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Sesqui- and diterpenes from the liverwort *Gackstroemia decipiens*☆

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Abstract

Six rosanes, 5β,11β-dihydroxy-ros-15-ene, 5β,12β-dihydroxy-ros-15-ene, 11β-hydroxy-7-oxo-rosa-5,15-diene, 1α,5β,11β-trihydroxy-7-oxo-ros-15-ene, 5β,20-epoxy-20-hydroxy-ros-15-ene and 5β,20-epoxy-20-methoxy-ros-15-ene along with the enantiomer of the already reported 11β-hydroxy-rosa-5,15-diene and the known 5β-hydroxy-ros-15-ene have been isolated from the liverwort *Gackstroemia decipiens*. Furthermore, the sesquiterpenes 3-acetoxy-7,11-dihydroxy-farnesa-1,5,9-triene and 1β,10β-epoxy-nardosin-7,11-diene were identified. Their structures were elucidated by NMR spectroscopy.

Keywords: *Gackstroemia decipiens*; Lepidolaenaceae; Hepaticae; Liverwort; Rosane; Nardosinane; Farnesane

1. Introduction

Liverworts have yielded a wide range of natural products, including some unique sesqui- and diterpenoids (Asakawa, 1995; Lorimer, Perry, Burgess & Foster, 1997). In the course of our investigations on terpenoids from liverworts, we have studied *Gackstroemia decipiens* Hässel (Lepidolaenaceae). This species grows on soil and logs in forests throughout Tierra del Fuego and Patagonia. So far, there has been only one detailed report on the chemistry of the genus *Gackstroemia*. Asakawa & Inoue (1984) used GC–MS to examine a lipophilic extract of *G. magellanica*. Within this studies, α-pinene, elemol, γ-muurolene, germacrene D, β-caryophyllene, and β-santalene were detected. The present paper describes the isolation and characterization of six new and two known rosane derivatives together with a new nardosinane- and a new farnesane-type sesquiterpenoid.

2. Results and discussion

A combination of size exclusion chromatography, vacuum liquid chromatography and HPLC of the ether extract of the plant led to the isolation of 11β-hydroxy-rosa-5,15-diene (**1**) whose ^{1}H- and ^{13}C-NMR were in good agreement with *ent*-11β-hydroxy-rosa-5,15-diene (Garcia-Alvarez, Rodriguez, Valverde, Fraga & Gonzalez, 1981). However, the isolated compound showed a positive rotation ($[\alpha]_D^{20} + 50.4°$) in contrast to the *ent*-rosane-derivative previously isolated. Therefore **1** belongs to the rosane-series. The same is true for 5β-hydroxy-ros-15-ene (**2**) which also showed a positive rotation ($[\alpha]_D^{20} + 71°$) in contrast to literature data (Bohlmann et al., 1984). Besides, the following six new rosane derivatives were isolated: 5β,11β-dihydroxy-ros-15-ene (**3**), 5β,12β-dihydroxy-ros-15-ene (**4**), 11β-hydroxy-7-oxo-rosa-5,15-diene (**5**), 1α,5β,11β-trihydroxy-7-oxo-ros-15-ene (**6**), 5β,20-epoxy-20-hydroxy-ros-15-ene (**7**), and 5β,20-epoxy-20-methoxy-ros-15-ene (**8**). Furthermore, the nardosinane, 1β,10β-epoxy-nardosin-7,11-diene (**9**) and the farnesane derivative, 3-acetoxy-7,11-dihydroxy-farnesa-1,5,9-triene (**10**) were obtained. Their structures were deduced from NMR and mass spectral data.

The spectroscopic data of **1** and **2**, together with

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Table 1
^{13}C-NMR spectral data of compounds **3**–**8**

C	3	4	5	6	7	8
C-1	24.4 *t*	21.3 *t*	30.0 *t*	66.7 *d*	20.3 *t*	20.2 *t*
C-2	22.1 *t*	21.4 *t*	21.8 *t*	31.2 *t*	23.8 *t*	24.3 *t*
C-3	36.7 *t*	36.7 *t*	40.2 *t*	33.1 *t*	37.1 *t*	37.2 *t*
C-4	39.0 *s*	39.0 *s*	37.7 *s*	39.3 *s*	35.0 *s*	35.1 *s*
C-5	76.8 *s*	77.2 *s*	169.6 *s*	83.1 *s*	87.4 *s*	86.9 *s*
C-6	32.4 *t*	32.7 *t*	120.9 *d*	49.5 *t*	31.5 *t*	31.7 *t*
C-7	24.5 *t*	25.0 *t*	201.1 *s*	212.5 *s*	27.9 *t*	29.7 *t*
C-8	40.9 *d*	41.8 *d*	42.6 *d*	52.5 *d*	37.6 *d*	37.6 *d*
C-9	42.8 *s*	36.7 *d*	43.3 *s*	50.3 *s*	50.5 *s*	50.8 *s*
C-10	49.1 *d*	49.2 *d*	30.7 *d*	55.8 *d*	49.7 *d*	49.6 *d*
C-11	77.8 *d*	40.8 *t*	77.2 *d*	73.1 *d*	22.9 *t*	22.8 *t*
C-12	43.1 *t*	74.4 *d*	49.2 *t*	40.5 *t*	33.7 *t*	33.8 *t*
C-13	37.0 *s*	42.0 *s*	36.5 *s*	34.9 *s*	35.8 *s*	35.8 *s*
C-14	39.2 *t*	32.8 *t*	30.8 *t*	30.8 *t*	41.4 *t*	41.6 *t*
C-15	150.0 *d*	146.5 *d*	149.3 *d*	149.1 *d*	151.0 *d*	151.1 *d*
C-16	109.1 *t*	114.7 *t*	109.8 *t*	109.6 *t*	109.0 *t*	108.9 *t*
C-17	24.2 *q*	24.3 *q*	23.5 *q*	22.8 *q*	21.8 *t*	21.9 *q*
C-18	24.0 *q*	24.0 *q*	29.2 *q*	29.0 *q*	25.5 *q*	25.3 *q*
C-19	24.7 *q*	24.1 *q*	29.2 *q*	23.5 *q*	25.0 *q*	25.1 *q*
C-20	6.7 *q*	15.0 *q*	6.7 *q*	9.2 *q*	97.4 *d*	103.8 *d*
OMe						54.9 *q*

optical rotation, led to the conclusion that **1** is 11β-hydroxy-rosa-5,15-diene (**1**) (Garcia-Alvarez, Rodriguez, Valverde, Fraga & Gonzalez, 1981), and **2** the enantiomer of the already described 5β-hydroxy-ros-15-ene (**2**) (Bohlmann et al., 1984).

Compound **3** was obtained as colourless needles with a molecular formula of $C_{20}H_{34}O$ as calculated from the EI mass spectrum (*m*/*z* 306 $[M]^+$). The ^{1}H-NMR spectrum displayed a characteristic ABX-system (δ_H 4.83, 1H, *dd*, *J* = 10.7, 1.1 Hz, H-16a; δ_H 4.87, 1H, *dd*, *J* = 17.5, 1.1 Hz, H-16b and δ_H 5.72, 1H, *dd*, *J* = 10.7, 17.5 Hz, H-15) besides four singlet methyl groups (δ_H 1.04, H-17; δ_H 0.99, H-18; δ_H 0.91, H-20; δ_H 0.83, H-19). This suggested the existence of a further rosane diterpenoid. The ^{13}C-NMR spectrum (Table 1) revealed the existence of two hydroxylated carbons (δ_C 76.8, *s*, C5 and δ_C 77.8, *d*, H-11). Based on its chemical shift the signal at δ_C 77.8 (compound **1**: 78.0) could be assigned to the carbon 11. The location of

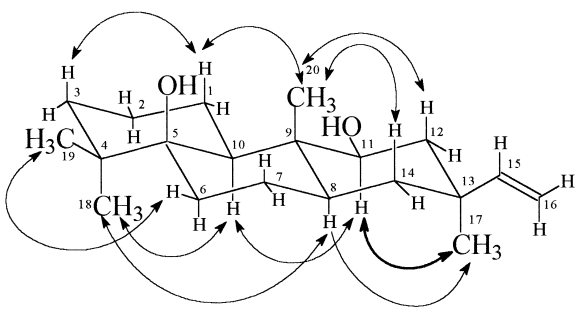


Fig. 1. Significant NOESY couplings of **3**.

the tertiary alcohol C-5 could be deduced from the HMBC spectrum (correlations between C-5 and H-18 and H-19 along with further cross peaks between C-5 and H-6α (δ_H 1.68, *m*) and H-6β (δ_H 1.50, *not resolved* (*nr*)). Furthermore, the β-position of the hydroxyl groups could be determined from NOESY spectra (Fig. 1). Thus, the structure of **3** was established as 5β,11β-dihydroxy-ros-15-ene.

Compound **4** (colourless needles) was assigned the molecular formula $C_{20}H_{34}O_2$ (EIMS, *m*/*z* 306 $[M]^+$). The ^{1}H- and ^{13}C-NMR spectra (Table 1) displayed signals assignable to a rosendiol with a tertiary hydroxyl group in position 5 (δ_C 77.2 *s*) and a secondary hydroxyl group. In the ^{1}H–^{1}H-COSY experiment the alcoholic proton (δ_H 3.56, 1H, *br s*, H-12) showed vicinal couplings to both methylene protons H-11 (α: 1.90, *m*; β: 1.24, *m*) and a cross peak to H-14α (δ_H 0.97, *nr*). From this observation the location of the secondary alcohol in position 12 can be assumed. Furthermore, the β-configuration of the hydroxyl group has been confirmed by cross peaks between H-12 and H-17 (δ_H 1.14, *s*) in the NOESY spectrum. Thus, **4** should be 5β,12β-dihydroxy-ros-15-ene.

The ^{13}C-NMR spectrum (Table 1) of compound **5**, $C_{20}H_{30}O_2$ (EIMS, *m*/*z* 302 $[M]^+$), revealed the existence of a ros-15-ene derivative containing a secondary alcohol in position 11 and an α,β-unsaturated ketone moiety (δ_C 169.9, *s*, C-5; δ_C 120.9, *d*, C-6, and δ_C 201.1, *s*, C-7). Since HMBC correlations from these olefinic carbons (δ_C 169.9, *s*, C-5; δ_C 120.9, *d*, C-6) to H-18 (δ_H 1.12, *s*) and H-19 (δ_H 0.83, *s*) could be detected, the structure of **5** must be 11β-hydroxy-7-oxo-rosa-5,15-diene.

Compound **6**, colourless needles, gave the molecular formula $C_{20}H_{32}O_4$ (CIMS, *m*/*z* 336 $[M]^+$). The ^{13}C-NMR spectrum (Table 1) displayed the signals due to a further rosane diterpenoid with an ethenyl side chain. Furthermore two secondary (δ_C 66.7, *d*, C-1 and δ_C 73.1, *d*, C-11) and a tertiary hydroxyl group (δ_C 83.1, *d*, C-5) beside a ketone function (δ_C 212.5, *s*, C-7) were detected. The location of these carbons have been deduced from the HMBC and HSQC spectra. The stereochemistry of the hydroxyl groups was determined by NOE experiments revealing correlations from H-1 (δ_H 3.90, *nr*) to both H-20 (δ_H 0.87, *s*) and H-3β (δ_H 1.77, *td*, *J* = 13.7, 4.4 Hz) and from H-11 (δ_H 3.76, *dd*, *J* = 5.3, 10.7 Hz) to H-17 (0.91, *s*), H-8 (δ_H 2.45, *dd*, *J* = 2.2, 12.8 Hz) and H-10 (δ_H 1.89, *d*, *J* = 9.7 Hz). These results established the hydroxyl groups as 1α, 5β and 11β. Therefore, the structure of **6** is represented as 1α,5β,11β-trihydroxy-7-oxo-ros-15-ene.

Compound **7** was obtained as colourless needles. The ^{1}H-NMR spectrum revealed the existence of a further ros-15-ene derivative. The ^{13}C-NMR spectrum indicated the presence of an oxygenated carbon (δ_C

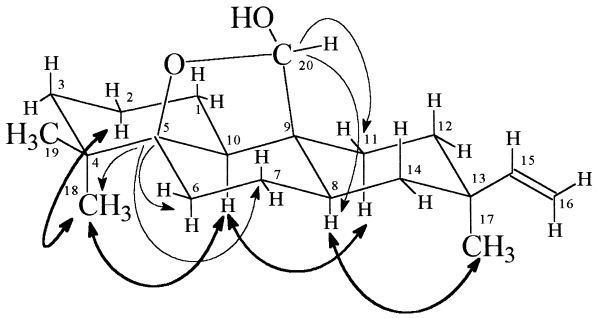


Fig. 2. Significant HMBC and NOESY (bold) couplings of **7**.

87.4, *d*, C-5) and an acetalic carbon (δ_C 97.4, *s*, C-20), each belonging to an epoxide moiety, since a molecular formula of $C_{20}H_{32}O_2$ (corresponding to a tetracyclic structure) could be calculated from EI mass spectrum (*m*/*z* 304, $[M]^+$). Based on ^{1}H–^{1}H-COSY, ^{1}H–^{13}C-COSY, and NOESY data (Fig. 2), structure **7**, 5β,20-epoxy-20-hydroxy-ros-15-ene, is assigned to this compound.

The CIMS of compound **8** displayed the molecular ion at *m*/*z* 318, corresponding to a molecular formula of $C_{21}H_{32}O_2$. The ^{1}H-NMR data were very similar to that of **7**, but showed a significant low field shift of H-20 (δ_H 4.64, *s*) and an additional singlet at δ_H 3.35 (3H), assignable to a methyl ether group. Thus, **8** must be 5β,20-epoxy-20-methoxy-ros-15-ene, the methylether of **7**, what could be proved by further HMBC-, HSQC-, and NOESY-experiments.

Compound **9** was obtained as a colourless oil with a molecular formula of $C_{15}H_{22}O$ as calculated from the EI mass spectrum (*m*/*z* 218, $[M]^+$). ^{1}H-NMR and ^{13}C-NMR displayed the signals of an exomethylene group (δ_H 4.85, 2H, *s*, H-12; δ_C 145.6, *s*, C-11; δ_C 115.7, *t*, C-12), and two methine protons, each belonging to a double bond (δ_H 5.50, 1H, *m*, H-7; δ_H 5.65, 1H, *m*, H-8; δ_C 129.9, *d*, C-7; δ_C 123.4, *d*, C-8). Based on their chemical shift the signals at δ_C 57.0 (*d*, C-1) and δ_C 61.6 (*s*, C-10) could be assigned to the bridgehead carbons of an epoxide ring. Furthermore, the ^{1}H-NMR spectrum showed signals due to three methyl groups (δ_H 1.83, *s*, H-13; δ_H 1.03, *s*, H-14; δ_H 0.76, *d*, J = 6.6 Hz, H-15). The ^{1}H- and ^{13}C-NMR assignments by ^{1}H–^{1}H-COSY, ^{1}H–^{13}C-COSY, DEPT experiments revealed the constitution of compound **9** as 1,10-epoxy-nardosin-7,11-diene. As there were NOESY correlations (Fig. 3) of H-14 with H-15, H-6 (δ_H 2.86, *dd*, J = 3.5, 2.7 Hz), and 9α (δ_H 1.91, *m*), together with cross peaks between H-4 (δ_H 1.67, *m*) and H-2β (δ_H 1.85, *m*), both methyl groups C-14 and C-15 had to be in the α-position, whereas the epoxide-ring has to be in the β-position, proved by further NOESY-signals between H-1 and H-9β (δ_H 2.73, *ddd*, J = 2.7, 19.2, 4.9 Hz). Therefore, the structure of **9** was established as 1β,10β-epoxy-nardosin-7,11-diene. The absolute configuration of this compound remained to be clarified.

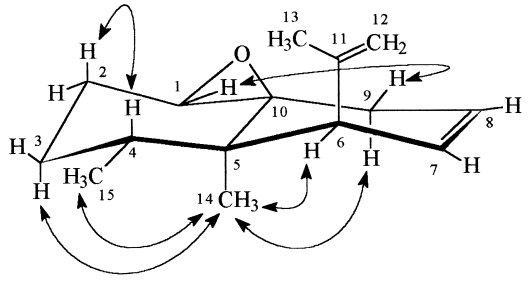
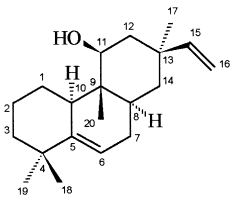


Fig. 3. Significant NOESY couplings of **8**.

Compound **10** with the molecular formula $C_{17}H_{28}O_4$ (EIMS, *m*/*z* 296, $[M]^+$) was obtained as a colourless oil. The ^{13}C-NMR spectrum showed signals due to four methyls, two methylenes, six olefinic carbons, three quaternary carbons with an oxygen shift, and a acetoxy group. Based on their chemical shifts the signals at δ_C 113.5 (*t*, C-1) and δ_C 141.5 (*d*, C-2) could be assigned to an exocyclic double bond. These spectroscopic data coupled with the molecular formula indicated a farnesane sesquiterpenoid. The location of the double bonds could be deduced from the HMBC and HSQC spectra, as correlations of C-11 (δ_C 70.6, *s*), C-12 (δ_C 29.9, *q*), and C-13 (δ_C 29.9, *q*) to H-10 (δ_H 5.68, *d*, J = 15.8) and H-9 (δ_H 5.60, *m*) along with cross peaks between C-14 (δ_C 27.9, *q*) and H-6 (δ_H 5.55, *nr*), and H-5 (δ_H 5.57, *nr*), respectively, were observed. On the basis of these results, structure **10**, 3-acetoxy-7,11-dihydroxy-farnesa-1,5,9-triene, was assigned to this compound.

Rosanes are new diterpenoids for Hepaticae whereas a nardosinane sesquiterpenoid and farnesane derivatives have been reported from different species (Asakawa, 1995). Rosanes arise by migration of the C-10 methyl group of pimaranes to C-9 and occur in both enantiomeric series predominantly in higher plants whereas nardosinanes, isolated from marine organism and higher plants, are eremophilanes in which the isopropyl group has migrated to carbon 6 (Connolly & Hill, 1992). Apart from the reported substances, β-santalane-type sesquiterpenoids and a bergamotane derivative, which showed an intensive odour, were isolated from *G. decipiens* (Geis & Becker, 1999).

Our results showed, that this species produces a considerable number of new and interesting compounds. In conclusion, *G. decipiens* has no chemotaxonomic relationships to any other liverworts, apart from the related species *G. magellanica* (Asakawa & Inoue, 1984).



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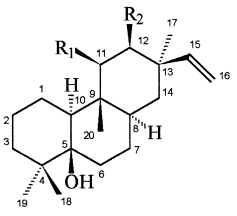
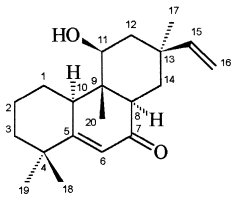


	R_1	R_2
2	H	H
3	OH	H
4	H	OH



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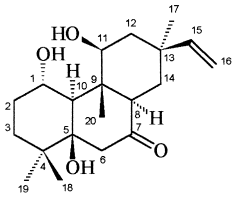

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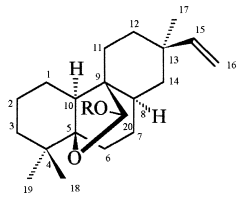
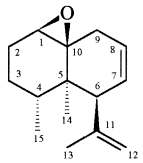


	R
7	H
8	CH_3



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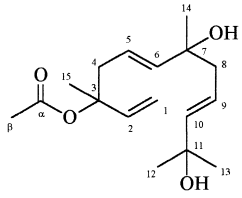

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3. Experimental

Solvents used for spectral measurements: $CDCl_3$ [^{1}H-NMR: 400 MHz; ^{13}C-NMR: 100 MHz for 1D, 500 and 125 MHz for 2D techniques, respectively. Chemical shifts are given in δ values (ppm) from TMS], $CHCl_3$ (UV, optical rotation).

3.1. Plant material

Gackstroemia decipiens Hässel was collected at the Paso Garibaldi, Tierra del Fuego in March 1997 and identified by Prof. Dr. R. Mues and Prof. Dr. U. Drehwald. A voucher specimen is deposited at Herbarium SAAR (No. 5478).

3.2. Extraction and isolation

The extraction scheme followed standard procedures of our group (Cullmann, Adam & Becker, 1993; Adam & Becker, 1994; Bungert, Gabler, Adam, Zapp & Becker, 1998; Geis, Buschauer & Becker, 1999). Powdered air dried plant material (287 g) was subsequently extracted with Et_2O and MeOH. The Et_2O extract (7.3 g) was chromatographed on Sephadex LH-20 (150 × 2.5 cm i.d.) with MeOH–CH_2Cl_2 (1:1) as eluent to give two fractions (I and II). Fraction I (3.6 g) was subjected to VLC on silica (silica gel 15 μm, 60 mm × 35 mm i.d., stepwise with a *n*-hexane–EtOAc gradient) to yield the fractions I-1 (100% *n*-hexane, 211 mg), I-2 (0.5–8% EtOAc, 265 mg), I-3 (8–15% EtOAc, 211 mg), I-4 (15–50% EtOAc, 977 mg), and I-5 (50–80% EtOAc, 386 mg). Fraction I-5 was further purified by HPLC on silica gel (LiChrospher Si 60, 5 μm, 4 × 250): *n*-hexane–EtOAc (50:50) for **10** (22 mg). Fraction II (4.4 g) was separated by VLC (silica gel 15 μm, 60 mm × 35 mm i.d., stepwise with a *n*-hexane–EtOAc gradient) and gave the fractions II-1 (0–0.5% *n*-hexane, 196 mg), II-2 (0.5–2% EtOAc, 824 mg), II-3 (2–3.5% EtOAc, 686 mg), II-4 (4–6% EtOAc, 316 mg), II-5 (6–8% EtOAc, 264 mg), II-6 (8–16% EtOAc, 332 mg), II-7 (16–18% EtOAc, 114 mg), II-8 (20–30% EtOAc, 317 mg), II-9 (30–40% EtOAc, 299 mg), II-10 (40–70% EtOAc, 250 mg), II-11 (70–90% EtOAc, 75 mg), II-12 (90–100% EtOAc, 22 mg). Fractions II-2, II-3, II-4 and II-6 were further purified by HPLC on diol-modified silicagel (LiChrospher diol 100, 5 μm, 4 × 250): *n*-hexane–EtOAc (99:1) for **9** (78 mg) and **2** (15 mg) $[\alpha]_D^{20}$ 50° (lit. $[\alpha]_D^{20}$ − 45°), *n*-hexane–EtOAc (98:2) for **1** (6 mg) $[\alpha]_D^{20}$ 71° (lit. $[\alpha]_D^{20}$ 41–84°), *n*-hexane–EtOAc (96:4) for 7 (11 mg), *n*-hexane–EtOAc (84:16) for **3** (50 mg), **4** (1 mg), **5** (15 mg), and **6** (1 mg).

The methanolic extract was evaporated in vacuo and distributed between EtOAc and H_2O. The organic layer (3.5 g) was chromatographed on Sephadex LH-20. For the EtOAc soluble fraction of the methanol extract MeOH–CH_2Cl_2 (4:1) was used as eluent to yield two fractions.

Fraction II (1.6 g) was chromatographed on diol-modified silicagel via VLC with a *n*-hexane–EtOAc-Gradient to give the fractions II-1 (100% *n*-hexane, 146 mg), II-2 (0–4% EtOAc, 288 mg), II-3 (5–7% EtOAc, 510 mg), II-4 (7–34% EtOAc, 170 mg), II-5 (34–70% EtOAc, 74 mg), and II-6 (70–90% EtOAc, 94 mg). Fraction II-1 was further purified by HPLC on silica gel (LiChrospher Si 60, 5 μm, 4 × 250): *n*-hexane–EtOAc (98:2) for **8** (3 mg).

3.2.1. 5β,11β-Dihydroxy-ros-15-ene (*3*)

$[\alpha]_D^{20}$ + 68° ($CHCl_3$; *c* 0.23); EIMS *m*/*z* (rel. int.): 306 $[M]^+$ (10), 291 (3), 273 (5), 208 (20), 207 (100), 194

(10), 173 (5), 161 (4), 147 (5), 135 (4), 123 (20), 55 (20); IR ν_{max}^{KBr} cm^{-1}: 3359, 2900, 2870; ^{1}H-NMR ($CDCl_3$) δ_H 5.72 (1H, *dd*, *J* = 10.7, 17.5 Hz, H-15), 4.87 (1H, *dd*, *J* = 17.5, 1.1 Hz, H-16a), 4.83 (1H, *dd*, *J* = 10.7, 1.1 Hz, H-16b), 3.57 (1H, *dd*, *J* = 11.1, 4.8 Hz, H-11), 1.04 (3H, *s*, H-17), 0.99 (3H, *s*, H-18), 0.91 (3H, *s*, H-20), 0.83 (3H, *s*, H-19), ^{13}C-NMR ($CDCl_3$): Table 1.

*3.2.2. 5β,12β-Dihydroxy-ros-15-ene (**4**)*

$[\alpha]_D^{20}$ + 57° ($CHCl_3$; *c* 0.27); EIMS *m*/*z* (rel. int.): 306 $[M]^+$ (17), 291 (90), 273 (12), 247 (20), 219 (85), 207 (12), 177 (10), 161 (10), 149 (20), 133 (20), 119 (25), 105 (25), 95 (45), 79 (55), 69 (60), 55 (100); IR ν_{max}^{KBr} cm^{-1}: 3300, 2950, 2870; ^{1}H-NMR ($CDCl_3$) δ_H 5.83 (1H, *dd*, *J* = 10.8, 17.4 Hz, H-15), 5.15 (1H, *d*, *J* = 10.8 Hz, H-16a), 5.12 (1H, *d*, *J* = 17.4 Hz, H-16b), 3.56 (1H, *br s*, H-11), 1.21 (3H, *s*, H-20), 1.14 (3H, *s*, H-17), 1.04 (3H, *s*, H-18), 0.83 (3H, *s*, H-19), ^{13}C-NMR ($CDCl_3$): Table 1.

*3.2.3. 11β-Hydroxy-7-oxo-rosa-5,15-diene (**5**)*

$[\alpha]_D^{20}$ + 76° ($CHCl_3$; *c* 0.41); EIMS *m*/*z* (rel. int.): 302 $[M]^+$ (17), 284 (15), 269 (20), 256 (10), 241 (20), 228 (18), 215 (25), 203 (25), 191 (27), 177 (40), 163 (100), 151 (40), 135 (30), 121 (80), 107 (45), 91 (45), 79 (55), 69 (30), 55 (60); IR ν_{max}^{KBr} cm^{-1}: 3400, 2950, 2900, 1645; ^{1}H-NMR ($CDCl_3$) δ_H 5.94 (1H, *br d*, *J* = 1.4 Hz, H-6), 5.79 (1H, *dd*, *J* = 10.6, 17.4 Hz, H-15), 4.96 (1H, *dd*, *J* = 17.4, 0.9 Hz, H-16a), 4.88 (1H, *dd*, *J* = 10.6, 0.9 Hz, H-16b), 3.91 (1H, *t*, *J* = 8.0 Hz, H-11), 1.12 (6H, *s*, H-17, H-18), 0.83 (3H, *s*, H-19), 0.73 (3H, *s*, H-20); ^{13}C-NMR ($CDCl_3$): Table 1.

*3.2.4. 1α,5β,11β-Trihydroxy-7-oxo-ros-15-ene (**6**)*

$[\alpha]_D^{20}$ + 76° ($CHCl_3$; *c* 0.17); EIMS *m*/*z* (rel. int.): 336 $[M]^+$ (20), 319 (70), 301 (100), 283 (30), 274 (5), 255 (7), 231 (4), 221 (18), 203 (20), 189 (7), 175 (5), 161 (10), 147 (10), 135 (8), 119 (10), 107 (10), 91 (20), 79 (25), 67 (20), 55 (25); IR ν_{max}^{KBr} cm^{-1}: 3400, 3200, 2950, 2900, 1680; ^{1}H-NMR ($CDCl_3$) δ_H 5.73 (1H, *dd*, *J* = 10.7, 17.5 Hz, H-15), 4.87 (1H, *dd*, *J* = 17.5, 0.8 Hz, H-16a), 4.79 (1H, *dd*, *J* = 10.7, 0.8 Hz, H-16b), 3.90 (1H, *m*, H-1), 3.76 (1H, *dd*, *J* = 5.3, 10.7 Hz, H-11), 1.02 (3H, *s*, H-19), 0.91 (3H, *s*, H-17), 0.87 (3H, *s*, H-20), 0.75 (3H, *s*, H-18); ^{13}C-NMR ($CDCl_3$): Table 1.

*3.2.5. 5β,20-Epoxy-20-hydroxy-ros-15-ene (**7**)*

$[\alpha]_D^{20}$ + 35° ($CHCl_3$; *c* 0.22); EIMS *m*/*z* (rel. int.): 304 $[M]^+$ (10), 289 (3), 275 (5), 258 (7), 243 (12), 215 (5), 202 (8), 193 (100), 178 (15), 163 (8), 147 (15), 133 (12), 119 (10), 107 (15), 91 (20), 79 (18), 67 (15), 55 (25); IR ν_{max}^{KBr} cm^{-1}: 3400, 3000, 2900, ^{1}H-NMR ($CDCl_3$) δ_H 5.78 (1H, *dd*, *J* = 10.7, 17.5 Hz, H-15), 5.20 (1H, *br d*, *J* = 3.9 Hz, H-11), 4.90 (1H, *dd*, *J* = 17.5, 1.0 Hz, H-16a), 4.83 (1H, *dd*, *J* = 10.7, 1.0 Hz, H-16b), 1.02 (3H, *s*, H-17), 0.93 (3H, *s*, H-18), 0.88 (3H, *s*, H-19); ^{13}C-NMR ($CDCl_3$): Table 1.

*3.2.6. 5β,20-Epoxy-20-methoxy-ros-15-ene (**8**)*

$[\alpha]_D^{20}$ + 33° ($CHCl_3$; *c* 0.12); EIMS *m*/*z* (rel. int.): 318 $[M]^+$ (10), 303 (5), 287 (3), 271 (2), 258 (10), 243 (12), 229 (4), 216 (5), 207 (100), 194 (10), 189 (7), 175 (4), 161 (8), 147 (35), 133 (12), 119 (12), 105 (15), 91 (20), 79 (18), 67 (15), 55 (25); IR ν_{max}^{KBr} cm^{-1}: 3400, 2950, 1650; ^{1}H-NMR ($CDCl_3$) δ_H 5.76 (1H, *dd*, *J* = 10.7, 17.5 Hz, H-15), 4.87 (1H, *dd*, *J* = 17.5, 1.3Hz, H-16a), 4.82 (1H, *dd*, *J* = 10.7, 1.3 Hz, H-16b), 4.64 (1H, *s*, H-20), 3.35 (1H, *s*, H-α), 1.00 (3H, *s*, H-17), 0.93 (3H, *s*, H-18), 0.85 (3H, *s*, H-19); ^{13}C-NMR ($CDCl_3$): Table 1.

*3.2.7. 1β,10β-Epoxy-nardosin-7,11-diene (**9**)*

$[\alpha]_D^{20}$ + 195° ($CHCl_3$; *c* 0.61); EIMS *m*/*z* (rel. int.): 218 $[M]^+$ (3), 203 (4), 189 (3), 175 (6), 160 (10), 145 (12), 133 (7), 121 (15), 105 (15), 95 (60), 79 (100), 67 (30), 55 (22); IR ν_{max}^{KBr} cm^{-1}: 2950, 2930; ^{1}H-NMR ($CDCl_3$) δ_H 5.65 (1H, *m*, H-8), 5.50 (1H, *m*, H-8), 4.85 (1H, *s*, H-12), 2.86 (1H, *dd*, *J* = 3.5, 2.7 Hz, H-6), 2.80 (1H, *t*, *J* = 2.3 Hz, H-1), 2.73 (1H, *ddd*, *J* = 2.7, 4.9, 19.2 Hz, H-9β), 1.85 (2H, *m*, H-2α, H-2β), 1.83 (3H, *s*, H-13), 1.67 (3H, *m*, H-4), 1.61 (3H, *m*, H-9α), 1.03 (3H, *s*, H-14), 0.76 (3H, *d*, *J* = 6.6 Hz, H-15); ^{13}C-NMR ($CDCl_3$): 145.6 (*s*, C-11), 129.9 (*d*, C-7), 123.4 (*d*, C-8), 115.7 (*t*, C-12), 61.6 (*s*, C-10), 57.0 (*d*, C-1), 54.1 (*d*, C-6), 37.8 (*s*, C-5), 32.7 (*t*, C-9), 29.1 (*d*, C-4), 25.5 (*t*, C-3), 22.4 (*t*, C-2), 20.7 (*q*, C-4), 17.6 (*q*, C-14), 16.4 (*q*, C-15).

*3.2.8. 3-Acetoxy-7,11-dihydroxy-farnesa-1,5,9-triene (**10**)*

$[\alpha]_D^{20}$ + 5° ($CHCl_3$; *c* 0.24); EIMS *m*/*z* (rel. int.): 296 $[M]^+$ (8), 279 (22), 261 (13), 233 (6), 219 (40), 201 (20), 151 (12), 137 (100), 121 (10), 109 (10), 95 (15), 82 (35), 71 (10), 55 (5); IR ν_{max}^{KBr} cm^{-1}: 3350, 2900, 2850; ^{1}H-NMR ($CDCl_3$) δ_H 5.90 (1H, *m*, H-2), 5.68 (1H, *d*, *J* = 15.8 Hz, H-10), 5.60 (1H, *m*, H-9), 5.57 (1H, nr, H-6), 5.55 (1H, nr, H-5), 5.11 (1H, *m*, H-1), 2.57 (1H, *m*, H-4), 2.19 (1H, *m*, H-8), 1.97 (3H, *s*, H-β), 1.48 (3H, *s*, H-15), 1.29 (6H, *s*, H-12, H-13), 1.23 (3H, *s*, H-14); ^{13}C-NMR ($CDCl_3$): 169.9 (*s*, C-α), 142.6 (*d*, C-10), 141.5 (*d*, C-2), 122.2 (*d*, C-5), 121.9 (*d*, C-9), 113.5 (*t*, C-1), 140.9 (*d*, C-6), 82.2 (*s*, C-3), 72.2 (*s*, C-7), 70.6 (*s*, C-11), 45.5 (*t*, C-8), 42.2 (*t*, C-4), 29.9 (*q*, C-12, C-13), 27.9 (*q*, C-14), 23.7 (*q*, C-15), 22.1 (*q*, C-β).

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