylkhayanolide B (8). Colorless needles from AcOEt, mp 297-299° C; HRFABMS m/z: 561.2335 $[M+1]^+$, Δ –0.1; $[\alpha]_D$ 0° (c 1.2); IR ν_{max} cm^{-1}: 3650-3200, 1730, 1720, 1635, 875 cm^{-1}; UV λ_{max} nm (ε): 211 (8000); CD: $\Delta\varepsilon_{220}$ –2.1 and $\Delta\varepsilon_{250}$ –2.3.

Methyl angolensate (1). A white amorphous powder; $C_{27}H_{34}O_7$; FABMS m/z: 471 $[M+1]^+$; $[\alpha]_D$ –40° (c 0.45); ^{13}C NMR: δ 13.8q (C-18), 21.5q (C-29), 21.6q (C-19), 23.7t (C-11), 25.9q (C-28), 29.3t (C-12), 32.7t (C-6), 33.8t (C-15), 39.4t (C-2), 41.5s (C-13), 42.9d (C-5), 44.0s (C-10), 48.0s (C-4), 51.0 (C-9), 52.1q (OMe), 77.2d (C-1), 79.6d (C-17), 80.2s (C-14), 109.9d (C-22), 111.5t (C-30), 120.8s (C-20), 140.8d (C-21), 142.6d (C-23), 145.8s (C-8), 170.0s (C-16), 173.9s (C-7), 213.0s (C-3).

Methyl 6-acetoxyangolensate (2). An amorphous powder, mp 208-210° C; $C_{29}H_{36}O_9$; HRFABMS m/z: 529.2416 $[M+1]^+$, Δ -2.2 mmu; $[\alpha]_D$ -75° (c 0.75); IR ν_{max} cm^{-1}: 3600-3250, 1745, 1720, 1618 and 875; UV λ_{max} nm (ε): 209 (6000); ^{13}C NMR: δ 13.7q (C-18), 22.7q (C-19), 23.9q (C-28), 24.1t (C-11), 24.5q (C-29), 28.8t (C-12), 33.8t (C-15), 39.1t (C-2), 41.5s (C-13), 44.6s (C-10), 46.7d (C-5), 48.8s (C-4), 50.8d (C-9), 53.0q (OMe), 72.4t (C-6), 78.2d (C-1), 79.5d (C-17), 80.7s (C-14), 109.9d (C-22), 111.7t (C-30), 120.8s (C-20), 140.8d (C-21), 142.8d (C-23), 145.9s (C-8), 169.7s (C-16), 170.9s (C-7), 211.0s (C-3).

Methyl 6-hydroxyangolensate (3). An amorphous powder, mp 130-132° C; $C_{27}H_{32}O_8$; HRFABMS m/z: 486.2267 $[M+1]^+$, Δ +2.5 mmu; $[\alpha]_D$ -56° (c 0.20); IR ν_{max} cm^{-1}: 3600-3200, 1740-1710, 1618 and 875; UV λ_{max} nm (ε): 209 (6000); ^{13}C NMR: δ 13.8q (C-18), 21.1q (Ac), 22.7q (C-19), 23.9q (C-28), 24.14 (C-11), 24.8q (C-29), 28.8t (C-12), 33.8t (C-15), 39.1t (C-2), 41.5s (C-13), 44.6s (C-10), 46.7d (C-

5), 48.8s (C-4), 50.8d (C-9), 53.0q (OMe), 72.4t (C-6), 78.2d (C-1), 79.5d (C-17), 80.7s (C-14), 109.9s (C-1), 111.7d (C-21), 120.8s (C-20), 140.8d (C-21), 142.8d (C-23), 145.9s (C-8), 169.7s (C-16), 170.0s (Ac), 170.9s (C-7).211.2 (C-3).

Seneganolide A (4). Colorless needles from acetone, mp 276-278˚ C; $C_{26}H_{30}O_8$; HRFABMS m/z: 471.2021 $[M+1]^+$, Δ +0.2 mmu; $[\alpha]_D$ +62˚ (c 0.92); IR ν_{max} cm^{-1}: 3580-3350, 1730, 1700, 1637 and 875; UV λ_{max} nm (ε): 210 (5000); CD: $\Delta\varepsilon_{255}$ –0.5, $\Delta\varepsilon_{270}$ –0.4 and $\Delta\varepsilon_{340}$ -0.2.

Khayanolide A (5). Colorless prisms from AcOEt, mp 237-239˚ C; $C_{27}H_{32}O_{10}$; HRFABMS m/z: 517.2092 $[M+1]^+$, Δ +1.8 mmu; $[\alpha]_D$ +62˚ (c 0.92); IR ν_{max} cm^{-1}: 3550-3350, 1735, 1720(sh), 1618, 1028 and 875; UV λ_{max} nm (ε): 211 (3000); CD: $\Delta\varepsilon_{210}$ +0.4, $\Delta\varepsilon_{245}$ -0.08 and $\Delta\varepsilon_{310}$ +0.4.

Khayanolide B (6). A white amorphous powder, mp 200-202˚ C; $C_{27}H_{32}O_{10}$; HRFABMS m/z: 517.2079 $[M+1]^+$, Δ +0.5 mmu; $[\alpha]_D$ +0.2˚ (c 0.38); IR ν_{max} cm^{-1}: 3550-3300, 1730-1690, 1238, 1032 and 875; UV λ_{max} nm (ε): 207 (12000); CD: $\Delta\varepsilon_{212}$ +1.8, $\Delta\varepsilon_{245}$ -4.3 and $\Delta\varepsilon_{358}$ –0.7.

Antifeedant test. The antifeedant potential of the isolated compounds was assessed by presenting them on leaf disks of a Chinese cabbage to the third instar larvae of *Spodoptera littoralis* (Boisduval), and visually comparing the treated and untreated disks eaten by the larvae.[12] Ten larvae were placed in a Petri dish with the five treated leaf disks with sample and the five untreated disks as control. The feeding assay terminated after the larvae had eaten approximately 50% of one of the disks. This choice test was done 200, 300, 500 and 1000 ppm concentrations to determine minimum inhibitory concentration for each of the compounds.

Antifeedant activity of the rings B,D-secolimonoids (1-8). The antifeedant potential; methyl angolensate (**1**): 500 ppm, methyl 6-hydroxy angolensate (**2**): 500 ppm, methyl 6-acetoxyangolensate (**3**): 500 ppm, seneganolide (**4**): 300 ppm, khayanolide A (**5**): 300 ppm, khayanolide B (**6**): 1000 ppm, khayalactol (**7**): 300 ppm and 1-*O*-acetykhayanolide B (**8**): 300 ppm. In this test, 50 ppm corresponds to a concentration of *ca.* 1 μg/leaf-cm^2.

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