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STEREOSTRUCTURES AND CONFORMATIONS OF FOUR DITERPENE LACTONES FROM *GELONIUM MULTIFLORUM**

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Key Word Index—*Gelonium multiflorum*; Euphorbiaceae; diterpene lactones; gelomulides G-J; molecular conformations; absolute configuration; X-ray crystallography.

Abstract—The stereostructures and molecular conformations of four more diterpene lactones, gelomulides G-J, isolated as minor constituents from the leaves of *Gelonium multiflorum* were established on the basis of their ^{1}H NMR, ^{13}C NMR and mass spectral evidence. Additionally, a 2D NMR spectral study and the ORTEP diagram derived from the X-ray crystallographic analysis of gelomulide I confirmed its proposed stereostructure and absolute configuration. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Gelonium multiflorum A. Juss was reported to yield pentacylic triterpenoids [3, 4] from its bark and a flavanoid glucoside [5] from its leaves. Previously we reported from the leaves six novel diterpene lactones designated gelomulides A-F (**1-6**) [6] (GM A-F) having an *ent*-abietane skeleton. Reinvestigation of the leaves of *G. multiflorum* led to the isolation of four minor closely-related diterpene lactones designated, in order of increasing polarity, gelomulides G, H, J and I (GM G-I)] [7, 8] along with the previously isolated gelomulides B, D, E, jolkinolide B (**11**) and sitosterol. Multiflorenol [6] was not isolated; instead baurenol [9] was obtained. In this paper we report the isolation, stereostructures and molecular conformations of the new diterpenes gelomulides G-J (**7**–**10**).

*This paper is dedicated to our teacher Professor (Mrs.) Asima Chatterjee on the occasion of her 80th birth anniversary with profound regards and best wishes. Presented at the Sixth National Bioorganic Symposium, Indian Institute of Science, Bangalore, 5–7 June, 1997, *Book of Abstracts*, IP 3, and at the 'National Symposium on Recent Developments in Natural Products', Andhra University, Visakhapatnam, 11–13 July, 1997, *Abstracts*, SL 11. Part 35 in the series 'Terpenoids and Related Compounds'. For Part 34 see ref. [1] for Part 33 see ref. [2].

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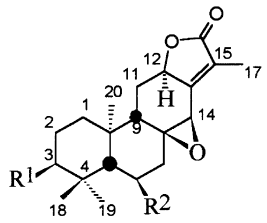
RESULTS AND DISCUSSION

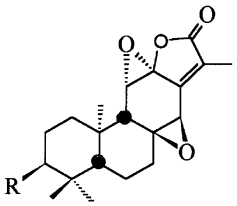
The petrol extract of the leaves of *G. multiflorum* furnished through silica gel column and flash chromatographies gelumulide G (**7**), gelomulide H (**8**) and gelomulide J (**10**) in low yields. The latter could not be purified in the conventional way because of an associated gum, and it was isolated as the acetate using acetic anhydride and pyridine and purified by chromatography followed by crystallization. The chloroform extract of the marc on chromatography gave gelomulide I (**9**).

Like gelomulides A-F (**1**–**6**) [6], gelomulides G-J showed an α, β-unsaturated γ-lactone absorption (1758–1785 cm^{-1}) in their IR spectra. The spectral data (IR, UV, ^{1}H NMR, ^{13}C NMR, Mass) were all commensurate with the proposed structures. However, the spectral data alone for gelomulide I could not identify its correct structure out of two possibilities. The ORTEP diagram obtained from the X-ray crystallography of gelomulide I confirmed its structure and absolute configuration as **9**.

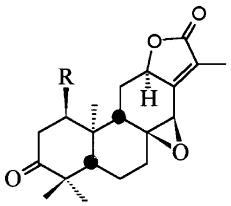
Gelomulide G (**7**), $C_{24}H_{32}O_7$ (m/z 432, M^+) showed evidence for two acetates [IR: 1738, 1732 and 1248 cm^{-1}; ^{1}H NMR: δ 2.07 (3H, *s*), 2.04 (3H, *s*); ^{13}C NMR: δ 20.94, 21.47 (two $OCOCH_3$), 169.77 and 170.05 (two $OCOCH_3$)] (Table 1). The presence of two acetoxyl groups in **7** was further supported by the loss of the elements of acetic acid (twice), as observed in its mass spectrum [m/z 432



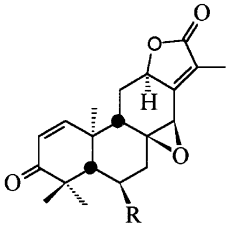
GM A,**1** : R^1=OAc, R^2=H
GM G,**7** : R^1=R^2=OAc



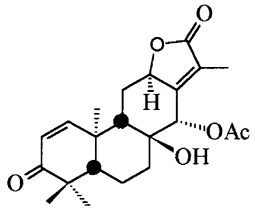
GM B,**2** : R=OAc
GM J,**10** : R=OH
11 : R=H



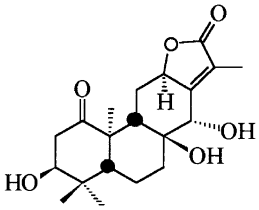
GM C,**3** : R=H
GM F,**6** : R=OAc



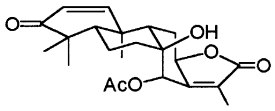
GM D,**4** : R=H
GM E,**5** : R=OAc



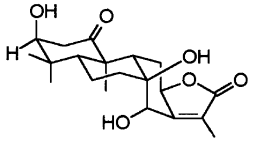
GM H,**8**



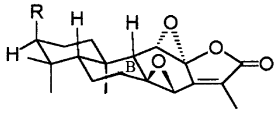
GM I,**9**



GM H, **8a**



GM I, **9a**



GM B, **2a** : R = OAc
GM J, **10a** : R = OH

Table 1. Comparison of the ^{1}H NMR signals (δ in ppm, multiplicity, coupling constants in Hz) of compounds **2**, **4**, **7**, **8** and **9**, in $CDCl_3$

Compound*	10-Acetate(≡ **2**) (300 MHz)	**4** (270 MHz)	**7** (300 MHz)	**8** (300 MHz)	**9** (500 MHz)
H-9	2.36 *br s*	2.66, *d*, 7.3	2.1, *d*, 6.9	2.32, *d*, 7.8	2.34, *brd*, 7, each signal $w_{1/2}$ 3
H-11 α (H-11β)	(4.01, *d*, 1.5)	2.73, *dd*, 14.0, 5.5	2.32, *dd*, 13.8, 5.5(1.40, *ddd*, 13.8, 13, 6.4)	2.93, *dd*, 14, 6.2	2.62, *ddd*, 14, 6.5, 2 (1.81, *m*, $W_{1/2}$ 33)
H-12	—	4.86, *ddd*, 13, 5.5, 2.0	4.90, *ddd*, 13.1, 5.1, 2.1	4.94, *ddd*, 12.3, 6.2, 2.0	5.13, *m*, $W_{1/2}$ 25
H-14	3.69, *s*	3.73, *s*	3.85, *s*	5.52, *s*	4.38, *s*
15-Me	2.04, *s*	1.98, *d*, 1.83	1.95, *d*, 2.0	1.95, *d*, 1.8	1.84, *d*, 1.8
Other important signals	3-OAc, 2.08, *s*; H-3, 4.7, *m*, $W_{1/2}$ 8; 3 Me s 0.83, 3H, *s*; 0.89, 6H, *s*	H-1, 6.44, *d* 10.38; H-2, 5.82, *d* 10.3; 3-Me's 1.14, 1.16, 1.36 (3H, *s* each)	3-OAc, 2.07, *s*; 6-OAc, 2.04, *s*; H-3, 4.63, *m*, $W_{1/2}$ 8; H-6, 5.16, *m*, $W_{1/2}$, 27; 3 Me's 1.23, 1.16, 1.00 (3H, *s* each)	H-1, 6.41, *d*, 10.2; H-2, 5.79, *d*, 10.2; 14-OAc, 2.13, *s*; 3 Me's, 1.50, 1.14, 1.11 (3H, *s* each)	H-3, 3.82, *dd* (*t*), 3.5; H-5, 1.76, *dd*, 13, 3; H-6α, 2.08, *dddd*, 13, 13, 13, 4; H-6β, 1.53, m, $W_{1/2}$ 22; H-7α, 2.26, *ddd*, 13, 13, 4; H-7, 1.62, *ddd* (= *td*), 13, 13, 5; H_3-18, 1.14, *s*; H_3-19, 1.01, *s*; H_3-20, 1.61, *s*

*For numbering of the compounds see structure **1**.

(M^+, 3), 372 (M^+-AcOH, 24), 312 (372-AcOH, 100). One proton multiplets at δ 4.63 ($W_{1/2}$ 8 Hz) and 5.16 ($W_{1/2}$ 27.2 Hz) are assignable to two acetoxymethine protons, H-3 and H-6, respectively. The placement was made on the basis of $W_{1/2}$. The 3-acetoxyl group was axial as revealed by the narrow half-width of H-3(e) involving J_{ea} and J_{ee}. The 6-acetoxyl group was equatorial as was evident from the broader half-width of H-6(a) involving J_{ae} and two J_{aa}s. The axial acetoxyl group was placed at C-3 as it is the biogenetically favoured site. Moreover, the appearance of a peak at m/z 81 originating from retro Diels-Alder collapse of ring A after deacetylation and loss of H in its mass spectrum supported its location. The placement also found support from its ^{13}C NMR spectral data (Table 2). Thus, **7** possessed [7, 10] structural features similar to those of **1** and an additional β-equatorial acetoxyl group at C-6. The coupling constants of H-12, H-11 and H-9 were also identical with those of **1** (Table 1). Hence, like **1**, compound **7** must possess a chair-chair-half chair conformation of rings A, B and C with *trans-transoid-cis*-configuration of the perhydrophenanthrene skeleton [6].

Gelomulide H (**8**), $C_{22}H_{28}O_6$ (m/z 388, M^+), isolated in a very low yield (0.001%), exhibited IR absorption bands at 1725 (ester C = 0) and 1217 cm^{-1} (O-CO stretching). It showed one acetoxymethine proton (ε 5.52, *s*), two *Z*-olefinic protons (δ 5.79 and 6.41, *d* each, *J* 10.2 Hz), one acetoxy methyl (ε 2.13, *s*) and one vinyl methyl (δ 1.95, *d*, *J* 1.8 Hz) groups. The narrowly split doublet of the latter is reminiscent of homoallylic coupling of this freely rotating methyl as in **1** and **3** to **7**. Unlike **1** to **7**, the epoxy proton (δ 3.73, *s*) is absent indicating thereby that the epoxy ring has opened in the 8,14-dioxygenated structure. Supportive evidence of this conjecture came from the appearance of one acetoxymethine proton at δ 5.52, (1H, *s*) for H-14 and the presence of an O—H band in its IR spectrum (3475 cm^{-1}, 8-OH). Its ^{13}C NMR spectrum (Table 2) exhibited oxygen bearing carbons at δ 70.01 and 73.12, in which the latter being monoprotonated is attributed to the acetoxymethine carbon C-14. The carbon shifts observed at δ 155.30 and 123.61 are assignable respectively to the monoprotonated olefinic carbons **1** and **2** conjugated with a carbonyl group (δ 205.5). Two other carbonyls at δ 168.54 and 174.10 are attributed to the acetoxy carbonyl and the conjugated lactonic carbonyl carbons (Table 2). Comparison of the ^{13}C and ^1H NMR spectral data of **8** with those of **4** (Tables 1 and 2) revealed that the structure of **8** is similar to that of **4** with a hydroxyl and an acetoxyl groups at C-8 and C-14 respectively instead of the 8,14-epoxy group in the latter. That **8** is not an artefact being formed from **4** during isolation was shown by the failure of the attempted opening of the epoxide ring of **4** to the corresponding 8,14-diol by subjecting the former to the isolation condition. Moreover, acetic acid was not used at any step during isolation to open up the epoxide ring and generate the 14-acetoxy-8-hydroxy compound **8**. The mass fragmentation pattern of **8** provides additional support to the proposed structure. Because of the presence of an α,β-unsaturated carbonyl system in ring A, the latter attains a flattened half chair conformation while, due to the absence

Table 2. Comparison of the ^{13}C chemical shifts* (in ppm, $CDCl_3$) of the diterpene lactones **1**, **4**, **7**, **8** and **9**.

Carbon	**1**	**7**	**4**	**8**	**9**
	75 MHz	75 MHz	75 MHz	67.5 MHz	125.70 MHz
1	33.8	33.8	155.3	155.5	216.0
2	22.7	22.1	124.0	124.0	43.9
3	77.0	78.5	204.3	205.5	80.1
4	36.7	36.6	49.4	49.0	39.0
5	48.9	52.3	49.6	49.8	51.1
6	20.4	69.3	20.9	21.6	21.5
7	34.6	39.9	34.8	40.4	42.3
8	60.9	59.4	60.6	73.1	75.9
9	48.7	48.2	39.6	46.8	48.7
10	38.9	38.9	36.6	36.3	54.4
11	23.8	24.0	26.3	31.2	32.7
12	75.5	74.9	76.1	73.7	78.9
13	155.5	154.4	154.9	155.0	164.8
14	56.1	55.2	55.9	70.0	73.5
15	128.8	129.4	128.4	126.9	122.8
16	174.2	173.3	173.9	174.1	177.2
17	8.8	8.6	8.8	8.5	8.3
18	28.4	31.1	31.5	31.6	28.5
19	22.2	22.2	22.3	20.9	22.7
20	19.2	20.3	17.8	17.4	16.9
-O*C*OCH$_3$	170.5	169.8 170.	—	168.5	—
-OCO*C*H$_3$	21.2	20.9 21.5	—	20.7	—

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

of the epoxide bridge, ring C assumed a chair conformation. Hence, the molecular conformation of **8** may be expressed as **8a** with half chair-chair-chair conformation rings A, B and C, respectively, having *trans-transoid-cis*-configuration of the perhydrophenanthrene system.

Gelomulide J (**10**) was isolated from a polar eluate fraction obtained at a later stage of chromatography only as its acetate derivative, thus removing its accompanying impurities, through flash chromatography and crystallization (*vide* experimental). The acetate, $C_{22}H_{28}O_6$ (*m/z*) 388 M^+) exhibited an identical ^{1}H NMR spectrum as that of gelomulide B (**2**) (Table 1). Thus, gelomulide J was identical with the hitherto unknown deacetylgelomulide B (**10**) and hence was a new diterpene lactone.

The tenth gelomulide, the most polar one, isolated from this plant material from its chloroform extract has been designated gelomulide I (**9**), $C_{20}H_{28}O_6$ (M^+ 364, 28%). It showed the presence of the hydroxyl (3490 cm^{-1}) and ketocarbonyl (1705 cm^{-1}) groups in addition to the α,β-unsaturated γ-lactone carbonyl (1738 cm^{-1}). Its ^{1}H NMR spectrum (500 MHz) showed the presence of the vinyl methyl protons (δ 1.84, *d*, J = 1.8 Hz) and two oxymethine protons [δ 3.82, *dd* (= *t*), J = 3.5 Hz and δ 4.38, *s*]. The narrow doublet indicated the presence of H-12α as in the cases of all gelomulides excepting **2** and **10** (Tables 1 and 4). However, the H-12 α (axial) appeared as a multiplet at δ 5.13 with $W_{1/2}$ = 25 Hz (approx.) which was caused by the overlapping of its J_{aa} and J_{ae} with H_2-11 and its homoallylic W-type coupling with the vinyl methyl at C-15 appearing as a doublet (J = 1.8 Hz) as in cases of the other gelomulides having H-12α. Like **8**, compound **9** had an epoxy opened/8,14-dioxygenated structure.

It is interesting to note that H_a-6α having two vicinal axial protons at C-5 and C-7 and a vicinal equatorial proton at C-7 appeared at an unexpectedly low field at δ 2.08, being recognized by its multiplicity, *dddd*, with $J_{gem} \approx J_{aa} \approx J_{aee} \approx 13$ Hz, $J_{ae} \approx 4$ Hz. Surprisingly, this proton was more deshielded than its equatorial counterpart (H_e-6β) which appeared at δ 1.53 as a multiplet ($W_{1/2}$ 22 Hz, involving a J_{gem}, two J_{ea}'s with H_a-5β and H_a-7β, and a J_{ee} with He-7α). The unexpected deshielding of H_a-6α was due to its presence, as evident from the Drieding model of **9**, in the anisotropic deshielding zone of the 14 α-OH (*vide* conformation **9a**). On the contrary, the equatorial counterpart H_e-6β of **9** was shielded to some extent because of its location in the shielding zone of the OH group. In this way, the *S*-configuration of C-14, having an axial α-OH, was also established. *This is a rare example where the equatorial proton is more shielded than its axial counterpart because of their particular geometry with respect to an OH group proximate in space* (*vide* **9a**).

The ^{13}C NMR spectrum of **9** showed two oxygen bearing secondary carbons (δ 73.48 and 80.13), one oxygen bearing tertiary carbon (δ 75.90), two carboxyl-carbons (δ 215.98 and 177.20) and one vinyl methyl carbon (δ 8.27) (Table 3).

The one-dimensional ^{1}H and ^{13}C NMR spectral analyses of **9** could not distinguish between its 1-keto-3-ol structure **9** and the alternative possibility of its corresponding 3-keto-1-ol structure. The conformation of **9** was thus expressed as chair-chair-chair (**9a**) of rings A, B and C with a *trans-transoid-cis*-configuration of the perhydrophenanthrene skeleton. In this gelomulide all three cyclohexane rings have assumed almost undistorted chair conformation. The mass spectral fragmentation exhibited by **9** was consistent with its proposed structure.

The two-dimensional ^{1}H-^{1}H and ^{13}C-^{1}H chemical shift correlation in the high resolution 500 MHz spectra provided detailed information regarding the structure and stereochemistry of **9**. The homonuclear proton-proton chemical shift correlation diagram indicated the two bond and three bond correlations between the protons which actually led to the assignment of each proton and the complete structure and stereochemistry of **9** (Table 3).

The two-dimensional heteronuclear carbon-proton chemical shift correlation diagram showed one bond correlation between each carbon bearing proton/s and the attached proton/s thus confirming the assignment of each carbon and proton shifts (Table 4). The chemical shift of each carbon was obtained from the noise decoupled ^{13}C NMR spectrum at 125.70 MHz.

The structure, stereochemistry and molecular conformation of **9**, as derived from its two-dimensional NMR spectral analyses, and the

Table 3. Two dimensional ^{1}H-^{1}H shift* correlation at 499.84 MHz for ^{1}H via two bond (bigger contours) and three bond (smaller contours)† couplings of **9**

1	Proton	H-2α	H-2β	H-3α	H-5β	H-6β	H-6α	H-7β	H-7α	H-9β	H-11β	H-11α	H-12α
2	Two bond correlation with proton	H-2β	H-2α	—	—	H-6α	H-6β	H-7α	H-7β	—	H-11α	H-11β	—
3	Three bond Correlation with proton	H-3α	H-3α	H-2α	H-6β	H-5β	H-5β	H-6β	H-6β	H-11β	H-9β	H-9β (v. w.)	H-11β
				H-2β	H-6α	H-7α H-7β	H-7α H-7β	H-6α	H-6β	H-11α	H-12α	H-12α	H-11α

*For chemical shifts of the particular protons Table 4 may be referred to.
†Five bond correlation contours between H-12α and 15-CH_3, and H-14β and 15-CH_3 (smaller contours) were also observed.

Table 4. One-bond ^{13}C-^{1}H correlation data of gelomulide I (**9**) from two-dimentional XHCORR diagram*

Carbon	δ_c ppm	One-bond correlation δ_H ppm (assignment)
C-1	215.98	—
C-2	43.94	2.23 (H_a-2α), 3.26 (H_e-2β)
C-3	80.13	3.82 (H_e-3α)
C-4	39.00	—
C-5	51.13	1.76 (H_a-5β)
C-6	21.49	1.53 (H_e-6β); 2.08 (H_a-6α)
C-7	42.26	1.62 (H_a-7β); 2.26 (H_e-7α)
C-8	75.90	—
C-9	48.66	2.34 (H-9β)
C-10	54.36	—
C-11	32.70	1.81 (H_a-11β); 2.62 (H_e-11α)
C-12	78.89	5.13 (H_a-12α)
C-13	164.80	—
C-14	73.48	4.38 (H_e-14β)
C-15	122.79	—
C-16	177.20	—
C-17	8.27	1.84 (H_3-17)
C-18	28.54	1.01 (H_3-18)
C-19	22.72	1.14 (H_3-19)
C-20	16.93	1.61 (H_3-20)

*125.70 MHz for ^{13}C; 499.84 MHz for ^{1}H.

absolute configuration of gelomulides proposed on the basis of their biogenesis [6] finally received unambiguous confirmation from the ORTEP diagram (Fig. 1) derived from the X-ray crystallographic analysis of **9**.

Gelonium multiflorum has thus been shown to produce a large number of diterpene lactones.

EXPERIMENTAL

General

Mps measured in open capillary tubes are uncorr. The absorption maxima of the UV spectra (in EtOH) are in nm and the IR spectra as KBr pellets are in cm^{-1}. Petrol refers to the 60–80° fraction. The silica gel (60–120 mesh, Qualigen) was used for column chromatography; the silica gel (230–400 mesh, SRL) was used for flash chromatography in an eyela EFC–2000 instrument. To monitor fractions TLC experiments were done using microscopic slides with silica gel G layers put on them by dipping in its $CHCl_3$ slurry, taking out and drying at ambient temperature. Spots were visualized under UV light and on exposure to I_2 vapour; similar fractions were combined. $CHCl_3$-Petrol was used for crystallisation, unless otherwise mentioned. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$. The peaks for TMS or solvent ($CHCl_3$: δ_H 7.26; $CDCl_3$: δ_c 77.0) were used as the internal standards. The *J*-values are given in Hz. The rotations were measured with a Perkin-Elmer 241 Polarimeter and the mass spectra were recorded in a MS-50 or RMU-6E with constant computer system operating at 70 eV. All known natural products were identified by direct comparison (mmp, superimposable IR and ^{1}H NMR) with authentic samples.

Plant material.

Leaves of *G. multiflorum* A. Juss [6] were collected for investigation from the neighbourhood of Calcutta and identified by comparison with the Voucher Specimen No. 646 kept at the herbarium, Botanical Survey of India, Sibpur Botanic Garden, Howrah, W. Bengal.

Extraction and isolation

Air-dried and powdered leaves of *G. multiflorum* (1.2 kg) were extracted in a Soxhlet apparatus with petrol and $CHCl_3$ successively, for 40 hr each.

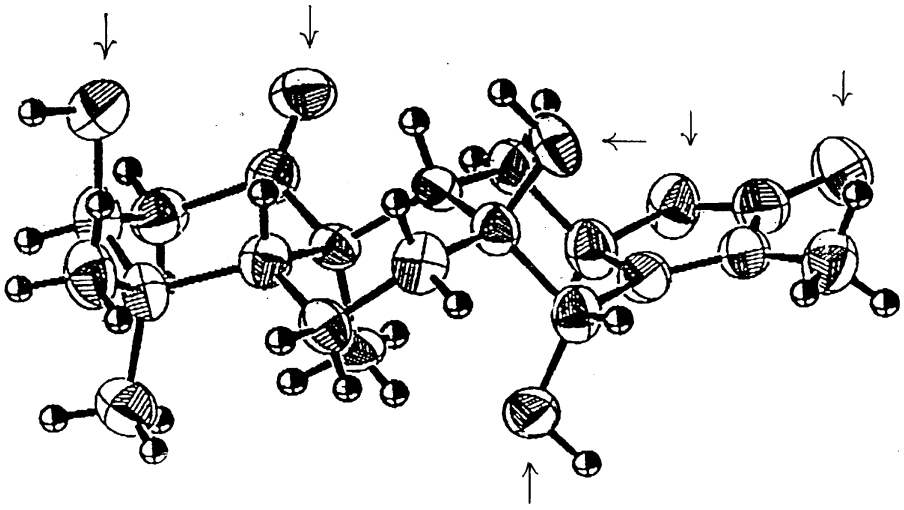


Fig. 1. ORTEP Diagram of gelomulide I (**9**). Arrows indicate Oxygen atoms (*cf* **9a**).

Treatment of the petrol extract concentrate

The residue (85.3 g) was chromatographed over silica gel (1.27 kg) using solvents and solvent mixtures of increasing polarity as eluents.

Bauerenol

The gummy concentrate of the petrol eluate fractions of the main chromatogram upon flash chromatography afforded bauerenol [3], crystallizing as colourless flakes ($CHCl_3$-MeOH), (yield 0.06%), mp 202°, $[\alpha]_D$−8.7° ($CHCl_3$, *c* 1.02). However, no multiflorenol [6] was isolated from this supply of plant materials.

Sitosterol, jolkinolide B (**12**)*, gelomulide B* (**2**)*, gelomulide D* (**4**) *and gelomulide E* (**5**)

The gummy concentrates obtained successively from the petrol-benzene (19:1), petrol-benzene (9:1), petrol-benzene (4:1), petrol-benzene (1:4) and benzene-$CHCl_3$ (4:1) eluate fractions of the main chromatogram upon separate flash chromatography afforded, sitosterol (0.004%), **12** (0.001%), **2** (0.002%), **4** (0.006%), and **5** (0.004%) respectively, all of which were reported by us earlier from this plant material in somewhat less yields [6]. However, gelomulides A, (C) and F (**1**, **3**, and **6**) were not found to occur in this batch of plant material.

Gelomulide G (**7**)

The brown residue (0.6 g) of the benzene-$CHCl_3$ (2:3) eluate fractions of the main chromatogram upon flash chromatography with the same solvent mixture afforded **7**, crystallizing from $CHCl_3$-MeOH as colourless needles, (0.002%), mp 205°, $C_{24}H_{32}O_7$ (M^+ 432), [R_f 0.58 $CHCl_3$-MeOH (19:1), silica gel G], $[\alpha]_D + 58.5°$ ($CHCl_3$, *c* 0.084), UV EtOH max nm (log ϵ): 228 (3.99); IR ν_{max} cm^{-1} 2940 *s*, 1758 *sh* (*s*) (α,β-unsaturated γ-lactone C = 0), 1738 *s* and 1732 *s*, (two acetate C = 0s), 1248 *s* (OC-C str.), 1458 *m*, 1440 *m*, 1380 *s*, 1180 *m*, 1108 *m*, 1020 *s*, 970 *m* and 872 m. ElMS *m*/*z* (rel. int.): 432 (M^+, 3), 372 (24), 354 (3), 339 (2), 330 (10), 312 (100), 297 (47), 279 (38), 269 (24), 251 (14), 244 (167), 218 (17), 201 (21), 187 (49), 173 (50), 159 (78), 145 (41), 133 (71), 119 (49), 105 (61), 81 (62). [Found: C. 65.9; H, 7.0. $C_{24}H_{32}O_7$ requires C. 66.7; H. 7.4%].

Gelomulide H (**8**)

The main chromatogram was next eluted with $CHCl_3$ (giving a dark oily residue) and then with EtOAc. The brown gummy residue (0.5 g) was flash chromatographed to give **8**, crystallizing in colourless fine needles (0.001%), mp 216°, $C_{22}H_{28}O_6$ (M^+ 388), $[\alpha]_D$−68.4° ($CHCl_3$, *c* 0.042); IR ν_{max} cm^{-1} 3380 m (0-H), 2960 m (C-H), 1750 s (α, β-unsaturated γ-lactone C = 0), 1725 s (acetate C = 0), 1217 s (acetate O-CO), 1670 s (α, β-unsaturated C = 0), 1448 w, 1365 m, 1025 s, 925 w, 817 w. ElMS *m*/*z* (rel. int.): 388 (40), 346 (10), 328 (100), 311 (32), 310 (17), 295 (11), 267 (19), 232 (28), 219 (20), 150 (79), 137 (86).

Gelomulide J Acetate (≡**2**)

The later EtOAc eluate fractions of the main chromatogram afforded a gummy residue (0.4 g) which showed only one spot, yet could not be induced to crystallize after repeated flash chromatography. The residue was treated with Ac_2O-Pyridine at room temp. overnight. The reaction mixture showing a much less polar spot, after usual work-up and flash chromatography, afforded the acetate of gelomulide J (**10**), mp 252° (0.002%), found to be identical with gelomulide B (**2**) by direct comparison (mmp, superposable IR and ^1H NMR).

Treatment of the $CHCl_3$ extract

The residue (20 g) obtained by conc. of the $CHCl_3$ extract under red. pres. (using Eyela aspirator) was chromatographed by eluting with solvents and solvent mixtures of increasing polarity.

Bauerenol

The dark oily residue (0.8 g) obtained from the petrol-EtOAc (4:1) eluate fractions of the main chromatogram was subjected to flash chromatography to furnish a further quantity of bauerenol (0.02%), mp 202°.

Gelomulide I (**9**)

The brown residue (0.5 g) obtained from the petrol-EtOAc (2:3) eluate fractions of the main chromatogram upon flash chromatography furnished **9**, crystallizing from $CHCl_3$-MeOH in colourless needles (0.002%), mp 276°; IR ν_{max}: 3490 vs (O-H), 1738 vs (α, β-unsaturated γ-lactone carbonyl), 1705 vs (keto C = O), 1445 m, 1380 m, 1335 m, 1250 m, 1120 m, 106, 1030 s, 910 m, 765 m, 740 m, 625 w, 575 m. EIMS *m*/*z* (rel. int.): 364 (M^+, 28), 346 (42), 347 (57), 328 (48), 310 (15), 285 (12), 267 (23), 232 (20), 214 (20), 192 (20), 177 (18), 168 (35), 150 (100), 137 (73), 123 (30), 110 (88). (Found C. 65.6; H. 7.9. $C_{20}H_{28}O_6$ requires: C. 65.9; H. 7.7%).

X-Ray crystallography of GM I(**9**)

The ORTEP diagram of **9** (Fig. 1) derived from X-ray crystallographic analyses was received through the kind courtesy of Professor Mugio Nishizawa, Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Yamashiro-Cho, Tokushima 770, Japan. The list of refined co-ordinates, together with other relevant data are not available with us and should be available with the X-ray crystallographic centre from which Professor Nishizawa received the ORTEP diagram and kindly sent to us.

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