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WITHAPERUVINS F AND G, TWO WITHANOLIDES OF *PHYSALIS PERUVIANA* ROOTS

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Key Word Index *Physalis peruviana*; Solanaceae; withaperuvins F and G; steroidal lactones.

Abstract Withaperuvins F and G, the minor constituents of the roots of *Physalis peruviana*, have been formulated respectively, as (3*R*,6*S*,17*S*,20*S*,22*R*)-4β,5β,17β,20α_f-tetrahydroxy-3α,6α-oxido-1-oxoergosta-14,24-dien-22,26-olide and (17*S*,20*S*,22*R*)-2β,3β:5β,6β-diepoxy-14α,17β,20α_f-trihydroxy-1-oxoergosta-24-en-22,26-olide.

INTRODUCTION

Withanolide, a term originally coined [1] to designate the steroidal lactones of *Withania somnifera*, embraces all naturally occurring C_{28}-steroidal lactones that may be chemically named as ergosta-22,26-olides or more commonly as 1-oxoergosta-2-en-22,26-olides because a great majority of this group of compounds have a steroidal Δ^2-1-one system. Withanolides occur only in the Solanaceae and their distribution is mainly restricted to the leaves [2]. The roots of *Physalis peruviana* are, however, quite rich in withanolides and the isolation and structural determination of several new withanolides from this source were reported previously [3-6]. The present communication describes the isolation of two minor withanolides, withaperuvins F and G from the roots of *P. peruviana* and advancement of their structures as (3*R*,6*S*,17*S*,20*S*,22*R*)-4β,5β,17β,20α_f-tetrahydroxy-3α,6α-oxido-1-oxoergosta-14,24-dien-22,26-olide (**1a**) and (17*S*,20*S*,22*R*)-2β,3β:5β,6β-diepoxy-14α,17β,20α_f-trihydroxy-1-oxoergosta-24-en-22,26-olide (**4**), respectively.

RESULTS AND DISCUSSION

Withaperuvin F (**1a**), $C_{28}H_{38}O_8$ was recognized to be a 17,20-dihydroxywithanolide, like its congeners [3-5], from its mass spectral peaks [7, 8] at *m/z* 125 (*a*), 152 (*b*) and 169 (*c*) and from the diagnostic ^{1}H NMR signal at δ4.66 as a double doublet [2] due to the carbinyl hydrogen at C-22. Unlike typical withanolides, withaperuvin F was found to be devoid of a Δ^2-1-one system and its IR absorption bands at 1690 and 1700 cm^{-1} were assigned, respectively, to α,β-unsaturated δ-lactone and cyclohexanone carbonyl groups. The ^{1}H NMR spectrum of withaperuvin F showed in addition to 3H singlets at δ1.16, 1.26 and 1.28, respectively, for 18-, 19- and 21-methyl groups, two vinylic methyl singlets at δ1.88 and 1.96 for 27- and 28-methyl groups. The lone olefinic hydrogen signal at δ5.20 (1H, broad) discernible in the spectrum and its band width are reminescent of the C-15 hydrogen signal of withaperuvin B (**2**) [4] and of physalolactone C [9]. The spectrum also showed signals for three carbinyl hydrogens at δ4.20, 4.33 and 4.44 in addition to one at δ4.66 for C-22-H. Of these three signals the one at δ4.44 was proved to be due to a secondary alcoholic group as it underwent a shift to δ5.29 in the spectrum of its monoacetate (**1b**), $C_{30}H_{40}O_9$ (M$^+$, 544), mp 132-133°, prepared by acetylation of withaperuvin F with acetic anhydride and pyridine. The remaining two carbinyl hydrogen signals at δ4.20 and 4.33, which remained unaffected on acetylation, were considered to be due to methine hydrogens bearing an oxide bridge. The geminally coupled hydrogen signals at δ2.43 (1H, *dd*, J = 18.2 and 3 Hz) and 2.60 (1H, *dd*, J = 18.2 and 1.6 Hz), observed in the ^{1}H NMR spectrum of **1b**, were assigned to a ketomethylene group, the presence of which was also corroborated from a positive Zimmermann test [10]. From irradiation experiments, this ketomethylene group in **1b** was proved to be a part of a $CO\,CH_2CHOCHOAcC$- system as is present in withaperuvin D acetate (**3b**). The irradiation at signal frequency for the methine multiplet at δ4.48 (δ4.33 in **1a**) transformed the doublet due to a hydrogen bound to the carbon bearing the acetoxy function at δ5.29 to a sharp singlet and the ketomethylene double doublets to clean geminally coupled doublets (J = 18 Hz) indicating it to be a carbinyl hydrogen flanked by the ketomethylene and the carbon bearing the acetoxy function. Based on this observation and from a ^{13}C NMR spectral comparison (Table 1) with withaperuvin B (**2**) and withaperuvin D (**3a**) [11], structure **1a** was advanced for withaperuvin F.

Rigorous evidence in favour of the proposed structure and stereochemistry of withaperuvin F came from its transformation to withaperuvin B (**2**) by prolonged heating with acetic acid. The identity of the enone, derived from withaperuvin F, with the naturally occurring withaperuvin B was disclosed from a comparison of their melting points, R_f values, IR and ^{1}H NMR spectra. Withaperuvin F is the second known withanolide bearing the novel 3,6-oxide bridge and the first for which the chemical evidence is provided.

Withaperuvin G (**4**), $C_{28}H_{38}O_8$ (M$^+$, 502), crystallized from chloroform as needles, mp 163° and showed IR bands for hydroxyl (3350 cm^{-1}), cyclohexanone (1700 cm^{-1}), and α,β-unsaturated δ-lactone (1690 cm^{-1}) groupings. The presence of an unsaturated δ-lactone

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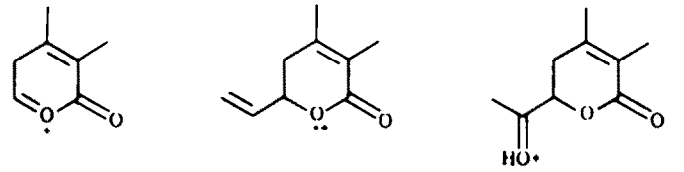
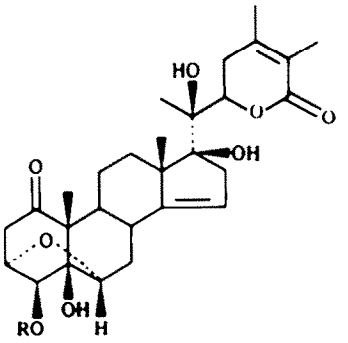


m/z 125 m/z 152 m/z 169

a b c



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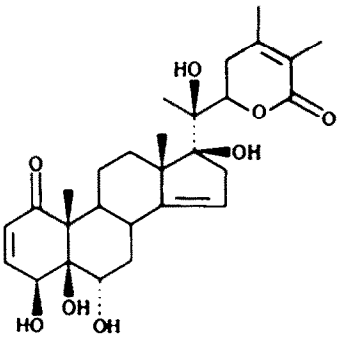

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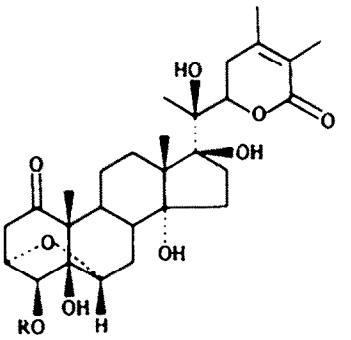

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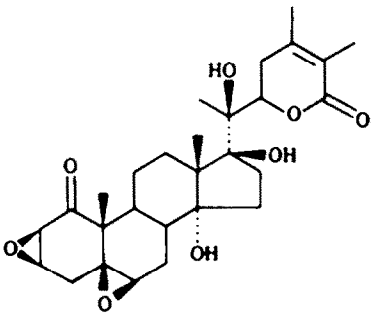
3b R = Ac



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chromophore was also corroborated from its UV absorption maximum at 236 nm (ε 7400). The mass spectral peaks at *m/z* 125, 152 and 169 and ^{1}H NMR signals at δ1.02, 1.10, 1.41, 1.86, 1.93 (3H, *s* each) and a one-proton triplet [12] at δ4.85 ($J \approx 8$ Hz) suggested it to be a 17,20-dihydroxywithanolide. The absence of the 2-en-1-one system in withaperuvin G became manifest from an examination of its ^{1}H NMR spectrum which did not show any olefinic hydrogen signal. Withaperuvin G is not acylable and, therefore, the presence of three carbinyl hydrogen signals at δ3.14 (*br*, $W_{1/2} \approx 4.5$ Hz), 3.48 (*d*, $J \approx 4.5$ Hz), and 3.60 (overlapped *dd*, $J = 4.5$ and 3.9 Hz) in its ^{1}H NMR spectrum suggested the probable presence of a disubstituted and trisubstituted ethylene oxide system in the molecule. The presence of two epoxides in withaperuvin G is also consistent with the observation that the molecule having eight oxygen atoms showed two carbonyl carbons and eight oxycarbons in its ^{13}C NMR spectrum (Table 1). A comparison of ^{1}H and ^{13}C NMR parameters of the carbinyl hydrogens and oxycarbons of withaperuvin G with those of withanolides of known structure and stereochemistry strongly suggested that the former is a 2β,3β- and 5β,6β-diepoxide like viscosalactone A (**5**) [12]. Accumulated evidence permitted advancement of the structure of withaperuvin G as **4** which may be regarded as 2β,3β-epoxide of withanolide E. In order to verify the correctness of this assumption, an attempt was made to prepare withaperuvin G (**4**) by epoxidation of withanolide E (**6a**) [13] using a methanolic solution of alkaline hydrogen peroxide as has been reported by Pelletier *et al.* [12] but the product was a mixture in our case, presumably due to Michael addition of methanol. The reaction was, however, smooth and complete within 5 min and gave a near-quantitative yield of withaperuvin G when epoxidation of withanolide E was performed in DMF medium.

Table 1. Carbon-13 shieldings in withaperuvin F (**1a**), withaperuvin G (**4**) and related withanolides

	(**1a**) ($CDCl_3$ + CD_3OD)	(**2**) (C_5D_5N)	(**3a**) (CD_3OD)	(**4**) (CD_3OD)	(**5**) ($CDCl_3$)
C-1	211.2 *s*	201.1	214.0	209.7	206.9
C-2	43.7 *t*	127.2	42.3	55.6	54.9
C-3	76.8 *d*	146.9	77.6	56.2	55.8
C-4	73.3 *d*	67.8	74.5	35.4	74.6
C-5	80.2 *s*	79.7	79.8	64.2	64.0
C-6	74.2 *d*	74.4	77.3	61.9	59.6
C-7	29.8 *t*	37.0	26.4	27.2	29.6
C-8	30.3 *d*	33.6	35.8	33.4	31.0
C-9	29.8 *d*	48.3	34.9	35.7	42.7
C-10	55.0 *s*	56.9	55.8	51.6	48.6
C-11	22.0 *t*	24.1	21.6	21.7	20.0
C-12	41.6 *t*	42.9	35.4	34.7	27.3
C-13	55.7 *s*	55.5	55.6	54.7	42.7
C-14	151.2 *s*	150.7	83.9	82.8	56.1
C-15	115.3 *d*	114.8	31.1	30.8	24.3
C-16	35.5 *t*	35.7	37.4	37.5	40.7
C-17	87.3 *s*	86.9	88.7	88.7	51.9
C-18	17.3 *q*	17.6	20.6	20.6	11.5
C-19	15.1 *q*	10.5	15.3	12.3	14.5
C-20	77.4 *s*	77.9	78.3	79.9	38.9
C-21	20.3 *q*	22.2	19.4	19.5	13.3
C-22	80.6 *d*	80.8	83.0	83.7	78.7
C-23	33.0 *t*	34.5	32.8	33.2	29.8
C-24	152.6 *s*	151.9	154.2	153.3	153.8
C-25	121.5 *s*	121.6	121.7	121.7	125.8
C-26	166.6 *s*	166.5	165.7	169.0	167.4
C-27	12.2 *q*	12.6	12.3	12.3	57.2
C-28	20.6 *q*	20.6	20.8	20.7	20.1

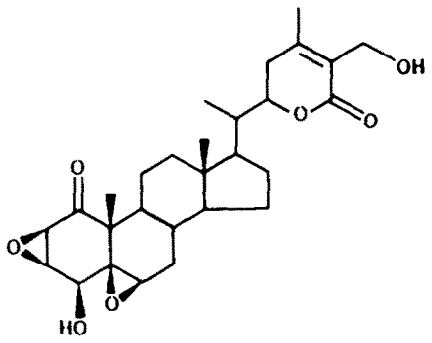
The orientation of the 2,3-epoxy function in semi-synthetic withaperuvin G was manifest from the observation that a nucleophile attacks the β-carbon of an enone system preferentially from the β-side in an analogous molecule. Thus when 4β-hydroxy withanolide E (**6b**) was treated with methanolic alkali at room temperature for a short while, it gave a methanol adduct (**7**), the ^{1}H NMR spectrum of which showed a one-proton multiplet at δ3.67 ($W/2 \approx 15$ Hz) due to the newly generated carbinyl hydrogen at C-3. The ^{1}H NMR parameters of this signal, which were found to be in perfect agreement with those reported for the C-3 hydrogen of physalactone (**8**) [15], indicated it to be an equatorial hydrogen in a A/B *cis*-fused ring system [16]. The methoxyl group at C-3 in this adduct was thus proved to be β. This observation, taken together with the fact that epoxidation of an enone with alkaline hydrogen peroxide proceeds through a mechanism analogous to the Michael addition reaction, clearly showed that the orientation of the 2,3-epoxide ring in **4** should be like the methoxy group in **7**. Withaperuvin G is the second natural withanolide with a 2,3-epoxy system.

EXPERIMENTAL

Isolation procedure. Roots of *Physalis peruviana* L. were collected near Varanasi (India) during the summer of 1979. Extraction of plant material was carried out as described elsewhere [3]. Repeated chromatography (silica gel) of EtOAc eluates of the Et_2O-soluble portion furnished a fraction which was found to be a mixture of two components on a TLC plate. Prep. TLC of this fraction on silica gel G plates yielded withaperuvin F (yield, 0.001 %) and withaperuvin G (0.0005 %).

Withaperuvin F (**1a**). Crystallized from $CHCl_3$ as needles, $C_{28}H_{38}O_8$ (M^+ 502), mp 174–175°, $[\alpha]_D$ +39.70° (*c* 0.26, $CHCl_3$); R_f 0.52 in hexane–EtOAc (1:4); UV λ_{max}^{MeOH}: 228 nm (ε 7078); IR $\nu_{max}^{CHCl_3}$: 3450, 1710, 1700 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ1.16 (3H, *s*, 18-CH_3), 1.26 (3H, *s*, 19-CH_3), 1.28 (3H, *s*, 21-CH_3), 1.88 (3H, *s*, 27-CH_3), 1.96 (3H, *s*, 28-CH_3), 2.32 (1H, *br d*, *J* = 16 Hz, 16-H), 2.91 (1H, *br d*, *J* = 16 Hz, 16-H), 2.49 (1H, *br*, 2-H), 2.62 (1H, *br*, 2-H), 4.20 (1H, *br*, 6-H), 4.33 (1H, *m*, 3-H), 4.44 (1H, *d*, *J* = 6.6 Hz, 4-H), 4.66 (1H, *dd*, *J* = 12 and 5 Hz, 22-H), 5.20 (1H, *br*, 15-H); MS *m/z* (rel. int. %): 502 (M^+, 2), 359 (15), 223 (16), 186 (12), 169 (80), 152 (100), 149 (85), 125 (80), 109 (76). Found: C, 66.50; H, 7.25%. Calc. for $C_{28}H_{38}O_8$: C, 66.93; H, 7.57%.

Withaperuvin F acetate (**1b**) was obtained (Ac_2O, py) as needles from EtOAc, mp 132–133°, $[\alpha]_D$ +40.2° (*c* 0.4 $CHCl_3$); IR $\nu_{max}^{CHCl_3}$: 3350, 1735, 1720, 1700 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ1.16 (3H, *s*, 18-CH_3), 1.25 (3H, *s*, 19-CH_3), 1.29 (3H, *s*, 21-CH_3), 1.88 (3H, *s*, 27-CH_3), 1.96 (3H, *s*, 28-CH_3), 2.10 (3H, *s*, OAc), 2.29 (1H, *br d*, *J* = 16.7 Hz, 16-H), 2.91 (1H, *br d*, *J* = 16.7 Hz, 16-H), 2.34 (1H, *dd*, *J* = 18.2 and 3 Hz, 2-H), 2.60 (1H, *dd*, *J* = 18.2 and 1.6 Hz, 2-H), 4.31 (1H, *dd*, *J* = 8.2 and 1.2 Hz, 6-H), 4.48 (1H, *m*, 3-H), 5.29 (1H, *d*, *J* = 6 Hz, 4-H), 4.65 (1H, *dd*, *J* = 10.6 and 6.1 Hz, 22-H), 5.19 (1H, *br s*, 15-H); ^{13}C NMR ($CDCl_3$ + CD_3OD): [C_1–C_{28}] 209.1 (*s*), 44.2 (*t*), 76.3 (*d*), 75.6 (*d*),



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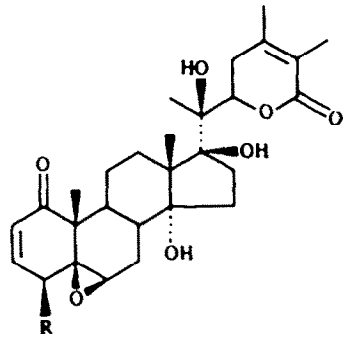

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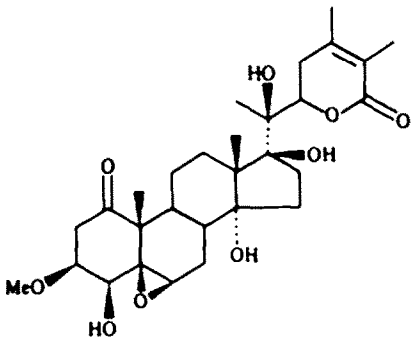
6b R = OH



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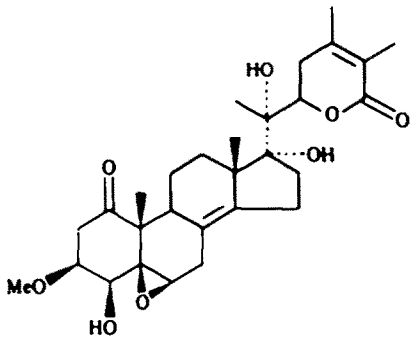

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78.5 (*s*), 71.2 (*d*), 29.8 (*t*), 30.2 (*d*), 29.8 (*d*), 54.9 (*s*), 22.3 (*t*), 41.7 (*t*), 56.1 (*s*), 150.6 (*s*), 115.1 (*d*), 35.4 (*t*), 87.2 (*s*), 17.4 (*q*), 15.3 (*q*), 77.0 (*s*), 20.5 (*q*), 80.3 (*d*), 33.0 (*t*), 152.2 (*s*), 121.6 (*s*), 165.8 (*s*), 12.4 (*q*), 20.5 (*q*), 172.6 (*s*, $-\underline{C}OCH_3$), 20.5 (*q*, $-CO\underline{C}H_3$). Found: C, 65.92; H, 7.29%. Calc. for $C_{30}H_{40}O_9$: C, 66.18; H, 7.35%.

Conversion of withaperuvin F (**1a**) *to withaperuvin B* (**2**). A solution of withaperuvin F (0.02 g) in HOAc (1 ml) was heated on a water bath for 72 hr. The solvent from the reaction mixture was removed *in vacuo* and the residue was subjected to prep. TLC. The lower band of the chromatogram, developed in C_6H_6–EtOAc (1:4), was scraped off, eluted with EtOAc and crystallized from MeOH to yield colourless plates, mp 268–270° R_f 0.57 (C_6H_6–EtOAc–MeOH, 2:6:1); indistinguishable from withaperuvin B (mp, co-TLC, IR); IR (KBr): 3450, 1700, 1665 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.13 (3H, *s*, 21-CH_3), 1.25 (3H, *s*, 18-CH_3), 1.28 (3H, *s*, 19-CH_3), 1.88 (3H, *s*, 27-CH_3), 1.94 (3H, *s*, 28-CH_3), 2.28 (1H, *br d*, J = 16 Hz, 16-H), 2.99 (1H, *br d*, J = 16 Hz, 16-H), 4.15 (1H, *dd*, J = 12 and 4 Hz, 22-H), 4.61 (1H, *t*, J = 8 Hz, 6-H), 5.10 (1H, *br s*, 4-H), 5.27 (1H, *br s*, 15-H), 5.96 (1H, *d*, J = 10 Hz, 2-H), 6.49 (1H, *d*, J = 10 Hz, 3-H).

Withaperuvin G (**4**). From $CHCl_3$ as needles, mp 163°; R_f 0.48 (hexane–EtOAc, 1:4); UV λ_{max}^{EtOH}: 236 nm (ε 7400); IR ν_{max}^{Nujol}: 3350, 1700, 1690 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.02 (3H, *s*, 18-CH_3), 1.10 (3H, *s*, 21-CH_3), 1.41 (3H, *s*, 19-CH_3), 1.86 (3H, *s*, 27-CH_3), 1.93 (3H, *s*, 28-CH_3), 3.14 (1H, *br s*, $W/2 \approx 4.5$ Hz, 6-H), 3.48 (1H, *d*, J = 4.5 Hz, 2-H), 3.60 (1H, overlapped *dd*, J = 4.5 and 3.9 Hz, 3-H), 4.85 (1H, *t*, J = 8 Hz, 22-H); MS *m/z* (rel. int.%): 502 (M^+, 3), 359 (38), 315 (25), 301 (28), 223 (38), 213 (67), 169 (90), 152 (100), 125 (90), 109 (90), 105 (80), 91 (94). Found: C, 66.75; H, 7.51%. Calc. for $C_{28}H_{38}O_8$: C, 66.93; H, 7.57%.

Epoxidation of withanolide E (**6a**). To a solution of withanolide E (0.05 g) in $HCONMe_2$ (2 ml) was added H_2O_2 (30%, 2 ml) and a pinch of KOH (*ca* 0.01 g) and the reaction mixture was kept at room temperature for 5 min. Dilution of the reaction mixture with water (10 ml), extraction with Et_2O (3 × 100 ml), chromatography of the ether extract over silica gel and elution with C_6H_6 EtOAc (2:3) yielded a solid (0.05 g) which crystallized from $CHCl_3$ as fine needles, mp 161–163°; IR ν_{max}^{Nujol}: 3350, 1700, 1690 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.02 (3H, *s*, 18-CH_3), 1.10 (3H, *s*, 21-CH_3), 1.42 (3H, *s*, 19-CH_3), 1.87 (3H, *s*, 27-CH_3), 1.93 (3H, *s*, 28-CH_3), 3.14 (1H, *br s*, $W/2 \approx 4.5$ Hz, 6-H), 3.48 (1H, *d*, J = 4.5 Hz, 2-H), 3.59 (1H, overlapped *dd*, J = 4.5 and 4 Hz, 3-H), 4.85 (1H, *t*, J = 8 Hz, 22-H). The compound was indistinguishable from withaperuvin G (mmp, co-TLC, IR).

Formation of methanol adduct (**7**) *from 4β-hydroxywithanolide E* (**6b**). To a solution of 4β-hydroxywithanolide E (0.1 g) in MeOH (10 ml) was added 1 N methanolic KOH (1 ml) and the reaction mixture was left at room temp. for 1 hr. The reaction mixture was then neutralized with cold dilute HCl and freed from solvent under reduced pressure to furnish a residue which was taken in water and extracted with $CHCl_3$. The $CHCl_3$ extract was washed, dried and crystallized from MeOH to yield **7**, mp 185°; ^1H NMR (270 MHz, $CDCl_3$): δ 1.02 (3H, *s*, 18-CH_3), 1.29 (3H, *s*, 19-CH_3), 1.42 (3H, *s*, 21-CH_3), 1.87 (3H, *s*, 27-CH_3), 1.93 (3H, *s*, 28-CH_3), 2.70 (1H, *dd*, J = 15 and 4.5 Hz, 2-H), 2.87 (1H, *dd*, J = 15 and 7 Hz, 2-H), 3.29 (1H, *br s*, $W/2 \approx 5$ Hz, 6-H), 3.33 (3H,

s, $-OCH_3$), 3.48 (1H, *br s*, $W/2 \approx 6.5$ Hz, 4-H), 3.67 (1H, *m*, $W/2 \approx 15$ Hz, 3-H), 4.85 (1H, *dd*, $J = 9$ and 7 Hz, 22-H). Found: C, 64.88; H, 7.78%. Calc. for $C_{29}H_{42}O_9$: C, 65.17; H, 7.86%.

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