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Three sesquiterpene hydrocarbons from the roots of *Panax ginseng* C.A. Meyer (Araliaceae)

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Abstract

The volatile constituents of the roots of *Panax ginseng* C.A. Meyer have been investigated after hydrodistillation and analysed by means of different analytical methods. Besides several compounds already known three sesquiterpene hydrocarbons have been isolated from the essential oil. Structure elucidation of the bicyclic panaxene as well as of the tricyclic panaginsene and ginsinsene was performed by MS and NMR. They have been identified as (1*R**,2*S**,5*S**)-2-ethenyl-1(1-methylethenyl)-2,6,6-trimethylbicyclo[3.2.0]heptane (panaxene), (1*S**,8*S**,11*R**)-4,7,7,11-tetramethyltricyclo[6.3.0.0^{1,5}]undec-4-ene (panaginsene) und (1*R**,6*R**,7*R**)-3,7,10,10-tetramethyltricyclo[4.3.2.0^{2,6}]undec-2-ene (ginsinsene).

Keywords: *Panax ginseng*; Araliaceae; Essential oil; Sesquiterpenes; Panaxene; Panaginsene; Ginsinsene

1. Introduction

Panax ginseng C.A. Meyer (Araliaceae) has been used in traditional medicine as Asian or Oriental ginseng since ancient times. Even today, this medicinal herb is listed in many pharmacopoeias and is still an important and high-grade health product.

Because of their biological activities, the ginsenosides (triterpenoid saponin glycosides) have frequently been investigated (Zhang et al., 2002). In addition, polyacetylenes were found in hexane extracts of the roots (Hirakura et al., 1991, 1992, 1994).

In previous studies, a number of terpenoids have been isolated (Iwabuchi et al., 1990; Ko et al., 1996). Among these, various sesquiterpene hydrocarbons as well as oxygenated sesquiterpenes have been identified. Here, we describe the isolation and structure elucidation of three new minor sesquiterpene hydrocarbons of ginseng roots which we like to call panaxene (**1**; 0.5%), panaginsene (**2**; 0.7%) and ginsinsene (**3**; 1.6%).

2. Result and discussion

2.7 ml (0.1%) essential oil was obtained by hydrodistillation from 2.7 kg plant material. The hydrodistillate of *Panax ginseng* was investigated by GC–MS. Most of the constituents could be identified by comparing their mass spectra and retention indices with data of a spectral library (König et al., 2004; Hochmuth, 2005). Major components were the monoterpene hydrocarbons α-pinene (1.7%) (**4**) and, β-pinene (2.3%) (**5**) as well as the sesquiterpene hydrocarbons β-panasinsene (6.6%) (**6**), african-2-ene (1.5%) (**7**), β-elemene (1.4%) (**8**), calarene (1.0%) (**9**), (E)-β-farnesene (3.1%) (**10**), α-humulene (8.4%) (**11**), α-neoclovene (4.3%) (**12**), 2-*epi*-(E)-β-caryophyllene (5.1%) (**13**), β-neoclovene (1.0%) (**14**), β-selinene (1.0%) (**15**) and bicyclogermacrene (4.0%) (**16**). In addition, the oxygenated compounds spath-

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✠ W.A. König deceased on November 19, 2004; his scientific achievements keep him among us.

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ulenol (5.5%) (**17**), humulene epoxide II (1.5%) (**18**), ginsenol (3.4%) (**19**), hexadecanoic acid (2.3%) (**20**), and falcarinol (3.8%) (**21**) could be identified (see Fig. 1).

Three unknown sesquiterpene hydrocarbons with a molecular ion signal at *m/z* 204 suggesting a molecular formula of $C_{15}H_{24}$, were selected for isolation and structural elucidation. Their investigation by 1- and 2-D NMR spectroscopy revealed novel skeletons for (**1**) and (**3**) (see Table 1). Structure (**2**) has previously been postulated as an intermediate in "senoxydene" – synthesis by Tori et al. (1985), but never been isolated before as a natural product.

2.1. Panaxene (*1*)

The ^{1}H NMR spectrum of panaxene (**1**) showed four singlets for methyl groups, three at δ 0.81, 1.03, 1.15 and one downfield shifted methyl group (δ 1.68). The ^{13}C NMR revealed two quaternary carbons (δ 55.6, 49.1) and two double bonds (δ 144.8, 109.5 and 150.0, 111.6). The HMBC spectrum showed two geminal methyl groups coupled to a quaternary carbon (δ 30.2, C-6; 1.15, 31.4, CH_3-14; 0.81, 23.7, CH_3-15). This quaternary carbon was linked to a tertiary carbon (δ 2.47, 50.5, C-5), which correlated with two methylene groups (δ 1.56–1.74, 24.6, C-4; 1.70–1.71, 40.5, C-3). On the other hand, C-6 was connected to a methylene group (δ 1.68–1.78, 41.5, C-7), followed by a quaternary carbon (δ 55.6, C-1), forming a cyclobutane ring to C-5. Connection of the methylene group C-3 with the quaternary carbon (δ 49.0, C-2) closed a cyclopentane ring.

C-2 was connected to a methyl group (δ 1.03, 18.5, CH_3-13) and two olefinic carbons (δ 4.90–4.95, 109.5, C-12; 5.86, 144.8, C-11). C-1 was found to be close to two other olefinic carbons (δ 150.0, C-8; 4.88–4.97, 111.6, C-9) one of which, C-8, carried a downfield shifted methyl group (δ 1.68, 21.2, C-10).

The structure for panaxene, resulting from these data, is 2-ethenyl-1(1-methylethenyl)-2,6,6-trimethylbicyclo[3.2.0]-heptane, shown in Fig. 2.

The relative configuration of the compound was derived from ^{1}H–^{1}H-NOE experiments. The methine proton H-5 showed a correlation with the methyl group H-14 and a weak signal to the methyl group H-10. The proton H-7a showed couplings to the methyl groups H-15 and H-13. Consequently, these protons are in-plane. The lack of correlation between H-5 and the methyl group H-15 indicates a *trans* configuration of these protons. The methyl group H-13 was found to interact with H-12a indicating *cis* configuration between the proton H-11 and H-12b. The compound, therefore, shows (1*R**,2*S**,5*S**) – configuration.

2.2. Panaginsene (*2*)

The ^{1}H NMR spectrum of panaginsene showed three singlets (δ 0.89, 0.97, 1.68) and one doublet (δ 0.99) for methyl groups. According to the HMQC NMR spectrum, 5 methylene groups (δ 29.5, C-9, 36.8, C-10, 40.3, C-3, 42.5, C-6, 44.1, C-2) and two methine groups (δ 46.7, C-11, 60.3, C-8) were found to be present.

The HMBC spectrum showed two geminal methyl groups coupled to a quaternary carbon (δ 43.0, C-7; 0.97, 25.4, C-13; 0.89, 32.0, C-14). This quaternary carbon was found to be adjacent to a tertiary carbon (δ 1.57, 60.0, C-8) and a methylene group (δ 1.66–1.85, 42.5, C-6). The latter was connected to a double bond (δ 129.1, C-5, 144.7, C-4), followed by two methylene groups (δ 2.14–2.7 and 40.3, C-3; 1.91–2.10 and 44.1, C-2). The C-2 carbon must be linked to a quaternary carbon C-1 (δ 69.3) closing a cylopentane ring.

One downfield shifted singlet methyl group (δ 1.68, C-12) coupled to C 4 (δ 144.7). The doublet methyl group C-15 (δ 0.99, $J = 6.9$ Hz) was connected to the methine carbon (δ 1.92 and 46.7, C-11) followed by two methylene groups (δ 1.08–1.62 and 36.8, C-10; 1.53–1.72 and 29.5, C-9) completed the tricyclic structure as C-9 was linked to the methine carbon C-8.

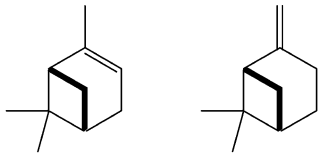
The structure for panaginsene, resulting from these data, is 4,7,7,11-tetramethyltricyclo[6.3.0.0^{1,5}]undec-4-ene, shown in Fig. 3. Panaginsene shows a new tricyclic sesquiterpene skeleton.

The relative configuration of (**2**) was established through ^{1}H–^{1}H-NOE experiments. The proton H-9b showed couplings to the methyl group H-13. The proton H-2b was observed to correlate with the methine proton H-8 as well as with the methyl group H-14. The methyl group H-15 coupled to H-3b. This can only be realized if C-11 is in *trans* position to H-8 and C-9 to C-2. The compound, therefore, shows (1*S**,8*S**,11*R**) – configuration.

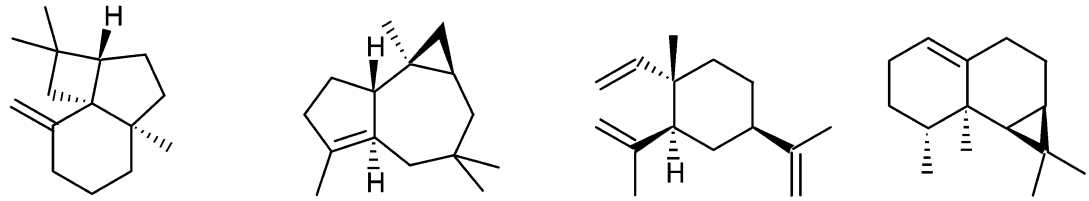
2.3. Ginsinsene (*3*)

The ^{1}H NMR spectrum of ginsinsene (**3**) showed three singlets (δ 0.99, 1.07, 1.65) and one doublet (δ 0.81) for methyl groups. The downfield shifted singlet methyl group (δ 1.65) indicated that it was attached to a double bond. The HMQC revealed five methylene groups (δ 1.45–1.70, 28.9, C-9, 1.20–1.45, 29.5, C-8, 1.54–1.93, 34.2, C-5, 2.35–2.56, 40.1, C-4, 0.96–1.61, 46.0, C-11) and two methin groups (δ 1.62 and 39.8, C-7, 1.90 and 44.7, C-1).

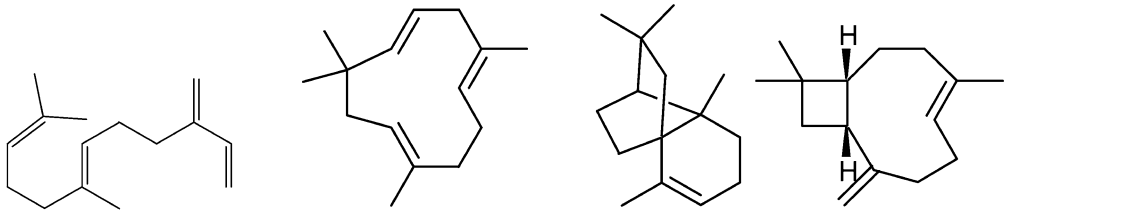
The HMBC spectrum pointed to the presence of one double bond (δ 151.2, 119.9) and two quaternary carbons (δ 61.1, 42.0), which the ^{13}C NMR did not show. In the HMBC spectrum two geminal methyl groups coupled to a quaternary carbon (δ 42.0, C-10; 0.99, 33.7, C-13; 1.07, 23.6, C-14). This quaternary carbon was found to be adjacent to a methylene group (δ 0.96–1.61, 46.0, C-11) and a tertiary carbon (δ 1.9, 44.7, C-1). The latter was connected to a double bond (δ 119.9, C-2, 151.2, C-3). A downfield shifted methyl group coupled with this C-3 carbon, followed by two methylene groups (δ 2.35–2.56 and 40.1, C-4; 1.54–1.93 and 34.2, C-5). A C-5 carbon was linked to the quaternary carbon C-6 (δ 61.1) as was C-11, two five membered rings were closed with C-6 (and C-2) as the bridge head. The doublet methyl group C-15 (δ 0.81,



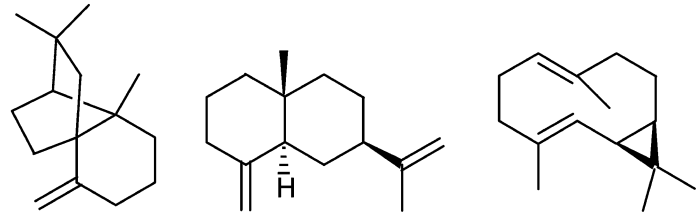
α-pinene (**4**) ß-pinene (**5**)



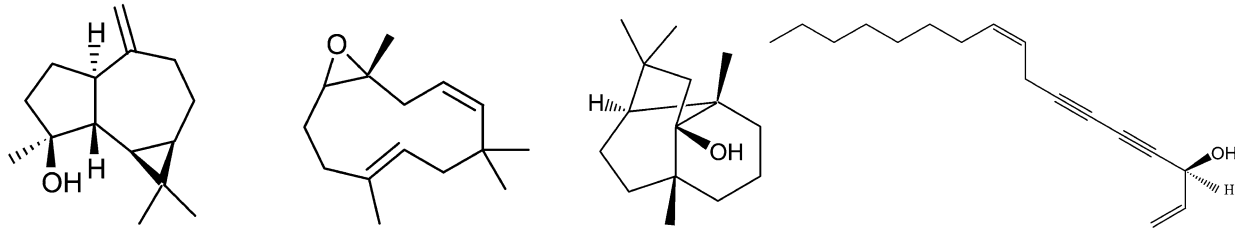
ß-panasinsene (**6**) african-2-ene (**7**) ß-elemene (**8**) calarene (**9**)



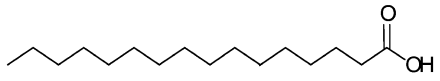
(*E*)-ß-farnesene (**10**) α-humulene (**11**) α-neoclovene (**12**) 2-*epi*-(*E*)-ß-caryophyllene (**13**)



ß-neoclovene (**14**) ß-selinene (**15**) bicyclogermacrene (**16**)



spathulenol (**17**) humulene epoxide II (**18**) ginsenol (**19**) falcarinol (**21**)



n-hexadecanoic acid (**20**)

Fig. 1. Volatile constituents of the roots of *Panax ginseng*.

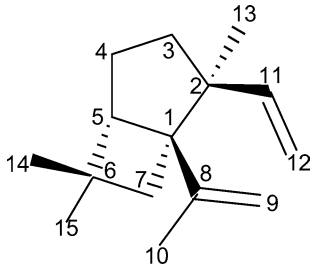


Fig. 2. Structure of panaxene **1** (1*R**,2*S**,5*S**)-2-ethenyl-1(1-methylethenyl)-2,6,6-trimethylbicyclo[3.2.0]heptane.

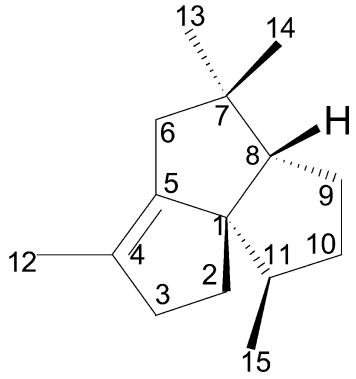


Fig. 3. Structure of panaginsene **2** (1*S**,8*S**,11*R**)-4,7,7,11-tetramethyltricyclo[6.3.0.0^{1,5}]undec-4-ene.

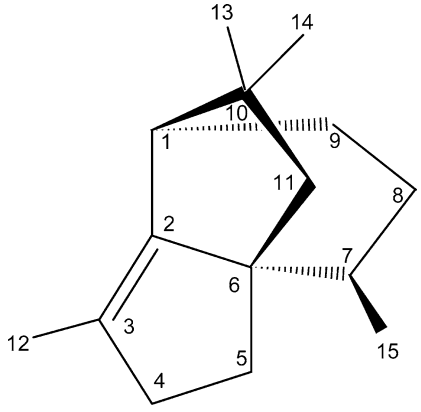


Fig. 4. Structure of ginsinsene **3** (1*R**,6*R**,7*R**)-3,7,10,10-tetramethyltricyclo[4.3.2.0^{2,6}]undec-2-ene.

$J = 6.6$ Hz) connected to the methine carbon (δ 1.62 and 39.8, C-7) followed by two methylene groups (δ 1.20–1.45 and 29.5, C-8; 1.45–1.70 and 28.9, C-9) completed the tricyclic structure of the compound, as C-9 was linked to the methine carbon C-1. The structure for ginsinsene, resulting from these data, is 3,7,10,10-tetramethyltricyclo[4.3.2.0^{2,6}]undec-2-ene. Ginsinsene shows a new tricyclic sesquiterpene skeleton (see Fig. 4).

The ^{1}H,^{1}H-COSY and NOE experiments revealed the basic structure with a relative configuration of (**3**). The methyl group C-15 (δ 0.81, 17.3) showed couplings to H-5b (δ 1.93, 34.2) and H-1 proton (δ 1.90 and 44.7) to the methyl group H-13 (δ 0.99, 33.7) with more intensity compared to the methyl group H-14 (δ 1.07, 23.6). The compound shows therefore (1*R**,6*R**,7*R**) – configuration.

3. Experimental

3.1. General experimental procedures

Gas chromatography was performed using a Orion Micromat 412 double column GC equipped with 25 m (0.25 mm I.D. × 0.25 μm) fused silica capillaries coated with polysiloxanes CPSil-5 CB and CPSil-19 CB (Chrompack), split injection; split ratio approx. 1:30; FID; carrier gas 0.5 bar H_2; injector and detector temperatures at 200 and 250 °C, respectively.

For preparative GC a modified Varian 1400 instrument was used, equipped with a stainless steel column (1.85 m × 4.3 mm) filled with 10% polydimethylsiloxane SE 52 on Chromsorb W-HP; flame ionisation detector; helium as carrier gas at a flow rate of 120 ml/min; injector and detector temperatures at 200 and 250 °C, respectively.

A HP 6890 gas chromatograph (FID) with autosampler was used, equipped with a 30 m megabore capillary column (0,53 mm i.d., film thickness 5 μm) DB 1 with He (60 ml/min) as carrier gas, coupled to an automatic fraction collector PFC system (Gerstel, Mühlheim, Germany).

GC–MS investigations (EI, 70 eV) were carried out with a Hewlett Packard HP 5890 gas chromatograph (25 m fused silica capillary column with polydimethylsiloxane CPSil-5 CB, film thickness 0.25 μm) coupled to a VG Analytical 70-250S mass spectrometer (ion source temperature: 250 °C).

NMR experiments were carried out with a Bruker WM 400 or WM 500 instrument. For panaxene (**1**) a Bruker NMR with cryo-head was used at 600/150 MHz. The internal standard was TMSi.

3.2. Plant material and isolation of the essential oil

Roots and rootlets of *Panax ginseng* were provided by Worlée NaturProdukte GmbH, Hamburg and Martin Bauer GmbH & Co. KG, Hamburg-Alveslohe. Other samples were obtained from Wischmann Flora Farm, Walsrode, Germany. In addition, authentic four-year-old material from South-Korea was analysed for comparison.

The volatile oil of the ground roots was obtained by hydrodistillation (4 h) with a clevenger type apparatus (Sprecher, 1963) and collected in 1 ml *n*-pentane. Solvents were distilled and dried before use.

3.3. Isolation of single components

The isolation of single constituents of the crude oil was carried out by column chromatography (60 g silica gel, 60 Å (ICN), eluent: 150 ml *n*-pentane). This fraction was concentrated to 5 ml and further subjected to preparative

Table 1
NMR-data for the new sesquiterpene hydrocarbons **1**–**3**

Carbons	^{13}C (ppm)	^{1}H (ppm)		HMBC-couplings
Panaxene (**1**)				
C-01	55.6			H-13, H-4b, H-10, H-7a, H-9a, H-9b
C-02	49.1			H-13,H-4b, H-7a, H-12b, H-12a
C-03	40.5	1.71 (*m*, 1H)	1.70 (*m*, 1H)	H-13
C-04	24.6	1.74 (*m*, 1H)	1.56 (*m*, 1H)	
C-05	50.5	2.47 (*d*, 1H, $J = 5.4$)		H-15, H-14, H-7b
C-06	30.2			H-15, H-14,H-4b, H-4a, H-7a
C-07	41.5	1.78 (*d*, $J = 12.0$)	1.68 (*m*, 1H)	H-15, H-14
C-08	150.0			H-10, H-7a
C-09	111.6	4.97 (*m*, 1H)	4.88 (*m*, 1H)	H-10
C-10	21.2	1.68 (*s*, 3H)		H-9a, H-9b
C-11	144.8	5.86 (*dd*, 1H, $J = 6.6$, 28.4 Hz)		H-13, H-12a
C-12	109.5	4.95 (*dd*, 1H, $J = 1.51$,17.5)	4.90 (*dd*, 1 H, $J = 1.6$, 10.9 Hz)	H-13
C-13	18.5	1.03 (*s*, 3H)		H-11
C-14	31.4	1.15 (*s*, 3H)		H-15, H-7a
C-15	23.7	0.81 (*s*, 3H)		
Panaginsene (**2**)				
C-01	69.3			H-15, H-6b
C-02	44.1	1.91 (1H)	2.1 (1H)	H-11, H-3a
C-03	40.3	2.14 (1H)	2.7 (1H)	H-12, H-2b
C-04	144.7			H-12, H-2a, H-2b, H-6b
C-05	129.1			H-12, H-2a, H-2b, H-6b
C-06	42.5	1.66 (1H)	1.85 (1H)	H-13, H-14
C-07	43.0			H-13, H-14
C-08	60.3	1.57 (1H)		H-13, H-14, H-9a, H-6b
C-09	29.5	1.53 (1H)	1.72 (1H)	
C-10	36.8	1.08 (*sept*, 1H)	1.62 (1H)	H-13
C-11	46.7	1.92 (1H)		H-15, H-10a, H-2a, H-2b
C-12	14.6	1.68 (*s*, 3H)		
C-13	25.4	0.97 (*s*, 3H)		H-14
C-14	32.0	0.89 (*s*, 3H)		H-13, H-6b,H-8
C-15	15.4	0.99 (*d*, 3H, $J = 6.9$ Hz)		H-10a, H-11
Ginsinsene (**3**)				
C-01	44.7	1.90 (*t*, 1H)		H-11a, H-13, H-14
C-02	119.9			H-12, H-1, H-4a, H-4b
C-03	151.2			H-12, H-1, H-4a, H-4b
C-04	40.1	2.35 (*m*, 1H)	2.56 (*m*, 1H)	
C-05	34.2	1.54 (*m*, 1H)	1.93 (*m*, 1H)	H-4a, H-4b
C-06	61.1	–		H-15, H-11a, H-11b, H-8a, H-5a, H-5b
C-07	39.8	1.62 (*m*, 1H)		H-8b, H-15, H-11a
C-08	29.5	1.45 (*m*, 1H)	1.20 (*m*, 1H)	H-15
C-09	28.9	1.45 (*m*, 1H)	1.70 (*m*, 1H)	H-8b
C-10	42.0	–		H-11a, H-13, H-14
C-11	46.0	0.96 (*d*, 1H, $J = 13.2$ Hz)	1.61 (*m*, 1H)	H-14, H-13, H-15
C-12	14.0	1.65 (*s*, 3H)		
C-13	33.7	0.99 (*s*, 3H)		
C-14	23.6	1.07 (*s*, 3H)		H-13, H-11a, H-8b
C-15	17.3	0.81 (*d*, 3H, $J = 6.6$ HZ)		H-11a, H-8b, H-7

GC. By using a SE-52 packed column (90–180 °C; 2 °C/min), the fraction was subsequently fractionated into eight subfractions. The sesquiterpenes (**1**), (**2**) and (**3**) were found in fraction 3. The purification of the compounds was achieved by means of GLC using a megabore DB-1 column (155 °C, isothermal).

3.4. Panaxene (*1*)

(1R,2S*,5S*)-2-Ethenyl-1(1-methylethenyl)-2,6,6-trimethylbicyclo[3.2.0]heptane*. R.I.$_{\text{CPSil 5}}$: 1312; ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.81 (3H, *s*, CH_3-15), 1.03 (3H, *s*, CH_3-13), 1.15 (3H, *s*, CH_3-14), 1.56 (1H, *m*, H-4b), 1.68 (1H, *m*, H-7b), 1.68 (3H, *s*, CH_3-10), 1.70 (1H, *m*, H-3b), 1.71 (1H, *m*, H-3a), 1.74 (1H, *m*, H-4a), 1.78 (1H, *m*, H-7a), 2.47 (1H, *d*, $J = 5.4$ Hz, H-5), 4.88 (1H, *s*, br, H-9b), 4.90 (1H, *dd*, $J = 1.6$, 10.9 Hz, H-12b), 4.95 (1H, *dd*, $J = 1.49$, 17.5 Hz, H-12a), 4.97 (1H, *s*, *br*, H-9a), 5.86 (1H, *dd*, $J = 10.9$, 17.5 Hz, H-11); ^{13}C NMR (600.1 MHz, C_6D_6): δ 18.5 (*q*, C-13), 21.2 (*q*, C-10), 23.7 (*q*, C-15), 24.6 (*t*, C-4), 30.2 (*s*, C-6), 31.4 (*q*, C-14), 40.5 (*t*, C-13), 41.5 (*t*, C-7), 49.1 (*s*, C-2), 50.5 (*d*, C-5), 55.6 (*s*,

C-1), 109.5 (*t*, C-12), 111.6 (*t*, C-9), 144.8 (*d*, C-11), 150.0 (*s*, C-8); MS (EI, 70 eV), *m/z* (rel. int.): 204 $[M]^+$ (3), 189 (36), 175 (12), 161 (30), 148 (70), 133 (65), 121 (100), 107 (56), 105 (58), 93 (72), 92 (54), 79 (40), 77 (26), 67 (18), 55 (22), 41 (41), 39 (15).

3.5. Panaginsene (**2**)

(1*S**, 8*S**, 11*R**)-*4,7,7,11-Tetramethyl-tricyclo*[*6.3. 0.0*^{1,5}]-*undec-4-ene*. R.I.$_{\text{CPSil 5}}$: 1336; ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.89 (3H, *s*, CH_3-14), 0.97 (3H, *s*, CH_3-13), 0.99 (3H, *d*, $J = 6.87$ Hz, CH_3-15), 1.08 (1H, *m*, H-10a), 1.53 (1H, *m*, H-9a), 1.57 (1H, *s*, H-8), 1.62 (1H, *m* , H-10b), 1.66 (1H, *m*, H-6a), 1.68 (3H, *s*, CH_3-12), 1.72 (1H, *m*, H-9b), 1.85 (1H, *m*, H-6b), 1.91 (1H, *m*, H-2a), 1.92 (1H, *m*, H-11), 2.10 (1H, *m*, H-2b), 2.14 (1H, *m*, H- 3a), 2.7 (1H, *m*, H-3b); ^{13}C NMR (600.1 MHz, C_6D_6): δ 14.6 (*q*, C-12), 15.4 (*q*, C-15), 25.4 (*q*, C-13), 29.5 (*t*, C-9), 32.0 (*q*, C-14), 36.8 (*t*, C-10), 40.3 (*t*, C-3), 42.5 (*t*, C-6), 43 (*s*, C-7), 44.1 (*t*, C-2), 46.7 (*d*, C-11), 60.3 (*d*, C-8), 69.3 (*s*, C-1), 129.1 (*s*, C-5), 144.7 (*s*, C-4) ; MS (EI, 70 eV), *m/z* (rel. int.): 204 $[M]^+$ (24), 189 (100), 175 (5), 161 (12), 147 (16), 133 (18), 119 (11), 105 (15), 91 (13), 79 (7), 77 (7), 69 (3), 67 (3), 65 (3), 55 (8), 53 (3), 41 (12), 39 (4).

3.6. Ginsinsene (**3**)

(*1R**, *6R**, *7R**)-*3,7,10,10-Tetramethyltricyclo*[*4.3.2.0*^{2,6}] *undec-2-ene*. R.I.$_{\text{CPSil 5}}$: 1353; ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.81 (3H, *d*, $J = 6.61$Hz, CH_3-15), 0.96 (1H, *d*, $J = 12.9$ Hz, H-11a), 0.99 (3H, *s*, CH_3-13), 1.07 (3H, *s*, CH_3-14), 1.20 (1H, *m*, H-8b), 1.45 (1H, *m*, H-9a), 1.45 (1H, *m*, H-8a), 1.54 (1H, *m*, H-5a), 1.60 (1H, *m*, H-9), 1.61 (1H, *m*, H-7b), 1.65 (3H, *s*, CH_3-12), 1.70 (1H, *m*, H-9b), 1.90 (1H, *t*, H-1), 1.93 (1H, *m*, H-1b), 2.34 (1H, *m*, H-2a), 2.59 (1H, *m*, H-2b); ^{13}C NMR (600.1 MHz, C_6D_6): δ 14.0 (*q*, C-12), 17.3 (*q*, C-15), 23.6 (*q*, C-14), 28.9 (*t*, C-9), 29.5 (*t*, C-8), 33.7 (*q*, C-13), 34.2 (*t*, C-5), 39.8 (*t*, C-7), 40.1 (*t*, C-4), 42.0 (*s*, C-10), 44.7 (*d*, C-1), 46.0 (*t*, C-11), 61.1 (5, C-6), 119.9 (5, C-2), 151.2(5, C-3); MS (EI, 70 eV), *m/z* (rel. int.): 204 $[M]^+$ (35), 189 (58), 175 (3), 161 (7), 148 (100), 133 (51), 119 (20), 105 (29), 91 (27), 79 (9), 77 (10), 69 (4), 67 (3), 65 (5), 55 (11), 41 (16), 39 (6).

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