Full Papers

Cycloartane Derivatives from *Tillandsia usneoides*

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Investigation of the extract of *Tillandsia usneoides* afforded 26 cycloartane derivatives, including the following novel ones: (22*E*)-25,26,27-trisnor-3-oxocycloart-22-en-24-al, (24*E*)-3-oxocycloart-24-en-26-al, 24-hydroxycycloart-25-en-3-one, (23*E*)-25-methoxycycloart-23-en-3-one, (23*E*)-25-hydroperoxycycloart-23-en-3-one, 25,26,27-trisnor-24-hydroxycycloartan-3-one, methyl (24*E*)-26-carboxy-3,4-*seco*-cycloart-4(29),24-dien-3-oate, methyl (23*E*)-25-hydroxy-3,4-*seco*-cycloart-23-en-3-oate, methyl (23*E*)-25-methoxy-3,4-*seco*-cycloart-23-en-3-oate, and methyl 24-hydroxy-3,4-*seco*-cycloart-25-en-3-oate. The structures were assigned on the basis of spectral data.

Previous studies of *Tillandsia usneoides* (Bromeliaceae) reported the presence of cycloartane derivatives[1] and flavonoids.[2] As part of our continued interest in the triterpenoids of this plane,[3] a systematic chemical investigation of the extract of the fresh plant was undertaken. Twenty-six triterpenoids with the cycloartane skeleton or 3,4-*seco* derivatives were isolated. Ten of these are new compounds. The structural assignments based on spectral data are presented and discussed.

Results and Discussion

The ^{1}H-NMR spectra of compounds **1**−**6** indicated the presence of a cycloartane skeleton with a keto group on C-3.[4] This fact was evidenced by H-2 multiplets at δ 2.31 and 2.71 and by the typical H-19 doublets at δ 0.59 and 0.81 (J = 4.2 Hz). Comparison of the ^{13}C-NMR spectra with the ^{13}C-NMR spectra of cycloartan-3-one and related compounds[4,5] confirmed that these are all 3-oxocycloartanes (Chart 1).

Compound **1** showed a molecular ion at m/z 396.3027 in its HREIMS corresponding to the molecular formula $C_{27}H_{40}O_2$. In the ^{1}H-NMR spectrum a proton signal assigned to an α,β-unsaturated aldehyde appeared at δ 9.49 (d, J = 7.7 Hz), and two protons of a trans double bond appeared at δ 6.07 (dd, J = 15.7, 7.7 Hz) and 6.73 (dd, J = 15.7, and 8.4 Hz). The presence of an α,β-unsaturated aldehyde was also supported by the ^{13}C-NMR spectrum, where signals at δ 194.4, 164.3, and 130.9 were observed. The ^{1}H-^{1}H COSY spectrum allowed us to obtain the structure of the side chain. Compound **1** was, therefore, established to be (22*E*)-25,26,27-trisnor-3-oxocycloart-22-en-24-al.

Compound **2** showed a molecular ion at m/z 438.3498 in the HREIMS corresponding to $C_{30}H_{46}O_2$. The ^{1}H-NMR spectrum showed an α,β-unsaturated aldehyde at δ 9.40 (s), a broad triplet at δ 6.49 (J = 6.7 Hz) belonging to the proton of the double bond attached to the aldehydic function, and a vinylic methyl signal at δ 1.76. The ^{13}C-NMR spectrum exhibited carbon resonances at δ 195.4, 155.6, 139.2, and 9.2, which confirmed the presence of a trans α,β-unsaturated aldehyde.[6] From this evidence, compound **2** was deduced to be (24*E*)-3-oxocycloart-24-en-26-al.

Compound **3** showed a molecular ion at m/z 440.3654 in the HREIMS, indicating a molecular formula of $C_{30}H_{48}O_2$. The ^{1}H-NMR spectrum displayed two olefinic signals at δ 4.84 (br s) and 4.93 (br s), a signal due to a proton attached to a carbon-bearing oxygen at δ 4.02 (t, J = 6.0 Hz), and a methyl group attached to a double bond at δ 1.73 (br s). The ^{13}C-NMR spectrum showed doubling of certain carbon resonance signals. These chemical shifts corresponded to a double bond with a quaternary carbon at δ 147.8, 147.5 and a sp^2 methylene carbon at δ 111.3, 110.8; a methylene at δ 31.7, 31.5; a methyl group at δ 17.6, 17.2, and a carbon bearing an oxygenated function at δ 76.7, 76.3. Because of the overlapping with $CDCl_3$ signals in the ^{13}C-NMR spectrum, these latter signals were better observed in a DEPT experiment. All these data resembled those of compound **7**,[7] and the doubling of the signals was consistent with the presence of a mixture of C-24 epimers.[8] Thus, structure **3** was assigned to 24-hydroxycycloart-25-en-3-one.

The structure of compound **4** was deduced from the MS and ^{1}H- and ^{13}C-NMR spectra. In the mass spectrum a fragment ion derived from the loss of 31 units from the molecular ion was observed in addition to typical fragment ions of the 3-oxocycloartane skeleton.[9,10] The ^{1}H-NMR spectrum showed a two-proton AB system assigned to a trans double bond at δ 5.54 (ddd, J = 15.8, 8.0, 5.5 Hz) and 5.40 (d, J = 15.8 Hz), a signal belonging to a methoxy group at δ 3.15, and a methyl singlet at δ 1.26 (6H) caused by the carbons C-26 and C-27 attached to a carbon-bearing oxygen. The presence of a double bond was confirmed by the ^{13}C-NMR spectrum, where chemical shifts at δ 136.7 and 128.6 were observed. In this spectrum two signals of carbon-bearing oxygen were observed: a methyl group at δ 50.2 and a quaternary carbon at δ 74.9, namely, the methoxyl and the site of attachment of this group.

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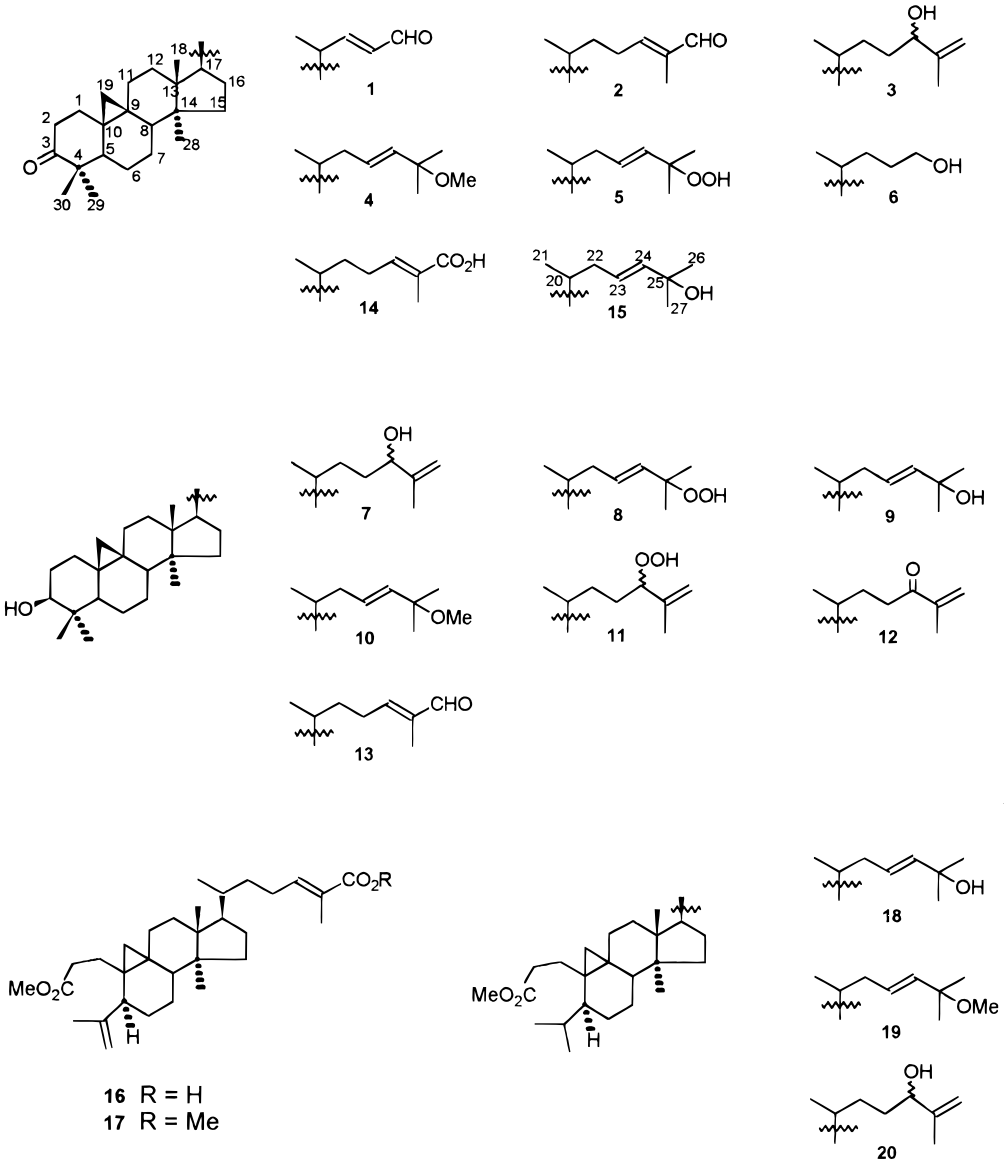
Chart 1



Taking into account the chemical shifts of the two methyl groups in ^{1}H NMR at δ 1.26 (6H, s), the coupling constants, and the multiplicities of the protons belonging to the double bond, this double bond should be *trans* and located at C-23 and C-24, and the methoxy group should be linked to C-25, establishing for compound **4** the structure (23*E*)-25-methoxycycloart-23-en-3-one.

NMR spectra showed that **4** and **5** were closely related. In the ^{1}H-NMR spectrum of **5** downfield displacements of the double bond system to δ 5.70 (ddd, J = 15.8, 8.0, 5.5 Hz) and 5.52 (d, J = 15.8 Hz) and of the methyl group to δ 1.35 (6H, s) and the appearance of a broad exchangeable singlet at δ 7.30 were the main differences. These data indicated that the side chain was very similar to that of compound **4** except for the presence of a different functional group on C-25. The MS suggested that this group should be a hydroperoxyl instead of a hydroxyl. Furthermore, in the ^{13}C-NMR spectrum, the chemical shifts of the side-chain carbons were identical to those recently reported by us for compound **8** from *Tillandsia recurvata*.[11] Thus, compound **5** was identified as (23*E*)-25-hydroperoxycycloart-23-en-3-one.

The 3-ketocycloartane **6** showed a molecular ion at m/z 400.3343 in the HRMS, corresponding to a molecular formula of $C_{27}H_{44}O_2$. The diagnostic ion at m/z 313, generated by the loss of the side chain,[9,10] suggested the presence of a hydroxy group in a short side chain. In addition to the common 3-ketocycloartane signals, the ^{1}H-NMR spectrum of **6** exhibited a triplet at δ 3.63 (2H, t, J = 6.2 Hz), indicating a primary alcohol function on the side chain. This conclusion was confirmed by the ^{13}C-NMR spectrum, which displayed a methylene carbon at δ 63.6. In order to determine the position of the hydroxyl in the side chain, HETCOR and ^{1}H$-^1$H COSY experiments were performed. In the latter, a methyl group at δ 0.90 (d) correlated to a methine proton at δ 1.43, allowing assignments of these signals to H-21 and H-20. The signal at δ 3.63 correlated with a complex signal of two methylene protons between δ 1.40 and 1.70, indicating that the primary alcohol was on C-24. Thus, the structure of compound **6** was established as 25,26,27-trisnor-24-hydroxycycloartan-3-one.

^{1}H-NMR and MS of compounds **9** and **10** were in good agreement with those reported for cycloart-23-ene-3β,-25-diol and 25-methoxycycloart-23-en-3β-ol.[1] In par-

Table 1. ^{1}H-NMR Chemical Shifts (δ) of Compounds **1** to **6** in $CDCl_3$ (J in Hz)

	compound					
proton	**1**	**2**	**3**	**4**	**5**	**6**
2	2.72 dt (6.2, 13.9), 2.31 m	2.71 dt (6.2, 13.8), 2.31 m	2.71 dt (6.2, 13.8), 2.31 m	2.71 dt (6.2, 13.9), 2.30 m	2.71 dt (6.2, 13.8), 2.30 m	2.71 dt (6.3, 14.0), 2.30 m
18	1.07 s	1.01 s	0.99 s	1.00 s	1.00 s	1.00 s
19-exo	0.59 d (4.2)	0.58 d (4.2)	0.57 d (4.2)	0.57 d (4.2)	0.57 d (4.2)	0.57 d (4.2)
-endo	0.81 d (4.2)	0.80 d (4.2)	0.79 d (4.2)	0.78 d (4.2)	0.79 d (4.2)	0.79 d (4.2)
21	1.10 d (6.5)	0.94 d (6.3)	0.89 d	0.88 d (6.4)	0.89 d (6.5)	0.90 d (6.5)
22	6.73 dd (15.7, 8.4)					
23	6.07 dd (15.7, 7.7)			5.54 ddd AB (15.8, 8.0, 5.5)	5.70 ddd AB (15.8, 8.0, 5.5)	
24	9.49 d (7.7)	6.49 bt (6.7)	4.02 t (6.0)	5.40 d AB (15.8)	5.52 d AB (15.8)	3.63 bt (6.2)
26		9.40 s	4.84 bs 4.93 bs	1.26 s	1.35 s	
27		1.76 s	1.73 bs	1.26 s	1.35 s	
28	0.93 s	0.91 s	0.90 s	0.89 s	0.90 s	0.91 s
29α	1.05 s	1.05 s	1.05 s	1.05 s	1.05 s	1.05 s
30β	1.10 s	1.10 s	1.10 s	1.10 s	1.10 s	1.10 s
OCH_3				3.15 s		
OOH					7.30 bs	

ticular, the large coupling constants (J = 15.8 Hz) observed in the ^{1}H-NMR spectrum for the double-bond signals in compound **10** indicated the *trans* nature of this bond. Compound **10** was identified as (23*E*)-25-methoxycycloart-23-en-3β-ol. In the case of compound **9**, both double bond protons were overlapped in a much more complex signal, and the coupling constants could not be measured. In a gated decoupling experiment, a similar pattern of long-range ^{1}H−^{13}C coupling constants was observed for C-24 in compounds **9** and **8**, suggesting a *trans* double bond in compound **9**.[12] Taking into account that reduction of compound **8** afforded compound **9**,[11] **8** was identified as (23*E*)-cycloart-23-ene-3β,25-diol.

Compounds **8** and **11** were identified by their ^{1}H- and ^{13}C-NMR spectra and MS, which were identical to those recently reported from *T. recurvata*.[11]

The known compounds **7** and **12**−**15** were identified by ^{1}H- and ^{13}C-NMR and EIMS spectra, which were in accordance with literature data.[6,7,13−16]

^{1}H- and ^{13}C-NMR spectra of compound **16** were similar to those of compound **17**.[3] The main difference appeared to be the absence of one methoxy group in the ^{1}H- and ^{13}C-NMR spectra of compound **16** and the presence of a carboxylic acid instead of an ester function at C-26. To corroborate this conclusion, compound **16** was treated with CH_2N_2, which yielded compound **17**. Compound **16** was therefore identified as methyl (24*E*)-26-carboxy-3,4-*seco*-cycloarta-4(29),24-dien-3-oate.

Compounds **18**, **19**, and **20** exhibited common characteristics in their ^{1}H-NMR spectra. A pair of doublets at δ 0.35 and 0.59, a methoxyl at δ 3.66 (similar to **16** and **17** for an ester methoxy group on C-3), and the same signals for methyl groups between δ 0.81 and 0.96 were common features in these spectra. This information suggested that these three compounds possessed the same 3,4-*seco*-skeleton with different side chains. As we were able to isolate only small amounts of compounds **19** and **20**, the structural elucidation of the skeleton was accomplished on compound **18**. The side chain of this compound was determined to be Δ^{23},25-hydroxy by direct comparison of ^{1}H- and ^{13}C-NMR spectra with those of compounds **9** and **15** and by 2D NMR experiments (^{1}H−^{1}H COSY, HETCOR, and COLOC). The ^{1}H−^{1}H COSY experiment correlated two methyl groups at δ 0.81 (d, J = 6.7 Hz) and 0.92 (d, J = 6.5 Hz) with a methine at δ 2.02 establishing the presence of an isopropyl group in the molecule, which was assigned as the substituent on C-5, taking into account that compound **18** was a 3,4-*seco*-cycloartane. Moreover, the shielding of C-6 (7.1 ppm) observed in the ^{13}C-NMR spectrum of **18** compared with those of compounds **16** or **17** was consistent with a γ effect produced by the presence of a more bulky group at C-5. Thus, compound **18** was identified as methyl (23*E*)-25-hydroxy-3,4-*seco*-cycloart-23-en-3-oate. The side chain of compounds **19** and **20** were identified by comparing their NMR spectra with those of compounds **4**, **10**, **3**, and **7**. Compound **19** was, therefore, identified as methyl (23*E*)-25-methoxy-3,4-*seco*-cycloart-23-en-3-oate and compound **20** as methyl 24-hydroxy-3,4-*seco*-cycloart-25-en-3-oate.

The known compounds cycloartanone, cycloartenone, 24-methylenecycloartanone, cycloartanol, cycloartenol, and 24-methylenecycloartanol were identified by their spectral data (EIMS, ^{1}H NMR, and ^{13}C NMR) according to literature reports.[9,10,13,14,17]

Compounds **1**−**6**, **16**, and **18**−**20** have not been reported previously. The presence of compounds **1**, **6**, **16**, and **18**−**20** is noteworthy because there are only a few reports of isolation of cycloartanes with short side chains[4,18,19] and 3,4-*seco*-cycloartanes.[20,21]

Compounds **3** and **7**, the latter isolated from many plants,[7,8] always appeared as an epimeric mixture at C-24, indicating a nonenzymatic process in their origin. Djerassi and McCrindle[22] suggested that compounds **7** and **9** originated from an oxidation of cycloartenol. The presence of hydroperoxide derivatives suggests that the oxidation process is one of photooxygenation. Taking into account the mild extraction and processing conditions employed and previous arguments,[11] this photooxygenation appears to proceed naturally in the plant.

The biogenetic origin of short-side-chain sterols was concluded to be an *in vivo* autooxidation of cholesterol mediated by 20- and 25-hydroperoxide derivatives.[23] These results suggest a similar origin for the short-side-chain cycloartanes. Cycloartenone, cycloartenol, 24-methylenecycloartanol, and compounds **7**, **9**, **10**, and **12** were isolated previously from *T. usneoides*.[1]

Table 2. ^{13}C-NMR Chemical Shifts (δ) of Compounds **1** to **6**, **16**, **23**, and **24** in $CDCl_3$

	compound									
carbon	**1**	**2**	**3**	**4**	**5**	**6**	**9**	**10**	**16**	**18**
1	33.4	33.4	33.4	33.4	33.4	33.4	32.0	31.9	29.1	28.4
2	37.4	37.4	37.4	37.5	37.4	37.4	30.4	30.4	31.5	31.7
3	216.5	216.4	216.5	216.5	216.5	216.5	78.9	78.8	174.4	174.5
4	50.2	50.2	50.2	50.2	50.2	50.2	40.5	40.5	149.5	28.9
5	48.4	48.4	48.4	48.4	48.4	48.4	47.1	47.1	45.9	41.1
6	21.5	21.5	21.5	21.5	21.5	21.5	21.1	21.1	27.8	20.7
7	25.8	25.8	25.8	25.8	25.8	25.8	26.0	26.2	25.0	25.3
8	47.8	47.9	47.9	47.9	47.8	47.9	47.9	47.9	47.7	48.1
9	21.0	21.1	21.1	21.1	21.1	21.1	20.0	20.0	21.3	21.4
10	26.1	26.0	26.0	26.0	26.0	26.0	26.1	26.0	27.1	27.5
11	26.7	26.7	26.7	26.7	26.7	26.7	26.5	26.4	27.0	27.0
12	32.7	32.8	32.8	32.7	32.7	32.8	32.8	32.8	33.1	33.0
13	45.9	45.5	45.3	45.4	45.4	45.3	45.3	45.3	45.2	45.1
14	48.8	48.8	48.7	48.7	48.8	48.8	48.8	48.8	49.0	49.0
15	35.6	35.5	35.5	35.6	35.5	35.5	35.6	35.6	35.6	35.7
16	28.2	28.2	28.1	28.1	28.1	28.1	28.1	28.0	28.1	28.0
17	51.3	52.2	52.2	52.0	52.1	52.2	52.0	51.9	52.2	52.0
18	18.4[a]	18.1	18.1	18.1	18.1	18.1	18.0	18.1	18.1	18.2
19	29.6	29.5	29.5	29.5	29.6	29.5	29.9	29.8	29.9	29.9
20	40.7	36.0	35.9	36.3	36.3	35.8	36.4	36.3	36.0	36.4
21	18.6[a]	18.1	18.3	18.4	18.3	18.3	18.3	18.3	18.1	18.2
22	164.3	34.8	31.9	39.3	39.3	32.1	39.0	39.3	34.8	39.0
23	130.9	26.1	31.5, 31.7	128.6	130.6	29.6	125.6	128.7	26.0	125.6
24	194.4	155.6	76.7, 76.3	136.7	134.5	63.6	139.3	136.6	145.8	139.4
25		139.2	147.8, 147.5	74.9	82.3		70.8	74.9	126.6	70.7
26		195.4	111.3, 110.8	26.2[a]	24.4[a]		29.9[a]	26.0[a]	172.9	29.9
27		9.2	17.6, 17.2	25.9[a]	24.3[a]		29.7[a]	25.7[a]	12.0	29.9
28	19.3	19.3	19.3	19.3	19.3	19.3	19.3	19.3	19.3	19.4
29	22.2	22.2	22.2	22.2	22.2	22.2	25.4	25.4	111.5	22.3[a]
30	20.8	20.7	20.7	20.8	20.8	20.8	14.0	14.0	19.8	17.0[a]
OCH_3				50.2				50.2	51.5	51.5

[a] Signals within same column may be interchangeable.

Experimental Section

General Experimental Procedures. HREIMS were recorded on a VG-ZAB mass spectrometer, and the EIMS were taken on a quadrupole mass spectrometer. NMR spectra were recorded on a Bruker AC 200 at 200.1 MHz for ^{1}H and 50.3 MHz for ^{13}C in $CDCl_3$ with TMS as internal standard.

Plant Material. *T. usneoides* was collected at Tigre, Buenos Aires, Argentina, in November 1993. A voucher specimen No. 17 913 is located at the Herbarium of Instituto Darwinion, San Isidro, Buenos Aires.

Extraction and Isolation. The fresh plant (7 kg) was extracted as previously reported.[3] The extract was fractionated by dry column flash chromatography on Si gel using hexane and mixtures of hexane−CH_2Cl_2−EtOAc of increasing polarity. Fraction 1, eluted with hexane−CH_2Cl_2 (8:2), yielded on HPLC (column: YMC C-18, 5 μm, 22.5 × 2.5 cm; eluent: MeOH) cycloartenone (76 mg), 24-methylenecycloartanone (13 mg), and cycloartanone (17 mg). Fraction 2, eluted with hexane−CH_2Cl_2(1:1) was further fractionated by the same technique. Subfractions eluted with hexane−CH_2Cl_2 (7:3 to 1:1) were chromatographed by HPLC (same conditions as above), yielding cycloartenol (1.56 g), 24-methylenecycloartanol (41 mg), cycloartanol (65 mg), and compounds **4** (5 mg), **17** (145 mg), and **19** (4 mg). Subfraction eluted with hexane−CH_2Cl_2(2:8) was first chromatographed on a Sephadex LH-20 column (MeOH) followed by HPLC (same conditions as above), yielding compounds **1** (4 mg), **2** (7 mg), **12** (53 mg), and **20** (2 mg). Fraction 3, eluted with CH_2Cl_2 to EtOAc, was chromatographed on Sephadex LH-20 (MeOH) to remove fatty acids and then chromatographed using dry column flash chromatography on reversed phase to remove sterols. The first fraction eluted with MeOH on HPLC (same conditions as above, except eluent: MeOH−H_2O 5%) afforded subfractions 31−37, which were further chromatographed by HPLC (eluent: CH_3-CN−H_2O 5%). Subfraction 31 yielded compounds **6** (8 mg), **7** (55 mg), **9** (45 mg), and **11** (26 mg). Subfraction 32 yielded compounds **8** (73 mg) and **10** (12 mg). Subfraction 33 afforded compound **3** (128 mg). Subfraction 34 yielded compound **5** (8 mg). Subfraction 35 provided compounds **14** (11 mg) and **15** (79 mg). Subfraction 36 yielded compound **16** (10 mg), and subfraction 37 afforded compounds **13** (12 mg) and **18** (10 mg).

Compound **1** was obtained as an amorphous solid: $[\alpha]^{25}_D$ +19° (*c* 0.073, $CHCl_3$); UV (CH_3CN) λ_{max} (log ϵ) 224 (3.6); HREIMS *m*/*z* 396.3027 ($C_{27}H_{40}O_2$), requires 396.3028; EIMS (70 eV) *m*/*z* M^+ 396 (25), 301 (17), 258 (19), 175 (100); ^{1}H NMR and ^{13}C NMR, see Tables 1 and 2.

Compound **2** was obtained as an amorphous solid: $[\alpha]^{25}_D$ +25° (*c* 0.06, $CHCl_3$); UV (CH_3CN) λ_{max} (log ϵ) 224 (3.9); HREIMS *m*/*z* 438.3498 ($C_{30}H_{46}O_2$), requires 438.3498; EIMS (70 eV) *m*/*z* $M^{\bullet+}$ 438 (10), 423 (6), 420 (2), 410 (3), 355 (4), 313 (10), 300 (14), 175 (25), 95 (100); ^{1}H NMR and ^{13}C NMR, see Tables 1 and 2.

Compound **3** was obtained as a white solid (Et_2O−hexane): mp 118−121 °C; $[\alpha]^{25}_D$ +20° (*c* 0.62, $CHCl_3$); UV (CH_3CN) λ_{max} (log ϵ) 220 (2.3); HREIMS *m*/*z* 440.3654 ($C_{30}H_{48}O_2$), requires 440.3654; EIMS (70 eV) *m*/*z* $M^{\bullet+}$ 440 (5), 422 (14), 407 (6), 379 (6), 355 (7), 313 (29), 302 (14), 175 (40), 95 (87), 55 (100); ^{1}H NMR and ^{13}C NMR, see Tables 1 and 2.

Compound **4** was obtained as an amorphous solid: $[\alpha]^{25}_D$ +14° (*c* 0.070, $CHCl_3$); UV (CH_3CN) λ_{max} (log ϵ) 220 (3.1); EIMS (70 eV) *m*/*z* $M^{\bullet+}$ 454 (1), 423 (25), 408

Table 3. ^{1}H-NMR Chemical Shifts (δ) of Compounds **16** and **18**−**20** in $CDCl_3$ (*J* in Hz)

	compound			
proton	**16**	**18**	**19**	**20**
18	0.97 s	0.96 s	0.96 s	0.95 s
19-exo	0.40 d (4.0)	0.35 d (4.2)	0.35 d (4.3)	0.34 d (4.4)
-endo	0.72 d (4.0)	0.59 d (4.2)	0.59 d (4.3)	0.59 d (4.4)
21	0.91 d (6.3)	0.86 d (6.5)	0.88 d (6.5)	0.89 d (6.2)
23		5.60 bs	5.54 ddd AB (15.9, 8.0, 5.5)	
24	6.91 bt (7.0)	5.60 bs	5.40 d AB (15.9)	4.02 bt (6.0)
26		1.32 bs	1.26 bs	4.83 bs
				4.92 bs
27	1.84 bs	1.32 bs	1.26 bs	1.72 bs
28	0.93 s	0.91 s	0.91 s	0.91 s
29	4.81 bs	0.81 d (6.7)	0.81 d (6.9)	0.81 d (6.8)
	4.73 bs			
30	1.68 bs	0.92 d (6.5)	0.92 d (6.5)	0.92 d (6.5)
C_3-OCH_3	3.64 s	3.66 s	3.66 s	3.66 s
C_{25}-OCH_3			3.15 s	

(10), 313 (28), 203 (24), 109 (7), 55 (100); ^{1}H NMR and ^{13}C NMR, see Tables 1 and 2.

Compound **5** was obtained as an amorphous solid: $[\alpha]^{25}_D$ +19° (*c* 0.13, $CHCl_3$); UV (CH_3CN) λ_{max} (log ϵ) 222 (2.6); EIMS (70 eV) *m*/*z* $M^{\bullet+}$ 456 (1), 438 (2), 422 (3), 313 (15), 203 (18), 175 (29), 147 (45), 95 (100); ^{1}H NMR and ^{13}C NMR, see Tables 1 and 2.

Compound **6** was obtained as a white solid (Et_2O−hexane): mp 143−146 °C; $[\alpha]^{25}_D$ +20° (*c* 0.11, $CHCl_3$); UV (CH_3CN) λ_{max} (log ϵ) 220 (2.5); HREIMS *m*/*z* 400.3343 ($C_{27}H_{44}O_2$), requires 400.3341; 385.3092 ($C_{26}H_{41}O_2$), requires 385.3107; 382.3229 ($C_{27}H_{42}O$), requires 382.3236; EIMS (70 eV) *m*/*z* $M^{\bullet+}$ 400 (25), 385 (14), 382 (14), 313 (67), 262 (38), 175 (46), 154 (100), 107 (84), 95 (62); ^{1}H NMR and ^{13}C NMR, see Tables 1 and 2.

Compound **16** was obtained as a colorless oil: $[\alpha]^{25}_D$ +64° (*c* 0.24, $CHCl_3$); UV (CH_3CN) λ_{max} (log ϵ) 220 (3.6); HREIMS *m*/*z* 484.3554 ($C_{31}H_{48}O_4$), requires 484.3553; 469.3323 ($C_{30}H_{45}O_4$), requires 469.3319; EIMS (70 eV) *m*/*z* $M^{\bullet+}$ 484 (8), 469 (20), 451 (6), 343 (5), 301 (6), 175 (30), 95 (100); ^{1}H NMR and ^{13}C NMR, see Tables 3 and 2, respectively.

Compound **18** was obtained as a colorless oil: $[\alpha]^{25}_D$ +24° (*c* 0.24, $CHCl_3$); UV (CH_3CN) λ_{max} (log ϵ) 222 (2.4); HREIMS *m*/*z* 454.3810 ($C_{31}H_{50}O_2$), requires 454.3811; EIMS (70 eV) *m*/*z* 454 (19); 439 (17), 412 (8), 345 (7), 343 (12), 302 (14), 269 (15), 203 (17), 109 (72), 43 (100); ^{1}H NMR and ^{13}C NMR, see Tables 3 and 2, respectively.

Compound **19** was obtained as a colorless oil: $[\alpha]^{25}_D$ +21° (*c* 0.13, $CHCl_3$); HREIMS *m*/*z* 486.4072 ($C_{32}H_{54}O_3$), requires 486.4073; 471.3831 ($C_{31}H_{51}O_3$), requires 471.3838; 454.3802 ($C_{31}H_{50}O_2$), requires 454.3811; EIMS (70 eV) *m*/*z* 454 (13), 439 (17), 373 (6), 345 (9), 343 (19), 301 (11), 284 (13), 269 (14), 207 (11), 203 (33), 175 (31), 55 (100); ^{1}H NMR, see Table 3.

Compound **20** was obtained as a colorless oil: $[\alpha]^{25}_D$ +30° (*c* 0.067, $CHCl_3$); HREIMS *m*/*z* 472.3912 ($C_{31}H_{52}O_3$), requires 472.3916; 454.3807 ($C_{31}H_{50}O_2$), requires 454.3811; EIMS (70 eV) *m*/*z* $M^{\bullet+}$ 472 (3), 457 (5), 454 (7), 439 (14), 345 (8), 302 (12), 175 (33), 95 (100); ^{1}H NMR, see Table 3.

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