

Sterols from the Fungus *Catathelasma imperiale*

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Eight ergostane-type sterols and three their derivatives (one mono-linoleate and two mono-glucosides) were isolated from the ethyl acetate soluble fraction of the fungus *Catathelasma imperiale*. Two of them are novel compounds, namely 22*E*, 24*R*-ergosta-7, 22-diene-3 β , 5 α -diol-6 β -linoleate (**1**) and 22*E*, 24*R*-ergosta-7, 22-diene-3 β , 5 β , 6 α -triol (**5**) with an uncommon *cis*-fused A/B ring. Structures of these compounds were demonstrated on the basis of their chemical evidences and spectroscopic methods, especially 2D NMR techniques.

Keywords fungus, *Catathelasma imperiale*, sterol

Introduction

Polyhydroxyl ergostane-type sterols and their derivatives occurring in fungi, soft corals and sponges, possess a variety of biological activities.^{1,2} *Catathelasma imperiale* (Fr.) Singer is a fungus mainly distributed in the west of China, such as Yunnan, Sichuan and Gansu provinces.³ The chemical investigation of this fungus was not reported previously. In an effort to understand the chemical composition of this fungus, a series of polyhydroxyl ergostane-type sterols, their mono-glucosides and mono-linoleate (**1**—**11**) has been isolated from the whole body of this fungus in our laboratory. Compounds **1** and **5** were elucidated to be new chemical entities, especially the new sterol, 22*E*, 24*R*-ergosta-7, 22-diene-3 β , 5 β , 6 α -triol (**5**) with an atypical *cis*-fused A/B ring. We report herein the isolation and the structural determination of these two new compounds (**1** and **5**), along with nine known steroids (**2**—**4**, **6**—**11**).

Results and discussion

The ¹H NMR and ¹³C NMR spectra indicated that compounds **1**—**11** (Fig. 1) present an ergostane-type side-chain with 22*E*, 24*R*-configuration.⁴ The absolute configuration of C-24 in the side chain of the ergostane-type sterols could be readily determined by analysis of its ¹³C NMR data.⁵ An ¹H NMR method was also developed to distinguish C-24 epimers (24*R* or 24*S*) and to assign the

methyl groups in the side chain.⁶ Although both the 24 α - and 24 β -configurations occur naturally, fungi, in general, only metabolite sterols with 24 β -configuration (H-24 β) (24*S* if a saturated side-chain, 24*R* if a Δ^{22} unsaturated side-chain).⁵ This is consistent with the assignment of configuration at C-24 in the side-chain for compounds **1**—**11** by ¹H NMR and ¹³C NMR spectroscopy.

22*E*, 24*R*-Ergosta-7, 22-diene-3 β , 5 α -diol-6 β -linoleate (**1**), with the molecular formula C₄₆H₇₆O₄ as deduced from the EIMS spectrum (*m/z* 412 corresponding to C₂₈H₄₄O₂[M - C₁₈H₃₂O₂]⁺) and chemical degradation, was obtained as colorless oil. Analysis of its ¹H NMR and ¹³C NMR spectra (Table 1), and also comparison with the literature⁴ inferred that **1** was a derivative of 22*E*, 24*R*-ergosta-7, 22-diene-3 β , 5 α , 6 β -triol (cervisterol). The only difference was that **1** linked with an unsaturated fatty acid moiety to form a cervisterol ester, which then underwent a hydrolysis (Scheme 1) to give compounds **1a** and **2**. The ¹H NMR and EIMS spectra of **1a** and **2** were consistent with those of linolic acid⁷ and cervisterol,^{2a,8} respectively, and the results were also confirmed by authentic samples on TLC. In the ¹H NMR spectrum, comparing with that of cervisterol, the proton signal of H-6 α (br. d, δ 4.79, *J* = 5.2 Hz) of **1** severely down field shifted by $\Delta\delta$ 1.17 caused by acylation effect, indicating that the linoleate moiety was located at 6 β position of cervisterol. The structure of **1** was thus determined to be 22*E*, 24*R*-ergosta-7, 22-diene-3 β , 5 α -diol-6 β -linoleate.

22*E*, 24*R*-Ergosta-7, 22-diene-3 β , 5 β , 6 α -triol (**5**) exhibited the molecular formula C₂₈H₄₆O₃ as determined by HR-EIMS at *m/z* 430.3449 [M]⁺ (calcd 430.3447). Its ¹H NMR spectra showed the presence of two tertiary methyls, four secondary methyls, two oxygenated methines and three olefinic protons. Its ¹³C NMR (Table 1) with DEPT spectra showed twenty-eight carbon signals, including six methyls, seven secondary carbons, eleven tertiary carbons and four quaternary carbons. The above-mentioned facts inferred that compound **5** was also an ergostane-type sterol. The EIMS showed typical fragmentation patterns of ergostane-type sterol at *m/z* 287 [M - H₂O

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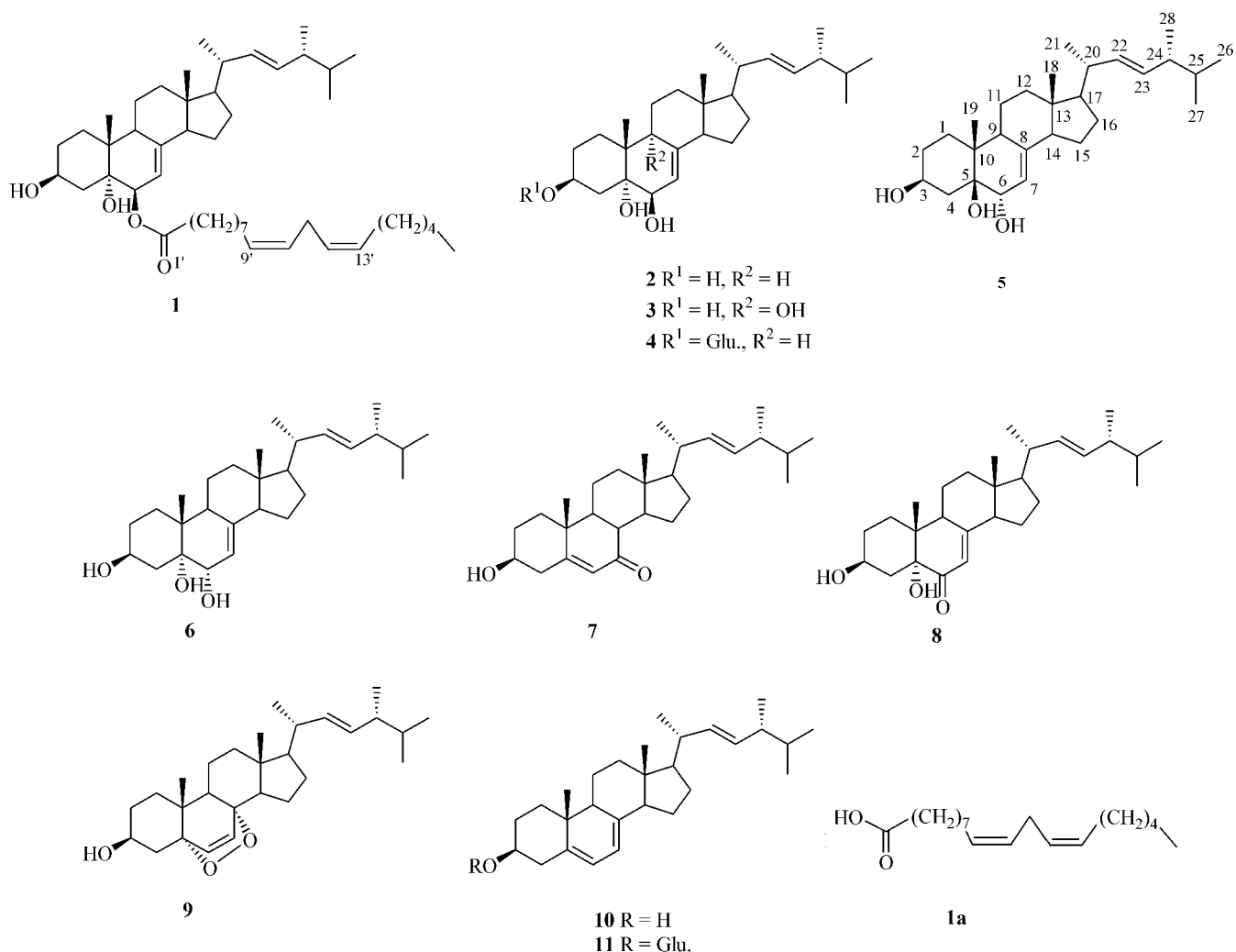


Fig. 1 Structures of compounds 1—11.

$-C_9H_{17}]^+$, m/z 314 $[M - H_2O - C_7H_{14}]^+$ and m/z 369 $[M - C_3H_7]^+$, clearly indicating the presence of a Δ^{22} double bond.^{1e,9} The coupling constant between the olefinic protons H-22 and H-23 ($J = 15.3$ Hz) definitely indicated the Δ^{22} double bond with *E* geometry. The C-24 was assigned to be 24*R*-configuration like other ergostane type sterols obtained from fungi. The HMQC and 1H - 1H COSY spectra were recorded (Fig. 2) to assign the protons to the corresponding carbons by 1H - ^{13}C correlations and to acquire the molecular fragments by 1H - 1H correlations, respectively. The carbon signals at δ 121.46 and δ 139.99 were assigned for the presence of a Δ^7 double bond. The relative high-field shifted methyl proton signal at δ 0.61 (s, H₃-18) also supported the presence of a Δ^7 double bond.^{2c,6,10} The proton signal of H-6 at δ 4.15 (br. s) indicated the C-6 bearing a hydroxyl. The proton signal of H-6 shifted to more down field was caused by the deshielding effect of Δ^7 double bond. Comparing the ^{13}C NMR data of compounds **5** and **6**, the carbon signals assigned for the C and D-rings in the both were very similar, suggesting that the oxygenated quaternary carbon signal at δ 77.43 was only assignable to the C-5 bearing a

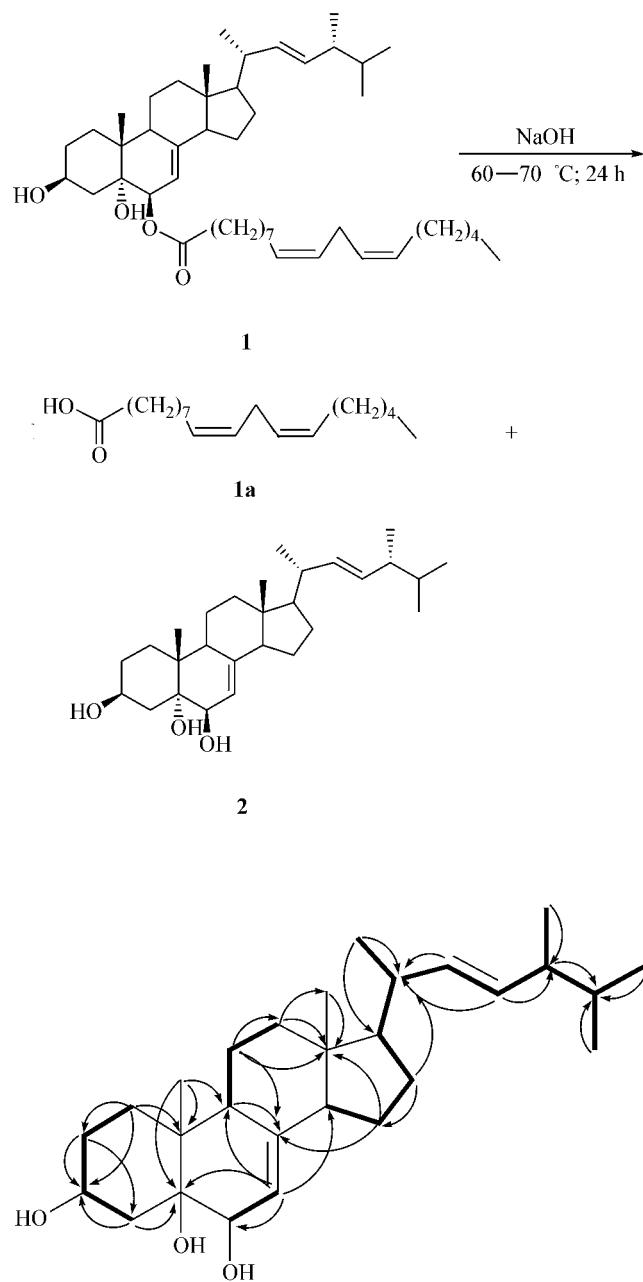
hydroxyl. The presence of 5-OH was supported by the broad singlet signal of H-6 at δ 4.15 in the 1H NMR spectrum.^{1g} The remaining oxygenated tertiary carbon signal at δ 67.38 was tentatively assigned to the C-3 bearing a 3 β -hydroxyl on the basis of a common biogenetic rule, like most of the natural sterols. The planar structure of **5** was thus outlined and confirmed by 1H - 1H COSY and HMBC. In the 1H - 1H COSY (Fig. 2), the correlations between the proton pairs of H-17/H₂-16, H₂-16/H₂-15, H₂-15/H-14, H₂-12/H₂-11, H₂-11/H-9, H-7/H-6, H₂-4/H-3, H-3/H₂-2 and H₂-2/H₂-1 were observed. In the HMBC spectrum (Fig. 2), the "loose ends" resulting from the insertion of quaternary carbons into the fragments established by 1H - 1H COSY and HMQC, could be fully connected. The olefinic proton signal of H-7 showing HMBC correlations with C-14, C-9 and C-6 further confirmed the presence of Δ^7 and 6-OH. The occurrence of C-5 hydroxyl was also confirmed by HMBC judging from the cross-peaks of H₃-19/C-5, H-7/C-5 and H₂-4/C-5. The singlet signal of the olefinic proton at δ 5.04 (H-7, br. s, $W_{1/2} \approx 7$ Hz) indicated that the H-6 took β -configuration. If the H-6 were in α -configuration, the coupling

Table 1 ^{13}C NMR Data (DEPT) of compounds **1**, **5** and **8**

Carbon No.	1 ^a	5 ^a	8 ^b
1	32.64	25.80	31.67
2	31.66	28.90	31.20
3	66.50	67.38	66.99
4	39.82	30.57	39.14
5	74.31	77.43	77.31
6	73.56	71.89	200.00
7	114.72	121.46	120.61
8	145.34	139.99	163.96
9	43.30	41.65	44.26
10	37.40	40.83	41.20
11	21.93	23.17	22.09
12	39.56	40.26	37.72
13	43.72	44.49	44.58
14	54.97	55.55	55.79
15	23.04	23.34	22.75
16	28.15	28.71	28.23
17	56.13	56.68	56.00
18	12.16	12.50	12.70
19	18.06	18.59	16.38
20	40.76	41.24	40.62
21	21.03	21.54	21.30
22	135.96	136.59	135.77
23	132.21	132.75	132.36
24	43.15	43.71	43.05
25	33.15	33.83	33.30
26	19.78	20.32	20.14
27	19.44	19.96	19.83
28	17.8	18.06	17.82
1'	172.90		
2'	34.59		
3'	25.66		
4', 5', 6', 7', 15'	29.16–31.11		
8', 14'	27.23		
9', 13'	130.14		
10', 12'	128.22		
11'	25.29		
16'	32.06		
17'	22.66		
18'	13.82		

^a Measured in acetone-*d*₆. ^b Measured in pyridine-*d*₅.

constant between the H-6 α and the olefinic proton H-7 would be around 5 Hz.^{1g, 2a, 10} The aforementioned evidence inferred that the planar structure of **5** is identical with that of **6**,¹¹ and the only difference likely results from the presence of a 5 β -OH in **5**, which allows the occurrence of an uncommon *cis*-fused A/B ring. In a *cis*-fused A/B ring sterol (Fig. 3), the broad singlet at δ 4.15 assignable for the H-3 ($W_{1/2} \approx 7$ Hz) indicated that the H-3 took an equatorial orientation, and 3-OH was

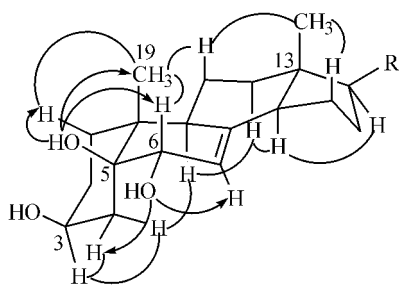
Scheme 1

— Correlations in the ^1H - ^1H COSY spectrum of **5**
 → Selected correlations in the HMBC spectrum of **5**

Fig. 2 ^1H - ^1H COSY and selected HMBC correlations of **5**.

definitely assigned as β -configuration.

The relative stereochemistry and conformation of **5** were finally determined by an outstanding performance of NOESY spectrum (Fig. 3), in which the presence of an uncommon *cis*-fused A/B ring, 3 β -OH, 5 β -OH and 6 α -OH were also confirmed. The ^1H NMR spectrum of **5** measured in pyridine-*d*₅ showed significant pyridine-induced deshielding effects^{4b, 12} (Fig. 3) on the signals of H-1 β , H-6 α and CH₃-19 (down-field shifted by *ca.* $\Delta\delta$ 0.46, 0.64 and 0.33, respectively) compared with those



— Key NOE correlations in the NOESY spectrum of **5**
 → Pyridine-induced deshielding effects of **5**

Fig. 3 Selected NOESY correlations and pyridine-induced deshielding effects of **5**.

of **5** acquired in acetone- d_6 caused by the presence of 5β -OH. The signals of H-4 β and H-7 were respectively down-field shifted by *ca.* $\Delta\delta$ 0.75 and 0.50 resulting from the occurrence of 6α -OH. Therefore, compound **5** was unambiguously elucidated as *22E, 24R*-ergosta-7, 22-diene-3 β , 5 β , 6 α -triol, with an uncommon *cis*-fused A/B ring.

Compounds **2**, **3**, **9**, **10** and **11** were respectively identified to be cerevisterol,⁴ *22E, 24R*-ergosta-7, 22-diene-3 β , 5 α , 6 β , 9 α -tetraol,^{12a} ergosterol peroxide,¹³ ergosterol^{11a, 14} and 3 β -*O*-glucopyranosylergosta-5, 7, 22-triene¹⁴ on the basis of the ¹H NMR, ¹³C NMR and authentic samples. Compounds **4**, **6**, **7** and **8** were respectively identified to be 3 β -*O*-glucopyranosyl-5 α , 6 β -dihydroxyergosta-7, 22-diene,¹⁴ *22E, 24R*-3 β , 5 α , 6 α -trihydroxyergosta-7, 22-diene,^{11b, 15} *22E, 24R*-3 β -hydroxyergosta-5, 22-diene-7-one^{1e} and *22E, 24R*-3 β , 5 α -dihydroxyergosta-7, 22-diene-6-one^{1b} on the basis of ¹H NMR and ¹³C NMR data. The ¹³C NMR data of **8** were assigned for the first time (see Table 1).

Experimental

General experiment procedures

Optical rotations were determined on a Perkin-Elmer 341 polarimeter. IR spectra were recorded on a Perkin-Elmer 577 spectrometer. NMR spectra were measured on a Bruker AM-400 spectrometer with TMS as internal standard. EIMS (70 eV) was carried out on a Finnigan MAT 95 mass spectrometer. All solvents used were of analytical grade (Shanghai Chemical Plant). Silica gel (200—300 mesh) was used for column chromatography, and pre-coated silica gel GF254 plates (Qingdao Haiyang Chemical Plant) were used for TLC. C18 reverse-phased silica gel (150—200 mesh, Merck) was also used for column chromatography.

Plant material

Catathelasma imperiale (Fr.) Singer was collected from Kunming area in Yunnan province of China and au-

thenticated by Prof. Zang Mu of Kunming Institute of Botany, where a voucher specimen with an access number HKAS 30226 was deposited.

Extraction and isolation

Fresh mushroom bodies (8 kg) were extracted with 95% ethanol to obtain 94 g of crude extract, which was partitioned with ethyl acetate (4 × 200 mL) to give ethyl acetate soluble fraction E (25.4 g) and water-soluble fraction W (68.8 g). The E fraction was separated over a silica gel column to afford fractions 1—12. Fraction 7 (3.99 g) was recrystallized from aqueous methanol (90%) to give 1.5 g of ergosterol (**10**). Fraction 8 (2.27 g) was purified on silica gel and C18 reverse-phased silica gel columns to yield **9** (10 mg). Fraction 9 (2.49 g) was extensively separated on silica gel and C18 reverse-phased silica gel columns to yield compounds **1** (50 mg), **5** (5 mg), **7** (20 mg) and **8** (10 mg). Fraction 11 (1.62 g) gave compounds **2** (32 mg), **3** (40 mg), **6** (10 mg) and **11** (10 mg) by extensive column chromatography on silica gel and C18 reverse-phased silica gel columns. Fraction 12 (1.06 g) was separated on silica gel column to afford compound **4** (20 mg).

22E, 24R-Ergosta-7, 22-diene-3 β , 5 α -diol-6 β -linoleate (**1**)

Colorless oil, $[\alpha]_D^{20}$ -37.6 (*c*, 0.91, acetone); ¹H NMR (acetone- d_6) δ : 5.29—5.36 (m, H-9', 10', 12', 13'), 5.23 (dd, *J* = 15.1, 6.8 Hz, H-23), 5.19 (dd, *J* = 15.1, 8.3 Hz, H-22), 5.17 (dd, *J* = 5.2, 2.7 Hz, H-7), 4.79 (br. d, *J* = 5.2 Hz, H-6), 3.94—3.99 (m, H-3), 2.76 (t, *J* = 6.8 Hz, H₂-11'), 2.24 (t, *J* = 7.3 Hz, H₂-2'), 1.26—2.14 (overlapped m, 40H), 1.04 (s, H₃-19), 1.02 (d, *J* = 6.8 Hz, H₃-21), 0.90 (d, *J* = 6.8 Hz, H₃-28), 0.86 (t, *J* = 6.8 Hz, H₃-18'), 0.82 (d, *J* = 6.8 Hz, H₃-27), 0.81 (d, *J* = 6.8 Hz, H₃-26), 0.60 (s, H₃-18); ¹³C NMR see Table 1; IR (film) ν_{\max} : 3412, 2928, 2870, 1732, 1458, 1383, 1252, 1175, 1026, 943, 723 cm^{-1} ; EIMS (70 eV) *m/z* (%): 412 (18), 394 (52), 376 (55), 361 (19), 337 (4), 291 (2), 280 (21), 269 (15), 252 (22), 251 (100), 227 (14), 209 (22), 197 (25), 181 (12), 157 (16), 125 (15), 109 (22), 95 (36), 81 (53), 69 (63), 55 (57).

Hydrolysis of *22E, 24R*-ergosta-7, 22-diene-3 β , 5 α -diol-6 β -linoleate (**1**)

10 mg of **1** (0.014 mmol) was hydrolyzed with sodium hydroxide (6.0 mol/L), and the reaction mixture was stirred for 24 h at 60—70 °C. After work-up, the products were purified by chromatography on silica gel column to yield **1a** (3.1 mg) and **3** (6.0 mg). **1a** was obtained as colorless oil. ¹H NMR (acetone- d_6) δ : 5.30—5.41 (m, H-9', 10', 12', 13'), 2.80 (t, *J* = 6.2 Hz, H₂-11'), 2.22 (t, *J* = 7.5 Hz, H₂-2'), 2.07—2.09 (m,

H₂-8', 14'), 1.55—1.59 (m, H₂-3'), 1.27—1.40 (m, H₂-4', 5', 6', 7', 15', 16', 17'), 0.88 (t, J = 7.0 Hz, H₃-18'); EIMS *m/z* (%): 280 (16), 263 (2.5), 248 (6), 203 (3), 189 (3), 186 (3), 150 (7), 149 (13.5), 135 (8), 123 (12), 110 (20), 109 (27), 95 (60), 81 (84), 67 (100), 55 (58).

22E 24R-Ergosta-7 22-diene-3β 5β 6α-triol (5)

Amorphous powder, [α]_D²⁰ + 26.2 (c, 0.61, pyridine); ¹H NMR (acetone-*d*₆) δ: 5.28 (dd, J = 15.3, 7.5 Hz, H-23), 5.22 (dd, J = 15.3, 7.2 Hz, H-22), 5.04 (br. s, W_{1/2} ≈ 7 Hz, H-7), 4.15 (br. s, H-6), 4.15 (br. s, H-3), 2.21—2.28 (m, H-9), 2.03—2.07 (m, H-20), 2.02—2.06 (m, H-12β), 1.93—1.98 (m, H-4β), 1.86—1.92 (m, H-14), 1.84—1.88 (m, H-16), 1.84—1.87 (m, H-1β), 1.80—1.84 (m, H-24), 1.7—1.93 (m, H-2), 1.60—1.72 (m, H-16), 1.47—1.63 (m, H₂-11, 15), 1.42—1.47 (m, H-25), 1.40—1.45 (m, H-4α), 1.34—1.36 (m, H-12α), 1.28—1.38 (m, H-17), 1.30—1.35 (m, H-2), 1.24—1.28 (m, H-1α), 1.05 (d, J = 6.6 Hz, H₃-21), 0.94 (d, J = 6.7 Hz, H₃-28), 0.91 (s, H₃-19), 0.86 (d, J = 6.8 Hz, H₃-27), 0.84 (d, J = 6.7 Hz, H₃-26), 0.61 (s, H₃-18); ¹H NMR (pyridine-*d*₅) δ: 5.54 (br. s, W_{1/2} ≈ 7 Hz, H-7), 5.18—5.31 (m, H-22, 23), 4.79 (br. s, W_{1/2} ≈ 7 Hz, H-6), 4.50 (br. s, W_{1/2} ≈ 7 Hz, H-3), 2.71 (br. d, J = 14.5 Hz, H-4β), 2.31 (dd, J = 15.2, 4.7 Hz, H-1β), 1.24 (s, H₃-19), 1.09 (d, J = 6.6 Hz, H₃-21), 0.97 (d, J = 6.8 Hz, H₃-28), 0.87 (d, J = 6.6 Hz, H₃-27), 0.87 (d, J = 6.6 Hz, H₃-26), 0.64 (s, H₃-18); ¹³C NMR see Table 1; IR (KBr) ν_{max}: 3400, 2956, 1720, 1672, 1595, 1458, 1371, 1165, 1105, 1061, 1005, 868 cm⁻¹; EIMS (70 eV) *m/z* (%): 430 (48), 414 (14), 413 (27), 412 (93), 395 (12), 394 (37), 383 (11), 379 (19), 377 (14), 376 (38), 369 (9), 358 (11), 355 (14), 314 (14), 287 (18), 269 (24), 252 (12), 251 (62), 209 (13), 197 (22), 195 (12), 175 (15), 159 (19), 157 (19), 155 (17), 147 (16), 145 (22), 139 (41), 133 (22), 125 (20), 121 (16), 119 (17), 109 (22), 95 (32), 81 (50), 69 (100), 55 (64). HREIMS (70 eV) *m/z*: 430.3449 [M]⁺ (calcd for C₂₈H₄₆O₃ 430.3447).

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