Camelliols A−C, Three Novel Incompletely Cyclized Triterpene Alcohols from Sasanqua Oil (*Camellia sasanqua*)

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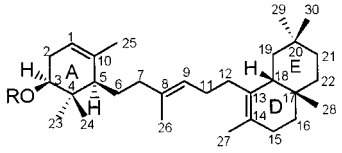
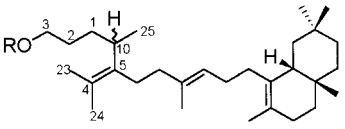
Received July 31, 1998

Three novel triterpene alcohols, camelliols A (**1**), B (**3**), and C (**5**), possessing a mono-, bi-, and tricyclic ring system, respectively, have been isolated, along with achilleol A, a known monocyclic triterpene alcohol, from the nonsaponifiable lipids of sasanqua oil (*Camellia sasanqua*). The structures of these new alcohols were determined on the basis of spectroscopic methods.

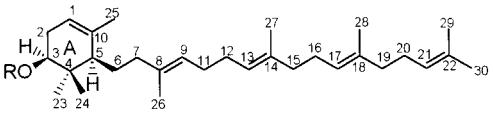
The seed oil of *Camellia sasanqua* Thunb. (Theaceae) (sasanqua oil) has a composition similar to camellia oil (from *C. japonica* L.)[1] and is occasionally used as a substitute for camellia oil.[2] These oils contain β-amyrin (olean-12-en-3β-ol), butyrospermol (eupha-7,24-dien-3β-ol), and Δ^7-tirucallol (tirucalla-7,24-dien-3β-ol) as the major triterpene alcohols from the nonsaponifiable lipid fraction.[3,4] Earlier investigations on the triterpene alcohol fractions of the nonsaponifiable lipid fraction of camellia and sasanqua oils have led to the isolation and characterization of eight novel compounds along with 21 known compounds.[5,6] In this paper, we report the isolation and structure elucidation as the acetyl derivatives of three novel incompletely cyclized triterpene alcohols from sasanqua oil. They were given the trivial names camelliol A (**1**), B (**3**), and C (**5**).



1 R = H **2** R = Ac



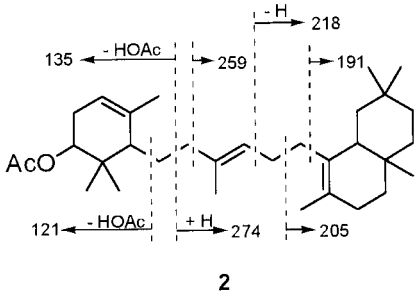
3 R = H **4** R = Ac



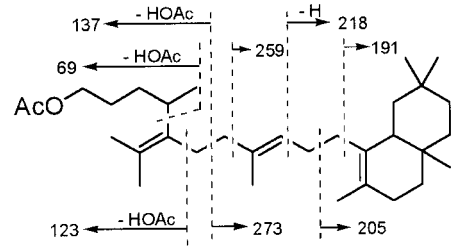
5 R = H **6** R = Ac

Results and Discussion

The molecular formula of compound **2** was established as $C_{32}H_{52}O_2$ (HREIMS). It was shown to have a secondary acetoxyl group [ν_{max} 1240, 1740 cm^{-1}; δ_C 76.7 (CH); δ_H 2.04 (3H, s, OAc)], two trisubstituted double bonds [ν_{max} 835, 800 cm^{-1}; δ_C 117.6 (CH) and 124.9 (CH); δ_H 5.17 (1H, br t, J = 6.4 Hz) and 5.22 (1H, m)], and one tetrasubstituted double bond (four quaternary sp^2 carbon signals with δ_C 123.9, 133.5, 135.0, and 137.0, two of which are associated with the trisubstituted double bonds), and five tertiary [δ_H



2



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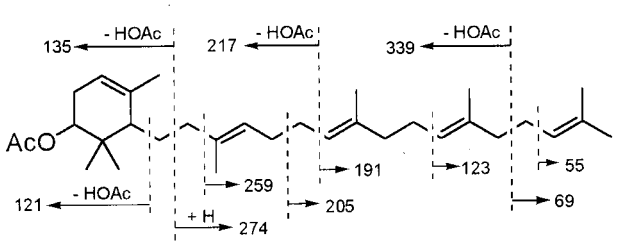

6

Figure 1. Mass spectral fragments (*m*/*z*) of **2**, **4**, and **6**.

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10.1021/np980336a CCC: $18.00
Published on Web 12/16/1998

Table 1. ^{13}C NMR Spectral Data (δ Values; 100.6 MHz; $CDCl_3$) of Three Novel Triterpene Alcohols and Their Acetyl Derivatives from Sasanqua Oil

carbon	**1**	**2**	**3**	**4**	**5**[a]	**6**[a]
1	118.3	117.6	31.6	31.7	118.3	117.6
2	31.8	28.7	31.2	27.0	31.8	28.8
3	75.1	76.7	63.4	64.9	75.1	76.7
4	38.1	36.8	125.2	125.5	38.1	36.8
5	48.9	48.9	135.1	135.3	49.0	48.9
6	27.1	27.1	26.8	26.8	27.2	27.4
7	42.0	41.8	40.3	40.2	42.0	41.8
8	135.1	135.0	135.6	135.6	135.2	135.2
9	124.9	124.9	124.1	124.1	124.7[b]	124.7[b]
10	137.1	137.0	35.6	35.5	137.1	137.0
11	27.2	27.2	27.1	27.1	28.3	28.3
12	31.6	31.6	31.5	31.6	28.3	28.3
13	133.9	133.5	133.6	133.6	124.3[b]	124.3[b]
14	123.9	123.9	123.8	123.9	134.9[c]	134.9[c]
15	29.5	29.5	29.5	29.5	39.8	39.8
16	26.5	26.5	26.5	26.5	26.7	26.7
17	31.4	31.4	31.4	31.4	124.3[b]	124.3[b]
18	42.3	42.2	42.2	42.2	135.4[c]	135.4[c]
19	43.0	43.0	42.9	42.9	39.8	39.8
20	31.0	31.0	31.0	31.0	26.8	26.8
21	34.6	34.6	34.6	34.6	124.4	124.4
22	36.6	36.6	36.5	36.6	131.3	131.3
23	25.3	25.5	20.1	20.1	25.4	25.6
24	16.1	18.0	20.9	21.0	16.2	18.2
25	22.6	22.7	19.6	19.6	22.6	22.7
26	16.0	16.0	16.0	16.0	16.0	16.0
27	18.7	18.7	18.7	18.7	16.1	16.1
28	27.0	27.0	27.0	27.0	16.1	16.1
29	33.2	33.2	33.2	33.2	17.7	17.7
30	24.2	24.2	24.2	24.2	25.7	25.7
OCO*Me*		21.3		21.0		21.3
O*C*OMe		170.8		171.2		170.8

[a] Determined at 125 MHz. [b,c] Assignments in each column are interchangeable.

0.82, 0.87, 0.89 (6H), and 0.92 (each s)] and three olefinic [δ_H 1.58, 1.63, and 1.72 (each s)] methyl groups. These data, in combination with EIMS fragment ions at *m*/*z* 121 $[C_9H_{13}]^+$ (ring A − HOAc) and 191 $[C_{14}H_{23}]^+$ (rings D and E), along with the other prominent ions (*m*/*z* 274, 259, 218, 205, and 135) shown in Figure 1, suggested that compound **2** was a triterpene with both a monocyclic (ring A) and a bicyclic (rings D/E) ring system. The secondary acetoxyl group, located most likely at C-3 of ring A, was deduced to be oriented equatorially from the shift and coupling constants of the adjacent methine ^1H signal [δ_H 4.71 (1H, dd, J = 5.9, 7.3 Hz)].[4] The close similarity of the ^{13}C NMR (Table 1), ^1H NMR (Table 2), and EIMS data (see Experimental Section) with those of achilleol B[7] suggested that **2** had a skeleton similar to that of achilleol B. Analysis of the ^{13}C DEPT, $^1H-^1H$ COSY, HMQC, and HMBC spectra revealed the structure of **2** to be 8,14; 9,10-bis-*seco*-oleana-1(10),8,13-trien-3β-yl acetate with a yet-to-be-determined stereochemistry. The stereochemistry of **2** was determined by NOE difference spectroscopy. Compound **2** showed significant NOE correlations between [H-2α−H-3α−H-23 (4α-Me)−H-5α] and [H-3α−H-5α] on the α-face and [H-2β−H-24 (4β-Me)] on the β-face of ring A of the molecule (Figure 2). This allowed the assignment of H-23 and H-24 signals and demonstrated the acetoxyl group at C-3 to be oriented at the β-face and the methine at C-5 at the α-face. Other significant NOE correlations observed between [H-28 (17β-Me)−H-18β and H-22β−H-30 (20β-Me)] on the β-face and [H-19α−H-29 (20α-Me)] on the α-face of rings D and E were consistent with those observed for β-amyrin acetate (Figure 2).[8] This suggested that **2** had a cis configuration in terms of the D/E-ring junction, orienting H-28 at the β-face. We conclude that structure **2** is 8,14; 9,10-bis-*seco*-oleana-1(10),8,13-trien-3β-yl acetate (camelliol A acetate). On alkaline hydrolysis, acetate **2** yielded a free alcohol, 8,14;9,10-bis-*seco*-oleana-1(10),8,13-trien-3β-ol (camelliol A, **1**).[10]

Compound **4** had the molecular formula $C_{32}H_{54}O_2$ (HRE-IMS) and IR absorptions at 1238, 1740 (acetoxyl), 800, and 824 cm^{-1} (trisubstituted double bond). The mass spectrum included diagnostic fragment ions at *m*/*z* 259, 218, 205, and 191 (Figure 1). The ^1H NMR spectrum included three tertiary (δ 0.83, 0.88, and 0.90) and two olefinic (δ 1.58 and 1.64) methyl singlets and an olefinic methine (δ 5.17, br t, J = 6.6 Hz) signal. These spectral features are similar to

Table 2. ^1H NMR Spectral Data (δ Values; 400 MHz; $CDCl_3$) of Compounds **1**−**6**[a]

proton(s)	**1**	**2**	**3**	**4**	**5**[b]	**6**[b]
1	5.24	5.22	1.36 (2H)	1.35 (2H)	5.24	5.21
2	2.24 (α), 1.98 (β)	2.28 (α), 2.00 (β)	1.48 (2H)	1.53 (2H)	2.24 (α), 1.97 (β)	2.27 (α), 2.04 (β)
3	3.47 (dd, 5.6, 8.0)	4.71 (dd, 5.9, 7.3)	3.61 (2H, t, 6.6)	4.02 (2H, dt, 1.9, 6.6)	3.46 (br t, 6.9)	4.70 (dd, 5.8, 7.0)
5	1.66	1.70			1.65	1.69
6	1.36, 1.76	1.35, 1.75	1.98 (2H)[c]	1.98 (2H)[c]	1.35, 1.76	1.37, 1.74
7	1.97, 2.16	1.96, 2.16	1.97 (2H)[c]	1.97 (2H)[c]	1.96, 2.16	1.98, 2.15
9	5.17 (br t, 6.4)	5.17 (br t, 7.3)	5.17 (br t, 6.6)	5.17 (br t, 6.6)	5.15	5.15
10			2.70 (dq, 7.3, 7.0)	2.70 (dq, 7.3, 7.0)		
11	1.96, 2.04	1.97, 2.05	1.95, 2.04	1.95, 2.03	2.02 (2H)	2.02 (2H)
12	1.74, 2.22	1.74, 2.23	1.74, 2.24	1.73, 2.24	2.02 (2H)	2.02 (2H)
13					5.15	5.15
15	1.89 (α), 2.02 (β)	1.89 (α), 2.03 (β)	1.90 (α), 2.03 (β)	1.90 (α), 2.02 (β)	1.98 (2H)	1.97 (2H)
16	1.91 (α), 0.81 (β)	1.91 (α), 0.81 (β)	1.91 (α), 0.81 (β)	1.92 (α), 0.81 (β)	2.07 (2H)	2.07 (2H)
17					5.12	5.12
18	1.66	1.66	1.65	1.66		
19	1.38 (α), 0.98 (β)	1.38 (α), 0.96 (β)	1.39 (α), 0.96 (β)	1.39 (α), 0.96 (β)	1.98 (2H)	1.97 (2H)
20					2.07 (2H)	2.07 (2H)
21	1.33 (α), 1.12 (β)	1.33 (α), 1.12 (β)	1.34 (α), 1.11 (β)	1.34 (α), 1.11 (β)	5.10	5.10
22	1.22 (α), 1.48 (β)	1.22 (α), 1.48 (β)	1.22 (α), 1.49 (β)	1.22 (α), 1.48 (β)		
23	0.97 (s)	0.92 (s)	1.66 (s)	1.65 (s)	0.97 (s)	0.91 (s)
24	0.83 (s)	0.89 (s)	1.68 (s)	1.68 (s)	0.83 (s)	0.89 (s)
25	1.72 (br s)	1.72 (br s)	0.97 (d, 7.2)	0.97 (d, 6.9)	1.72 (br s)	1.72 (br s)
26	1.63 (s)	1.63 (s)	1.64 (br s)	1.64 (br s)	1.60 (s)	1.62 (s)
27	1.58 (s)	1.58 (s)	1.58 (s)	1.58 (s)	1.60 (s)	1.60 (s)
28	0.82 (s)	0.82 (s)	0.83 (s)	0.83 (s)	1.60 (s)	1.60 (s)
29	0.87 (s)	0.87 (s)	0.88 (s)	0.88 (s)	1.60 (s)	1.60 (s)
30	0.90 (s)	0.89 (s)	0.90 (s)	0.90 (s)	1.68 (s)	1.68 (s)
3-OAc		2.04 (s)		2.04 (s)		2.04 (s)

[a] J Values (Hz) are bracketed. J values not included were not determined. [b] Determined at 500 MHz. [c] Assignments in each column are interchangeable.

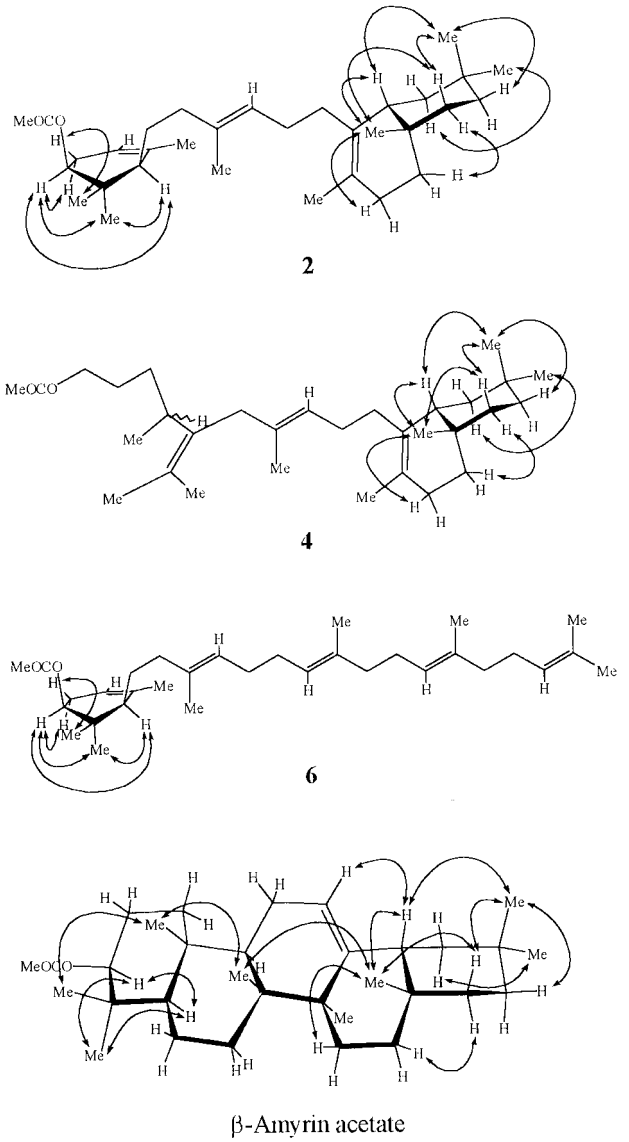

Figure 2. Major NOE correlations (↔) for **2**, **4**, **6**, and *β*-amyrin acetate.

those of **2**. It appeared that **2** and **4** had the same right-hand portion (carbons 7−30) of the molecule. The ^{1}H NMR spectrum of **4** included signals corresponding to an isopropylidene [δ_H 1.65 and 1.68 (each 3H and s)], a secondary methyl (δ_H 0.97, d, J = 6.9 Hz) associated with an allylic methine (δ_H 2.70, tq, J = 7.3, 7.0 Hz), and an acetoxy methylene (δ_H 2.04, 3H, s, and δ_H 4.02, 2H, dt, J = 1.9, 6.6 Hz), which are consistent with a 3,4-*seco*-triterpene-3-yl acetate structural moiety.[6] This was supported by the fragments having *m*/*z* 123 $[C_9H_{15}]^+$ (Figure 1), formed by cleavage of the C-5 and C-6 bond and loss of acetic acid, and *m*/*z* 69 $[C_5H_9]^+$, due to the cleavage of the C-5 and C-10 bond with concomitant loss of acetic acid. The above evidence in combination with the ^{13}C (Table 1) and ^{1}H NMR data (Table 2), in addition to analysis of ^{1}H−^{1}H COSY, HMQC, and HMBC spectra, indicated that **4** possessed a 3,4;8,-14;9,10-tris-*seco*-oleana-4,8,13-trien-3-yl acetate structure. Compound **4** showed the same significant NOE correlations in terms of ring D/E with those of compound **2** (Figure 2),[8] and hence, **4** was established as (10ζ)-3,4;8,14;9,10-tris-*seco*-oleana-4,8,13-trien-3-yl acetate (camelliol B acetate), with the stereochemistry at C-10 remaining undetermined. On alkaline hydrolysis, acetate **4** yielded a free alcohol, (10ζ)-3,4;8,14;9,10-tris-*seco*-oleana-4,8,13-trien-3-ol (camelliol B, **3**).[10]

The molecular formula of compound **6** was determined as $C_{32}H_{52}O_2$ by HREIMS. Its IR spectrum showed absorption bands for an acetoxyl group (1240, 1720 cm^{-1}) and a trisubstituted double bond (800, 835 cm^{-1}). The ^{1}H NMR spectrum of **6** displayed signals due to a secondary acetoxyl group [δ_H 2.04 (3H, s, OAc) and 4.70 (1H, dd, J = 5.8, 7.0 Hz)], a trisubstituted double bond [δ_H 5.22 (1H, m)], and two tertiary methyl groups [δ_H 0.89 and 0.91 (each s)] and an olefinic (δ_H 1.72, s) methyl group, which were almost indistinguishable from those arising from the ring A protons of **2** (Table 2). This information, in combination with a diagnostic EIMS fragment ion at *m*/*z* 121 $[C_9H_{13}]^+$, formed by cleavage of the C-5 and C-6 bond and loss of acetic acid (Figure 1), suggested that compound **6** was a triterpene with the same monocyclic (ring A) moiety in the molecule as compound **2**. Further, the ^{1}H NMR signals for five olefinic methyl groups [δ_H 1.60 (9H, s), 1.62 (3H, s), and 1.68 (3H, s)] and four trisubstituted double bonds [δ_H 5.10−5.15 (4H, m)] (Table 2) and the EIMS fragmentation pattern (Figure 1) of **6**, arising from four isoprene units contained as a side chain in the molecule, were consistent with those of achilleol A acetate.[11] The above evidence in combination with the ^{13}C (Table 1) and ^{1}H NMR (Table 2) data in addition to ^{1}H−^{1}H COSY, HSQC, HMBC, difference NOE, and phase-sensitive NOESY spectra indicated that **6** possesses the structure 8,14;9,10;13,18;17,22-tetra-*seco*-neogammacera-1(10),8,13,17,21-pentaen-3*β*-yl acetate (Figure 2).[8] Alkaline hydrolysis of **6** yielded camelliol C (**5**; 8,14;9,10;13,18;17,22-tetra-*seco*-neogammacera-1(10),8,13,-17,21-pentaen-3*β*-ol; $C_{30}H_{50}O$).[10]

Two triterpene alcohols structurally related to compounds **1**, **3**, and **5** have previously been reported from *Achillea odorata* L. (Compositae),[7,11] viz., achilleols A and B. We also isolated the first of these two known compounds from sasanqua oil. It is a double-bond isomer of camelliol C (**5**). Achilleol B differs from camelliol A (**1**) in that it has an exocyclic double bond in the A ring and a trans configuration of the decalin residue (D/E ring). Sasanqua oil contains *β*-amyrin (25% of the triterpenes). It is interesting to note that a bicyclic squalene 2,3-oxide, possessing the same ring system (D/E ring) as **1** and **3**, afforded *β*-amyrin on enzymatic cyclization.[12] Thus, **1** and **3** might be byproducts of the biosynthesis of *β*-amyrin.

Experimental Section

General Experimental Procedures. TLC plates [silica gel−$AgNO_3$ (4:1, w/w)] were developed with cyclohexanes−EtOAc (9:1). Reversed-phase HPLC was carried out on octadecyl silica gel columns (25 cm × 10 mm i.d.), on a Superiorex ODS S-5 *μ*m column (Shiseido Co., Ltd., Tokyo, Japan) (HPLC I) and on a TSK ODS-120A 5 *μ*m column (Toso Co., Tokyo, Japan) (HPLC II), at 25 °C with MeOH (4 mL/min) as mobile phase. GLC was performed using a DB-17 fused-silica capillary column (30 m × 0.3 mm i.d., column temperature 275 °C). For both HPLC and GLC, cholesterol (cholest-5-en-3*β*-ol) was the standard for the determination of Rt_R(I) of hydroxy triterpenes; cholesteryl acetate was the standard for the determination of Rt_R(II) for the acetoxy triterpenes. EIMS and HREIMS were recorded at 70 eV. NMR spectra were recorded, if not otherwise specified, at 400 MHz (^{1}H NMR) and 100.6 MHz (^{13}C NMR) in $CDCl_3$ with tetramethylsilane (TMS) (^{1}H NMR) and $CDCl_3$ at *δ* 77.0 (^{13}C NMR) as internal standard. Chemical shifts are *δ* values. IR spectra were recorded as liquid films. Specific rotations were measured at 25 °C in $CHCl_3$. Acetylation (Ac_2O−pyridine) and hydrolysis of acetates (5% KOH in MeOH) were performed at room temperature overnight.

Materials. Crude sasanqua oil (*Camellia sasanqua* Thunb.) was donated by Nikko Fine Products Co. (Tokyo, Japan). A reference specimen of β-amyrin acetate was isolated from sasanqua oil.[5]

Extraction and Isolation. Alkaline hydrolysis (5% KOH in MeOH, reflux, 3 h) of sasanqua oil (5.0 kg) followed by diisopropyl ether extraction yielded a neutral nonsaponifiable lipid fraction (19.2 g). Column chromatography over silica gel afforded a triterpene alcohol fraction (6.7 g), which was acetylated. Yield: 5.2 g. Argentation TLC followed by HPLC of the acetylated fraction yielded 29 compounds[5,6] and, furthermore, four incompletely cyclized triterpene alcohols as the acetyl derivatives: **2** (5 mg), **4** (5 mg), **6** (8 mg), and achilleol A acetate (10 mg).

Camelliol A (1): amorphous gum; $[\alpha]^{25}_D$ +4.0° (*c* 0.2, $CHCl_3$); IR ν_{max} 3400, 800 cm^{-1}; EIMS *m/z* 426 $[M]^+$ (24), 411 (16), 408 (6), 393 (5), 287 (3), 274 (14), 259 (6), 231 (3), 218 (30), 205 (58), 191 (17), 189 (11), 175 (6), 163 (6), 149 (21), 139 (4), 135 (30), 121 (48), 109 (100); HREIMS *m/z* 426.3879 (calcd for $C_{30}H_{50}O$, 426.3859), 411.3642 (calcd for $C_{29}H_{47}O$, 411.3624), 408.3751 (calcd for $C_{30}H_{48}$, 408.3753), 274.2639 (calcd for $C_{20}H_{34}$, 274.2658), 259.2398 (calcd for $C_{19}H_{31}$, 259.2424), 218.2065 (calcd for $C_{16}H_{26}$, 218.2033), 205.1916 (calcd for $C_{15}H_{25}$, 205.1955), 191.1780 (calcd for $C_{14}H_{23}$, 191.1797), 139.1120 (calcd for $C_9H_{15}O$, 139.1122), 135.1160 (calcd for $C_{10}H_{15}$, 135.1173), 121.1009 (calcd for C_9H_{13}, 121.1016); Rt_R(I) 0.65 (HPLC I), 0.78 (GLC).

Camelliol A acetate (2): amorphous gum; $[\alpha]^{25}_D$ −3.1° (*c* 0.2, $CHCl_3$); IR ν_{max} 1740, 1240, 835, 800 cm^{-1}; EIMS *m/z* 468 $[M]^+$ (11), 453 (5), 408 (10), 393 (9), 274 (24), 259 (11), 244 (2), 231 (3), 229 (4), 218 (26), 205 (63), 191 (12), 189 (16), 181 (1), 175 (11), 149 (26), 135 (43), 121 (72), 111 (95), 97 (85), 43 (100); HREIMS *m/z* (assignment) 468.3942 ($C_{32}H_{52}O_2$), 453.3746 ($C_{31}H_{49}O_2$), 408.3712 ($C_{30}H_{48}$,), 274.2664 ($C_{20}H_{34}$), 259.2404 ($C_{19}H_{31}$), 218.2088 ($C_{16}H_{26}$), 205.1972 ($C_{15}H_{25}$), 191.1784 ($C_{14}H_{23}$), 181.1248 ($C_{11}H_{17}O_2$), 135.1155 ($C_{10}H_{15}$), 121.0989 (C_9H_{13}); Rt_R-(II) 0.51 (HPLC I), 0.26 (HPLC II), 0.68 (GLC). On alkaline hydrolysis, **2** yielded a free alcohol (**1**).

Camelliol B (3): amorphous gum; $[\alpha]^{25}_D$ +1.7° (*c* 0.4, $CHCl_3$); IR ν_{max} 3340, 800 cm^{-1}; EIMS *m/z* 428 $[M]^+$ (25), 413 (10), 341 (1), 273 (3), 257 (5), 236 (5), 222 (3), 218 (5), 205 (28), 191 (5), 189 (5), 163 (3), 149 (13), 137 (18), 135 (16), 123 (15), 121 (17), 109 (50), 95 (61), 87 (55), 81 (66), 69 (100); HREIMS *m/z* (assignment) 428.4019 ($C_{30}H_{52}O$), 413.3760 ($C_{29}H_{49}O$), 273.2541 ($C_{20}H_{33}$), 218.2064 ($C_{16}H_{26}$), 205.1900 ($C_{15}H_{25}$), 191.1746 ($C_{14}H_{23}$), 137.1317 ($C_{10}H_{17}$), 123.1171 (C_9H_{15}), 69.0702 (C_5H_9); Rt_R(I) 0.60 (HPLC I), 0.60 (GLC).

Camelliol B acetate (4): amorphous gum; $[\alpha]^{25}_D$ −3.6° (*c* 0.1, $CHCl_3$); IR ν_{max} 1740, 1238, 840, 800 cm^{-1}; EIMS *m/z* 470 $[M]^+$ (37), 455 (14), 273 (3), 264 (3), 259 (2), 257 (2), 218 (9), 205 (45), 191 (8), 189 (12), 149 (18), 137 (45), 123 (18), 121 (31), 109 (78), 95 (100), 81 (77), 69 (70); HREIMS *m/z* (assignment) 470.4100 ($C_{32}H_{54}O_2$), 455.3848 ($C_{31}H_{51}O_2$), 273.2580 ($C_{20}H_{33}$), 259.2364 ($C_{19}H_{31}$), 218.2073 ($C_{16}H_{26}$), 205.1978 ($C_{15}H_{25}$), 191.1812 ($C_{14}H_{23}$), 137.1309 ($C_{10}H_{17}$), 123.1144 (C_9H_{15}), 69.0700 (C_5H_9); Rt_R(II) 0.51 (HPLC I), 0.24 (HPLC II), 0.57 (GLC). On alkaline hydrolysis, **4** yielded a free alcohol (**3**).

Camelliol C (5): amorphous gum; $[\alpha]^{25}_D$ −12.9° (*c* 0.2, $CHCl_3$); IR ν_{max} 3393, 800 cm^{-1}; EIMS *m/z* 426 $[M]^+$ (2), 408 (1), 383 (1), 357 (1), 339 (1), 315 (1), 286 (1), 274 (2), 259 (1), 243 (1), 231 (2), 217 (2), 205 (3), 203 (6), 191 (2), 175 (3), 161 (5), 151 (7), 149 (9), 136 (20), 135 (15), 123 (25), 121 (29), 81 (96), 69 (100), 55 (31); HREIMS *m/z* (assignment) 426.3830 ($C_{30}H_{50}O$), 408.3753 ($C_{30}H_{48}$), 357.3208 ($C_{25}H_{41}O$), 339.3018 ($C_{25}H_{39}$), 274.2630 ($C_{20}H_{34}$), 259.2483 ($C_{19}H_{31}$), 217.1974 ($C_{16}H_{25}$), 205.1909 ($C_{15}H_{25}$), 191.1779 ($C_{14}H_{23}$), 135.1184 ($C_{10}H_{15}$), 123.1153 (C_9H_{15}), 121.0991 (C_9H_{13}), 69.0717 (C_5H_9), 55.0557 (C_4H_7); Rt_R-(I) 0.39 (HPLC I), 0.85 (GLC).

Camelliol C acetate (6): amorphous gum; $[\alpha]^{25}_D$ −6.5° (*c* 0.8, $CHCl_3$); IR ν_{max} 1720, 1240, 835, 800 cm^{-1}; EIMS *m/z* 468 $[M]^+$ (1), 408 (1), 339 (1), 274 (3), 271 (1), 259 (1), 257 (1), 231 (2), 217 (1), 205 (3), 203 (5), 191 (2), 175 (2), 149 (9), 147 (1), 135 (20), 134 (37), 123 (20), 121 (27), 81 (74), 69 (100), 55 (19); HREIMS *m/z* (assignment) 468.3968 ($C_{32}H_{52}O_2$), 408.3734 ($C_{30}H_{48}$), 339.3064 ($C_{25}H_{39}$), 274.2678 ($C_{20}H_{34}$), 259.2407 ($C_{19}H_{31}$), 217.1949 ($C_{16}H_{25}$), 205.1942 ($C_{15}H_{25}$), 191.1781 ($C_{14}H_{23}$), 135.1165 ($C_{10}H_{15}$), 123.1188 (C_9H_{15}),121.1016 (C_9H_{13}), 69.0701 (C_5H_9), 55.0551 (C_4H_7); Rt_R(II) 0.22 (HPLC II), 0.74 (GLC). On alkaline hydrolysis, **6** yielded a free alcohol (**5**).

References and Notes

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NP980336A