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Triterpenoids from *Parthenium argentatum x P. tomentosa*

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Abstract

Four tetracyclic triterpenoids and lupeol were isolated from the hybrid *Parthenium argentatum x P. tomentosa*. The new triterpenoids were identified as 16, 24-epoxy-3α-hydroxylanost-8-ene (argentatin E); 16, 24-epoxy-25-hydroxycycloart-1, 11, 22-trien-3-one (argentatin F); 16,24-dihydroxycycloart-20, 25-dien-3-one (argentatin G) and 16, 24-dihydroxycycloart-25-en-3-one (argentatin H). The chemical identities of these compounds were confirmed by the different spectrometric measurements.

Keywords: Triterpenoids; *Parthenium argentatum x P. tomentosa*; Asteraceae; Lupeol; Argentatins E, F, G and H

1. Introduction

Parthenium argentatum Gray, Asteraceae (guayule), is a rubber plant common to northern Mexico and Southwest Texas (Whitworth and Whitehead, 1991; Castillon and Cornish, 1999). Six different triterpenoids have been isolated from guayule resin. These triterpenes are incanilin, argentatins A, B, C and D and iso-argentatin B. All these triterpenoids are C30 oxygenated cycloartane or lanost-8-ene derivatives (Komoroski et al., 1986; Romo De Vivar et al., 1990; Rodriguez-Hahn et al., 1970). The sesquiterpene esters guayulins A, B, C and D were also isolated (Romo et al., 1970; Proksch et al., 1981; Schloman et al., 1983). In a previous communication, we reported the isolation of antifungal eudesmanoids from the resin of the hybrid *P. argentatum x P. tomentosa* (Maatooq et al., 1996; Maatooq and Hoffmann, 1996). In this paper we describe the isolation and structure elucidation of four new tritepenoids belonging to the cycloartane and lanost-8-ene series, in addition to lupeol.

2. Results and discussion

The investigation of the resin of guayule hybrid *P. argentatum x P. tomentosa* has led to isolation and identification of five different triterpenes, four of them are new ones **2–5**. The known pentacyclic triterpene, lupeol (**1**), was isolated from guayule for the first time as needles, mp, 202 °C (Du Shang-jiang et al., 1985). The spectroscopic data of **1** are in full agreement with those reported for lupeol (Wenkert et al., 1978; Reynolds et al., 1986; Rasool et al., 1989; Hui and Li, 1976; Ahmad et al., 1985). Further structure connectivity confirmations came through DEPT, H–H-COSY and HETCOR experiments.

The investigation of the spectral data of **2** indicated that its structure is 16,24-epoxy-3α-hydroxylanost-8-ene (argentatin E). The ^{1}H and ^{13}C NMR data of **2** were found to be close to those reported for isoargentatin B, **7** (Komoroski et al., 1986), with few differences. The signal at δ 4.29, integrated for 1H, was assigned for C-24 carbinol methine proton and was found to be multiplet rather than a double doublet. This indicated the likely absence of the 25-hydroxyl group and the presence of a methine proton at C-25. Moreover, the 26 and 27-methyl groups protons signals appeared as doublets ($J = 7.5$ Hz, each). ^{13}C NMR spectrum showed three carbinol methine signals (DEPT) at δ 84.2, 76.3

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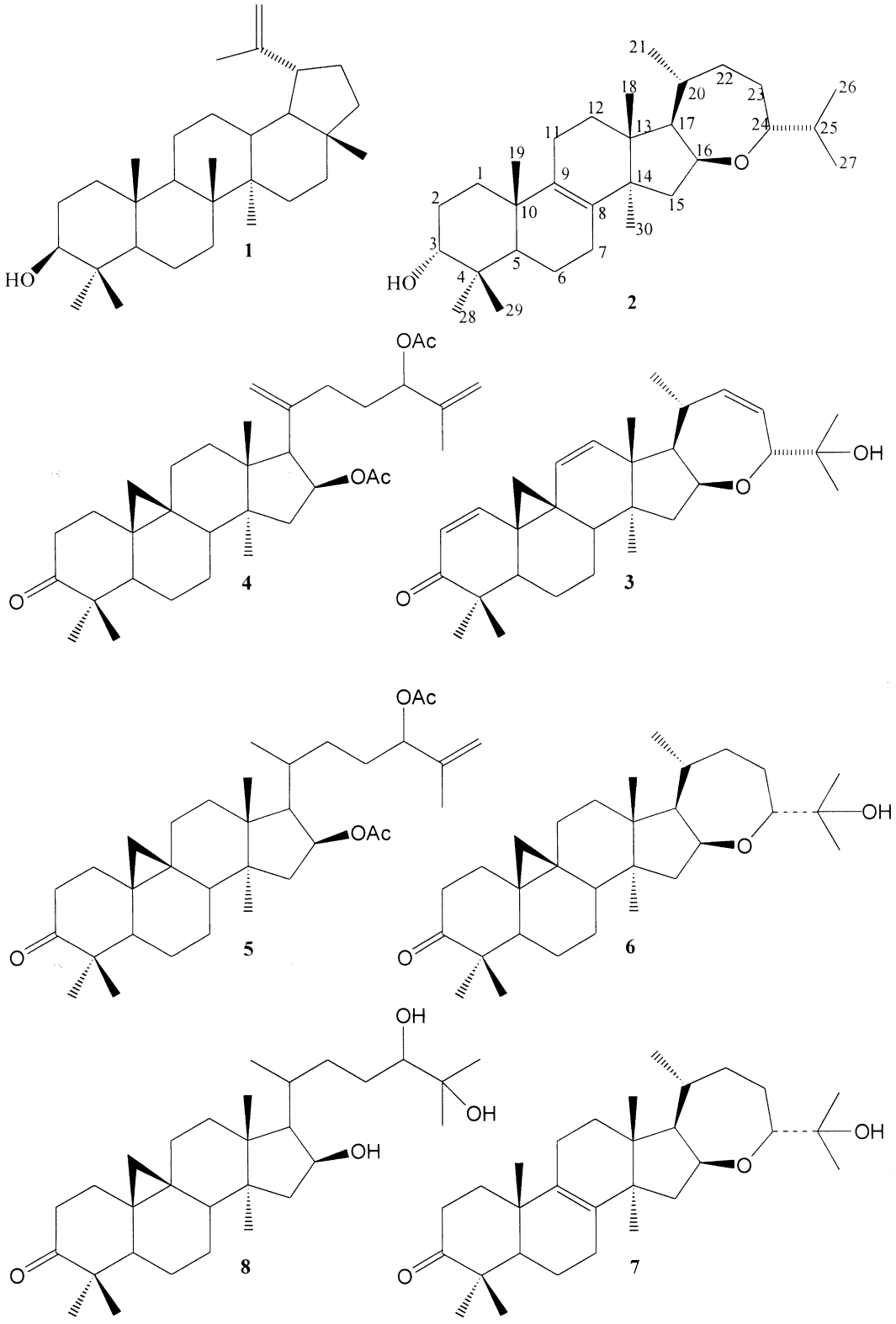

and 74.5. The signals at δ 84.2 and 74.3 ppm were assigned to C-24 and C-16, respectively, forming an epoxy bridge (Komoroski et al., 1986). The carbon signal at δ 76.3 and the proton signal at δ 3.53 ppm were assigned to a carbinol methine group at C-3. The 3-OH was found to be α-oriented, since the carbinol methine proton signal appeared as a double doublet with a small coupling constants ($J = 1.5$ and 5.0 Hz), inferring its equatorial orientation. Furthermore, the δ 76.3 value is consistent with the 3β-hydroxylanostane

skeleton (Komoroski et al., 1986; Rodriguez-Hahn et al., 1970). The EI–MS of **2** gave *m/z* 442 analyzed for $C_{30}H_{50}O_2$ which is in agreement with the proposed structure for **2**.

Compound **3** was identified as 16,24-epoxy-25-hydroxy-cycloart-1,11,22-trien-3-one (argentatin F). The ^{1}H NMR spectrum of **3** showed seven methyl signals at δ 0.87, 0.98, 1.04, 1.09, 1.17, 1.26 and 1.26, indicating the possible presence of argentatin B, **6,** skeleton. The upfield pair of doublets at δ 0.52 and 0.81 ($J = 5.0$ Hz, each) were assigned to the cyclopropane methylene protons at C-19. The carbinol methine proton signals at δ 4.38 (multiplet) and 4.92 (doublet, $J = 5.5$ Hz) were assigned to H-16 and H-24, respectively. The ^{13}C NMR spectrum displayed 30 carbon signals and their multiplicities were discriminated by DEPT experiment into seven methyl groups, four methylene groups, twelve methine groups and seven quaternary carbons. Among the quaternary signals, the one at δ 204.1 was assigned to 3-oxo group with a likely α,β-unsaturation between C-1 and C-2 (Nick et al., 1994), which was supported by presence of the IR absorption band at 1680 cm^{-1}. This made it possible to assign the pair of doublets ($J = 11.5$ Hz, each) at δ 7.73 and 6.49 for H-2 and H-1, respectively. These two doublets were correlated to the olefinic methine signals at δ 128.2 and 146.5, respectively. Another pair of doublets ($J = 10$ Hz, each) at δ 5.41 and 5.39 were correlated to the olefinic methine carbon signals at δ 128.3 and 127.8 and were assigned to C-11 and C-12, respectively, based on their multiplicities. Irradiation (9 Hz) of the cyclopropyl methylene proton signals at δ 0.51 and 0.81 by selective INEPT experiment causes enhancement of the carbon signals at δ 47.1 (C-5), 48.1 (C-8), 20.9 (C-9), 128.3 (C-11) and 127.8 (C-12). A third set of olefinic protons signals was represented by a pair of broad triplets at δ 5.53 and 5.56, correlated to the olefinic carbon signals at δ 118.1 and 131.5 were assigned to C-22 and C-23, respectively. The locations of these triplets were excluded from 6 and 7-positions, based on the observed deshielding of the 24-position carbinol methine proton signal (at δ 4.92, but normally around ca. δ 3.20–3.60; Komoroski et al., 1986). Furthermore, this H-24 signal appeared as a doublet ($J = 5.5$ Hz) rather than a double doublet supporting this conclusion. The rest of the molecule chemical shift values are in agreement with those reported for argentatin B (**6**) (Komoroski et al., 1986). The CI–MS (CH_4) spectrum of compound **3** gave *m/z* 433 analyzed for $[M–H_2O + 1]^+$ indicating a molecular formula of $C_{30}H_{42}O_3$, which is consistent with the proposed structure for **3**.

Compounds **4** and **5** were obtained by acetylation after excluding the presence of any natural acetate by IR. The analysis of the spectral data for **4** indicated the presence of argentatin B (**6**) skeleton, since the proton NMR spectrum demonstrated the presence of the upfield proton signals characteristic for the cyclopropane ring system at δ 0.57 and 0.83 (each as a doublet, $J = 4.5$ Hz). The two downfield proton signals, each integrated for 3H, observed at δ 1.97 and 2.03 and the two pairs of carbon signals at δ 170.3 and 21.2 ppm and δ 170.3 and 21.3 were assigned to these two acetate groups. H-16 and H-24 signals were found to be deshielded and appeared at δ 5.33 (*ddd*, $J = 5.0$, 4.5, 5.0 Hz) and 5.12 (*dd*, $J = 5.5$, 5.5 Hz) and were correlated to the carbon signals at δ 74.7 and 76.8, respectively. This indicated the likely opening of the epoxide bridge between C-16 and C-24. The analysis of the multiplicities of the carbon signals of **4** by DEPT experiment indicated the presence of two downfield shifted methylene groups at δ 112.8 and 114.9, assigned for two different terminal methylene groups. The presence of these two terminal methylene groups

Table 1
^{13}C NMR spectral data for compounds **2**–**5**[a]

Compound no.	2	3	4	5
1	38.2	146.5	33.4	33.3
2	26.8	128.2	37.4	37.4
3	76.3	204.1	216.3	216.3
4	41.5	37.6	50.2	50.2
5	52.7	47.1	48.3	48.3
6	20.5	22.2	21.6	21.4
7	26.7	26.6	26.1	26.4
8	136.5	48.1	48.2	47.9
9	135.0	20.9	20.9	20.7
10	37.1	27.5	26.4	26.3
11	21.4	128.3	25.9	25.9
12	32.2	127.8	33.2	32.4
13	48.4	50.1	45.8	45.7
14	48.1	46.2	46.8	47.0
15	46.2	44.8	44.9	45.9
16	74.5	72.4	74.7	75.4
17	56.5	56.4	54.1	54.9
18	17.3	18.0	19.9	18.0
19	19.0	30.6	29.7	29.9
20	30.7	32.4	143.7	30.7
21	21.7	20.2	114.9	19.9
22	34.5	118.1	35.9	31.6
23	23.8	131.5	29.2	30.7
24	84.2	81.3	76.8	77.6
25	35.5	71.1	143.0	143.2
26	25.1[b]	25.5[b]	112.8	112.7
27	25.2[b]	25.8[b]	21.5	18.6
28	22.8	20.6	20.8	20.8
29	27.8	21.5	21.3	22.2
30	21.9	19.1	20.8	18.1
16-Ac	–	–	170.3	170.4
	–	–	21.3	21.3
24-Ac	–	–	170.3	170.6
	–	–	21.2	21.1

[a] At 62.5 MHz, using $CDCl_3$ as a solvent, TMS is the internal standard and the chemical shifts (δ) are expressed in ppm. Assignements were made possible by DEPT, HETCOR and selective INEPT.
[b] Assignement may be interchangeable.

was supported by the appearance of two sets of double doublets at δ 4.86, 4.91 ($J=1.5$ Hz, each) and δ 4.93 and 5.01 ($J=1.5$ Hz, each), integrated to four exomethylene protons.

The appearance of only five methyl skeletal methyl protons singlets at δ 0.95, 1.02, 1.07, 1.22 and 1.71, indicated the conversion of two skeletal methyls into terminal methylene groups and one of these should be C-21, due to the disappearance of its corresponding doublet. The deshielded methyl proton singlet at δ 1.71, assigned to 3H-27, which indicated that C-26 has to be the second terminal methylene group. The appearance of H-24 signal as a double doublet, indicated the absence of any protons at C-25 and confirmed our conclusion. The rest of the molecule chemical shifts deviations are insignificant and were consistent with those reported for argentatins B, **6** and C, **8** and iso-argentatin B, (**7**) (Komoroski et al., 1986). The CI–MS of **4** gave m/z 419 as a base peak calculated for $[M-2HOAc+1]^+$ which is consistent with the proposed structure for **4** as 16, 24-dihydroxycycloart-20, 25-dien-3-one diacetate (argentatin G diacetate).

The spectral data for **5** are very close to those of **4** with few differences. The ^1H NMR spectrum showed only one set of exomethylene double doublets at δ 4.87 and 4.90 ppm ($J=1.0$ Hz, each), assigned to 2H-26. This indicated that the other terminal methylene group at C-21 in compound **4** was absent. The 3H doublet at δ 0.94 ($J=7.0$ Hz) was assigned to 21-methyl group. The ^{13}C NMR demonstrated the presence of six skeletal methyl signals and two olefinic carbon signals at δ 143.2 and 112.7, assigned to C-25 and C-26, respectively, confirming the presence of only one terminal methylene group. The CI–MS spectrum of **5** gave an ion peaks at m/z 541 $[M+1]^+$, 481 $[M-HOAc+1]^+$ and 421 $[M-2HOAc+1]^+$ to confirm the proposed structure for **5** to be 16, 24-dihydroxycycloart-25-en-3-one diacetate (argentatin H diacetate).

3. Experimental

3.1. General instrumentation

Melting points are uncorrected. ^1H NMR and ^{13}C NMR were measured on a Bruker WM 250 NMR Spectrometer, at 250 and 62.5 MHz, respectively, with $CDCl_3$ as a solvent and TMS as the internal standard. The chemical shifts are expressed in δ ppm. DEPT, Selective INEPT, HETCOR and COSY were measured on a Bruker WM 300 NMR Spectrometer. EI–MS (70 eV) and CI–MS (CH_4) were conducted on a Hewlett Packard 5988A Spectrometer, equipped with a Hewlett Packard RTE-6/VM data system. IR was conducted on Beckman Acculab I IR spectrometer. UV data was obtained from Beckman Model 26 Spectrophotometer. ORDs were measured on Autopole III Automatic Polarimeter (Rudolph Scientific).

3.2. Isolation

For the primary resin treatment and initial fractionations see Maatooq et al. (1996). Then, a portion of the derubberized resin (1334 g) was column chromatographed (2 columns, 10×50 cm, 2.0 kg silica gel 60, 63–200 μm). The eluent was 20.0 l each of C_6H_{14}, C_6H_{14}–EtOAc 98:2, 96:4, 90:10, 80:20 and 70:30.

The frs eluted with C_6H_{14} (68.0 g oil) were adsorbed onto a top of 500 g Rp-C18 silica gel in a sentered glass funnel and washed with 2.0 l each of 100% MeOH, 100% Me_2CO and 50% Me_2CO/C_6H_{14}. The Me_2CO wash afforded 162 mg solid mass which was purified by prep TLC on 1 mm-thick silica gel GF_{254} plates using 5% *iso*-PrOH/C_6H_{14} ($R_f=0.39$). This afforded 38 mg of **1** as needles. Compound **1** gave an orange color after spraying with vanillin/H_2SO_4 spray reagent. The MeOH wash gave 67.0 g residue. This residue was adsorbed onto a top of 900 g silica gel 63–200 μm, 5×50 cm column. Five frs were generated using 2.0 l each of 50% CH_2Cl_2/C_6H_{14}, CH_2Cl_2, 50% Me_2CO/CH_2Cl_2,100% Me_2CO and 100% MeOH. The 50% Me_2CO/CH_2Cl_2 wash gave 382 mg solid mass. After prep TLC on 1 mm-thick silica gel GF_{254} plates using 15% *iso*-pr-OH/C_6H_{14} ($R_f=0.34$), 20 mg of **2** were obtained as needles. Compound **2** gave yellow and greyish-brown colors after spraying with vanillin//H_2SO_4 and cerium sulfate spray reagents, respectively.

The frs eluted with C_6H_{14}–EtOAc, 80:20, gave 140 g residue. Forty-two grams of incanilin were obtained by repeated crystallization from C_6H_{14} or MeOH. A 5 g-fr of the mother liquor was subjected to repeated c.c., 200 g silica gel 63–200 μm, 2.5×45 cm, first using 500 ml each of C_6H_{14}, C_6H_{14}–CH_2Cl_2 50:50, 75:25, 100:0, CH_2Cl_2–Me $_2$CO 98:2, 97:3, 90:10, 50:50 and 100:0. The frs eluted with 100% CH_2Cl_2 through 10% Me_2CO/CH_2Cl_2 (2.8 g) were rechromatographed on a similar column using C_6H_{14}–EtOAc, one liter portions of 95:5, 90:10, 85:15, 75:25, 50:50 and 100:0. The frs eluted with C_6H_{14}–EtOAc 90:10–75:25 (1.5 g) were processed in a similar way, but the elution solvent was 1.0 l C_6H_{14}–EtOAc, 80:20, 3.0 l 75:25 and 1.0 l 50:50. The frs eluted with C_6H_{14}–EtOAc 80:20, displayed one major spot (161 mg). After purification on 1 mm-thick silica gel GF_{254} prep TLC plates using 10% Me_2CO/CH_2Cl_2 as the solvent system ($R_f=0.71$), it afforded 76 mg of **3** as a solid gum. The earlier fractions eluted with C_6H_{14}–EtOAc 75:25 (120 mg) were subjected to acetylation (acetic anhydride/pyridine). Final purification was achieved by prep TLC on 1 mm-thick silica gel

GF_{254} plates using 10% Me_2CO/CH_2Cl_2 as the solvent system ($R_f = 0.65$) to give 34 mg of **4** acetate as solid gum. The middle frs eluted with C_6H_{14}–EtOAc 75:25 (168 mg) were treated the same way as **4** to give 47 mg pure **5** acetate as a solid gum ($R_f = 0.56$). All **3**, **4** and **5** are quenching under UV light and gave a reddish-brown color after spraying with vanillin/H_2SO_4 spray reagent followed by heating for 5–10 s with a heat gun.

3.3. Compound *1*; lup-20(29)-en-3β-ol; lupeol

Needles, mp 202 °C, for the spectroscopic data see (Wenkert et al., 1978; Reynolds et al., 1986; Rasool et al., 1989; Hui and Li, 1976; Ahmad et al., 1985).

3.4. Compound *2*; 16,24-epoxy-3α-hydroxylanost-8-ene; argentatin E

Needles, mp 168–170 °C, $[\alpha]_D^{25}$, −45 (CH_2Cl_2; *c* 2.0). IR $\upsilon_{max}{}^{cm-1}$; 3410, 2960, 2890, 1640, 1460, 1370, 1010 and 900. UV λ_{max} nm; 229.0. EI–MS, 70 eV, *m*/*z* (rel. int.); 442 $[M]^+$ (1), 406 $[M–2H_2O]^+$ (30), 405 (82), 343 (24), 325 (20), 324 (38), 327 (100), 311 (10), 253 (12), 156 (24) and 28 (40). ^1H NMR (250 MHz, $CDCl_3$, δ ppm, *J* = Hz); 4.72 (1H, *m*, H-16), 3.53 (1H, *dd*, 1.5, 5.0, H-3), 4.29 (1H, *m*, H-24),1.15 (3H, *s*, H-29),1.14 (3H, *s*, H-30), 1.09 (3H, *d*, 7.5, H-27), 1.08 (3H, *s*, H-28), 1.07 (3H, *d*, 7.5, H-26), 0.96 (3H, *d*, 7.0, H-21) and 0.93 (6H, *s*, H-18 and H-19). ^{13}C NMR data for compounds **2**–**5** are listed in Table 1.

3.5. Compound *3*; 16,24-epoxy-25-hydroxycycloart-1,11,22-trien-3-one; argentatin F

Solid gum, $[\alpha]_D^{25}$, +3.5 (CH_2Cl_2; *c* 2.0). IR $\upsilon_{max}{}^{cm-1}$; 3430, 2970. 2930, 2840, 1680, 1645, 1470, 1360, 1230, 1100, and 990. UV λ_{max} nm; 268.0. CI–MS (CH_4), *m*/*z* (rel. int.); 433 $[M–H_2O+1]^+$ (1), 418 $[M–H_2O–CH_3+1]^+$ (3), 217 (15),189 (10), 149 (100), 131 (73) and 109 ((44). ^1H NMR (250 MHz, $CDCl_3$, δ ppm, *J* = Hz); 7.73 (1H, *d*, 11.5, H-2), 5.56 (1H, *br t*, H-23), 5.53 (1H, *br t*, H-22), 5.41 (1H, *d*, 10, H-11), 5.39 (1H, *d*, 10, H-12), 6.49 (1H, *d*, 11.5, H-1), 4.92 (1H, *d*, 5.5, H-24), 4.38 (1H, *m*, H-16), 1.26 (6H, *s*, H-26 and H-27), 1.17 (3H, *s*, H-29), 1.09 (3H, *s*, H-30), 1.04 (3H, *s*, H-28), 0.98 (3H, *d*, 7.0, H-21), 0.87 (3H, *s*, H-18), 0.81 (1H, *d*, 5.0, H-19) and 0.58 (1H, *d*, 5.0, H-19‘).

3.6. Compound *4*; 16,24-dihydroxycycloart-20,25-dien-3-one diacetate; argentatin G diacetate

A solid gum, $[\alpha]_D^{25}$, +25.6 (CH_2Cl_2; *c* 2.5). IR $\upsilon_{max}{}^{cm-1}$; 3045, 2950, 2845, 1720, 1695, 1640, 1460, 1370, 1240, 1110 and 890. UV λ_{max} nm; 232.0. CI–MS (CH_4), *m*/*z* (rel. int.); 419 $[M–2HOAc+1]^+$ (100), 311 (35), 217 (30), 215 (20), 203 (25), 201 (20), 219 (20), 109 (98), 107 (20) and 95 (23). ^1H NMR (250 MHz, $CDCl_3$, δ ppm, *J* = Hz); 5.33 (1H, *ddd*, 5.0, 4.5, 5.0, H-16), 5.12 (1H, *dd*, 5.5, 5.5, H-24), 5.01 (1H, *d*, 1.5, H-21), 4.93 (1H, *d*, 1.5, H-21′), 4.91 (1H, *d*, 1.5, H-26), 4.86 (1H, *d*, 1.5, H-26′), 2.03 (3H, *s*, H-16Ac), 1.97 (3H, *s*, H-24Ac), 1.71 (3H, *s*, H-27), 1.22 (3H, *s*, H-29), 1.07 (3H, *s*, H-30), 1.02 (3H, *s*, H-28), 0.95 (3H, *s*, H-18), 0.83 (1H, *d*, 4.5, H-19) and 0.57 (1H, *d*, 4.5, H-19′).

3.7. Compound *5*; 16,24-dihydroxycycloart-25-en-3-one diactate; argentatin H diacetate

A solid gum, $[\alpha]_D^{25}$, +18.2 (CH_2Cl_2; *c* 2.5). IR $\upsilon_{max}{}^{cm-1}$; 3040, 2930, 2825, 1720, 1690, 1630, 1470, 1360, 1240, 1120 and 890. UV λ_{max} nm; 231 CI–MS (CH_4), *m*/*z* (rel. int.); 541 $[M+1]^+$ (6), 481 $[M–HOAc+1]^+$ (12), 421 $[M–2HOAc+1]^+$ (100), 365 (5), 311 (8), 297 (4), 245 (2), 217 (6), 163 (2), and 109 (10). ^1H NMR (250 MHz, $CDCl_3$, δ ppm, *J* = Hz); 5.26 (1H, *ddd*, 5.0, 4.5, 5.0, H-16), 5.07 (1H, *dd*, 5.5, 5.5, H-24), 4.90 (1H, *d*, 1.0, H-26), 4.87 (1H, *d*, 1.0, H-26′), 2.05 (3H, *s*, H-16Ac), 2.04 (3H, *s*, H-24Ac), 1.71 (3H, *s*, H-27), 1.17 (3H, *s*, H-29), 1.09 (3H, *s*, H-30), 1.05 (3H, *s*, H-28), 0.94 (3H, *d*, 7.0, H-21), 0.91 (3H, *s*, H-18), 0.80 (1H, *d*, 4.5, H-19) and 0.60 (1H, *d*, 4.5, H-19′).

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