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STEREOSTRUCTURES AND MOLECULAR CONFORMATIONS OF SIX DITERPENE LACTONES FROM *GELONIUM MULTIFLORUM*†‡

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Key Word Index—*Gelonium multiflorum*; Euphorbiaceae, diterpene lactones; gelomulides A–F; molecular conformations; multiflorenol, jolkinolide B.

Abstract—The stereostructures and molecular conformations of six novel diterpene lactones, gelomulides A–F, isolated from the leaves of *Gelonium multiflorum* were established on the basis of NMR, mass spectral and chemical evidence

INTRODUCTION

The bark of *Gelonium multiflorum* A. Juss was reported to yield a number of pentacyclic triterpenoids [2, 3]. The present work on the leaves shows it to be a rich source of diterpenes and we report the isolation, stereostructures and molecular conformations of six novel diterpene lactones, trivially named gelomulides A–F, in order of increasing polarity.

RESULTS AND DISCUSSION

The dried leaves of *Gelonium multiflorum* were extracted with petrol and the lipid extract separated by silica gel chromatography into nine homogeneous crystalline constituents. Common spectral features possessed by gelomulide A (**1**), gelomulide B (**2**), gelomulide C (**3**), gelomulide D (**4**), gelomulide E (**5**) and gelomulide F (**6**) are characteristic IR bands and UV absorptions for an α,β-unsaturated γ-lactone moiety and the following ^{1}H NMR signals (Table 1): a one proton singlet in the region δ3.67–3.86 attributable to an epoxy proton at C-14 and a vinyl methyl linked to C-15 in the region δ1.91–2.04.

A literature survey showed that only jolkinolide A (**8**) and jolkinolide B (**7**) reported from *Euphorbia jolkini* [4] and caudicifolin (**9**) (possessing a vinyl hydroxymethyl) isolated from *E caudicifolia* [5] possess the above-mentioned spectral features. In fact, one of the remaining three constituents isolated, was identified as jolkinolide B (**7**) from its physical and spectral characteristics, the other two being multiflorenol and sitosterol. Jolkinolide A was shown to have stereostructure **8** by X-ray crystallography [6]. The absolute configuration of caudicifolin (**9**) was displayed [7] as the mirror image of **9**, although the ORTEP drawing derived from the X-ray crystallographic analysis [7] seems to correspond to **9** itself. The absolute configuration was, however, undefined [7]

Gelomulide A (**1**) contained an axial β-acetoxy group at C-3 (**1a**) since the acetate methine proton appeared at δ4.7 as a multiplet ($W_{1/2} \sim 8$ Hz) involving J_{ee} and J_{ea}. Further, the vinyl 15-Me, showing homoallylic coupling with H-12, appeared at δ1.97 as a doublet ($J = 2.0$ Hz). In gelomulide B (**2**) the homoallylic splitting of 15-Me and the H-12 signal were absent Additionally, another epoxy proton appeared at δ 4.0 (*d*, $J = 1.5$ Hz) assignable to H-11 (β-), placing the second α-epoxy at C-11/C-12 since the C-12 oxygen bond in ring D must be equatorial and β- (as evident from the Dreiding model). The acetoxy group in **2** is located at C-3 as in **1**, based on ^{13}C NMR data (*ca* +3 ppm shift of 4-carbon compared to that of **7**) and on the mass peaks originating through AcOH elimination, followed by collapse of ring B, as shown in Scheme 1 to form the ion with *m/z* 135 (base peak) or by RDA collapse of ring A and H loss to form the ion with *m/z* 81 [CH_2=CH–CH=C(Me)CH_2^+]. A plausible pathway for the genesis of the base peak, *m/z* 150 is also shown. The acetoxy methine proton (δ4.7, *m*, $W_{1/2} \sim 8$ Hz) is equatorial, and hence 3-acetoxy in **2** also is β- and axial.

Gelomulide C (**3**), D (**4**), E (**5**) and F (**6**) showed homoallylic coupling of 15-Me with H-12 which in each case appeared as a well-resolved *ddd* in the region δ4.8–4.99 (Table 1). They all contain an additional CO group at C-3 which in the cases of **4** and **5** constitutes a part of an α,β-unsaturated CO moiety, as evident from the appearance of two *cis*-coupled olefinic protons. In the mass spectrum of **4** the fragment ions having ring A or rings A/B intact possesses *m/z* values with 2 mass units less compared to those for the saturated ketone **3** showing that gelomulide C (**3**) is presumably 1,2-dihydrogelomulide D. Gelomulide F (**6**) is shown to be 1-acetoxygelomulide C since its mass fragmentation pattern after the elimination of acetic acid became identical with that of gelomulide D (**4**). Gelomulide E (**5**) is shown to have the 6β-acetoxygelomulide D structure. The acetoxy methine proton appeared at δ5.14 (*m*, $W_{1/2} \sim 28$ Hz) and its $W_{1/2}$ was slimmed around 11.6 Hz when H-5 (δ2.04, *d*, J = 11.6 Hz) was saturated. Moreover, the ^{1}H NMR spectra of both **3** and **6** showed the presence of ketomethylene

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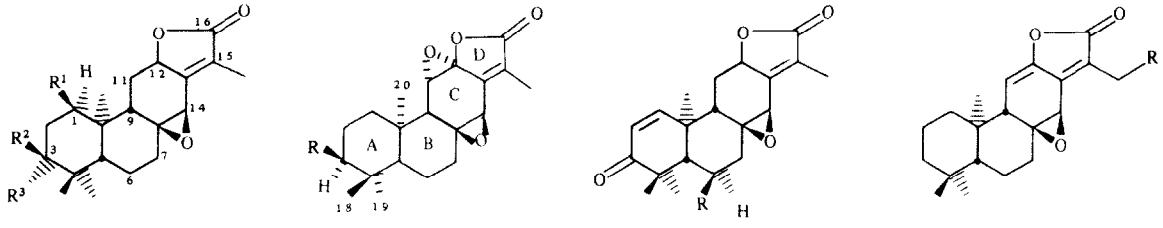
Table 1 ^{1}H NMR signals (δ, $CDCl_3$), of compounds **1**–**7** (coupling constants in Hz)

Compound*	H-9	H-11β (H-11α)	H-12	H-14	15-Me	Other important signals
1	2.05,	2.29, *dd*,	4.99, *ddd*	3.72,	1.97,	3-OAc 2.07, s, H-3, 4.7, *m*, $W_{1/2}$ ~ 8,
300 MHz	*d*, 6.7	13.4, 5.6	12.9, 5.3, 2.1	s	*d*, 2.0	3 Me's 0.92, 0.98, 1.10 (3H s each)
2	2.35,	(4.0, *d*,		3.67,	2.04,	3-OAc 2.07, s, H-3, 4.7, *m*, $W_{1/2}$ ~ 8,
100 MHz	*br s*	15)		s	s	3 Me's 0.83 (3H, s), 0.89 (6H, s)
3	2.58,	2.41, *dd*,	4.83, *ddd*,	3.70,	1.91,	H-2β 2.79, *m*, $W_{1/2}$ ~ 24, H-2α 2.14,
300 MHz	*d*, 7.3	14.2, 5.8	12.9, 5.6, 2.0	s	*d*, 2.0	*m*, $W_{1/2}$ ~ 28, 3 Me's 0.93, 1.07, 1.34 (3H s each)
4	2.66,	2.73,† *dd*,	4.86, *ddd*,	3.73,	1.98,	H-1 6.44, *d*, 10.38, H-2 5.82, *d*
270 MHz	*d*, 7.3	14.0, 5.5	13, 5.5, 2.0	s	*d*, 1.83	10.73, 3 Me's 1.14, 1.16, 1.36 (3H s each)
5	2.69,	2.62,† *dd*,	4.81, *ddd*,	3.86,	1.98,	H-1 6.33, *d*, 10.37, H-2 5.84, *d*,
270 MHz	*d*, 7.3	14.3, 5.8	13, 5.5, 1.8	s	*d*, 1.83	10.37, 6-OAc 2.12, s, H-6 5.14, *m*, $W_{1/2}$ ~ 28, H-5 2.04,† *d*, 11.6, 3 Me's 1.19, 1.32, 1.39 (3H s each)
6	2.69,	2.50, *dd*,	4.84, *ddd*,	3.73,	1.95,	H-2β 3.17, *dd*, 13.5, 2.9, H-2α
300 MHz	*d*, 7.2	14.0, 5.8	13, 5.4, 2.1	s	*d*, 1.9	2.39, *dd*, 13.5, 3.8, 1-OAc 2.04, s, H-1 5.03, *m*, $W_{1/2}$ ~ 8, 3 Me's 0.98, 1.22, 1.41 (3H s each)
7‡	2.29,	(4.04,	—	3.68,	2.08,	3 Me's 0.83, 0.85, 0.94 (3H s each)
270 MHz	*br s*	*br s*)		s	s	

* For numbering see structure **1**

† Data obtained by decoupling experiment

‡ The values are consistent with jolkinolide B



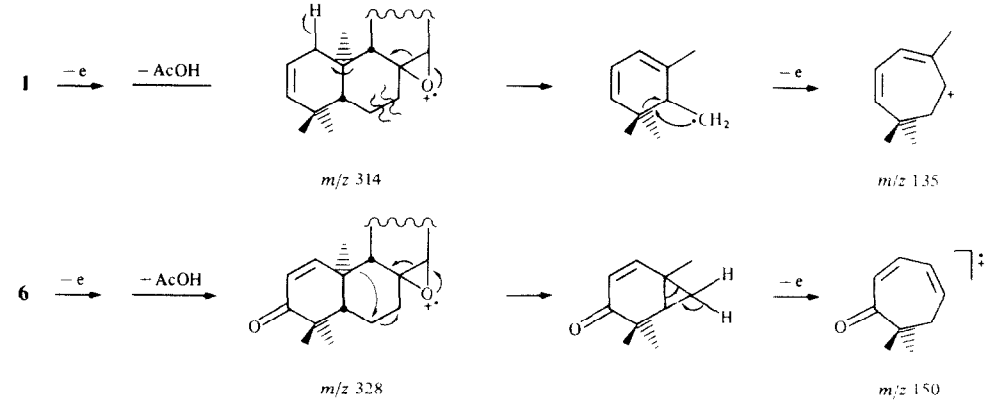
1 R^1 = R^3 = H R^2 = OAc
3 R^1 = H R^2 R^3 = O
6 R^1 = OAc R^2, R^3 = O

2 R = OAc
7 R = H

4 R = H
5 R = OAc

8 R = H
9 R = OH

Scheme 1



protons. In **6** H-2 (β,*e*) showed the signal at δ3.17 (*dd*, *J* = 13.5, 2 9 Hz) and H-2 (α, a) at δ2.39 (*dd*, *J* = 13 5, 3.8 Hz), the smaller *J*-values of each indicating equatorial orientation of H-1. Again, H-1 appeared at δ5.03 (*m*, $W_{1/2} \sim 8$ thus reaffirming its α- and equatorial orientation and hence the β-axial orientation of 1-acetoxy group.

Gelomulide C (**3**) and gelomulide D (**4**) underwent Lewis acid catalysed rearrangement upon treatment with boron trifluoride-etherate to give the corresponding 14-ketones, **10** and **11**, respectively The ^{13}C NMR spectral data [8] (Table 2), as well as mass fragmentation patterns, are consistent with the structures of gelomulides A–F The ^{13}C NMR assignments of only one such diterpene lactone, caudicifolin [5] (**9**) was reported [7] recently.

The high resolution ^{1}H NMR spectral data of the gelomulides were used to deduce their stereostructures and molecular conformations **1a–6a** The coupling constants and multiplicities of H-12, H_2-11 and H-9 determined the stereochemistry of H-12 and H-9, hence the conformations of the gelomulides because of the steric dependence of the *J*-values in a more or less rigid system; *e.g.* in gelomulide F (**6**) H-12 appeared as a *ddd* (*J* = 13, 5.4, 2.1 Hz), while H-11 showed a *dd* (*J* = 14.0, 5.8 Hz) and H-9 showed a doublet (*J* = 7.2 Hz). These coupling constants necessitate the following approximate dihedral angles: H-12α, H-11β 180°; H-12α, H-11α 40°; H-9β, H-11α 80°; H-9β, H-11β 38°; in conformity with the assigned chiralities and molecular conformation **6a**. By the same token conformations of other gelomulides and that of jolkinoide B (**7a**) can be deduced Compounds **8** and **9** possess similar conformation as **7a** Ring A becomes a flattened half-chair to accommodate the α,β-unsaturated ketone moiety in **4** and **5** while it assumes a chair form when saturated as in **1**, **2**, **3**, and **6** having a chair–chair–half chair conformation with *trans–anti–cis* configuration of the perhydrophenanthrene skeleton. The (*R*)-configuration at C-12 could also be predicted by Dreiding model studies which revealed that the γ-lactone ring in **1** and **3–6** can only be constructed with the C-12 oxygen bond β- and equatorial with respect to ring C, making H-12 α- and axial. Like **2**, in jolkinolide **B** the second epoxide at C-11/C-12 is α-oriented and in **2** and **7** the C ring obviously becomes more flattened and planar.

The biogenesis of these novel diterpene lactones may involve the following pathway. The geranylgeranyl pyrophosphate undergoes appropriate folding and all *trans* cyclization to form an *ent*-A/B system, followed by further cyclization, being triggered by the expulsion of the pyrophosphate group to form an 8,14-ene (**12**) carrying a vinyl group at C-13. The latter through terminal epoxidation, methyl group migration to C-15, H-15 elimination forms the vinylogous allyl alcohol **13** which undergoes oxidation to the acid, allylic oxidation at C-12 β- and epoxidation at the $\Delta^{8(14)}$-double bond from the less hindered β-face (the exact sequence being unpredictable) and lactonization to form the diterpene lactones **1** or **3–6** with H-12 α- and axial. Enzymatic dehydrogenation at C-12 and C-11 followed by epoxidation at the α-face, keeping the lactone ring at the less strained and only possible β-face, would give rise to the diepoxylactone **2** or **7**

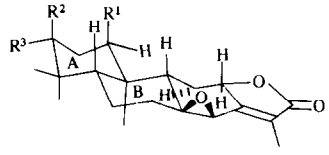
EXPERIMENTAL

General Mps: uncorr The UV spectra were taken in EtOH and IR spectra as KBr pellets Petrol refers to the 60–80° fraction, the silica gel (60–120 mesh) was used for chromatography, and crystallizing solvent was $CHCl_3$–petrol (60–80°) in each case, unless otherwise stated. The TLC experiments were done using microscopic slides with silica gel G layers to monitor the fractions and similar fractions were combined.

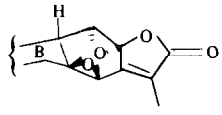
Extraction Air-dried and milled leaves of *Gelonium multiflorum* (1.1 kg) were extracted in a Soxhlet apparatus with petrol and $CHCl_3$ successively for 40 hr each The marc left was then extracted with MeOH at room temp for 21 days The residue (82 6 g), left upon concn of the petrol extract, was chromatographed using solvents and solvent mixtures of increasing polarity as eluents.

Multiflorenol. The gummy concentrate of the petrol eluates of the main chromatogram on rechromatography furnished multiflorenol (yield 0.06%), crystallizing as colourless flakes, mp 192°, $[\alpha]_D$ −8 7° ($CHCl_3$, *c* 1.012) The IR, ^{1}H NMR and mass spectral data were found to be similar to those for multiflorenol [2].

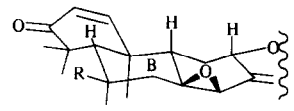
Sitosterol The petrol–EtOAc (19 · 1) eluates afforded sitosterol (0 002%), mp and mmp with an authentic sample 137°, $[\alpha]_D$ −38° ($CHCl_3$; *c* 0 42)



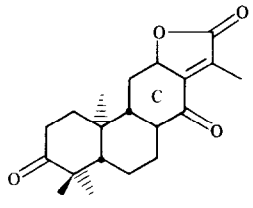
1a R^1 = R^3 = H, R^2 = OAc
3a R^1 = H R^2 R^3 = O
6 R^1 = OAc, R^2, R^3 = O



2a
7a



4a R = H
5a R = OAc



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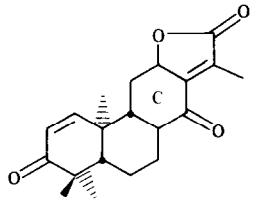

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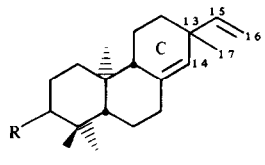

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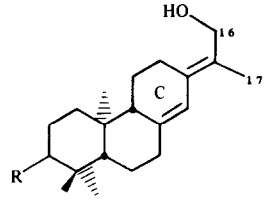

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Table 2 ^{13}C Chemical shifts *(δ, $CDCl_3$) of diterpene lactones **1**-**7** and **9** [MHz]

C	**1** [67 5]	**2** [75]	**3** [20]	**4** [67 5]	**5** [67 5]	**6** [75]	**7** [75]	**9** [7] [100 5]
1	33 80	32 42	42 63	155 32	156 21	80 49	39 10	39 87
2	22 66	22 46	33 29	124 02	122 69	39 51	20 79	18 40
3	76 98	76 81	214 60	204 29	202 54	210 15	41 25	41 48
4	38 93	38 75	53 14	49 41	49 01	53 14	35 54	35 51
5	48 92	47 86	55 87	49 58	51 77	51 36	53 47	53 47
6	20 41	20 28	20 81	20 85	69 19	20 06	18 32	20 79
7	34 61	35 37	34 61	34 75	40 17	34 63	35 54	33 94
8	60 90	65 69	60 51	60 64	58 79	60 26	65 86	61 31
9	48 66	47 79	40 82	39 62	38 79	40 95	48 02	51 74
10	36 65	36 77	35 49	36 61	36 59	37 16	39 10	41 44
11	23 78	60 51	25 92	26 29	26 20	25 95	60 77	106 55
12	75 50	84 98	76 91	76 10	75 84	75 67	85 08	147 28[a]
13	155 49	148 30	154 86	154 85	153 96	154 60	148 53	146 61[a]
14	56 12	55 21	56 33	55 86	55 66	55 96	55 23	54 41
15	128 80	130 34	129 53	128 42	129 08	128 70	130 08	127 42
16	174 20	170 22[a]	173 73	173 94	173 71	173 60	169 38	169 23
17	8 78	8 56	8 60	8 78	8 84	8 58	8 48	56 29
18	28 39	27 93	32 46	31.53	34 06	27 60	33 37	33 46
19	22 23	21 88[b]	22 51	22 34	22 20	22 06	21 73	21 89
20	19 15	15 21	16 90	17 82	19 15	16 78	15 28	15 08
OCOMe	170 52	170 10[a]			169 86	169 82		
OCOMe	21 22	21 05[b]			21 57	20 75		

* Assignments were made by the use of proton noise decoupling, SFORD and APT techniques, by comparison with appropriate literature values and with the data of the compounds included.
[a, b] Interchangeable

Jolkinolide B The gummy concentrate of the petrol–benzene (7 3) eluates on rechromatography afforded jolkinolide B (0 0003%), crystallizing as colourless needles, mp 220°d, $[\alpha]_D$ +177 3° ($CHCl_3$, *c* 0 029), UV λ_{max}^{EtOH} nm (log ε) 237 (4 27), IR ν_{max}^{KBr} cm^{-1} 2920 (C-H), 1775 (α,β-unsaturated γ-lactone C =O), 1450, 1385, 1359, 1250, 1048, 1006, 960, 872, 830, 802, ^1H NMR see Table 1, ^{13}C NMR see Table 2; MS *m/z* (rel int) 330 $[M]^+$ (11, $C_{20}H_{26}O_4$), 312 (4), 301 (13), 285 (11), 151 (100), 137 (89), 123 (71), 109 (53)

Gelomulide A The gummy concentrate of the petrol–C_6H_6 (1 1) eluates on rechromatography afforded gelomulide A (0 04%), crystallizing as colourless needless, mp 240°, $[\alpha]_D$ +95°, ($CHCl_3$, *c* 0 08, UV λ_{max}^{EtOH} nm (log ε) 223 (4 02), IR ν_{max}^{KBr} cm^{-1} 2950 (C-H), 1753 (α,β-unsaturated γ-lactone C=O), 1720 and 1250 (acetate C=O and CO–O), 1450, 1372, 1175, 1095, 1025, 980, 901, 870, ^1H NMR, see Table 1, ^{13}C NMR see Table 2, MS *m/z* (rel int) 374 $[M]^+$ (9, $C_{22}H_{30}O_5$), 314 (44), 299 (15), 281 (13), 180 (55), 161 (22), 135 (100), 133 (65), 120 (33), 81 (33)

Gelomulide B The gummy concentrate of petrol–C_6H_6 (1 3) eluates on rechromatography afforded gelomulide B (0 001%), crystallizing as colourless needles, mp 252°, $[\alpha]_D$ +126 7°, ($CHCl_3$, *c* 0 015), UV λ_{max}^{EtOH} nm (log ε) 238 (4 27), IR ν_{max}^{KBr} cm^{-1} 2940 (C-H), 1785 (α,β-unsaturated γ-lactone C=O), 1715 and 1250 (acetate C=O and CO–O), 1459, 1370, 1045, 1000, 955, 870, 815, ^1H NMR see Table 1, ^{13}C NMR see Table 2, MS *m/s* (rel int) 388 $[M]^+$ (3, $C_{22}H_{28}O_6$), 328 (5), 313 (9), 299 (16), 281 (15), 177 (36), 161 (37), 135 (100), 121 (33), 81 (26)

Gelomulide C The oily concentrate of the petrol–C_6H_6 (1 3) eluates (later fractions) on rechromatography afforded gelomulide C (0.006%), crystallizing as colourless needles, mp 173°, $[\alpha]_D$ −27° ($CHCl_3$, *c* 0 077), UV λ_{max}^{EtOH} nm (log ε) 224 (4 16), IR ν_{max}^{KBr} cm^{-1} 2940 (C-H), 1750 (α,β-unsaturated γ-lactone C =O), 1700 (ketone C=O), 1444, 1310, 1091, 1022, 870, 828, 767, ^1H NMR see Table 1, ^{13}C NMR see Table 2, MS *m/z* (rel int); 330 $[M]^+$ (70, $C_{20}H_{26}O_4$), 312 (16), 297 (14), 287 (28), 269 (32), 241 (26), 232 (18), 214 (17), 160 (24), 152 (100), 137 (38)

Gelomulide D The oily concentrate of the C_6H_6 eluates on rechromatography afforded gulomulide D (0 005%), crystallizing as colourless needles, mp 220°, $[\alpha]_D$ +7 58° ($CHCl_3$, *c* 0 079); UV λ_{max}^{EtOH} nm (log ε) 226 (4 43), IR ν_{max}^{KBr} cm^{-1} 2920 (C-H), 1746 (α,β-unsaturated γ-lactone C=O), 1665 (α,β-unsaturated ketone C=O), 1438, 1363, 1249, 1090, 1023, 899, 864, 815, ^1H NMR see Table 1, ^{13}C NMR see Table 2; MS *m/z* (rel int) 328 $[M]^+$ (38, $C_{20}H_{24}O_4$), 310 (19), 295 (8), 285 (5), 267 (18), 239 (5), 232 (17), 214 (25), 160 (13), 150 (100), 137 (53), 135 (26)

Gelomulide E The concentrate of the C_6H_6–$CHCl_3$ (3 1) and C_6H_6–$CHCl_3$ (1 1) eluates on rechromatography afforded gelomulide E (0 003%), crystallizing as colourless needles, mp 241°, $[\alpha]_D$ −12 5° ($CHCl_3$, *c* 0 08), UV λ_{max}^{EtOH} nm (log ε) 226 (4 36), IR ν_{max}^{KBr} cm^{-1} 2960 (C-H), 1758 (α,β-unsaturated γ-lactone C =O), 1730 and 1240 (acetate C=O and CO–O), 1668 (α,β-unsaturated ketone C=O), 1460, 1378, 1092, 1025, 950, 875, 836, ^1H NMR see Table 1, ^{13}C NMR. see Table 2, MS *m/z* (rel int) 386 $[M]^+$ (16, $C_{22}H_{26}O_6$), 326 (45), 308 (41), 293 (17), 283 (9), 265 (33), 237 (8), 230 (10), 212 (11), 163 (16), 137 (100), 122 (11)

Gelomulide F The concentrate of the C_6H_6–$CHCl_3$ (1 1) and $CHCl_3$ eluates on rechromatography afforded gelomulids F (0 005%), crystallizing as colourless needles, mp 220°, $[\alpha]_D$ +10 98° ($CHCl_3$, *c* 0 082), UV λ_{max}^{EtOH} nm (log ε) 223 (4 14), IR ν_{max}^{KBr} cm^{-1} 2950 (C–H), 1765 (α,β-unsaturated γ-lactone C=O), 1742 and 1238 (acetate C=O and CO–O), 1712 (ketone C=O), 1428, 1375, 1092, 1060, 1024, 975, 930, 870, 814, ^1H NMR

see Table 1, ^{13}C NMR· see Table 2, MS *m/z* (rel int) 388 $[M]^+$ (26, $C_{22}H_{28}O_6$), 328 (47), 310 (28), 395 (16), 285 (10), 267 (27), 239 (9), 232 (11), 214 (40), 160 (13), 150 (100), 137 (59), 135 (27)

Treatment of gelomulide C (**3**) *with* BF_3–Et_2O *to yield compound* **10**. To a soln of gelomulide C (20 mg) in dry C_6H_6 (6 ml) 4 drops of BF_3–Et_2O were added and the mixture was kept at room temp for 24 hr The residue obtained on usual work-up gave a product which was purified by chromatography and then crystallized to afford **10** as colourless needles (3 mg), mp 190°, IR ν_{max}^{KBr} cm^{-1} 2920 (C–H), 1745 (α,β-unsaturated γ-lactone C=O), 1720, 1710 (ketone C=O), 1450, 1370, 1150, 1100, 1020, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0 9, 1 03, 1 36 (3H each for three Me's), 2 17 (3H, *d*, *J* = 2 2 Hz, 15-Me), 1 4–2 85 (13H, *m*, CH_2 and CH protons) and 5 1 (1H, *m*, $W_{1/2} \sim 24$ Hz, H-12)

Treatment of gelomulide D (**4**) *with* BF_3–Et_2O *to yield compound* **11** Gelomulide D (20 mg) was treated with BF_3–Et_2O (*vide* preparation of **10**) at room temp. for 24 hr The product after usual work-up was purified by chromatography and crystallized to afford **11** (6 mg) mp 214°, IR ν_{max}^{KBr} cm^{-1} 2960 (C-H), 1758 (α,β-unsaturated γ-lactone C=O), 1693 (ketone C=O), 1678 (α,β-unsaturated ketone C=O), 1457, 1433, 1370, 1320, 1228, 1170, 1090, 1028, 995, ^{1}H NMR ($CDCl_3$, 100 MHz) δ 1 08, 1.11, 1 33 (3H each for three Me's), 2 21 (3H, *d*, *J* = 2 0 Hz, 15-Me), 1 72–2.76 (9H, *m*, CH_2 and CH protons), 5 15 (1H, *m*, $W_{1/2} \sim 23$ Hz, H-12), 5 8 (1H, *d*, *J* = 10 Hz, H-1), MS. $[M]^+$ 328 (42, $C_{20}H_{24}O_4$), 300 (2), 174 (23), 163 (9), 149 (38), 137 (100), 135 (24), 121 (15), 107 (15)

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