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(24*R*)- and (24*S*)-24-hydoxy-24-vinyllathosterols and other sterols from the aerial part of *Bryonia dioica*

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Abstract

The structures of four sterols isolated from the nonsaponifiable lipids of the aerial part extract of white bryony (*Bryonia dioica*) were established to be (24*R*)- and (24*S*)-24-hydroxy-24-vinyllathosterols, and (24*R*,24[1]*R*)- and (24*S*,24[1]*S*)-24(24[1])-epoxyisoavenasterols.

Keywords: *Bryonia dioica*; Cucurbitaceae; Aerial part; Sterol; 24-Hydroxy-24-vinyllathosterol; 24(24[1])-Epoxyisoavenasterol

1. Introduction

Bryonia dioica Jacq. (white bryony) is a climbing perennial herb with tuberous roots which occurs in temperate Europe, North Africa, and western Asia (The Staff of the L.H. Bailey Hortorium, Cornell University, 1986). The roots of *B. dioica* are characterized by the presence of cucurbitacins, oxygenated tetracyclic triterpenoids possessing a wide range of biological activities (Lavie & Glotter, 1971). We have recently reported the isolation and characterization of eight sterols and four triterpenoids from the roots (Akihisa, Kimura, Kokke, Itoh & Tamura, 1996a; Akihisa, Kimura, Kokke, Takase, Yasukawa & Tamura, 1996b), and a triterpenoid from its aerial portion (Akihisa, Kimura, Koike, Kokke, Nikaido & Tamura, 1998) of this plant. We now report the isolation from the aerial part and the structure elucidation of four sterols, (24*R*)- (**1a**) and (24*S*)-24-hydroxy-24-vinyllathosterols (**1b**), and (24*R*,24[1]*R*)-(**1c**) and (24*S*,24[1]*S*)-24(24[1])-epoxyisoavenasterols (**1d**), along with a known synthetic sterol, 24-oxolathosterol (**1e**).

2. Results and discussion

The nonsaponifiable lipids obtained from the chloroform extract of the dried aerial part of *B. dioica* were subjected to column chromatography which yielded a fraction containing several dihydroxy triterpenoids (Akihisa et al., 1998) and oxygenated sterols. Acetylation of the fraction followed by reversed phase HPLC of the acetate fraction yielded two mixtures of oxygenated steryl acetates, **2a**/**2b** and **2c**/**2d**, and a steryl acetate **2e**, in addition to the acetates of three dihydroxy triterpenoids reported recently (Akihisa et al., 1998). Compound **2e** and its hydrolysis product **1e** were identified as 24-oxo-5α-cholest-7-en-3β-yl acetate and 24-oxo-5α-cholest-7-en-3β-ol (24-oxolathosterol), respectively, by ^{1}H-NMR spectroscopic and MS comparison (see Table 1 for the ^{1}H-NMR data of **2e**) with the literature data (Sucrow & Radüchel, 1969).

The mixture of compounds **2a** and **2b** showed the

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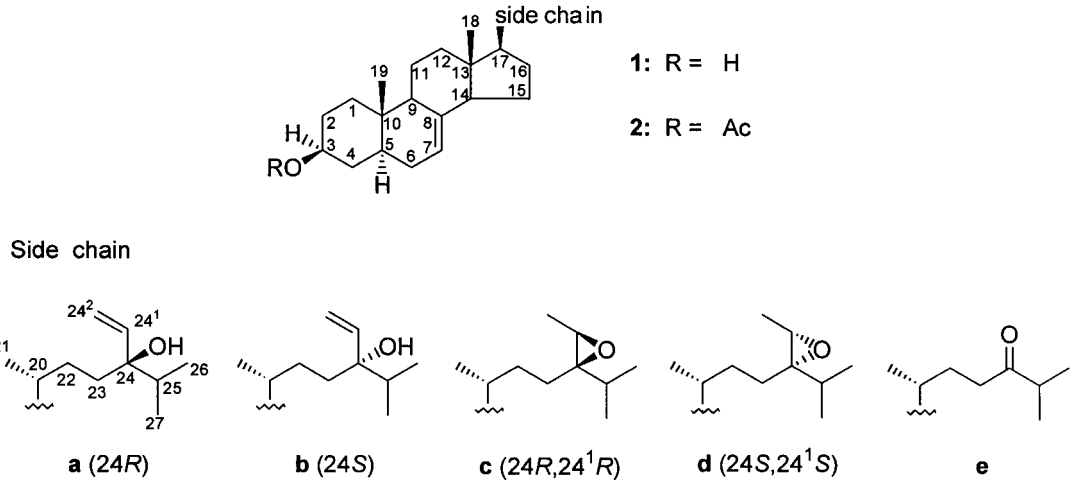
Table 1
^{1}H-NMR data (400 MHz, $CDCl_3$) of the sterols[a] isolated from the aerial part of *Bryonia dioica*[b]

H	**2a**[c]	**2b**[c]	**2c**	**2d**	**2e**
H-3	4.69 (*tt*)	4.69 (*tt*)	4.69 (*tt*)	4.69 (*tt*)	4.69 (*tt*)
	(4.6, 11.3)	(4.6, 11.3)	(4.7, 11.3)	(4.8, 11.3)	(4.4, 11.0)
H-7	5.15 (*m*)	5.15 (*m*)	5.16 (br *dd*)	5.16 (br *dd*)	5.15 (*m*)
			(2.0, 4.8)	(2.0, 5.0)	
H-18 (*s*)	0.53	0.53	0.54	0.54	0.53
H-19 (*s*)	0.81	0.81	0.81	0.81	0.81
H-21 (*d*)	0.93	0.93	0.95	0.94	0.92
	(6.6)	(6.7)	(6.6)	(6.6)	(6.3)
H-25	1.74 (m)	1.72 (m)	1.75 (m)	1.78 (m)	2.61 (*sept.*)
					(7.0)
H-26 (*d*)	0.87[d]	0.87[d]	0.91[d]	0.89[d]	1.09
	(7.0)	(7.0)	(6.8)	(6.8)	(6.9)
H-27 (*d*)	0.89[d]	0.90[d]	0.92[d]	0.92[d]	1.09
	(6.7)	(6.7)	(7.2)	(6.8)	(6.9)
H-24^1	5.81 (*dd*)	5.80 (*dd*)	2.90 (*q*)	2.90 (*q*)	
	(10.7, 17.1)	(11.0, 17.4)	(5.5)	(5.5)	
H-24^2	5.14 (*dd*)	5.13 (*dd*)	1.27 (*d*)	1.28 (*d*)	
	(1.5, 11.0)	(1.5, 11.0)	(5.8)	(5.8)	
	5.19 (*dd*)	5.18 (*dd*)			
	(1.5, 17.4)	(1.5, 17.4)			
3-OAc (*s*)	2.02	2.02	2.03	2.03	2.03

[a] Spectra were taken as the C-3 acetyl derivatives.
[b] Figures in parentheses denote *J* values (Hz).
[c] Determined at 500 MHz.
[d] Assignments in each column are interchangeable.

presence of acetoxyl (1269, 1715 cm^{-1}) and hydroxyl (3526 cm^{-1}) groups, terminal methylene (916, 1640, 3094 cm^{-1}) and a trisubstituted double bond (828, 840 cm^{-1}) in the IR spectrum, and $[M]^+$ at *m/z* 470.3783 ($C_{31}H_{50}O_3$) in the EI-MS accompanied with diagnostic fragment ions at *m/z* 392 $[M–HOAc–H_2O]^+$, 313 [M–side chain (s.c.; $C_{10}H_{19}O$)–2H]$^+$ and 255 [M–s.c.–HOAc]$^+$. The skeletal ^{1}H-NMR signals of the mixture **2a**/**2b** were in accord with the corresponding signals of Δ^7-sten-3β-yl acetate (Akihisa et al., 1996a; Goad & Akihisa, 1997) and **2e**, suggesting that it has a skeletal structure of Δ^7-sten-3β-yl acetate. The ^{1}H-NMR spectrum of **2a**/**2b** exhibited further the presence of a vinyl group attached to a tertiary carbon atom (ABX system: H_A δ 5.18–5.19, H_B δ 5.13–5.14, H_X δ 5.80–5.81; $J_{AX} \approx 11$ Hz, $J_{BX} \approx 17$ Hz) and three secondary methyl groups. These data, in combination with the mass fragments at *m/z* 427, formed by loss of an isopropyl group by cleavage of C-24–C-25, 409 (*m/z* 427-H_2O), and 356 $[M–C_7H_{14}O]^+$, formed by cleavage of C-22–C-23 with the concomitant 1H loss, suggested that **2a**/**2b** possesses a 24-hydroxy-24-vinyl side chain (Ikekawa, Tsuda & Morisaki, 1966; Catalan, Kokke, Duque & Djerassi, 1983). We concluded that **2a**/**2b** was 24-ethyl-5α-cholesta-7,24^1(24^2)-diene-3β,24-diyl 3-acetate (24-hydroxy-24-vinyllathosteryl acetate). Normal-phase HPLC enabled the separation of the mixture **2a**/**2b** into the slower eluted more-polar **2a** and faster eluted less-polar **2b**. The full consistency of the side chain ^{1}H signals of **2a** and **2b** (Table 1) with the corresponding signals of (24*R*)-saringosterol [(24*R*)-24-ethylcholesta-5,24^1(24^2)-diene-3β,24-diol] (Catalan et al., 1983) and (24*S*)-saringosterol (Catalan et al., 1983), respectively, allowed us to assign **2a** as (24*R*)-24-hydroxy24-vinyllathosteryl acetate and **2b** as its (24*S*)-epimer.

The molecular formula of the mixture **2c**/**2d** was determined as $C_{31}H_{50}O_3$ based on the EI-MS (*m/z* 470.3770 $[M]^+$). Its IR spectrum indicated acetoxyl (1249, 1733 cm^{-1}) and epoxy (805 cm^{-1}) groups, and a trisubstituted double bond (824, 840 cm^{-1}). The MS exhibited diagnostic fragments at *m/z* 395 [M–Me–HOAc]$^+$, 313 [M–s.c. ($C_{10}H_{19}O$)–2H]$^+$ and 255 [M–s.c.–2H]$^+$ indicating that the compound possessed a mono-unsaturated skeleton and an epoxylated C_{10} side chain. The skeletal ^{1}H signals of **2c**/**2d** were in accord with the corresponding signals of **2a**/**2b** and **2e**, whereas the ^{1}H signals of a methine (δ_H 2.90, *q*, *J* = 5.5 Hz; H-24^1) and a methyl (δ_H 1.27–1.28, *d*, *J* = 5.5 Hz; H-24^2) group attached to an oxygen bearing carbon (C-24^1) and associated with the side chain protons are consistent with those of 24-ethyl-24(24^1)-epoxy-cholest-5-en-3β-ol [24(24^1)-epoxyfucosterol] (Catalan et al., 1983) and its benzoate (Fujimoto, Murakami & Ikekawa, 1980). The combined evidence suggested that **2c**/**2d** was the C-24 epimeric mixture of 24-ethyl-24(24^1)-epoxy-5α-cholest-7-en-3β-yl acetate. Normal-phase HPLC of the mixture **2c**/**2d** enabled the separ-



ation into less-polar **2c** and more-polar **2d**. Compound **2c** exhibited the side chain ^{1}H signals (H-26, H-27, H-24^1 and H-24^2) (Table 1) consistent with those of (24*R*,24^1*R*)-24(24^1)-epoxyfucosterol (Catalan et al., 1983), and **2d** with those of (24*S*,24^1*S*)-24(24^1)-epoxyfucosterol (Catalan et al., 1983), which allowed us to assign **2c** as (24*R*,24^1*R*)-24-ethyl-24(24^1)-epoxy-5α-cholest-7-en-3β-yl acetate [(24*R*,24^1*R*)-24(24^1)-epoxyisoavenasteryl acetate] and **2d** as its (24*S*,24^1*S*)-epimer.

This is the first report of the isolation from a natural source of (24*R*)- (**1a**) and (24*S*)-24-hydroxy-24-vinyllathosterols (**1b**), (24*R*,24^1*R*)- (**1a**) and (24*S*,24^1*S*)-24(24^1)-epoxyisoavenasterols (**1b**), and 24-oxolathosterol (**1e**), all of which were isolated and characterized as their C-3 acetyl derivatives, although **1e** has previously been known as a synthetic sterol (Sucrow & Radüchel, 1969). The Δ^5-isomer of **1a**/**1b**, *viz*., saringosterol [(24ξ)-24-hydroxy-24-vinylcholest-5-en-3β-ol], has been reported to occur in some marine brown algae (Ikekawa et al., 1966; Knights, 1970; Ikekawa, Morisaki & Hirayama, 1972; Virtue & Nichols, 1994; Milkova, Talev, Christov, Dimitrova-Konaklieva & Popov, 1997), and this was shown to be a mixture of epimers at C-24 (Catalan et al., 1983). Saringosterol has been suggested as an artifact produced during the isolation procedure by oxidation of fucosterol {[24(24^1)*E*]-stigmasta-5,24(24^1)-dien-3β-ol}, which also was a component of the algae (Knights, 1970; Milkova et al., 1997). On the other hand, it has been demonstrated that oxidation of the sterols takes place under physiological conditions induced by linoleic acid hydroperoxides in photoautotrophic cell cultures of *Chenopodium rubrum* (Meyer & Spiteller, 1997). Whether the five oxygenated sterols, **1a**–**1e**, are formed artificially from isoavenasterol {[24(24^1)*E*]-5α-stigmasta-7,24(24^1)-dien-3β-ol}, a component sterol of *B. dioica* aerial parts (Akihisa et al., 1998) (see Section 3), during the isolation procedure, or whether they are natural products in the tissue (Meyer & Spiteller, 1997; Francisco, Cambaut, Teste, Tarchini & Djerassi, 1979) remains to be clarified.

The fully assigned ^{1}H- and ^{13}C-NMR spectral data for **2a**, **2b**, **2c** and **2d** are given in Section 3.

3. Experimental

3.1. General

Crystallizations were performed in Me_2CO–MeOH. Mp: uncorr. Reverse phase HPLC (HPLC I): Superiorex ODS S 5 μm column (25 cm × 10 mm i.d.; temp. 25°; Shiseido, Tokyo), MeOH as mobile phase (flow rate 4 ml min^{-1}); Normal-phase HPLC (HPLC II): Senshu Pak Silica-4251-N column (25 cm × 10 mm i.d.; temp. 25°; Senshu Scientific, Tokyo), *n*-hexane–EtOAc (97 : 3) as mobile phase (4 ml min^{-1}); GC: DB-17 fused-silica capillary column (30 m × 0.3 mm i.d.), column temperature 275°. RR_t on HPLC and GC expressed relative to cholesteryl (cholest-5-en-3β-yl) acetate. IR: KBr. EI-MS (70 eV): probe. NMR spectra were recorded at 400 or 500 MHz (^{1}H-NMR) and 100 or 125 MHz (^{13}C-NMR) in $CDCl_3$ with TMS for ^{1}H-NMR and the solvent peak (δ_C 77.0, $CDCl_3$) for ^{13}C-NMR as internal standard. Acetylation: Ac_2O-pyridine, at room temperature overnight. Hydrolysis of acetate: 5% KOH in MeOH, at room temperature overnight. Signal assignment of ^{1}H- and ^{13}C-NMR spectra was made by comparison with literature data of relevant compounds (Akihisa et al., 1996a; Goad & Akihisa, 1997), and using the results of the following NMR experiments: ^{13}C-DEPT, ^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY, HMBC, and NOESY spectroscopy. Source of the plant material was described in our previous paper (Akihisa et al., 1998).

3.2. Isolation procedure

Dried and ground aerial parts (450 g) of *B. dioica* (2.5 kg) were extracted at room temperature × 3 for 3 days each with $CHCl_3$. The nonsaponifiable lipids (14 g) obtained from the extract by alkaline hydrolysis were chromatographed on a silica gel column which yielded a fraction (140 mg; R_f 0.18 on TLC) containing dihydroxy triterpenoids (Akihisa et al., 1998) and oxygenated sterols, and a fraction (450 mg; R_f 0.28) containing other sterols. Acetylation of the former fraction afforded the acetate fraction which was subjected to HPLC I yielding three dihydroxy triterpenoids as the acetyl derivatives (Akihisa et al., 1998), and, in addition, two mixtures **2a**/**2b** and **2c**/**2d**, and **2e** (2.0 mg). Normal-phase HPLC of the mixtures **2a**/**2b** and **2c**/**2d** allowed the isolation of individual components: **2a** (2.9 mg), **2b** (2.4 mg), **2c** (1.9 mg) and **2d** (1.4 mg). The sterol fraction (R_f 0.28) was constituted with isoavenasterol (46% of the fraction) and (24ξ)-stigmast-7-en-3β-ol (39%) (Akihisa et al., 1998).

3.3. Mixture of (24*R*)-(**2a**) and (24*S*)-24-hydroxy-24-vinyllathosteryl acetates (**2b**)

RR_t 0.19 (HPLC I), 3.45 (GC). IR ν_{max} cm^{-1}: 3526, 3094, 1715, 1640, 1269, 916, 848, 828. EI-MS *m*/*z* (rel. int.): 470.3783 $[M]^+$ (3, $C_{31}H_{50}O_3$, requires 470.3757), 455.3487 (1, $C_{30}H_{47}O_3$), 452.3671 (5, $C_{31}H_{48}O_2$), 437.3437 (5, $C_{30}H_{45}O_2$), 427.3220 (22, $C_{28}H_{43}O_3$), 410.3362 (5, $C_{29}H_{46}O$), 409.3123 (8, $C_{28}H_{41}O_2$), 392.3447 (18, $C_{29}H_{44}$), 356.2722 (4, $C_{24}H_{36}O_2$), 313.2153 (56, $C_{21}H_{29}O_2$), 288.2086 (3, $C_{19}H_{28}O_2$), 273.1862 (4, $C_{18}H_{25}O_2$), 255.2100 (23, $C_{19}H_{27}$), 43.0172 (100, C_2H_3O).

3.4. (24*R*)-24-Hydroxy-24-vinyllathosteryl acetate (**2a**)

Mp 154–156°. $[\alpha]_D^{25}$ +16.9° ($CHCl_3$, *c* 0.30). RR_t 28.8 (HPLC II). ^{13}C- (125 MHz) and ^{1}H-NMR (500 MHz) ($CDCl_3$): C-1 [δ_C 36.9;δ_H 1.12 (α), 1.83 (*β*)], C-2 [27.5; 1.80 (α), 1.46 (*β*)], C-3 [73.5; 4.69 (*tt*, *J* = 4.6, 11.3 Hz)], C-4 [33.8; 1.72 (α), 1.34 (*β*)], C-5 [40.1; 1.41], C-6 [29.6; 1.73 (2H)], C-7 [117.4; 5.15], C-8 [139.5], C-9 [49.3; 1.65], C-10 [34.2], C-11 [21.5; 1.53 (α), 1.44 (*β*)], C-12 [39.5; 1.21 (α), 2.00 (*β*)], C-13 [43.4], C-14 [55.0; 1.78], C-15 [22.9; 1.52 (α), 1.38 (*β*)], C-16 [27.9; 1.87 (α), 1.23 (*β*)], C-17 [55.9; 1.22], C-18 [11.9; 0.53 (*s*)], C-19 [12.9; 0.81 (*s*)], C-20 [36.6; 1.33], C-21 [19.0; 0.93 (*d*, *J* = 6.6 Hz)], C-22 [29.0; 1.03, 1.40]; C-23 [34.9; 1.36, 1.62], C-24 [77.9], C-25 [35.9; 1.74], C-26 and C-27 [16.5 and 17.6; 0.87 (*d*, *J* = 7.0 Hz) and 0.89 (*d*, *J* = 6.7 Hz)], C-24^1 [142.5; 5.81, *dd*, *J* = 10.7, 17.1 Hz], C-24^2 [113.0; 5.14 (*dd*, *J* = 1.5, 11.0 Hz), 5.19 (*dd*, *J* = 1.5, 17.4 Hz)], 3-O<u>C</u>OMe [170.7], 3-OCO<u>Me</u> [21.5; 2.02 (*s*)].

3.5. (24*S*)-24-Hydroxy-24-vinyllathosteryl acetate (**2b**)

Mp 148–150°. $[\alpha]_D^{25}$ +3.8° ($CHCl_3$, *c* 0.24). RR_t 23.1 (HPLC II). ^{13}C- (125 MHz) and ^{1}H-NMR (500 MHz) ($CDCl_3$): C-1 [δ_C 36.9; δ_H 1.13 (α), 1.83 (*β*)], C-2 [27.5; 1.82 (α), 1.47 (*β*)], C-3 [73.5; 4.69 (*tt*, *J* = 4.6, 11.3 Hz)], C-4 [33.9; 1.74 (α), 1.37 (*β*)], C-5 [40.1; 1.41], C-6 [29.6; 1.76 (2H)], C-7 [117.4; 5.15], C-8 [139.5], C-9 [49.3; 1.65], C-10 [34.2], C-11 [21.5; 1.55 (α), 1.44 (*β*)], C-12 [39.5; 1.22 (α), 2.01 (*β*)], C-13 [43.4], C-14 [55.0; 1.80], C-15 [23.0; 1.52 (α), 1.38 (*β*)], C-16 [27.9; 1.89 (α), 1.28 (*β*)], C-17 [55.9; 1.23], C-18 [11.9; 0.53 (*s*)], C-19 [12.9; 0.81 (*s*)], C-20 [36.4; 1.38], C-21 [18.9; 0.93 (*d*, *J* = 6.7 Hz)], C-22 [29.1; 1.02, 1.43]; C-23 [34.7; 1.42, 1.58], C-24 [77.7], C-25 [36.2; 1.72], C-26 and C-27 [16.5 and 17.6; 0.87 (*d*, *J* = 7.0 Hz) and 0.90 (*d*, *J* = 6.7 Hz)], C-24^1 [142.6; 5.80, *dd*, *J* = 11.0, 17.4 Hz], C-24^2 [112.9; 5.13 (*dd*, *J* = 1.5, 11.0 Hz), 5.18 (*dd*, *J* = 1.5, 17.4 Hz)], 3-O<u>C</u>OMe [170.7], 3-OCO<u>Me</u> [21.5; 2.02 (*s*)].

3.6. Mixture of (24*R*,24^1*R*)-(**2c**) and (24*S*,24^1*S*)-24(24^1)-epoxyisoavenasteryl acetates (**2d**)

Mp 151–153°. RR_t 0.20 (HPLC I), 3.07 (GC). IR ν_{max} cm^{-1}: 1733, 1249, 840, 805. EI-MS *m*/*z* (rel. int.): 470.3770 $[M]^+$ (3, $C_{31}H_{50}O_3$, requires 470.3757), 455.3550 (1, $C_{30}H_{47}O_3$), 427.3390 (2, $C_{28}H_{43}O_3$), 410.3565 (2, $C_{29}H_{46}O$), 395.3351 (2, $C_{28}H_{43}O$), 356.2709 (6, $C_{24}H_{36}O_2$), 313.2143 (30, $C_{21}H_{29}O_2$), 288.2090 (2, $C_{19}H_{28}O_2$), 273.1837 (2, $C_{18}H_{25}O_2$), 255.2109 (10, $C_{19}H_{27}$), 43.0152 (100, C_2H_3O).

3.7. (24*R*,24^1*R*)-24(24^1)-epoxyisoavenasteryl acetate (**2c**)

RR_t 4.83 (HPLC II). ^{13}C- (100 MHz) and ^{1}H-NMR (400 MHz) ($CDCl_3$): C-1 [δ_C 36.8; δ_H 1.15 (α), 1.84 (*β*)], C-2 [27.5; 1.81 (α), 1.48 (*β*)], C-3 [73.5; 4.69 (*tt*, *J* = 4.7, 11.3 Hz)], C-4 [33.8; 1.75 (α), 1.37 (*β*)], C-5 [40.1; 1.45], C-6 [29.5; 1.77 (2H)], C-7 [117.4; 5.16 (br *dd*, *J* = 2.0, 4.8 Hz)], C-8 [139.4], C-9 [49.2; 1.67], C-10 [34.2], C-11 [21.5; 1.58 (α), 1.46 (*β*)], C-12 [39.5; 1.22 (α), 2.02 (*β*)], C-13 [43.3], C-14 [55.0; 1.82], C-15 [23.0; 1.54 (α), 1.40 (*β*)], C-16 [28.0; 1.94 (α), 1.25 (*β*)], C-17 [55.6; 1.26], C-18 [11.8; 0.54 (*s*)], C-19 [12.9; 0.81 (*s*)], C-20 [36.8; 1.38], C-21 [18.8; 0.95 (*d*, *J* = 6.6 Hz)], C-22 [31.6; 1.18, 1.45]; C-23 [25.3; 1.26, 1.75], C-24 [66.3], C-25 [32.5; 1.75], C-26 and C-27 [18.0 and 18.2; 0.91 (*d*, *J* = 6.8 Hz) and 0.92 (*d*, *J* = 7.2 Hz)], C-24^1 [57.0; 2.90, *q*, *J* = 5.5 Hz], C-24^2 [14.3; 1.27 (*d*, *J* = 5.8 Hz)], 3-O<u>C</u>OMe [170.7], 3-OCO<u>Me</u> [21.5; 2.03 (*s*)].

3.8. (24S,24^{1}S)-24(24^1)-epoxyisoavenasteryl acetate (**2d**)

RR_t 5.19 (HPLC II). ^{13}C (100 MHz) and ^{1}H-NMR (400 MHz) ($CDCl_3$): C-1 [δ_C 36.8; δ_H 1.15 (α), 1.84 (β)], C-2 [27.5; 1.81 (α), 1.48 (β)], C-3 [73.5; 4.69 (*tt*, J = 4.8, 11.3 Hz)], C-4 [33.8; 1.75 (α), 1.37 (β)], C-5 [40.1; 1.45], C-6 [29.5; 1.77 (2H)], C-7 [117.4; 5.16 (br *dd*, J = 2.0, 4.8 Hz)], C-8 [139.4], C-9 [49.2; 1.67], C-10 [34.2], C-11 [21.5; 1.58 (α), 1.46 (β)], C-12 [39.5; 1.22 (α), 2.02 (β)], C-13 [43.4], C-14 [55.0; 1.82], C-15 [23.0; 1.54 (α), 1.40 (β)], C-16 [28.0; 1.94 (α), 1.25 (β)], C-17 [55.8; 1.24], C-18 [11.8; 0.54 (*s*)], C-19 [12.9; 0.81 (*s*)], C-20 [36.7; 1.38], C-21 [18.8; 0.94 (*d*, J = 6.6 Hz)], C-22 [31.2; 1.14, 1.53]; C-23 [25.6; 1.42, 1.56], C-24 [66.2], C-25 [32.1; 1.78], C-26 and C-27 [17.8 and 18.4; 0.89 (*d*, J = 6.8 Hz) and 0.92 (*d*, J = 6.8 Hz)], C-24^1 [56.5; 2.90, *q*, J = 5.5 Hz], C-24^2 [14.3; 1.27 (*d*, J = 5.8 Hz)], 3-OCOMe [170.7], 3-OCOMe [21.5; 2.03 (*s*)].

3.9. 24-Oxolathosteryl acetate (**2e**) and 24-oxolathosterol (**1e**)

2e: RR_t 0.18 (HPLC I), 2.52 (GC). EI-MS m/z (rel. int.): 442.3424 $[M]^+$ (34, $C_{29}H_{46}O_3$, requires 442.3443), 427 (9), 382 (22), 367 (17), 356 (6), 341 (3), 313 (25), 288 (4), 273 (7), 255 (38), 228 (7), 213 (38), 43 (100). **1e**: EI-MS **m/z** (rel. int.): 400.3309 $[M]^+$ (67, $C_{27}H_{44}O_2$, requires 400.3338), 385 (22), 382 (4), 367 (10), 357 (2), 314 (18), 299 (6), 273 (16), 271 (30), 255 (40), 246 (9), 231 (18), 213 (28), 43 (100).

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