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DITERPENES FROM *EUPHORBIA HELIOSCOPIA*

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Key Word Index—*Euphorbia helioscopia*; Euphorbiaceae; toxic diterpenes; euphoscopins; epieuphoscopins; euphornins; euphohelioscopins; euphohelionone.

Abstract—A number of diterpenes have been isolated from *Euphorbia helioscopia* and their stereostructures elucidated on the basis of the spectral data together with some chemical evidence. The absolute configuration of euphoscopin A and euphornin in particular have been unambiguously determined by means of X-ray crystallographic analysis.

INTRODUCTION

Plants of the Euphorbiaceae contain a number of toxic diterpenes (jatrophone [1], kansuinin [2], lathylol [3], ingenol [4], phorbol [5], jatropholane [6], crotofolin A [7] and others), some of which have antitumour activity or promote cancer development in tumour formation. In 1975, Evans *et al.* isolated some phorbol-type diterpenes from *E. helioscopia* [8]. We also examined substances from the same plant (Todai Gusa in Japanese) and have isolated the diterpenes euphoscopin A, epieuphoscopin A, euphornin, euphohelioscopin A and euphohelionone.

RESULTS AND DISCUSSION

Fresh leaves and roots of *E. helioscopia* collected in Kanagawa Prefecture early in May afforded 31 new diterpenes.

Euphoscopin A (**1**), molecular formula $C_{31}H_{40}O_8$, exhibited an IR spectrum of 3500, 1740 and 1770 cm^{-1}, and its ^1H NMR spectrum indicated one benzoyloxyl group [δ7.35–7.65 (3H), 7.99 (2H)], two acetoxyl groups (δ2.15, 2.18) and five methyls [δ0.91 (*d*, $J = 7$ Hz), 1.08 (*s*), 1.10 (*d*, $J = 7$ Hz), 1.22 (*s*), 1.81 (*d*, $J = 1.5$ Hz)]. Furthermore, the ^1H NMR spectrum with the aid of decoupling experiments indicated the presence of the following partial structures ([A], [B] and [C] Fig. 1), wherein the benzoyloxyl group and one of the two acetoxyl groups are included in [A] and [C], respectively. On sodium borohydride reduction (room temp, 19 hr), euphoscpoin A (**1**) was converted into the corresponding hydroxy compound (**2**) in good yield, indicating that there was one ketonic carbonyl group in the compound. Finally, the stereostructure of euphoscopin A including the absolute configuration was unambiguously determined by means of an X-ray crystallographic analysis of the corresponding *p*-bromobenzoate (**3**), produced on treatment of **1** with *p*-bromobenzoyl chloride in pyridine [9, 10].

The spectral data of euphoscopin B (**4**), molecular formula $C_{33}H_{42}O_9$, were similar to those of **1** except for the following data. The former had no D_2O exchangeable protons, but instead exhibited signals for acetoxy groups

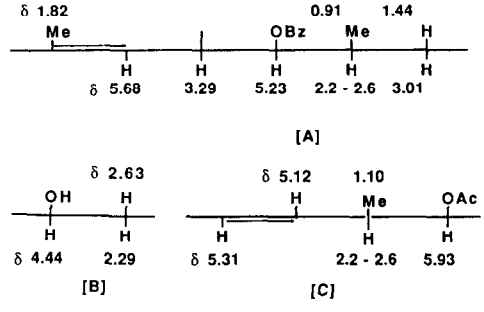


Fig. 1. Partial structures present in euphoscopin A (**1**).

(δ1.26, 2.14, 2.20), whereas **1** exhibited a signal at 3400 cm^{-1} in its IR spectrum and signals for two acetoxyl groups (δ2.15, 2.18) in its ^1H NMR spectrum. When treated with acetic anhydride in pyridine (70°, 1 hr), euphoscopin A (**1**) was readily converted into euphoscopin B (**4**) in almost quantitative yield. It was noted that in the ^1H NMR spectrum a signal due to a newly formed acetoxyl group in **4** was observed at an unusually high magnetic field (δ1.26), possibly because of an anisotropic effect of the benzoyloxyl group at C-3.

Euphoscopin C (**5**), molecular formula $C_{38}H_{44}O_9$, was similar to **4** in its spectral data. However, some differences were observed in relation to functional groups. The former exhibited signals for two acetoxy groups (δ2.15, 2.19) and two benzoyloxyl groups [δ6.88–7.04 (3H, *m*), 7.19–7.40 (2H, *m*), 7.46–7.62 (3H, *m*), 7.85 (2H, *m*)] in its ^1H NMR spectrum, whereas there were three acetoxyl signals and one benzoyloxyl signal in the spectrum of **4**. Clearly, the additional benzoyloxyl group must be located at C-7, because the ^1H NMR signals assigned to the two acetoxy groups were observed in a normal region. Finally, on benzoylation with benzoyl chloride in pyridine (room temp., overnight), **1** was readily converted into euphoscopin C (**5**).

Euphoscopin D (**6**), molecular formula $C_{31}H_{38}O_8$, shows IR absorption bands at 1740, 1710 and 1670 cm^{-1}

but exhibited no hydroxyl absorption band, indicating that this diterpene may be regarded as an α,β-unsaturated ketone (IR 1670 cm^{-1}). On the basis of the ^1H NMR spectrum, euphoscopin D also possessed two AcO groups (δ2.15, 2.22) and one benzoyloxyl group [δ7.40–7.57 (3H, *m*), 7.92 (2H, *m*)], seen in **1**. From these data, therefore, the secondary hydroxyl group at C-7 in **1** corresponded to the α,β-unsaturated carbonyl group in **6**. Thus, on oxidation with manganese dioxide in benzene (70–80°, 24 hr) **1** was successfully converted into **6**.

Euphoscopin E (**7**), molecular formula $C_{29}H_{36}O_7$, exhibited IR absorption bands at 3500, 1735 and 1710 cm^{-1}. This diterpene had one secondary hydroxyl group [δ4.35 (1H, *dd*, J=6, 10 Hz)], one acetoxyl group (δ2.27) and one benzoyloxyl group [δ7.42–7.64 (3H, *m*), 8.02 (2H, *m*)] as shown by its ^1H NMR spectrum which is similar to that of **1** except for the doublet at δ5.93 assigned to the proton (AcO–C_{14}—H) in **1** which is not observed in **7**. On acetylation with acetic anhydride–pyridine, euphoscopin E was readily converted into euphoscopin F (**8**) [$C_{31}H_{38}O_8$; IR 1735, 1710 cm^{-1}]. In the ^1H NMR spectrum of **8**, the singlet assigned to the newly formed acetoxyl group was observed at δ1.30, indicating that euphoscopin E possessed a secondary hydroxyl group at C-7. From these data, the structures of euphoscopin E and F are represented by **7** and **8**, respectively. Finally, **1** and **7** were chemically correlated, as follows. Euphoscopin A (**1**) was converted into the corresponding silyl ether (**9**) in quantitative yield (^{t}BuMe$_2$SiCl–imidazole; room temp., 5.7 hr) which was then subjected to hydrolysis using potassium carbonate in methanol (room temp., 24 hr) followed by oxidation (PCC–Celite in CH_2Cl_2; room temp., 6 hr) to afford a diketone (**10**). This diketone (**10**) was also derived from euphoscopin E (**7**) through a silyl ether (**11**) in two steps [(1) ^{t}BuMe$_2$SiCl–imidazole in DMF (room temp, 17 min); (2) K_2CO_3 in MeOH (room temp, 15 hr)].

In addition to the benzoyloxyl group at C-3, euphoscopin G, I and K (**12**, **14** and **16**), molecular formula $C_{29}H_{38}O_7$, possessed two OH groups and one acetoxyl group, whereas euphoscopin H and J (**13** and **15**), molecular formula $C_{31}H_{40}O_8$, contained one hydroxyl group and two acetoxyl groups, as judged from their IR and ^1H NMR spectra, by comparison to those of euphoscopin A and B (**1** and **4**). However, some differences were observed in the chemical shifts of the protons located at C-7 and C-14, (Table 1). On a detailed comparison of the ^1H NMR spectra of euphoscopin G, H and K (**12**, **13** and **16**), an acetoxyl group was located at C-14 in **12** and at C-7 in **16**, respectively. Clearly, euphoscopin H (**13**) had two acetoxyl groups at C-7 and C-14. On acetylation with acetic anhydride–pyridine, **12** was readily converted into **13**. Finally, the structures of these diterpenes were unambiguously determined by chemical transformation of **1** to **13** and **16**: the silyl ether (**9**) of euphoscopin A was treated with potassium carbonate in methanol (room temp.,

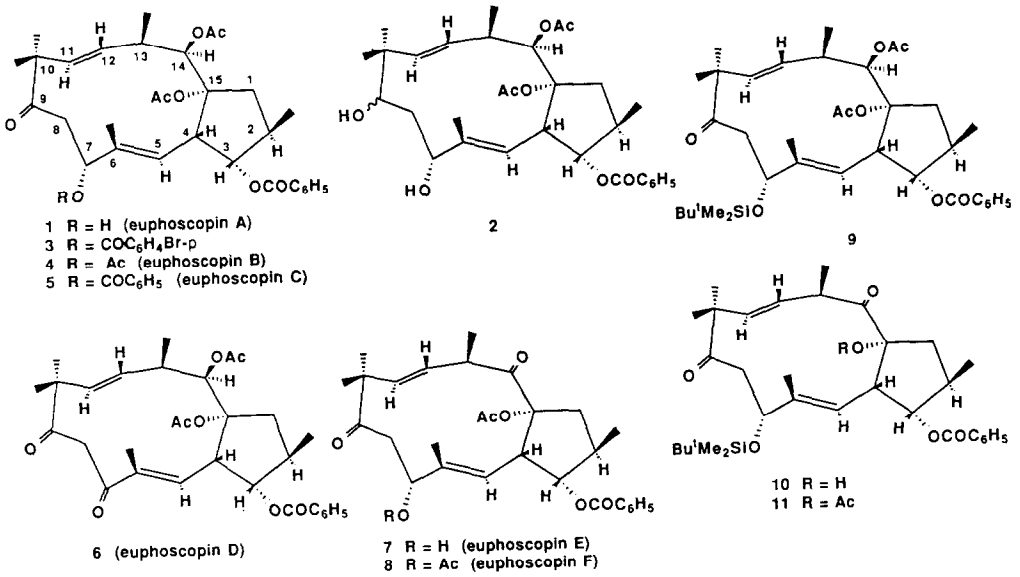
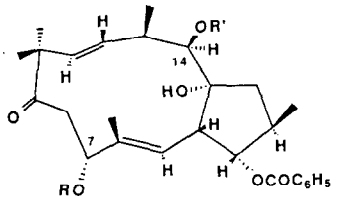
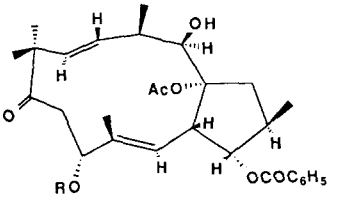


Table 1. ^1H NMR spectral data (δ-value) of euphoscopins

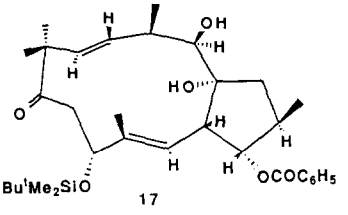
Compound	H-7	OAc-7	H-14	OAc-14	OAc-15
Euphoscopin A (**1**)	4.44	—	5.93	2.15	2.18
Euphoscopin B (**4**)	5.31	1.26	5.88	2.14	2.20
Euphoscopin G (**12**)	4.39	—	5.14	2.16	—
Euphoscopin H (**13**)	5.36	1.27	5.15	2.16	—
Euphoscopin I (**14**)	4.36	—	4.46	—	2.17
Euphoscopin J (**15**)	5.35	1.22	4.50	—	2.21
Euphoscopin K (**16**)	5.32	1.27	3.67	—	—



12 R = H, R' = Ac (euphoscopin G)
13 R = R' = Ac (euphoscopin H)
16 R = Ac, R' = H (euphoscopin K)



14 R = H (euphoscopin I)
15 R = Ac (euphoscopin J)



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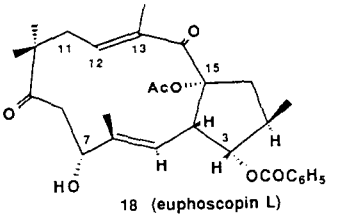


18 (euphoscopin L)

24 hr) to afford a diol (**17**) which was then desilylated (HOAc in MeOH–H_2O; 50°, 12.5 hr) and then treated with acetic anhydride–pyridine (room temp., 3 hr) to give rise to a mixture of **13** and **16** in 53 and 32% yields, respectively.

The structures of **14** and **15** were based on the ^1H NMR spectral data (Table 1) coupled with some chemical evidence. On acetylation with acetic anhydride–pyridine, both **14** and **15** afforded euphoscopin B (**4**) in almost quantitative yields.

Euphoscopin L (**18**), molecular formula $C_{29}H_{36}O_7$, exhibited IR absorption bands at 3480 (OH), 1740 (ester CO), 1720 (CO) and 1680 cm^{-1} (α,β-unsaturated CO). Furthermore, signals in its ^1H NMR spectrum strongly suggested that both secondary OH and AcO (δ2.18) groups were located at C-7 [δ4.13 (1H, *m*) (C-7H)] and C-15, respectively, in addition to the benzoyloxyl group at C-3, as seen in other euphoscopins. However, we proposed a partial structure [D] (Fig. 2) for euphoscopin L (**18**), as judged from its ^1H NMR spectral data, wherein no NOE was observed between C-13 Me and C-12H indicating that this conjugated double bond is in a *trans* configuration. From these data coupled with the following experiment, the structure of euphoscopin L is represented by **18**; when treated with sodium acetate in DMF (50°, 3 days), euphoscopin E (**7**) was converted into euphoscopin L (**18**) in 86% yield.

Epieuphoscopin A (**19**), molecular formula $C_{31}H_{40}O_8$, was similar to **1** in its IR and ^1H NMR spectra, indicating the presence of two acetoxyl groups (δ2.12, 2.14), one hydroxyl group (IR 3480 cm^{-1}), one benzoyloxyl group [δ7.3–7.5 (3H, *m*), 7.93 (2H, *m*) and one carbonyl group (IR 1720 cm^{-1}). However, some differences between **1** and **19** are observed in their ^1H NMR spectra. Although the chemical shifts of the proton (AcO–C_{14}–H) were similar (δ5.93 in **1**; δ5.92 in **19**), the coupling constant of the former ($J = 1.5$ Hz) was different from that of epieuphoscopin A ($J = 10$ Hz), indicating that epieuphoscopin A may be regarded as a stereoisomer of euphoscopin A (**1**) around C-13 and/or C-14. Finally, these two diterpenes were correlated, as follows. Epieuphoscopin A (**19**) afforded a silyl ether (**20**) (^{t}BuMe$_2$SiCl–imidazole in DMF), which was subjected to hydrolysis (K_2CO_3 in MeOH) followed by oxidation [DMSO–Ac_2O (room temp, 2 days)] to give rise to a diketone (**21**) in 92% yield. However, this compound was not identical with the diketone (**10**) derived from **1** in all respects. Both diketones (**10** and **21**) were isomerized with sodium acetate in DMF (80°, 4 days) to afford the same α,β-unsaturated ketone (**22**). Therefore, epieuphoscopin A (**19**) is regarded as the stereoisomer of **1** at C-13.

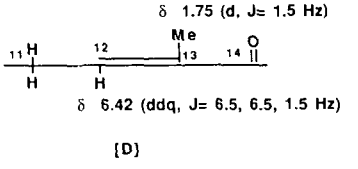


Fig. 2. Partial structure for euphoscopin L (**18**).

Epieuphoscopin B (**23**), molecular formula $C_{33}H_{42}O_9$, was similar to **19** except for an extra acetoxyl group (δ1.52) at C-7. On acetylation with acetic anhydride–pyridine, **19** was readily converted into epieuphoscopin B (**23**).

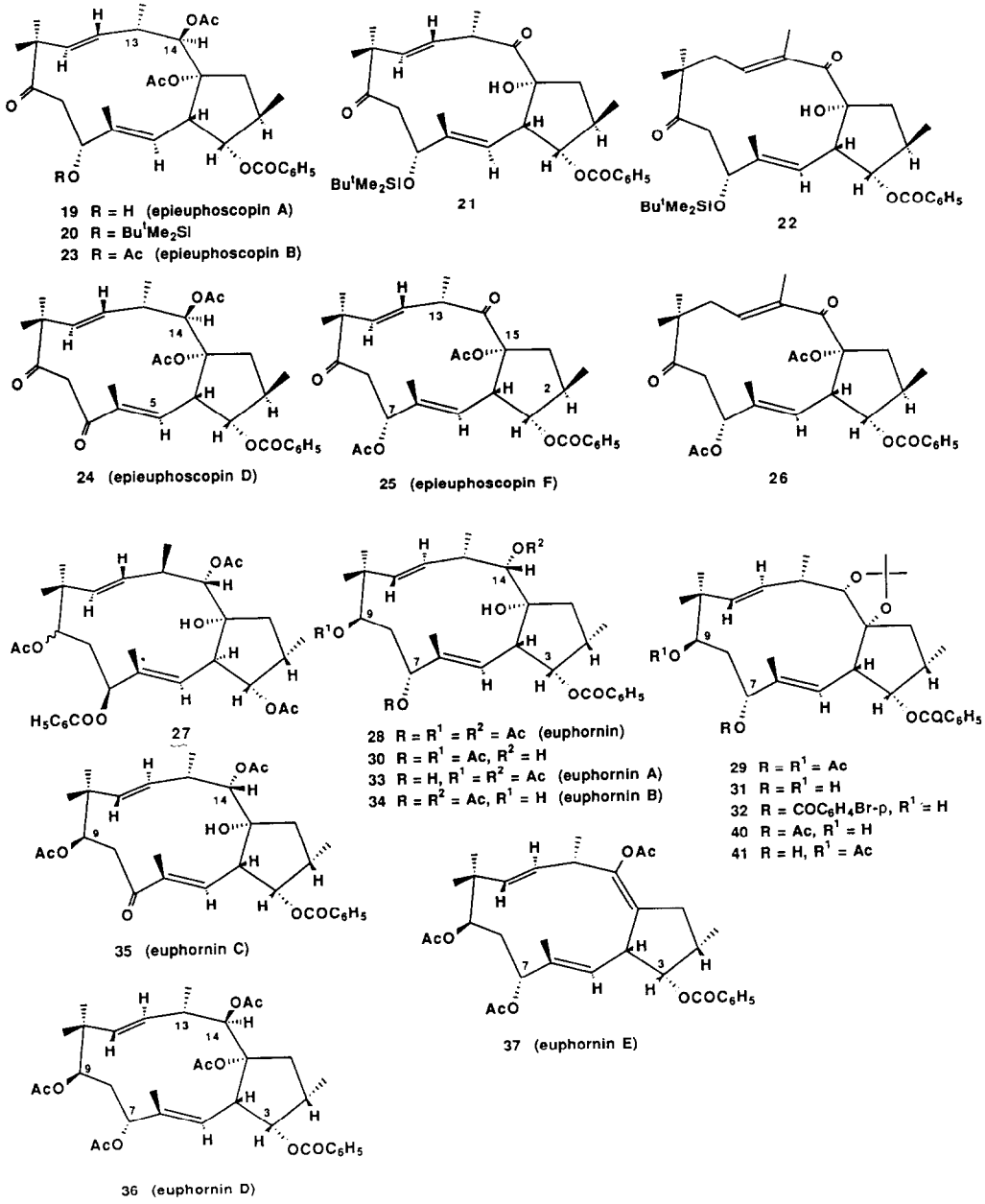
Epieuphoscopin D (**24**), molecular formula $C_{31}H_{38}O_8$, exhibited IR absorption bands at 1745 (ester CO), 1720 (CO) and 1655 cm^{-1} (α,β-unsaturated CO). The ^1H NMR spectrum of **24** was similar to that of epieuphoscopin A (**19**) [δ5.92 (1H, *d*, $J = 10$ Hz) AcO–C_{14}–H) in **19**; δ5.99 (1H, *d*, $J = 10.2$ Hz) in **24**]. However, the proton assigned to C-7 is absent in epieuphoscopin D (**24**). In addition, the ^1H NMR signal due to the olefinic proton at C-5 in **19** (δ5.46) shifted to a lower magnetic field (δ7.00) in **24**. From these data, the structure of epieuphoscopin D can be represented as **24**, which was confirmed by the following experiment. Epieuphoscopin A (**19**) was oxidized with active manganese dioxide in benzene (reflux, 4 days) to give the corresponding diketone, which was identical with epieuphoscopin D (**24**) in all respects.

Epieuphoscopin F (**25**), molecular formula $C_{31}H_{38}O_8$, is regarded as a stereoisomer of **8**, as judged from its spectral data [IR 1740 (ester CO), 1710 (CO) cm^{-1}; δ1.43 (3H, *s*), 5.11 (1H, *dd*, $J = 4.5$, 10.5 Hz) (CH–OAc), 2.26 (3H,

s), (AcO–C), 5.33 (1H, dd, $J = 3.5$, 6.5 Hz), 7.4–7.6 (3H, m), 7.98 (2H, m) C_6H_5COO–CH)]. In the ^1H NMR spectrum, the signals for one of the two acetoxyl groups was assigned to C-7, as seen in **8** (δ1.3). Thus, possible stereoisomers at C-2, C-13 and/or C-15 are proposed for epieuphoscopin F. However, **25** was shown to be the epimer of **8** at C-13 by the following experiments. When treated with sodium acetate in DMF (75°, 4 hr), both epieuphoscopin F and euphoscopin F were converted into the same α,β-unsaturated ketone (**26**) in 73 and 17% yields, respectively.

Euphornin having antitumour activity against PS cell was first isolated by Bohlmann *et al.* from *E. maddeni* [11], and its tentative structure (**27**) was also given by the same authors [11]. However, the stereostructure of euphornin was corrected as **28** by the present experiments, as described below.

Euphornin (**28**), molecular formula $C_{33}H_{44}O_9$, was also isolated from *E. helioscopia* [12] and exhibited IR absorption bands at 3550 (OH), 1730 (ester CO), 1600 and 1580 cm^{-1}. As judged from ^1H NMR, euphornin exhibited one benzoyloxyl group [δ7.4–7.6 (3H, m), 8.06 (2H, m)], three acetoxyl groups (δ1.18, 1.96, 2.22) and five methyls [δ0.88 (3H, s), 0.96 (6H, d, $J = 6$ Hz), 0.96 (3H, s), 1.75 (3H, d, $J = 1.5$ Hz)]. in addition to three olefinic protons [δ5.06 (1H, d, $J = 15.5$ Hz), 5.65 (1H, dd, $J = 9.5$, 15.5 Hz), 5.74 (1H, dd, $J = 1.5$, 10 Hz)]. Furthermore, its ^{13}C NMR spectrum indicated the presence of four ester carbonyls (δ165.1, 168.4, 169.0, 170.6), five carbon atoms bearing an oxygen atom [δ72.8 73.4 (d), (d), 80.6 (d), 80.7 (d), 83.5 (s)] and two double bonds [δ119.8 (d), 128.6 (d), 133.4 (s), 137.5 (d)] in addition to the benzoyloxyl group. From these data, euphornin has the structure **27** as proposed by Bohlmann *et al.* [11] and confirmed in his



laboratory. In connection with **1** and related diterpenes, however, the benzoyloxyl group and one of the three acetoxyl groups must be located at C-3 and C-7, respectively, as judged from ^{1}H NMR spectral data: δ5.42 (1H, *dd*, J=3, 4.5 Hz) (C_6H_5COO–C_3–H), 1.18 (3H, *s*) (C-7 OAc. In spite of these data, it seems difficult to decide the stereochemistry of euphornin by means of ^{1}H NMR because of the flexibility of the 12-membered ring in **28**. In addition to euphornin itself, a number of euphornin derivatives had been subjected to an X-ray crystallographic analysis without success. Finally, however, the stereostructure of euphornin (**28**), including absolute configuration, was determined from X-ray crystallographic analysis of the corresponding *p*-bromobenzoate (**32**) derived from euphornin [10, 12], wherein the flexible 12-membered ring in euphornin was fixed by ketal formation, as follows. When hydrolysed with potassium carbonate in methanol (room temp, 10.5 hr), **28** was converted into monodeacetyleuphornin (**30**), in 70% yield, which was further treated with 2,2-dimethoxypropane–*p*-TsOH in acetone to afford the corresponding acetonide (**29**). This acetonide was hydrolysed again (K_2CO_3 in MeOH; room temp, 60 hr) to give a diol (**31**) which was then treated with *p*-bromobenzoyl chloride–pyridine to afford **32** in 31% yield.

As judged from their ^{1}H NMR spectra, the conformations of **1** and **28** are considerably different. Molecular mechanics calculations and the ^{1}H NMR spectrum of the former indicated that **1** adopts the most stable conformation similar to the stereostructure elucidated by X-ray crystallographic analysis [9, 10]. In the case of **28** [12], the coupling constants in its ^{1}H NMR spectrum are roughly compatible with the corresponding ones calculated on the basis of the most stable conformer which is deduced by molecular mechanics calculations (to be reported in detail elsewhere). However, some remarkable differences are observed in coupling constants ($J_{H\text{-}8\text{-}H\text{-}9}$; $J_{H\text{-}8'\text{-}H\text{-}9}$), strongly suggesting that the conformation of **28** is flexible around C-8 and C-9. In fact, in the variable temperature ^{1}H NMR spectrum of **28** in $CDCl_3$, the broad triplet due to H-9 became sharp gradually with an increase of temperature (30°–85°).

Both euphornin A and B (**33** and **34**), molecular formula $C_{31}H_{42}O_8$, are regarded as deacetyl derivatives of euphornin on the basis of exhaustive comparison of the ^{1}H NMR spectral data among these three diterpenes. As judged from the ^{1}H NMR spectrum, **33** exhibited two acetoxyl groups (δ2.05, 2.22) and one secondary OH group [δ4.09 (HO–C_7–H)]. Euphornin B (**34**) also exhibited two acetoxyl groups [δ1.26, 2.21; 4.92 (AcO–C_7–H), 4.92 (AcO–C_{14}–H)]and one secondary OH group [δ3.34 (HO–C_9–H)] in addition to the benzoyloxyl group at C-3. Clearly, the latter has the acetoxyl group at C-7, the methyl singlet of which was observed at high magnetic field because of the anisotropic effect of the benzoyloxyl group at C-3. Finally, when treated with acetic anhydride–pyridine, **33** and **34** afforded euphornin **28** in *ca* 50% yields, indicating that their stereostructures must be represented by **33** and **34**, respectively.

Euphornin C (**35**), molecular formula $C_{31}H_{40}O_8$ exhibited IR absorption bands at 3500 (OH), 1720 (ester CO) and 1650 (α,β-unsaturated CO) cm^{-1}. Its ^{1}H NMR spectrum indicated the presence of two acetoxyl groups [δ2.01, 2.19; 4.78 (AcO–C_9–H), 4.93 (AcO–C_{14}–H)] and one benzoyloxyl group [δ7.3–7.5 (3H, *m*), 7.92 (2H, *m*)]. As seen in the ^{13}C NMR spectrum, **35** has one CO group (δ199.3), three ester carbonyls (δ165.7, 170.2, 170.5), and four sp^3 carbon atoms bearing an oxygen atom [δ77.2 (*d*), 80.8 (*d*), 81.4 (*d*), 84.4 (*s*)]. From these data together with observation of the broad doublet (J=9 Hz) at lower magnetic field [δ6.93 (H-5)], clearly, the structure of euphornin C is represented by **35**, which has been confirmed by the following chemical evidence. When oxidized with PCC in dichloromethane (room temp, 23 hr), euphornin A was readily converted into **35** in 92% yield.

Euphornin D **36**, molecular formula $C_{35}H_{46}O_{10}$, exhibited IR absorption bands at 1740 cm^{-1} and no OH band. Furthermore, the ^{1}H NMR spectrum indicated the presence of four acetoxyl groups (δ1.10, 1.94, 2.14, 2.29) in addition to the benzoyloxyl group at C-3. Some remarkable differences between euphornin and euphornin D are observed (Table 2). The methyl doublet due to H-14 in the latter (**36**) was exhibited at a lower magnetic field (δ5.97) when compared to the corresponding signal at δ4.95 in **28** by *ca* 1 ppm. This suggests that the acetoxyl group at C-14 in the former is in a β-configuration. In addition, the coupling constant (J=10 Hz) in **36** is larger than the corresponding one (J=3 Hz) in euphornin, indicating that the two vicinal protons (H-13 and H-14) are in a *trans* relationship. From these data, clearly, euphornin D has the structure **36**. This was also confirmed by chemical evidence, as discussed later.

Euphornin E (**37**), molecular formula $C_{33}H_{42}O_8$, had three acetoxyl groups (δ1.31, 1.97, 2.19) in addition to the benzoyloxyl group. As seen in **28**, one of the three acetoxyl groups was located at C-7. This ^{1}H NMR signal was exhibited at a higher magnetic field (δ1.31) because of an anisotropic effect of the benzoyloxyl group at C-3. The ^{13}C NMR spectrum of euphornin E indicated the presence of four ester carbonyls [δ165.1 (*s*), 168.7 (*s*), 169.6 (*s*), 169.7 (*s*)] three sp^3 carbons bearing an oxygen atom [δ72.5 (*d*), 74.6 (*d*), 78.7 (*d*)] and three double bonds [δ122.4 (*d*), 129.6 (*d*), 130.3 (*s*), 131.4 (*s*), 136.0 (*s*), 142.8 (*s*)]. As seen in both **1** and **28**, euphornin E also had one trisubstituted double bond [δ5.32 (1H, *br d*, J=10 Hz)] and one disubstituted one [δ5.09 (1H, *d*, =15.5 Hz), 5.29

Table 2. ^{1}H NMR spectral data (δ-value) of euphornins

Compound	H-3	H-7	H-9	H-14
Euphornin (**28**)	5.42 (*dd*, J=3, 4.5 Hz)	4.95 (*dd*, J=1, 6.5 Hz)	4.77 (*t*, J=3.5 Hz)	4.95 (*d*, J=3 Hz)
Euphornin D (**36**)	5.45 (*dd*, J=3, 4.5 Hz)	4.92*	4.92*	5.97 (*d*, J=10 Hz)
Euphornin G (**39**)	5.43 (*dd*, J=3, 4.5 Hz)	5.04 (*dd*, J=3, 9 Hz)	—	4.94 (*d*, J=3 Hz)
Euphornin H (**44**)	5.46 (*dd*, J=3, 4.5 Hz)	4.86–5.26 (3H, complex)†	—	5.93 (*d*, J=9.5 Hz)

*Overlapped with other signals.

†^{1}H NMR signal due to H-7 must be included.

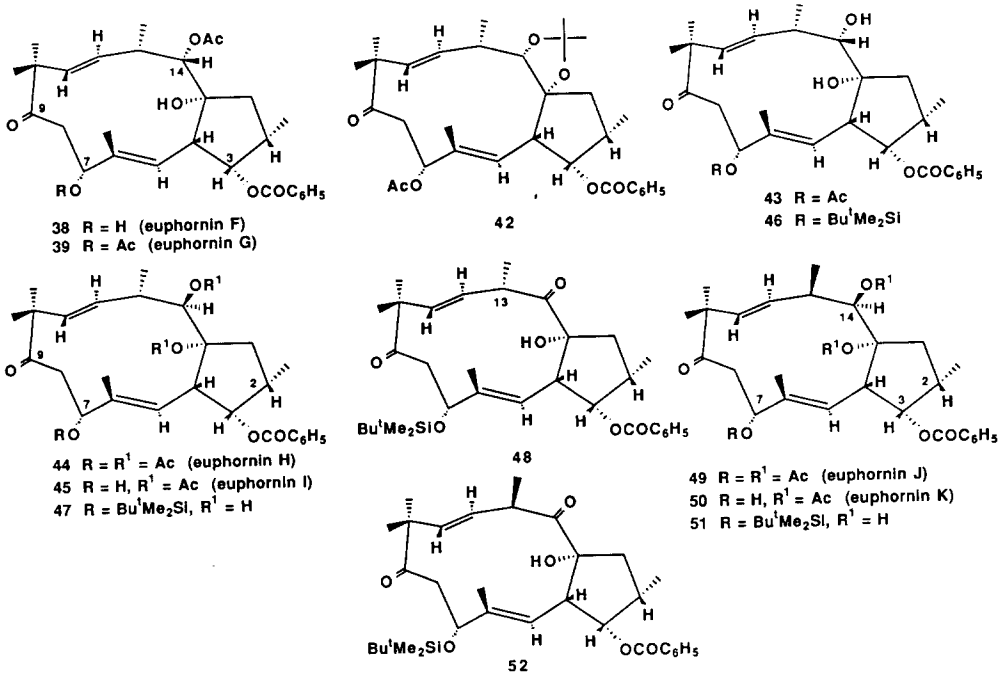
(1H, *dd*, $J = 8.0$, 15.5 Hz)]. The remaining double bond was fully substituted and the ^{1}H NMR signal due to the C-14 proton was absent from the spectrum of euphornin E. From these data, the structure of euphornin E is represented by **37**. Thus, on treatment with thionyl chloride in pyridine containing a trace amount of DMAP (room temp., 100 min), **28** was readily converted into a mixture of two dehydration products, one of which was identical to euphornin E in all respects.

Euphornin F (**38**), molecular formula $C_{29}H_{38}O_7$, exhibited IR absorption bands at 3570 and 3520 (OH), 1720 *br* (ester CO) and 1680 (CO) cm^{-1}. The ^{1}H NMR spectrum indicated the presence of one AcO group (δ2.20) at C-14 [δ4.90 (1H, *d*, $J = 3.0$ Hz)] and one OH group at C-7 [δ4.16 (1H, *dd*, $J = 2.0$, 9.0 Hz)] in addition to the benzoyloxyl group at C-3 [δ5.41 (*dd*, $J = 2.0$, 5.0 Hz)]. Euphornin G (**39**), molecular formula $C_{31}H_{40}O_8$, was similar to **38** in its ^{1}H NMR spectrum except for an extra acetoxyl group [δ1.32 (3H, *s*), 5.04 (1H, *dd*, $J = 3.0$, 9.0 Hz)] instead of the hydroxyl group at C-7. Thus, on acetylation with acetic anhydride–pyridine (room temp., overnight), euphornin F was readily converted into euphornin G in 67% yield. On an exhaustive comparison of ^{1}H NMR spectra between **28** and **39** (Table 2) the chemical shifts (H-3, H-14) and coupling constants both are similar. As judged from the ^{1}H NMR spectral data (δ1.18 in **28**; δ1.32 in **39**), the AcO group at C-7 is in an α-configuration in both diterpenes. However, the ^{1}H NMR signal due to C-7H in euphornin G was different from the corresponding one in **28** in both chemical shift and coupling constant, because of the presence of the CO group at C-9.

Finally, the structures of **38** and **39** were unambiguously determined by means of chemical evidence, as follows. The acetonide (**31**) derived from **28** was treated with acetic anhydride–pyridine (room temp, 6 days) to afford a mixture of two monoacetates (**40** and **41**) in 17 and 36% yields, respectively. The former had the newly formed acetoxyl group (δ1.38) at C-7, whereas the corresponding one (δ2.06) was located at C-9 in **41**. Compound **40** was further oxidized with PCC–Celite in dichloromethane (room temp, 3 days) to afford the corresponding ketone (**42**), in 65% yield, which was also derived from **39** via a deacetyl compound (**43**) in two steps [(1) K_2CO_3 in MeOH (room temp, 2 hr); (2) 2,2-dimethoxypropane–*p*-TsOH in Me_2CO (room temp, 18 hr)].

Euphornin H (**44**), molecular formula $C_{33}H_{42}O_9$, exhibited IR absorption bands at 1740 *br* cm^{-1} and no hydroxyl band. The ^{1}H NMR spectrum of **44** indicated the presence of three acetoxyl groups (δ1.32, 2.14, 2.20) in addition to the benzoyloxyl group. The stereostructure of euphornin H was similar to that of euphornin D (**36**) (Table 2) except for the absence of a ^{1}H NMR signal due to C-9H, but instead the carbonyl group was assigned to that position. Euphornin I (**45**), molecular formula $C_{31}H_{40}O_8$, exhibited IR absorption bands at 3490 (OH), 1740 and 1720 (ester CO), and 1680 (CO) cm^{-1}. Its ^{1}H NMR spectrum indicated the presence of two acetoxyl groups (δ2.13, 2.17), none of which were located at C-7. On acetylation with acetic anhydride–pyridine, euphornin I was converted into euphornin H (**44**). Finally, chemical correlation between euphornin F and I was successfully carried out. Euphornin F (**38**) was treated with ^{t}BuMe$_2$SiCl–imidazole in DMF (room temp, 20 min) and then hydrolysed (K_2CO_3 in MeOH, room temp, 18 hr) to afford a dihydroxy silyl ether (**46**) in good yield. According to essentially the same procedure as described above, **45** was also converted into the corresponding dihydroxy silyl ether (**47**). These two silyl ethers (**46** and **47**) are not identical in their IR and ^{1}H NMR spectra. However, on oxidation (Ac_2O–DMSO, room temp, 3 days), both compounds were converted into the same ketone (**48**) in 78 and 85% yields, respectively.

Euphornin J (**49**), molecular formula $C_{33}H_{42}O_9$, exhibited IR absorption bands at 1740 br cm^{-1} and no OH absorption band. On the basis of its ^{1}H NMR spectrum,

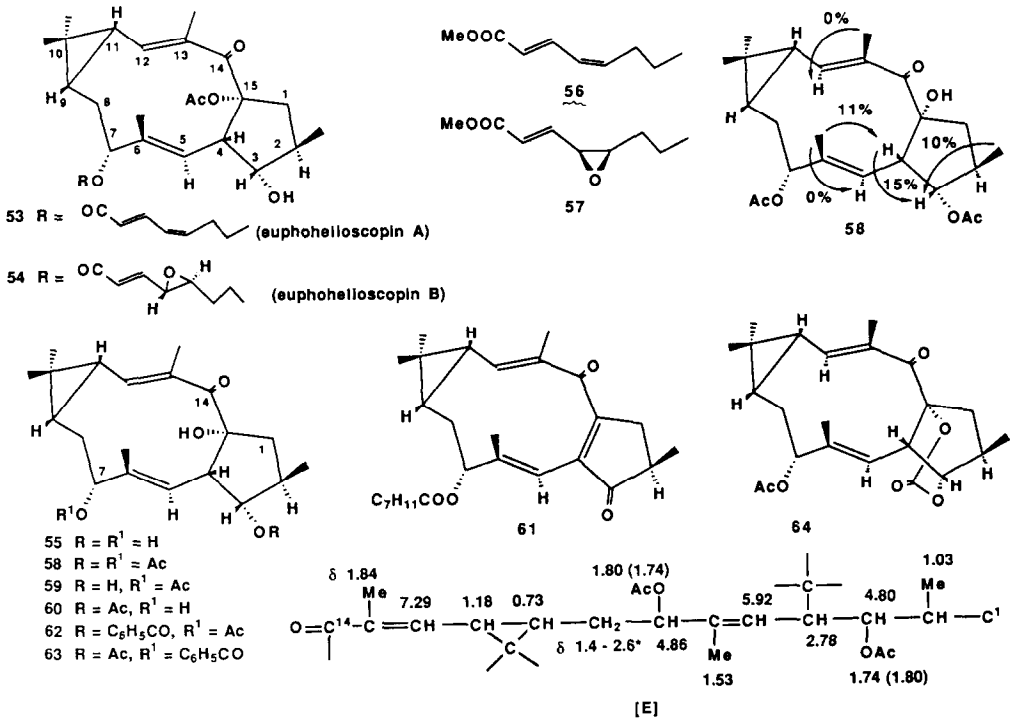


euphornin J had three AcO groups (δ1.33, 2.17, 2.25) and a benzoyloxyl group at C-3, as seen in the case of euphornin H (**44**). However, its ^{1}H NMR signals due to C-7H and C-14H are different from the corresponding ones of **44** in both chemical shifts and coupling constants except for the signal due to C-3H (see Tables 2 and 3). Clearly, euphornin J is similar to **4** (Table 3) in its stereostructure except at C-2, wherein the secondary methyl group was in an α-configuration as seen in **44**. Euphornin K (**50**), molecular formula $C_{31}H_{40}O_8$, has two acetoxyl groups (δ2.13, 2.16) and one hydroxyl group [IR 3500 cm^{-1}; δ4.41 (1H, *m*) (HO-C-7H)], and is regarded as deacetyleuphornin J. On acetylation with acetic anhydride–pyridine, as expected, euphornin K was readily converted into euphornin J (**49**). From these data, the stereostructures of euphornin J and K can be represented by **49** and **50**, respectively, and confirmed by the following chemical evidence. Euphornin K was treated with ^{t}BuMe$_2$SiCl–imidazole in DMF (room temp, overnight) and then hydrolysed (K_2CO_3 in MeOH, room temp, overnight) to afford the corresponding dihydroxy silyl ether (**51**), in good yield, which was not identical with either **46** or **47**. Furthermore, the dihydroxy compound (**51**) was subjected to oxidation using acetic anhydride–DMSO to afford to ketone (**52**), in 77% yield, which was also not identical with the ketone (**48**) derived from euphornin F and I (**38** and **45**), although their spectral data are similar. However, when treated with sodium acetate in DMF (80°, two days), the ketone (**48**) was converted into **52**, in 27% yield, wherein the α-secondary methyl group at C-13 adjacent to the carbonyl group was epimerized to the β-secondary Me group.

Euphohelioscopin A (**53**), molecular formula $C_{30}H_{42}O_6$, exhibited IR absorption bands at 3500, 1735, 1710 and 1620 cm^{-1}. Euphohelioscopin B (**54**) contains an extra oxygen atom in its molecular formula $C_{30}H_{42}O_7$ as compared with euphohelioscopin A. As judged from ^{1}H NMR spectra, both exhibited one acetoxyl group [**53**: $\delta(C_6D_6)$ 1.93; **54**: $\delta(CDCl_3)$ 2.03] and six methyls [**53**: $\delta(C_6D_6)$ 0.72 (3H, *t*, J = 6.5 Hz), 0.85 (3H, *s*), 0.96 (3H, *s*), 1.00 (3H, *d*, J = 6 Hz), 1.58 (3H, *br s*), 1.65 (3H, *s*); **54**: $\delta(CDCl_3)$ 0.96 (3H, *t*, J = 6.5 Hz), 1.07 (3H, *d*, J = 6 Hz), 1.08 (3H, *s*), 1.18 (3H, *s*), 1.55 (3H, *br s*), 1.83 (3H, *s*)], indicating that euphohelioscopin A and B have the same carbon skeleton. On treatment with potassium carbonate in methanol (room temp, 18 hr), they were converted into the same triol (**55**) having the molecular formula $C_{20}H_{30}O_4$, in high yield. In the case of **53**, an $\alpha\beta,\gamma\delta$-unsaturated ester (**56**) was obtained, whose structure was unambiguously determined on the basis of ^{1}H NMR. The geometries of the two double bonds in particular are based on the coupling constants of these four olefinic

Table 3. Comparison of ^{1}H NMR spectral data (δ-value) between euphoscopin B and euphornin J

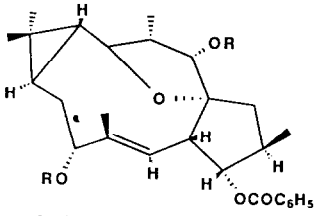
Compound	H-3	H-7	H-9	H-14
Euphoscopin B (**4**)	5.11 (*dd*, J = 3.5, 7 Hz)	5.31 (*dd*, J = 5, 10.5 Hz)	—	5.88 (*d*, J = 1.5 Hz)
Euphornin J (**49**)	5.59 (*dd*, J = 3, 4.5 Hz)	5.26 (*dd*, J = 7, 10.5 Hz)	—	6.07 (*d*, J = 1.5 Hz)



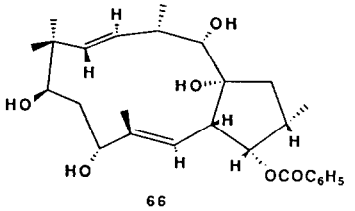
protons [δ5.84 (1H, *dt*, J=7, 10.5 Hz), 5.87 (1H, *d*, J =15 Hz), 6.14 (1H, *dd*, J=10.5, 11 Hz), 7.64 (1H, *dd*, J =11, 15 Hz)]. In the case of euphohelioscopin B (**54**) the corresponding methyl ester was not isolated. However, it should have an α,β-unsaturated ester group containing an epoxide ring at the C-4′–C-5′ position, on the basis of an exhaustive comparison of ^{1}H NMR spectra between **53** and **54** (δ5.56, 5.98, 6.00, 7.87 in **53**; δ2.89, 3.17, 6.12, 6.71 in **54**). The geometry of the epoxide ring must be *trans*, as judged from the coupling constant (J=2 Hz) between H-4′–H-5′, while the corresponding J value is 4.5 Hz in the *cis* epoxide (**57**) which was produced on treatment of **56** with mCPBA. When treated with acetic anhydride (two equivalents)–pyridine (room temp, 10 hr), the triol (**55**) so far obtained was converted into a diacetate (**58**) in addition to two monoacetates (**59** and **60**). On the basis of ^{1}H NMR with the aid of decoupling experiments, a partial structure [E] is present in **58**. In the light of the co-occurrence of euphoscopin A and B (**1** and **4**), euphohelioscopin A has the structure (**53**), in which the partial structure [E] is accommodated, except for the stereochemistry and position of the two ester groups. On oxidation with PCC in dichloromethane (room temp, 10 hr), euphohelioscopin A (**53**) was converted into a conjugated dione (**61**), in 60% yield, exhibiting IR absorption bands at 1745, 1710 and 1665 cm^{-1}. Its ^{1}H NMR spectrum indicated that this oxidation product had neither an acetoxyl group nor a H-4. These results indicate that the $\alpha\beta,\gamma\delta$-unsaturated ester group and the acetoxyl group are located at C-7 and C-15, respectively. The stereochemistry of euphohelioscopin A (**53**) was elucidated by means of NOE experiments in the ^{1}H NMR spectrum of the diacetate (**58**) together with some chemical evidence. When treated with benzoyl chloride–pyridine (room temp, 9 hr), the monoacetates (**59** and **60**) were converted into the corresponding benzoates (**62** and **63**), respectively, which exhibited the following ^{1}H NMR signals: δ1.28 (3H, *s*) (C-7OAc), 5.02 (1H, *dd*, J=6, 8.5 Hz) (C-3H) in **62**; δ1.56 (3H, *s*) (C-3OAc), 5.06 (1H, *dd*, J=3, 11 Hz) in **63**. As seen in the case of **4**, the ^{1}H NMR signal due to the acetoxyl group at C-7 in **62** was observed at a higher magnetic field (δ1.28) than that of **59** (δ2.01), indicating that the two ester groups are present on the same side of the molecule. Furthermore, the stereochemistry of C-15 was elucidated on the basis of some chemical evidence. On treatment with 1,1-carbonyldiimidazole (room temp, 1.5 hr and then 140°, 3 days), **59** was successfully converted into a carbonate ester (**64**), exhibiting IR absorption bands at 1770 cm^{-1}, indicating the both acetoxyl and hydroxyl groups are also present on the same side of the molecule. Finally, the stereochemistry at C-9 and C-11 of euphohelioscopin A (**53**) was unambiguously determined by means of molecular mechanics calculations of the diacetate (**58**), as reported in a previous paper [3]. Thus, the structures of euphohelioscopin A and B are represented by **53** and **54**, respectively, which belong to a group of lathylane-type diterpenes [3].

Euphohelionone (**65**), molecular formula $C_{41}H_{44}O_7$, exhibited IR absorption bands at 1720, 1600, 1580, 1265 and 1110 cm^{-1}, and no OH absorption band. Its ^{1}H NMR spectrum indicated the presence of three benzoyloxyl groups [δ6.85–8.14 (15H, complex)], five methyls [δ0.97 (3H, *d*, J=6.5 Hz), 1.01 (3H, *s*), 1.09 (3H, *s*), 1.14 (3H, *d*, J=7 Hz), 1.84 (3H, *br s*)] and two protons attached to the cyclopropane ring [δ0.10 (1H, *dd*, J=5.5, 6 Hz), 0.90 (1H, *m*)]. Particularly, the coupling constant (J =5.5 Hz) between the two vicinal protons on the cyclopropane ring indicates that they are *trans* to each other. Furthermore, on the basis of the ^{1}H NMR spectrum with the aid of NOE experiments, euphohelionone had two moieties [F and G], which would be accommodated in the skeletons of euphoscopin A (**1**), euphornin (**28**) and euphohelioscopin A (**53**). This suggests that euphohelionone had the tentative structure (**65**) although the stereochemistry remains unsettled. Finally, its stereo structure was unambiguously determined by successful synthesis of euphohelionone from euphornin (**28**).

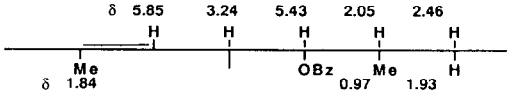
When hydrolysed with potassium carbonate in methanol (room temp., 10.5 hr), euphornin was converted into deacetyleuphornin (**66**) in 20% yield, in addition to monodeacetyleuphornin (**30**). The hydrolysis product (**66**) was further treated with *p*-TsOH in acetone (room temp,



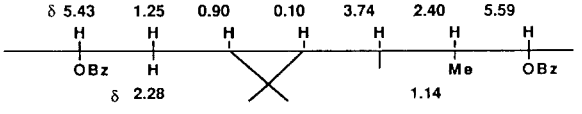
65 R = C_6H_5CO (euphohelionone)
67 R = H



66



[F]



[G]

5.5 hr) to afford a tricyclic compound (**67**) in 76% yield. The newly formed cyclopropane ring was supported by the ^{1}H NMR spectrum: δ0.16 (1H, *t*, J = 5.5 Hz), 0.84 (1H, *dd*, J = 5.5, 11 Hz). Finally, this tricyclic compound (**67**) was treated with benzoyl chloride–pyridine (room temp, 37 hr) to give euphohelionone in 74% yield. Euphohelionone (**65**) is regarded as the first tricyclic diterpene with a *trans* cyclopropane ring different from the lathylane-type such as euphohelioscopin A and B (**53** and **54**) which containing a *cis* cyclopropane ring.

EXPERIMENTAL

Mps: uncorr. Optical rotations were measured in $CHCl_3$. ^{1}H NMR (90 or 200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded in $CDCl_3$ or C_6C_6 with TMS as int st. Mass spectra (70 eV) were measured with a direct inlet system.

Extraction and isolation. Fr leaves and roots of *E. helioscopia* L. (*ca* 100 kg) were collected in Kanagawa Prefecture early in May, directly immersed in MeOH (340 l) at room temp for 30 days, and then concd to leave a greenish oil which was partitioned between H_2O and EtOAc. The EtOAc soln was concd under red pres. to give a greenish oil (*ca* 580 g), which was partitioned between 90% aq MeOH and isooctane. The 90% aq MeOH exts were further partitioned between MeOH–H_2O (17:1) and CCl_4. The CCl_4 layer was dried (Na_2SO_4) and then filtered. The filtrate was concd under red. pres. to give a dark green oil (*ca* 290 g), which was subjected to CC on silica gel (Wakogel C-200) (800 g) using a gradient of hexane–EtOAc (100:0–0:100) to afford 35 frs. Each fr. was further sepd using a Harrison Research Chromatotron Model 7924 [Kieselgel 60 GF_{254}, 4 mm; Me_2CO–hexane (1–20%) and then finally purified by repeated prep. TLC (Kieselgel 60 PF_{254}, 0.25, 0.4 or 1 mm) using hexane–EtOAc (2 or 3), $CHCl_3$–Me_2CO (8 or 10) and/or C_6H_6–EtOAc (6, 7 or 10) to afford 31 new compounds in a pure state.

Euphoscopin A. (**1**, 876 mg) colourless oil: $[\alpha]_D^{25}$ −62.0° ($CHCl_3$; *c* 1.03); IR ν_{max}^{film} cm^{-1}: 3500, 1740, 1710, 1600, 1580; ^{1}H NMR ($CDCl_3$): δ0.91 (3H, *d*, J = 7 Hz), 1.10 (3H, *d*, J = 7 Hz), 1.08 (3H, *s*), 1.22 (3H, *s*), 1.44 (1H, *dd*, J = 9.5, 15 Hz), 1.82 (3H, *dm* J = 1.5 Hz), 2.15 (3H, *s*), 2.18 (3H, *s*), 2.2–2.6 (2H, complex), 2.63 (1H, *dd*, J = 5, 15.5 Hz), 2.99 (1H, *dd*, J = 10.5, 15.5 Hz), 3.01 (1H, *dd*, J = 7, 15 Hz), 3.29 (1H, *dd*, J = 7, 9 Hz), 4.44 (1H, *dd*, J = 5, 10.5 Hz), 5.12 (1H, *dd*, J = 7.5, 15 Hz), 5.23 (1H, *dd*, J = 3.5, 7 Hz), 5.36 (1H, *d*, J = 15 Hz), 5.68 (1H, *dq*, J = 9, 1.5 Hz), 5.93 (1H, *d*, J = 1.5 Hz), 7.35–7.65 (3H, *m*), 7.99 (2H, *m*); MS *m/z*: 540.2706 [M]$^+$ (calc. for $C_{31}H_{40}O_8$ *m/z*: 540.2720).

Euphoscopin B. (**4**, 1.73 g) colourless oil: $[\alpha]_D^{25}$ +19.4° ($CHCl_3$; *c* 0.84); IR ν_{max}^{film} cm^{-1}: 1735, 1720, 1600, 1580; ^{1}H NMR ($CDCl_3$): δ0.92 (3H, *d*, J = 7 Hz), 1.10 (3H, *s*), 1.10 (3H, *d*, J = 7 Hz), 1.25 (3H, *s*), 1.26 (3H, *s*), 1.43 (1H, *dd*, J = 9.5, 15 Hz), 1.85 (3H, *d*, J = 1.5 Hz), 2.14 (3H, *s*), 2.20 (3H, *s*), 2.2–2.6 (2H, complex), 2.63 (1H, *dd*, J = 5, 15.5 Hz), 2.8–3.1 (2H, complex), 3.24 (1H, *dd*, J = 7, 9 Hz), 5.08 (1H, *dd*, J = 7.5, 15 Hz), 5.11 (1H, *dd*, J = 3.5, 7 Hz), 5.31 (1H, *dd*, J = 5, 10.5 Hz), 5.33 (1H, *d*, J = 15 Hz), 5.61 (1H, *dq*, J = 9, 1.5 Hz), 5.88 (1H, *d*, J = 1.5 Hz), 7.25–7.6 (3H, *m*), 7.95 (2H, *m*); MS *m/z*: 582.2806 [M]$^+$ (calc. for $C_{33}H_{42}O_9$ *m/z*: 582.2826).

Euphoscopin C. (**5**, 15 mg) colourless oil: $[\alpha]_D^{25}$ +32.1° ($CHCl_3$; *c* 0.38); IR ν_{max}^{film} cm^{-1}: 1715 br, 1600, 1580; ^{1}H NMR ($CDCl_3$): δ0.93 (3H, *d*, J = 7 Hz), 1.08 (3H, *d*, J = 7 Hz), 1.13 (3H, *s*), 1.29 (3H, *s*), 1.94 (3H, *d*, J = 1.5 Hz), 2.15 (3H, *s*), 2.19 (3H, *s*), 2.38–3.50 (5H, complex), 5.13 (1H, *dd*, J = 2, 7 Hz), 5.17 (1H, *dd*, J = 7.5, 16 Hz), 5.43 (1H, *d*, J = 16 Hz), 5.70 (1H, *dd*, J = 4.5, 11 Hz), 5.88 (1H, *br d*, J = 11 Hz), 5.95 (1H, *d*, J = 1.5 Hz), 6.88–7.04 (3H, *m*), 7.19–7.40 (2H, *m*), 7.46–7.62 (3H, *m*), 7.85 (2H, *m*); MS *m/z*: 644.2975 [M]$^+$ (calc. for $C_{38}H_{44}O_9$ *m/z*: 644.2982).

Euphoscopin D. (**6**, 42 mg) colourless oil: $[\alpha]_D^{25}$ +22.0° ($CHCl_3$; *c* 0.50); IR ν_{max}^{film} cm^{-1}: 1740, 1710, 1675, 1600, 1580; ^{1}H NMR ($CDCl_3$): δ0.91 (3H, *d*, J = 7 Hz), 1.15 (3H, *s*), 1.18 (3H, *d*, J = 7 Hz), 1.32 (3H, *s*), 1.83 (3H, *d*, J = 1.5 Hz), 2.15 (3H, *s*), 2.22 (3H, *s*), 2.35–2.62 (2H, complex), 3.02 (1H, *d*, J = 15 Hz), 3.11 (1H, *dd*, J = 7.5, 15 Hz), 3.27 (1H, *t*, J = 7.5 Hz), 4.50 (1H, *d*, J = 15 Hz), 5.27 (1H, *dd*, J = 8, 15 Hz), 5.32 (1H, *dd*, J = 3, 7.5 Hz), 5.55 (1H, *d*, J = 15 Hz), 5.88 (1H, *d*, J = 1.5 Hz), 6.77 (1H, *br d*, J = 7.5 Hz), 7.40–7.57 (3H, *m*), 7.92 (2H, *m*); MS *m/z*: 538.2545 [M]$^+$ (calc. for $C_{31}H_{38}O_8$ *m/z*: 538.2564).

Euphoscopin E. (**7**, 514 mg) colourless oil: $[\alpha]_D^{25}$ −53.4° ($CHCl_3$; *c* 0.36); IR ν_{max}^{film} cm^{-1}: 3500, 1735, 1710, 1600, 1580; ^{1}H NMR ($CDCl_3$): δ1.10 (3H, *s*), 1.12 (3H, *d*, J = 7 Hz), 1.16 (3H, *s*), 1.21 (3H, *d*, J = 7 Hz), 1.54 (3H, *d*, J = 1.5 Hz), 2.27 (3H, *s*), 2.54–2.92 (2H, complex), 3.11 (1H, *dd*, J = 6, 10 Hz), 3.38 (1H, *dd*, J = 7, 10 Hz), 4.35 (1H, *br dd*, J = 6, 10 Hz), 5.05 (1H, *dd*, J = 9, 16 Hz), 5.16 (1H, *dd*, J = 2, 7 Hz), 5.49 (1H, *d*, J = 16 Hz), 5.81 (1H, *dq*, J = 10, 1.5 Hz), 7.42–7.64 (3H, *m*), 8.02 (2H, *m*); MS *m/z*: 496.2471 [M]$^+$ (calc. for $C_{29}H_{36}O_7$ *m/z*: 496.2461).

Euphoscopin F. (**8**, 76 mg) colourless oil: $[\alpha]_D^{25}$ +16.5° ($CHCl_3$; *c* 0.66); IR ν_{max}^{film} cm^{-1}: 1735, 1710, 1600, 1580; ^{1}H NMR ($CDCl_3$): δ1.10 (3H, *s*), 1.15 (3H, *d*, J = 7 Hz), 1.22 (3H, *s*), 1.26 (3H, *d*, J = 7 Hz), 1.30 (3H, *s*), 1.66 (3H, *d*, J = 1.5 Hz), 2.34 (3H, *s*), 2.59–3.36 (4H, complex), 3.49 (1H, *dd*, J = 2, 7.5 Hz), 5.02 (1H, *dd*, J = 9, 15 Hz), 5.13–5.36 (2H, complex), 5.55 (1H, *d*, J = 15 Hz), 5.73 (1H, *dq*, J = 9, 1.5 Hz), 7.44–7.59 (3H, *m*), 8.05 (2H, *m*); MS *m/z*: 538.2602 [M]$^+$ (calc. for $C_{31}H_{38}O_8$ *m/z*: 538.2564).

Euphoscopin G. (**12**, 1.6 mg) colourless oil: $[\alpha]_D^{25}$ *ca* +4° ($CHCl_3$; *c* 0.025); IR ν_{max}^{film} cm^{-1}: 3500, 1740, 1600, 1580; ^{1}H NMR ($CDCl_3$): δ0.93 (3H, *d*, J = 7 Hz), 1.08 (3H, *d*, J = 7 Hz), 1.09 (3H, *s*), 1.22 (3H, *s*), 1.82 (3H, δ, J = 1.5 Hz), 2.16 (3H, *s*), 2.43 (1H, *m*), 2.70 (1H, *dd*, J = 4.5, 15.5 Hz), 2.94 (1H, *m*), 2.96 (1H, *dd*, J = 10, 15.5 Hz), 3.16 (1H, *dd*, J = 7, 8.5 Hz), 4.39 (1H, *dd*, J = 4.5, 10 Hz), 5.14 (1H, *d*, J = 1.5 Hz), 5.15 (1H, *dd*, J = 9, 16 Hz), 5.16 (1H, *dd*, J = 4, 7 Hz), 5.44 (1H, *d*, J = 16 Hz), 5.61 (1H, *dq*, J = 8.5, 1.5 Hz), 7.4–7.6 (3H, *m*), 7.95 (2H, *m*); MS *m/z*: 480.2533 [M−H_2O]$^+$ (calc. for $C_{29}H_{38}O_7$ *m/z*: 480.2510).

Euphoscopin H. (**13**, 31 mg): mp 177–179° (from hexane–EtOAc); $[\alpha]_D^{25}$ +71.5° ($CHCl_3$; *c* 0.20); IR ν_{max}^{film} cm^{-1}: 3500, 1735, 1715, 1600, 1580; ^{1}H NMR ($CDCl_3$): δ0.95 (3H, *d*, J = 7 Hz), 1.08 (3H, *d*, J = 7 Hz), 1.10 (3H, *s*), 1.24 (3H, *s*), 1.27 (3H, *s*), 1.87 (3H, *d*, J = 1.5 Hz), 2.15 (3H, *s*), 2.38 (1H, *m*), 2.71 (1H, *dd*, J = 5, 16 Hz), 3.00 (1H, *m*), 3.13 (1H, *dd*, J = 6.5, 8 Hz), 3.16 (1H, *dd*, J = 11, 16 Hz), 5.11 (1H, *dd*, J = 3, 6.5 Hz), 5.15 (1H, *d*, J = 1.5 Hz), 5.18 (1H, *dd*, J = 8.5, 16 Hz), 5.36 (1H, *dd*, J = 5, 11.5 Hz), 5.48 (1H, *d*, J = 16 Hz), 5.64 (1H, *dq*, J = 8, 1.5 Hz), 7.2–7.5 (3H, *m*), 7.95 (2H, *m*); MS *m/z*: 540.2693 [M]$^+$ (calc. for $C_{31}H_{40}O_8$ m/z: 540.2720).

Euphoscopin I. (**14**, 15 mg) colourless oil: IR ν_{max}^{film} cm^{-1}: 3490, 1730, 1710, 1600, 1580; ^{1}H NMR ($CDCl_3$): δ1.03 (3H, *d*, J = 7 Hz), 1.10 (3H, *s*), 1.16 (3H, *d*, J = 7 Hz), 1.22 (3H, *s*), 1.79 (3H, *d*, J = 1.5 Hz), 1.5–1.87 (2H, complex), 2.17 (3H, *s*), 2.32 (1H, *m*), 2.62 (1H, *dd*, J = 5, 15.5 Hz), 2.85 (1H, *m*), 2.98 (1H, *dd*, J = 10.5, 15.5 Hz), 3.52 (1H, *dd*, J = 7, 9 Hz), 4.36 (1H, *dd*, J = 5, 10.5 Hz), 4.46 (1H, *dd*, J = 1, 1.5 Hz), 5.1–5.3 (2H, complex), 5.42 (1H, *d*, J = 15.5 Hz), 5.67 (1H, *dq*, J = 9, 1.5 Hz), 7.35–7.63 (3H, *m*), 8.01 (2H, *m*); MS *m/z*: 498.2632 [M]$^+$ (calc. for $C_{29}H_{38}O_7$ *m/z*: 498.2615).

Euphoscopin J. (**15**, 8.7 mg) colourless oil: $[\alpha]_D^{25}$ +49.4° ($CHCl_3$; *c* 0.31); IR ν_{max}^{film} cm^{-1}: 3540, 1735, 1715, 1600, 1585; ^{1}H NMR ($CDCl_3$): δ1.06 (3H, *d*, J = 7 Hz), 1.10 (3H, *s*), 1.17 (3H, *d*, J = 7 Hz), 1.22 (3H, *s*), 1.24 (3H, *s*), 1.73 (1H, *m*), 1.83 (3H, *d*, J = 1.5 Hz), 2.18 (1H, *m*), 2.21 (3H, *s*), 2.37 (1H, *m*), 2.67 (1H, *dd*, J = 4.5, 15.5 Hz), 2.96 (1H, *dd*, J = 8, 14.5 Hz), 3.13 (1H, *dd*, J = 11.5, 15.5 Hz), 3.48 (1H, *dd*, J = 7, 8 Hz), 4.50 (1H, *br s*), 5.24 (1H, *dd*, J = 2.5, 7 Hz), 5.35 (1H, *dd*, J = 4.5, 11.5 Hz), 5.3–5.44

(2H, complex), 5.65 (1H, *dq*, *J* = 8, 1.5 Hz), 7.35–7.6 (3H, *m*), 8.10 (2H, *m*); MS *m/z*: 540.2710 $[M]^+$ (calc. for $C_{31}H_{40}O_8$ *m/z*: 540.2720).

Euphoscopin K. (**16**, 6.6 mg) amorphous powder: $[\alpha]_D^{25}$ +63.7° ($CHCl_3$; *c* 0.22); IR ν_{max}^{film} cm^{-1}: 3500, 1715, 1695, 1600, 1580; ^1H NMR ($CDCl_3$): δ 1.09 (3H, *d*, *J* = 8 Hz), 1.09 (3H, *s*), 1.16 (3H, *d*, *J* = 7 Hz), 1.23 (3H, *s*), 1.27 (3H, *s*), 1.84 (3H, *d*, *J* = 1.5 Hz), 2.38 (1H, *m*), 2.67 (1H, *dd*, *J* = 5, 15.5 Hz), 2.93 (1H, *m*), 3.15 (1H, *dd*, *J* = 11, 15.5 Hz), 3.28 (1H, *dd*, *J* = 7, 10 Hz), 3.67 (1H, *d*, *J* = 5.5 Hz), 5.16 (1H, *dd*, *J* = 2.5, 7 Hz), 5.29 (1H, *dd*, *J* = 8, 16 Hz), 5.32 (1H, *dd*, *J* = 5, 11 Hz), 5.48 (1H, *d*, *J* = 16 Hz), 5.62 (1H, *dq*, *J* = 10, 1.5 Hz), 7.4–7.6 (3H, *m*), 7.94 (2H, *m*); MS *m/z*: 498.2638 $[M]^+$ (calc. for $C_{29}H_{38}O_7$ *m/z*: 498.2615).

Euphoscopin L. (**18**, 5 mg) colourless oil: IR ν_{max}^{film} cm^{-1}: 3480, 1740, 1720, 1680, 1670, 1600, 1580; ^1H NMR ($CDCl_3$): δ 1.06 (3H, *s*), 1.17 (3H, *d*, *J* = 7 Hz), 1.23 (3H, *s*), 1.42 (3H, *d*, *J* = 1.5 Hz), 1.75 (3H, *d*, *J* = 1.5 Hz), 2.18 (3H, *s*), 2.97–3.18 (2H, complex), 4.13 (1H, *m*), 5.02 (1H, *dd*, *J* = 4, 7.5 Hz), 5.95 (1H, *dq*, *J* = 10, 1.5 Hz), 6.42 (1H, *ddq*, *J* = 6.5, 6.5, 1.5 Hz), 7.34–7.67 (3H, *m*), 8.06 (2H, *m*); MS *m/z*: 496.2458 $[M]^+$ (calc. for $C_{29}H_{36}O_7$ *m/z*: 496.2458).

Epieuphoscopin A. (**19**, 73 mg) colourless oil: $[\alpha]_D^{25}$ −79.5° ($CHCl_3$; *c* 0.48); IR ν_{max}^{film} cm^{-1}: 3480, 1740, 1720, 1680, 1600, 1580; ^1H NMR ($CDCl_3$): δ 0.96 (3H, *d*, *J* = 7 Hz), 1.03 (3H, *d*, *J* = 7 Hz), 1.08 (3H, *s*), 1.18 (3H, *s*), 1.57 (3H, *d*, *J* = 1.5 Hz), 2.12 (3H, *s*), 2.14 (3H, *s*), 3.00 (1H, *br dd*, *J* = 2, 14 Hz), 3.55 (1H, *dd*, *J* = 9, 11 Hz), 3.89 (1H, *m*), 4.56 (1H, *d*, *J* = 8 Hz), 4.64 (1H, *t*, *J* = 9 Hz), 5.12 (2H, *m*), 5.46 (1H, *dq*, *J* = 11, 1.5 Hz), 5.92 (1H, *d*, *J* = 10 Hz), 7.3–7.5 (3H, *m*), 7.93 (2H, *m*); MS *m/z*: 540.2706 $[M]^+$ (calc. for $C_{31}H_{40}O_8$ *m/z*: 540.2720).

Epieuphoscopin B. (**23**, 1.04 g): mp 148–150° (from hexane–C_6H_6); $[\alpha]_D^{25}$ −25.2° ($CHCl_3$; *c* 0.78); IR ν_{max}^{film} cm^{-1}: 1740, 1720, 1600, 1580: ^1H NMR ($CDCl_3$): δ 1.02 (3H, *d*, *J* = 6.5 Hz), 1.12 (3H, *d*, *J* = 7 Hz), 1.13 (3H, *s*), 1.18 (3H, *s*), 1.52 (3H, *s*), 1.74 (3H, *d*, *J* = 1.5 Hz), 2.14 (3H, *s*), 2.15 (3H, *s*), 2.2–2.5 (3H, complex), 2.73 (1H, *dd*, *J* = 3.5, 14 Hz), 2.93 (1H, *dd*, *J* = 9.5, 14 Hz), 2.93 (1H, *dd*, *J* = 7.5, 14 Hz), 3.33 (1H, *dd*, *J* = 7.5, 9.5 Hz), 5.01 (1H, *dd*, *J* = 5.5, 15.5 Hz), 5.08 (1H, *dd*, *J* = 3.5, 9.5 Hz), 5.26 (1H, *d*, *J* = 15.5 Hz), 5.34 (1H, *dd*, *J* = 6.5, 15.5 Hz), 5.66 (1H, *dq*, *J* = 9, 1.5 Hz), 5.87 (1H, *d*, *J* = 8.5 Hz), 7.3–7.6 (3H, *m*), 7.95 (2H, *m*); MS *m/z*: 582.2795 $[M]^+$ (calc. for $C_{33}H_{42}O_9$ *m/z*: 582.2826).

Epieuphoscopin D. (**24**, 5.6 mg) colourless oil: $[\alpha]_D^{25}$ +31.1° ($CHCl_3$; *c* 0.23); IR ν_{max}^{film} cm^{-1}: 1745, 1720, 1655, 1600, 1580; ^1H NMR ($CDCl_3$): δ 0.92 (3H, *d*, *J* = 6.5 Hz), 1.13 (3H, *d*, *J* = 7 Hz), 1.21 (3H, *s*), 1.24 (3H, *s*), 1.89 (3H, *d*, *J* = 1 Hz), 2.15 (1H, *m*), 2.16 (3H, *s*), 2.33 (3H, *s*), 2.80 (1H, *dd*, *J* = 7.5, 15 Hz), 3.32 (1H, *d*, *J* = 13.5 Hz), 3.47 (1H, *dd*, *J* = 7.5, 10 Hz), 3.88 (1H, *d*, *J* = 13.5 Hz), 5.03 (1H, *d*, *J* = 16 Hz), 5.18 (1H, *dd*, *J* = 4.5, 7.5 Hz), 5.32 (1H, *dd*, *J* = 10, 16 Hz), 5.99 (1H, *d*, *J* = 10 Hz), 7.00 (1H, *dq*, *J* = 10, 1 Hz), 7.4–7.6 (3H, *m*), 8.00 (2H, *m*); MS *m/z*: 538.2554 $[M]^+$ (calc. for $C_{31}H_{38}O_8$ *m/z*: 538.2564).

Epieuphoscopin F. (**25**, 3.1 mg): mp 142–143° (from hexane–EtOAc); IR ν_{max}^{film} cm^{-1}: 1740, 1710, 1600, 1580: ^1H NMR ($CDCl_3$): δ 1.10 (3H, *s*), 1.15 (3H, *d*, *J* = 7.5 Hz), 1.21 (3H, *s*), 1.30 (3H, *d*, *J* = 7.5 Hz), 1.43 (3H, *s*), 1.63 (3H, *d*, *J* = 1.5 Hz), 2.26 (3H, *s*), 3.45 (1H, *dd*, *J* = 6.5, 7.5 Hz), 5.11 (1H, *dd*, *J* = 4.5, 10.5 Hz), 5.24 (1H, *d*, *J* = 15 Hz), 5.33 (1H, *dd*, *J* = 3.5, 6.5 Hz), 5.50 (1H, *dq*, *J* = 7.5, 1.5 Hz), 5.53 (1H, *dd*, *J* = 7, 15 Hz), 7.4–7.6 (3H, *m*), 7.98 (2H, *m*); MS *m/z*: 538.2545 $[M]^+$ (calc. for $C_{31}H_{38}O_8$ *m/z*: 538.2564).

Euphornin. (**28**, 5.04 g): mp 206–208° (from hexane–EtOAc); $[\alpha]_D^{25}$ −3.2 ($CHCl_3$; *c* 0.70); IR ν_{max}^{film} cm^{-1}: 3550, 1730 *br*, 1600, 1580: ^1H NMR ($CDCl_3$): δ 0.88 (3H, *s*), 0.96 (6H, *d*, *J* = 6 Hz), 0.96 (3H, *s*), 1.18 (3H, *s*), 1.75 (3H, *d*, *J* = 1.5 Hz), 1.96 (3H, *s*), 2.22 (3H, *s*), 2.57 (1H, *ddq*, *J* = 3, 9.5, 6.5 Hz), 2.88 (1H, *dd*, *J* = 4.5, 10 Hz), 4.77 (1H, *t*, *J* = 3.5 Hz), 4.95 (1H, *d*, *J* = 3 Hz), 4.95 (1H, *dd*, *J* = 1, 6.5 Hz), 5.06 (1H, *d*, *J* = 15.5 Hz), 5.42 (1H, *dd*, *J* = 3, 4.5 Hz), 5.65 (1H, *dd*, *J* = 9.5, 15.5 Hz), 5.74 (1H, *dd*, *J* = 1.5, 10 Hz), 7.4–7.6 (3H, *m*), 8.06 (2H, *m*); ^{13}C NMR ($CDCl_3$): δ 13.5 (*q*), 16.1 (*q*), 19.3 (*q*), 19.7 (*q*), 20.2 (*q*), 20.9 (*q*), 20.9 (*q*), 22.6 (*q*), 32.3 (*t*), 36.6 (*d*), 39.3 (*d*), 39.5 (*s*), 46.2 (*t*), 47.7 (*d*), 72.8 (*d*), 73.4 (*d*), 80.6 (*d*), 80.7 (*d*), 83.5 (*s*), 119.8 (*d*), 128.1 (*d* × 2), 128.6 (*d*), 129.4 (*d* × 2), 130.0 (*s*), 132.4 (*d*), 133.4 (*s*), 137.5 (*d*), 165.1 (*s*), 168.4 (*s*), 169.0 (*s*), 170.6 (*s*); MS *m/z* 542.2891 $[M-C_2H_2O]^+$ (calc. for $C_{33}H_{44}O_9$ *m/z*: 542.2877).

Euphornin A. (**33**, 700 mg): mp 98–102° (from hexane–EtOAc); $[\alpha]_D^{25}$ −14.3° ($CHCl_3$; *c* 1.33); IR ν_{max}^{film} cm^{-1}: 3470, 1710 br, 1600, 1580; ^1H NMR ($CDCl_3$): δ 0.94 (6H, *s*), 0.96 (3H, *d*, *J* = 7 Hz), 0.99 (3H, *d*, *J* = 7 Hz), 1.68 (3H, *br s*), 2.05 (3H, *s*), 2.22 (3H, *s*), 2.97 (1H, *dd*, *J* = 5, 10.5 Hz), 4.09 (1H, *br d*, *J* = 6 Hz), 4.37 (1H, *dd*, *J* = 1.5, 4.5 Hz), 4.95 (1H, *d*, *J* = 3 Hz), 5.05 (1H, *d*, *J* = 16.5 Hz), 5.41 (1H, *dd*, *J* = 4, 5 Hz). 5.63 (1H, *dd*, *J* = 9, 16.5 Hz), 5.82 (1H, *br d*, *J* = 10.5 Hz), 7.4–7.6 (3H, *m*), 8.07 (2H, *m*); MS *m/z*: 525.2870 $[M-OH]^+$ (calc. for $C_{13}H_{41}O_7$ *m/z*: 525.2850).

Euphornin B. (**34**, 18 mg) colourless oil: IR ν_{max}^{film} cm^{-1}: 3530, 1730 *br*, 1600, 1580; ^1H NMR ($CDCl_3$): δ 0.85 (3H, *s*), 0.95 (6H, *d*, *J* = 6 Hz), 1.10 (3H, *s*), 1.26 (3H, *s*), 1.72 (3H, *br s*), 2.21 (3H, *s*), 2.86 (1H, *dd*, *J* = 4.5, 10 Hz), 3.34 (1H, *dd*, *J* = 3, 3.5 Hz), 4.92 (1H, *br d*, *J* = 6 Hz), 4.92 (1H, *d*, *J* = 3 Hz), 5.05 (1H, *d*, *J* = 15 Hz), 5.36–5.74 (3H, complex), 7.4–7.6 (3H, *m*), 8.06 (2H, *m*); MS *m/z*: 524.2879 $[M-H_2O]^+$ (calc. for $C_{31}H_{42}O_7$ *m/z*: 524.2877).

Euphornin C. (**35**, 16 mg) colourless oil: $[\alpha]_D^{25}$ +30.3° ($CHCl_3$; *c* 0.35); IR ν_{max}^{film} cm^{-1}: 3500, 1720 *br*, 1650 *br*, 1600, 1580; ^1H NMR ($CDCl_3$): δ 0.91 (3H, *d*, *J* = 6 Hz), 0.93 (3H, *s*), 0.97 (3H, *d*, *J* = 6 Hz), 1.15 (3H, *s*), 1.81 (3H, *br s*), 2.01 (3H, *s*), 2.17 (3H, *s*), 2.85 (1H, *dd*, *J* = 4.5, 9 Hz), 3.23 (1H, *br dd*, *J* = 2, 13.5 Hz), 4.78 (1H, *dd*, *J* = 2, 9 Hz), 4.93 (1H, *d*, *J* = 2 Hz), 5.03 (1H, *d*, *J* = 16.5 Hz), 5.49–5.74 (2H, complex), 6.93 (1H, *br d*, *J* = 9 Hz), 7.3–7.5 (3H, *m*), 7.92 (2H, *m*); ^{13}C NMR ($CDCl_3$): δ 12.2 (*q*), 14.4 (*q*), 19.8 (*q*), 20.8 (*q*), 21.0 (*q*), 23.9 (*q*), 25.7 (*q*), 36.4 (*t*), 37.8 (*t*), 39.7 (*d*), 40.0 (*s*), 49.1 (*t*), 50.1 (*d*), 77.2 (*d*), 80.8 (*d*), 81.4 (*d*), 84.4 (*s*), 128.5 (*d* × 2), 128.9 (*d*), 129.7 (*d* × 2), 130.1 (*s*), 133.0 (*d*), 137.8 (*s*), 138.1 (*d*), 140.5 (*d*), 165.7 (*s*), 170.2 (*s*), 170.5 (*s*), 199.3 (*s*); MS *m/z*: 540.2682 $[M]^+$ (calc. for $C_{31}H_{40}O_8$ *m/z*: 540.2720).

Euphornin D. (**36**, 9.1 mg) colourless oil: IR ν_{max}^{film} cm^{-1}: 1740, 1680, 1600, 1580; ^1H NMR ($CDCl_3$): δ 0.91 (6H, *s*), 0.93 (6H, *d*, *J* = 6 Hz), 1.10 (3H, *s*), 1.74 (3H, *br s*), 1.94 (3H, *s*), 2.14 (3H, *s*), 2.29 (3H, *s*), 3.28 (1H, *dd*, *J* = 4.5, 11 Hz), 4.92 (2H complex), 4.94 (1H, *d*, *J* = 16 Hz), 5.25 (1H, *d*, *J* = 16 Hz), 5.45 (1H, *dd*, *J* = 3, 4.5 Hz), 5.81 (1H, *br d*, *J* = 11 Hz), 5.97 (1H, *d*, *J* = 10 Hz), 7.4–7.7 (3H, *m*), 8.03 (2H, *m*); MS *m/z*: 626.3111 $[M]^+$ (calc. for $C_{35}H_{46}O_{10}$ *m/z*: 626.3088).

Euphornin E. (**37**, 2.9 mg) colourless oil: $[\alpha]_D^{25}$ −41.4° ($CHCl_3$; *c* 1.08); IR ν_{max}^{film} cm^{-1}: 1750, 1725, 1600, 1580; ^1H NMR ($CDCl_3$): δ 0.90 (3H, *s*), 1.02 (3H, *d*, *J* = 7 Hz), 1.06 (3H, *d*, *J* = 6.5 Hz), 1.31 (3H, *s*), 1.64 (3H, *d*, *J* = 1 Hz), 1.93 (2H, complex), 1.97 (3H, *s*), 2.19 (3H, *s*), 2.24–2.38 (3H, complex), 2.99 (1H, *dq*, 8, 7 Hz), 3.94 (1H, *dd*, *J* = 7, 10 Hz), 4.77 (1H, *t*, *J* = 3.5 Hz), 4.91 (1H, *br t*, *J* = 4 Hz), 5.09 (1H, *d*, *J* = 15.5 Hz), 5.29 (1H, *dd*, *J* = 8, 15.5 Hz), 5.32 (1H, *br d*, *J* = 10 Hz), 5.56 (1H, *dd*, *J* = 5, 7 Hz), 7.37–7.56 (3H, *m*), 7.99 2H, m). An $[M]^+$ peak was not been observed in the HRMS but the stereostructure is supported by the above mentioned spectral data.

Euphornin F. (**38**, 59 mg) colourless oil: IR ν_{max}^{film} cm^{-1}: 3570, 3500, 1720 *br*, 1680, 1600, 1580; ^1H NMR ($CDCl_3$): δ 1.17 (3H, *s*), 1.22 (3H, *s*), 1.72 (3H, *d*, *J* = 1.5 Hz), 2.20 (3H, *s*), 2.45 (1H, *dd*, *J* = 7, 15 Hz), 2.88 (1H, *dd*, *J* = 5, 12.5 Hz), 3.06 (1H, *dd*, *J* = 2, 15 Hz), 4.16 (1H, *ddd*, *J* = 2, 7, 9 Hz), 4.90 (1H, *d*, *J* = 3 Hz), 5.23 (1H, *d*, *J* = 15.5 Hz), 5.41 (1H, *dd*, *J* = 2, 5 Hz), 5.54 (1H, *dq*, *J* = 12.5, 1.5 Hz), 5.76 (1H, *dd*, *J* = 8.5, 15.5 Hz), 7.3–7.6 (3H, *m*), 8.02 (2H, *m*); MS *m/z*: 498.2603 $[M]^+$ (calc. for $C_{29}H_{38}O_7$ *m/z*: 498.2615).

Euphornin G. (**39**, 164 mg) colourless oil: IR ν_{max}^{film} cm^{-1}: 3520,

1730 *br*, 1600, 1580; ^{1}H NMR ($CDCl_3$): δ0.96 (3H, *d*, J = 5.5 Hz), 0.99 (3H, *d*, J = 7 Hz), 1.11 (3H, *s*), 1.20 (3H, *s*), 1.33 (3H, *s*), 1.76 (3H, *d*, J = 1.5 Hz), 2.22 (3H, *s*), 2.46–2.07 (5H, complex), 4.94 (1H, *d*, J = 3 Hz), 5.04 (1H, *dd*, J = 3, 9 Hz), 5.14 (1H, *d*, J = 15.5 Hz), 5.43 (1H, *dd*, J = 3, 4.5 Hz), 5.68 (1H, *dq*, J = 10, 1.5 Hz), 5.74 (1H, *dd*, J = 8, 15.5 Hz), 7.4–7.5 (3H, *m*), 8.04 (2H, *m*); MS *m/z*: 540.2692 $[M]^+$ (calc. for $C_{31}H_{40}O_8$ *m/z*: 540.2720).

Euphornin H. (**44**, 57 mg) colourless oil: $[\alpha]_D^{25}$ +1.5° ($CHCl_3$; *c* 0.46); IR ν_{max}^{film} cm^{-1}: 1740 *br*, 1600, 1580; ^{1}H NMR ($CDCl_3$): δ0.91 (3H, *d*, J = 6 Hz), 0.98 (3H, *d*, J = 6 Hz), 1.13 (3H, *s*), 1.16 (3H, *s*), 1.32 (3H, *s*), 1.81 (3H, *d*, J = 1.5 Hz), 2.14 (3H, *s*), 2.20 (3H, *s*), 3.24 (1H, *dd*, J = 4.5, 10.5 Hz), 4.86–5.26 (3H, complex), 5.46 (1H, *dd*, J = 3, 4.5 Hz), 5.71 (1H, *dq*, J = 10.5, 1.5 Hz), 5.93 (1H, *d*, J = 9.5 Hz), 7.3–7.7 (3H, complex), 7.98 (2H, *m*); MS *m/z*: 582.2803 $[M]^+$ (calc. for $C_{33}H_{42}O_9$ *m/z*: 582.2825).

Euphornin I. (**45**, 33 mg) colourless oil: IR ν_{max}^{film} cm^{-1}: 3490, 1745, 1720, 1680, 1600, 1580; ^{1}H NMR ($CDCl_3$): δ0.91 (3H, *d*, J = 6.5 Hz), 0.94 (3H, *d*, J = 7 Hz), 1.09 (3H, *s*), 1.19 (3H, *s*), 1.71 (3H, *d*, J = 1.5 Hz), 2.13 (3H, *s*), 2.17 (3H, *s*), 3.02 (1H, *dd*, J = 2, 16.5 Hz), 3.25 (1H, *dd*, J = 4.5, 11 Hz), 4.16 (1H, *m*), 5.10 (1H, *d*, J = 15 Hz), 5.30 (1H, *dd*, J = 7, 15 Hz), 5.43 (1H, *dd*, J = 4, 4.5 Hz), 5.58 (1H, *dq*, J = 11, 1.5 Hz), 5.91 (1H, *d*, J = 10 Hz), 7.3–7.7 (3H, *m*), 7.97 (2H, *m*); MS *m/z*: 540.2686 $[M]^+$ (calc. for $C_{31}H_{40}O_8$ *m/z*: 540.2720).

Euphornin J. (**49**, 6.6 mg) colourless oil: IR ν_{max}^{film} cm^{-1}: 1740 *br*, 1600, 1580; ^{1}H NMR ($CDCl_3$): δ0.91 (3H, *d*, J = 6 Hz), 0.92 (3H, *d*, J = 7 Hz), 1.10 (3H, *s*), 1.21 (3H, *s*), 1.33 (3H, *s*), 1.87 (3H, *d*, J = 1.5 Hz), 2.17 (3H, *s*), 2.25 (3H, *s*), 2.66 (1H, *dd*, J = 7, 15 Hz), 3.06 (1H, *dd*, J = 10.5, 15 Hz), 3.28 (1H, *dd*, J = 4.5, 7.5 Hz), 5.11 (1H, *dd*, J = 8, 16.5 Hz), 5.26 (1H, *dd*, J = 7, 10.5 Hz), 5.40 (1H, *d*, J = 16.5 Hz), 5.59 (1H, *dd*, J = 3, 4.5 Hz), 5.72 (1H, *dq*, J = 7.5, 1.5 Hz), 6.07 (1H, *d*, J = 1.5 Hz), 7.4–7.7 (3H, *m*), 7.99 (2H, *m*); MS *m/z*: 582.2808 $[M]^+$ (calc. for $C_{33}H_{42}O_9$ *m/z*: 582.2826).

Euphornin K. (**50**, 55 mg) colourless oil: IR ν_{max}^{film} cm^{-1}: 3500, 1740, 1710, 1600, 1580; ^{1}H NMR ($CDCl_3$): δ0.89 (3H, *d*, J = 6.5 Hz), 0.94 (3H, *d*, J = 6 Hz), 1.08 (3H, *s*), 1.15 (3H, *s*), 1.85 (3H, *d*, J = 1.5 Hz), 2.13 (3H, *s*), 2.16 (3H, *s*), 3.28 (1H, *dd*, J = 4, 8 Hz), 4.41 (1H, *m*), 5.07 (1H, *dd*, J = 8, 16 Hz), 5.35 (1H, *d*, J = 16 Hz), 5.54 (1H, *dd*, J = 4, 4.5 Hz), 5.75 (1H, *dq*, J = 8, 1.5 Hz), 6.06 (1H, *d*, J = 1.5 Hz), 7.5–7.6 (3H, *m*), 7.95 (2H, *m*); MS *m/z*: 540.2708 $[M]^+$ (calc. for $C_{31}H_{40}O_8$ *m/z*: 540.2720).

Euphohelioscopin A. (**53**, 5.78 g) colourless oil: IR ν_{max}^{film} cm^{-1}: 3500, 1735, 1710, 1620; ^{1}H NMR (C_6D_6): δ0.72 (3H, *t*, J = 6 Hz), 0.85 (3H, *s*), 0.96 (3H, *s*), 1.00 (3H, *d*, J = 6 Hz), 1.58 (3H, *br s*), 1.65 (3H, *s*), 1.93 (3H, *s*), 2.61 (1H, *dd*, J = 7, 11 Hz), 2.93 (1H, *dd*, J = 7.5, 14 Hz), 3.57 (1H, *dd*, J = 4, 7 Hz), 5.00 (1H, *dd*, J = 3, 10.5 Hz), 5.56 (1H, *dt*, J = 4, 7 Hz), 5.98 (1H, *d*, J = 15 Hz), 6.00 (1H, *br t*, J = 11 Hz), 6.31 (1H, *br d*, J = 11 Hz), 6.62 (1H, *br d*, J = 11 Hz), 7.87 (1H, *dd*, J = 11, 15 Hz); MS *m/z*: 498.2986 $[M]^+$ (calc. for $C_{30}H_{42}O_6$ *m/z*: 498.2979).

Euphohelioscopin B. (**54**, 8.2 mg) colourless oil: IR ν_{max}^{film} cm^{-1}: 3500, 1720 *br*, 1645, 1615; ^{1}H NMR ($CDCl_3$): δ0.96 (3H, *t*, J = 6.5 Hz), 1.07 (3H, *d*, J = 6 Hz), 1.08 (3H, *s*), 1.18 (3H, *s*), 1.24 (3H, *s*), 1.55 (3H, *br s*), 1.83 (3H, *s*), 2.03 (3H, *s*), 2.59 (1H, *dd*, J = 11 Hz), 2.89 (1H, *dt*, J = 2, 5.5 Hz), 3.17 (1H, *dd*, J = 2, 7 Hz), 3.83 (1H, *dd*, J = 3, 6.5 Hz), 4.90 (1H, *dd*, J = 3, 10.5 Hz), 6.04 (1H, *br d*, J = 11 Hz), 6.12 (1H, *d*, J = 15.5 Hz), 6.56 (1H, *br, d*, J = 11 Hz), 6.71 (1H, *dd*, J = 7, 15.5 Hz); MS *m/z*: 514.2964 $[M]^+$ (calc. for $C_{30}H_{42}O_7$ *m/z*: 514.2928).

Euphohelionon. (**65**, 5.2 mg) colourless oil: $[\alpha]_D^{25}$ −19.7° ($CHCl_3$; *c* 0.41); IR ν_{max}^{film} cm^{-1}: 1720, 1600, 1580; ^{1}H NMR ($CDCl_3$): δ0.10 (1H, *dd*, J = 5.5, 6 Hz), 0.90 (1H, *m*), 0.97 (3H, *d*, J = 6.5 Hz), 1.01 (3H, *s*), 1.09 (3H, *s*), 1.14 (3H, *d*, J = 7 Hz), 1.25 (1H, *m*), 1.84 (3H, *br s*), 1.93 (1H, *d*, J = 12.5 Hz), 2.05 (1H, *m*), 2.28 (1H, *br d*, J = 15 Hz), 2.40 (1H, *m*), 2.46 (1H, *dd*, J = 5.5, 12.5 Hz), 3.24 (1H, *dd*, J = 5.5, 10.5 Hz), 3.74 (1H, *dd*, J = 3.5, 6 Hz), 5.38–5.47 (2H, complex), 5.59 (1H, *d*, J = 5.5 Hz), 5.85 (1H, *br d*, J = 10.5 Hz), 6.85–8.14 (15H, complex); MS *m/z*: 648.3103 $[M]^+$ (calc. for $C_{14}H_{44}O_7$ *m/z*: 648.3084).

$NaBH_4$ reduction of euphoscopin A (**1**). To a soln of **1** (31 mg) in DMF (3 ml) was added $NaBH_4$ (30 mg) and the reaction mixt stirred at room temp for 19 hr. It was then made acidic with HOAc under cooling and extracted with EtOAc. The EtOAc soln was washed well with satd aq NaCl and then concd under red pres. to give an oil which was sepd by prep. TLC (Kieselgel 60 PF_{254}, 1 mm) to afford a viscous oil (**2**, 7 mg), IR ν_{max}^{Nujol} cm^{-1}: 3450, 1740, 1710, 1600, 1580; ^{1}H NMR ($CDCl_3$): δ0.89 (3H, *s*), 0.94 (3H, *d*, J = 6 Hz), 0.99 (3H, *s*), 1.11 (1H, *dd*, J = 7 Hz), 1.86 (3H, *d*, J = 1.5 Hz), 2.17 (6H, *s*), 3.07 (1H, *dd*, J = 7.5, 15 Hz), 3.28 (1H, *dd*, J = 7.5, 9 Hz), 4.04 (1H, *br dd*, J = 3.5, 12 Hz), 5.32 (3H, complex), 5.73 (1H, *br d*, J = 9 Hz), 5.95 (1H, *br s*), 7.4–7.63 (3H, *m*), 7.98 (2H, *m*); MS *m/z*: 542.2853 $[M]^+$ (calc. for $C_{31}H_{42}O_8$ *m/z*: 542.2877).

Formation of euphoscopin A p-*bromobenzoate* (**3**). A soln of euphoscopin A (34 mg) and *p*-bromobenzoyl chloride (65 mg) in pyridine (2 ml) was stirred at room temp. overnight and then heated at 60° for 1 hr. The reaction mixt. was partitioned between EtOAc and H_2O. The EtOAc ext was washed with satd aq NaCl and then dried (Na_2SO_4). Removal of the solvent under red press afforded a solid (45 mg), which was recrystallized from EtOAc–Me_2CO to give colourless prisms (**3**, 45 mg), mp 203–204°; IR ν_{max}^{film} cm^{-1}: 1740, 1720 *br*, 1710, 1585; MS *m/z*: 724.2108 $[M]^+$ (calc. for $C_{38}H_{43}O_9Br$ *m/z*: 724.2110). A single crystal was subjected to X-ray crystallographic analysis [10].

Acetylation of euphoscopin A (**1**). A soln of **1** (20 mg) in Ac_2O (1 ml) and pyridine (1 ml) was heated at 70° for 1 hr. The reaction mixt. was partitioned between EtOAc and H_2O. The organic layer was dried (Na_2SO_4) and then concd under red pres. to give an almost colourless oil, which was purified by prep. TLC (Kieselgel 60 PF_{254}, 0.4 mm) using hexane–EtOAc (3:1) to afford 16 mg of euphoscopin B (**4**) (IR and ^{1}H NMR).

Benzoylation of euphoscopin A (**1**). A soln of **1** (15 mg) in pyridine (0.5 ml) containing benzoyl chloride (30 μl) was allowed to stand at room temp overnight. After addition of EtOAc (20 ml), the EtOAc soln was washed with satd aq NaCl and then dried (Na_2SO_4). The organic layer was concd under red pres. to leave an oil, which was purified by prep. TLC (Kieselgel 60 PF_{254}, 0.4 mm) using EtOAc–C_6H_6 (1:3) to afford a colourless oil (12 mg) of euphoscopin C (**5**) (IR and ^{1}H NMR).

Oxidation of euphoscopin A (**1**) *with* MnO_2. To a soln of **1** (30 mg) in C_6H_6 (2 ml) was added MnO_2 (30 mg), with stirring, at room temp. After further addition of the reagent (60 mg × 2), the reaction mixt was heated at 70–80° for 24 hr with stirring. After filtration, the filtrate was concd under red. pres. and then sepd by prep. TLC (Kiesel-gel 60 PF_{254}, 1 mm) using hexane–EtOAc (2:1) to afford a colourless oil (4.7 mg), which was identical with euphoscopin D (**6**) (IR and ^{1}H NMR).

Acetylation of euphoscopin E (**7**). Using the same procedure as described above, **7** (10 mg) was converted into euphoscopin F (**8**, 9 mg) (IR and ^{1}H NMR).

Silylation of euphoscopin A (**1**). A soln of **1** (161.8 mg), ^{t}BuMe$_2$SiCl (447 mg) and imidazole (200 mg) in DMF (10 ml) was stirred at room temp for 5.7 hr under Ar, and then poured into H_2O and extracted with EtOAc. The EtOAc soln was washed with satd aq NaCl and dried (Na_2SO_4). Removal of solvent afforded a solid, which was purified by prep. TLC (Kiesel gel 60 PF_{254}, 1 mm) using Me_2CO–$CHCl_3$ (1 : 5) to give a silyl ether (**9**, 199 mg), mp 176–177° (from hexane-EtOAc); IR ν_{max}^{film} cm^{-1}: 1740, 1715, 1700, 1600, 1580; ^{1}H NMR ($CDCl_3$): δ −0.27 (3H, *s*), −0.12 (3H, *s*), 0.62 (9H, *s*), 0.93 (3H, *d*, J = 7 Hz), 1.07 (3H, *d*, J = 7 Hz), 1.09 (3H, *s*), 1.25 (3H, *s*), 1.75 (3H, *d*, J = 1.5 Hz), 2.14 (3H, *s*), 2.19 (3H, *s*), 3.25 (1H, *dd*, J = 5, 9 Hz), 4.48 (1H, *dd*, J = 5,

10.5 Hz), 5.01 (1H, *dd*, $J=2$, 5 Hz), 5.14 (1H, *dd*, $J=7.5$, 16 Hz), 5.43 (1H, *d*, $J=16$ Hz), 5.83 (1H, *dq*, $J=9$, 1.5 Hz), 5.96 (1H, *d*, $J=1.5$ Hz), 7.35–7.62 (3H, *m*), 8.00 (2H, *m*); MS *m/z*: 654.3580 $[M]^+$ (calc. for $C_{37}H_{54}O_8Si$ *m/z*: 654.3584).

Hydrolysis of silyl ether (**9**). A soln of **9** (104 mg) and K_2CO_3 (20 equiv) in MeOH (5 ml) was stirred at room temp overnight. After usual work-up, the amorphous powder was sepd by prep. TLC (Kieselgel 60 PF_{254}, 1 mm) using hexane–EtOAc (4:1) to afford colourless needles of the deacetyl compound (40.1 mg), mp 93–94° (from hexane–EtOAc); IR ν_{max}^{film} cm^{-1}: 3530, 1700, 1600, 1580; ^1H NMR ($CDCl_3$): δ −0.29 (3H, *s*), −0.12 (3H, *s*), 0.65 (9H, *s*), 1.07 (3H, *d*, $J=7$ Hz), 1.13 (3H, *d*, $J=7$ Hz), 1.21 (3H, *s*), 1.71 (3H, *d*, $J=1.5$ Hz), 2.54 (1H, *m*), 3.19 (1H, *dd*, $J=5$, 11 Hz), 3.63 (1H, *br s*), 4.39 (1H, *dd*, $J=5$, 11 Hz), 5.04 (1H, *br d*, $J=5$ Hz), 5.26 (1H, *dd*, $J=6.5$, 15.5 Hz), 5.50 (1H, *d*, $J=15.5$ Hz), 5.72 (1H, *dq*, $J=9$, 1.5 Hz), 7.35–7.6 (3H, *m*), 7.89 (2H, *m*); MS *m/z*: 570.3397 $[M]^+$ (calc. for $C_{33}H_{50}O_6Si$ *m/z*: 570.3374).

Formation of diketone (**10**). A mixt. of the deacetyl compound (48 mg), PCC (100 mg) and Celite (26 mg) in CH_2Cl_2 (2 ml) was allowed to stand at room temp. for 6 hr with stirring. After filtration of insol. material, the filtrate was concd under red pres. and then subjected to prep. TLC (Kieselgel 60 PF_{254}, 0.4 mm) using hexane–EtOAc (4:1) to give the diketone (**10**, 22 mg), mp 194–195° (from hexane–EtOAc); IR ν_{max}^{film} cm^{-1}: 3350, 1710, 1600, 1580; ^1H NMR ($CDCl_3$): δ −0.27 (3H, *s*), −0.13 (3H, *s*), 0.62 (9H, *s*), 1.10 (3H, *d*, $J=7$ Hz), 1.10 (3H, *s*), 1.22 (3H, *d*, $J=7$ Hz), 1.27 (3H, *s*), 1.48 (3H, *d*, $J=1.5$ Hz), 2.45 (1H, *dd*, $J=4.5$, 15 Hz), 2.98 (1H, *dd*, $J=11$, 15 Hz), 3.57 (1H, *dd*, $J=6$, 10.5 Hz), 4.17 (1H, *m*), 4.41 (1H, *dd*, $J=4.5$, 11 Hz), 5.07 (1H, *dd*, $J=2$, 6 Hz), 5.31 (1H, *dd*, $J=7.5$, 15 Hz), 5.53 (1H, *d*, $J=15$ Hz), 5.84 (1H, *dq*, $J=11$, 1.5 Hz), 7.43–7.65 (3H, *m*), 8.01 (2H, *m*); MS *m/z*: 568.3208 $[M]^+$ (calc. for $C_{33}H_{48}O_6Si$ *m/z*: 568.3217).

Silylation of euphoscopin E (**7**). A soln of **7** (25.2 mg), ^{t}BuMe$_2$SiCl (18 mg) and imidazole (9 mg) in DMF (2 ml) was stirred at room temp. for 17 min and then worked-up in usual way to give an oil which was purified by prep. TLC (Kieselgel 60 PF_{254}, 1 mm) using hexane–EtOAc (4:1) to give a colourless oil of euphoscopin E silyl ether (**11**, 21 mg): IR ν_{max}^{film} cm^{-1}: 1720, 1710, 1600, 1580; ^1H NMR ($CDCl_3$): δ −0.33 (3H, *s*), 0.13 (3H, *s*), 0.64 (9H, *s*), 1.10 (3H, *s*), 1.14 (3H, *d*, $J=6$ Hz), 1.18 (3H, *s*), 1.23 (3H, *d*, $J=6$ Hz), 1.46 (3H, *d*, $J=1.5$ Hz), 2.30 (3H, *s*), 2.52 (1H, *dd*, $J=6$, 15 Hz), 3.02 (1H, *dd*, $J=10.5$, 15 Hz), 3.07 (1H, *dd*, $J=5$, 10.5 Hz), 3.41 (1H, *dd*, $J=7$, 9 Hz), 4.38 (1H, *dd*, $J=6$, 10.5 Hz), 5.00 (1H, *br d*, $J=5$ Hz), 5.06 (1H, *dd*, $J=10$, 15.5 Hz), 5.59 (1H, *d*, $J=15.5$ Hz), 5.96 (1H, *dq*, $J=10.5$, 1.5 Hz), 7.36–7.65 (3H, *m*) 8.06 (2H, *m*); MS *m/z*: 610.3300 $[M]^+$ (calc. for $C_{35}H_{50}O_7Si$ *m/z*: 610.3323).

Hydrolysis of euphoscopin E silyl ether (**11**). A soln of **11** (22 mg) and K_2CO_3 (15 mg) in MeOH (2 ml) was stirred at room temp. for 15 hr and then worked-up as usual to give an amorphous powder, which was sepd by prep. TLC (Kieselgel 60 PF_{254}, 0.4 mm) using hexane–EtOAc (6:1) to afford the diketone (**10**, 5.6 mg) and a conjugated ketone (6.9 mg) with the following spectral data: IR ν_{max}^{film} cm^{-1}: 1740, 1720, 1710, 1660, 1600, 1580; ^1H NMR ($CDCl_3$): δ −0.24 (3H, *s*), −0.10 (3H, *s*), 0.51 (9H, *s*), 1.10 (3H, *s*), 1.17 (3H, *d*, $J=7$ Hz), 1.35 (3H, *s*), 1.53 (3H, *d*, $J=1.5$ Hz), 1.72 (3H, *br s*), 2.04 (3H, *s*), 3.08 (1H, *dd*, $J=5$, 10 Hz), 4.44 (1H, *dd*, $J=4.5$, 9 Hz), 5.05 (1H, *br d*, $J=5$ Hz), 6.17 (1H, *dq*, $J=10$, 1.5 Hz), 6.53 (1H, *br t*, $J=5$ Hz), 7.40–7.63 (3H, *m*), 8.08 (2H, *m*); MS *m/z*: 610.3313 $[M]^+$ (calc. for $C_{35}H_{50}OSi$ *m/z*: 610.3322).

Desilylation of deacetyleuphornin A silyl ether (**17**) *followed by acetylation.* A soln of **17** (8 mg) in HOAc–MeOH–H_2O (3:2:1) was stirred at 50° for 12.5 hr and then dil. with aq. $NaHCO_3$ and extracted with EtOAc. The EtOAc soln was dried (Na_2SO_4) and then concd under red pres. to give an oil which was purified by prep. TLC (Kieselgel 60 PF_{254}, 0.25 mm) using EtOAc–hexane (1:2) to afford colourless needles of deacetyleuphornin A (5.3 mg), mp 182–183° (from hexane–C_6H_6); IR ν_{max}^{film} cm^{-1}: 3500, 3400, 3300, 1710, 1690, 1600; ^1H NMR ($CDCl_3$): δ 1.07 (3H, *d*, $J=6.5$ Hz), 1.14 (3H, *s*), 1.18 (3H, *d*, $J=7$ Hz), 1.23 (3H, *s*), 1.79 (3H, *d*, $J=1.5$ Hz), 1.96 (1H, *dd*, $J=9$, 12 Hz), 2.22–2.53 (2H, complex), 2.64 (1H, *dd*, $J=6$, 16 Hz), 2.96 (1H, *dd*, $J=11$, 16 Hz), 3.31 (1H, *dd*, $J=7.5$, 9 Hz), 3.66 (1H, *br*), 4.38 (1H, *br dd*, $J=6$, 11 Hz), 5.21 (1H, *dd*, $J=3.5$, 7.5 Hz), 5.21 (1H, *dd*, $J=8$, 16 Hz), 5.47 (1H, *d*, $J=16$ Hz), 5.60 (1H, *dq*, $J=9$, 1.5 Hz), 7.3–7.65 (3H, *m*), 7.95 (2H, *m*); MS *m/z*: 456.2487 $[M]^+$ (calc. for $C_{27}H_{36}O_6$ *m/z*: 456.2509).

A soln of deacetyleuphoscopin A (7.2 mg) in pyridine (0.5 ml) and Ac_2O (0.3 ml) was allowed to stand at room temp for 3 hr and then worked-up in usual way to afford an oil which was sepd by prep. TLC (Kieselgel 60 PF_{254}, 0.25 mm) using hexane–EtOAc (2:1) to give euphoscopin H (**13**, 4.5 mg) and euphoscopin K (**16**, 2.5 mg) (IR and ^1H NMR).

Formation of euphoscopin L (**18**) *from euphoscopin E* (**7**). A soln of **7** (20 mg) and NaOAc (20 mg) in DMF (2.5 ml) was stirred at 50° for 3 days and then partitioned between EtOAc and H_2O. The organic layer was washed with satd aq NaCl and dried (Na_2SO_4). Removal of solvent gave an oil which was purified by prep. TLC (Kieselgel 60 PF_{254}, 0.4 mm) using hexane–EtOAc (4:1) to afford a colourless oil of euphoscopin L (**18**, 17.2 mg) IR and ^1H NMR).

Silylation of epieuphoscopin A (**19**). To a soln of **19** (114 mg) in DMF (5 ml) were added ^{t}BuMe$_2$SiCl (95 mg) and imidazole (43 mg) with stirring. The reaction mixt. was stirred at room temp for 4 hr and then worked-up as usual to leave a solid, which was purified by prep. TLC (Kieselgel 60 PF_{254}, 1 mm) using hexane–EtOAc (4:1) to afford white crystal of epieuphoscopin A silyl ether (**20**, 125 mg), mp 160–161° (from hexane–EtOAc); IR ν_{max}^{film} cm^{-1}: 1740, 1720, 1600, 1580; ^1H NMR ($CDCl_3$); δ −0.33 (3H, *s*), −0.06 (3H, *s*), 0.76 (9H, *s*), 0.98 (3H, *d*, $J=7$ Hz), 1.09 (3H, *s*), 1.18 (3H, *d*, $J=7$ Hz), 1.20 (3H, *s*), 1.56 (3H, *d*, $J=1.5$ Hz), 2.10 (3H, *s*), 2.13 (3H, *s*), 2.88 (1H, *dd*, $J=9.5$, 15 Hz), 3.11 (1H, *t*, $J=8$ Hz), 4.29 (1H, *dd*, $J=3$, 11 Hz), 5.10 (1H, *dd*, $J=4$, 8.5 Hz), 5.18 (1H, *d*, $J=15.5$ Hz), 5.42 (1H, *dd*, $J=6$, 15.5 Hz), 5.58 (1H, *d*, $J=7$ Hz), 5.90 (1H, *br d*, $J=8.5$ Hz), 7.32–7.58 (3H, *m*), 7.96 (2H, *m*); MS *m/z*: 654.3584 $[M]^+$ (calc. for $C_{37}H_{54}O_8Si$ *m/z*: 654.3584).

Hydrolysis of epieuphoscopin A silyl ether (**20**) *followed by oxidation.* A soln of **20** (125 mg) and K_2CO_3 (52.7 mg) in MeOH was stirred at room temp. for 15 hr and then worked-up in the usual way to give an oil, which was purified by prep. TLC (Kieselgel 60 PF_{254}, 1 mm) using hexane–EtOAc (4:1) to afford a colourless oil of the corresponding diol (70.3 mg): IR ν_{max}^{film} cm^{-1}: 3450, 1700, 1600, 1580; ^1H NMR ($CDCl_3$): δ −0.40 (3H, *s*), −0.17 (3H, *s*), 0.72 (9H, *s*), 1.06 (3H, *s*), 1.10 (3H, *d*, $J=6$ Hz), 1.13 (3H, *s*), 1.17 (3H, *d*, $J=6$ Hz), 1.52 (3H, *br s*), 3.66 (1H, *d*, $J=8$ Hz), 4.60 (1H, *dd*, $J=4.5$, 9.5 Hz), 4.96 (1H, *dd*, $J=5.5$, 6.5 Hz), 5.18 (1H, *d*, $J=15.5$ Hz), 5.58 (1H, *d*, $J=9$ Hz), 5.75 (1H, *d*, $J=6.5$ Hz), 7.30–7.58 (3H, *m*), 7.93 (2H, *m*); MS *m/z*: 570.3393 $[M]^+$ (calc. for $C_{33}H_{50}O_6Si$ *m/z*: 570.3372). To a soln of this diol (70.3 mg) in DMSO (2 ml) was added Ac_2O (115 μl, 10 equiv) with stirring. The reaction mixt. was stirred at room temp for 2 days and then worked-up as usual to give an oil which was purified by prep. TLC (Kieselgel 60 PF_{254}, 1 mm) using hexane–EtOAc (2:1) to afford a colourless oil of diketone (**21**, 64.5 mg): IR ν_{max}^{film} cm^{-1}: 3400, 1700, 1600, 1580; ^1H NMR ($CDCl_3$): δ −0.33 (3H, *s*), −0.13 (3H, *s*), 0.60 (9H, *s*), 1.09 (3H, *s*), 1.16 (3H, *s*), 1.25 (3H, *d*, $J=7$ Hz), 1.29 (3H, *d*, $J=7$ Hz), 1.50 (3H, *br s*), 2.78 (1H, *dd*, $J=9$, 15 Hz), 3.31 (1H, *t*, $J=5$ Hz), 3.58 (1H, *quint*, $J=7$ Hz), 4.30 (1H, *dd*, $J=4$, 9 Hz), 5.21 (1H, *d*, $J=15.5$ Hz), 5.33 (1H, *m*), 5.41 (1H, *dd*, $J=8$, 15.5 Hz), 5.66 (1H,

br d, $J=6$ Hz), 7.33–7.55 (3H, *m*), 8.05 (2H, *m*); MS *m/z*: 568.3231 $[M]^+$ (calc. for $C_{33}H_{48}O_6Si$ *m/z*: 568.3218).

Isomerization of **21**. A soln of **21** (39 mg) and NaOAc (6 equiv) in DMF (3.5 ml) was heated at 80° for 4 days with stirring. The reaction mixt. was dil. with H_2O and then extracted with EtOAc. The EtOAc soln was washed with satd aq NaCl and then dried (Na_2SO_4). Removal of solvent afforded an oil, which was sepd by prep. TLC (Kieselgel 60 PF_{254}, 1 mm) using hexane–EtOAc (4:1) to give a colourless oil of α,β-unsaturated ketone (**22**, 4.8 mg): IR ν_{max}^{film} cm^{-1}: 3500, 1720, 1700, 1650, 1600, 1580; ^1H NMR ($CDCl_3$): δ −0.42 (3H, *s*), −0.23 (3H, *s*), 0.66 (9H, *s*), 1.12 (3H, *s*), 1.22 (3H, *d*, $J=7.5$ Hz), 1.40 (3H, *s*), 1.53 (3H, *d*, $J=1.5$ Hz), 1.76 (3H, *s*), 3.06 (1H, *t*, $J=6.5$ Hz), 3.20 (1H, *dd*, $J=9.5$, 16 Hz), 4.43 (1H, *dd*, $J=4.5$, 9.5 Hz), 5.31 (1H, *dd*, $J=1.5$, 6.5 Hz), 5.98 (1H, *br d*, $J=10.5$ Hz), 6.98 (1H, *br t*, $J=6.5$ Hz), 7.4–7.7 (3H, *m*), 8.02 (2H, *m*); MS *m/z*: 568.3247 $[M]^+$ (calc. for $C_{33}H_{48}O_6Si$ *m/z*: 568.3244).

Isomerization of diketone (**10**) *derived from euphoscopin A* (**1**). According to the same procedure as described above, the α,β-unsaturated ketone (**22**, 3.2 mg) was also obtained from **10** (15 mg).

Isomerization of epieuphoscopin F (**25**). A soln of **25** (15.9 mg) and NaOAc (30 mg) in DMF (1.8 ml) was stirred at 75° for 4 hr and then worked-up as described for **21**, to afford an oil which was subjected to prep. TLC (Kieselgel 60 PF_{254}, 0.4 mm) using hexane–EtOAc (4:1) to give a colourless oil of α,β-unsaturated ketone (**26**, 11.6 mg): IR ν_{max}^{film} cm^{-1}: 1730 *br*, 1660, 1600, 1580; ^1H NMR ($CDCl_3$): δ 1.14 (3H, *s*), 1.17 (3H, *d*, $J=7$ Hz), 1.28 (3H, *s*), 1.54 (3H, *s*), 1.63 (3H, *d*, $J=1.5$ Hz), 1.72 (3H, *br s*), 2.19 (3H, *s*), 2.97 (1H, *dd*, $J=8.5$, 11 Hz), 3.15 (1H, *dd*, $J=9$, 16.5 Hz), 5.16 (1H, *br d*, $J=8.5$ Hz), 5.18 (1H, *dd*, $J=5.5$, 9 Hz), 5.90 (1H, *br d*, $J=11$ Hz), 6.43 (1H, *br t*, $J=6$ Hz), 7.4–7.9 (3H, *m*), 8.08 (2H, *m*); MS *m/z*: 538.2580 $[M]^+$ (calc. for $C_{31}H_{38}O_8$ *m/z*: 536.2564).

Isomerization of euphoscopin F (**8**). According to the same procedure as described above, **8** (5.0 mg) was converted into the same α,β-unsaturated ketone (**26**, 0.8 mg) (TLC, IR and ^1H NMR).

Hydrolysis of euphornin (**28**). A soln of **28** (172.5 mg) and K_2CO_3 (46.9 mg) in MeOH (4 ml) was stirred at room temp for 10.5 hr and then worked-up as usual to give an oil which was sepd by prep. TLC (Kieselgel 60 PF_{254}, 1 mm) using hexane–EtOAc (1:1) to afford monodeacetyleuphornin (**30**, 112 mg) and deacetyleuphornin (**66**, 27.5 mg): **30** colourless oil: IR ν_{max}^{film} cm^{-1}: 3550, 1730 *br*, 1600, 1580; ^1H NMR ($CDCl_3$): δ0.88 (3H, *s*), 0.92 (3H, *d*, $J=6$ Hz), 0.93 (3H, *s*), 1.06 (3H, *d*, $J=7$ Hz), 1.19 (3H, *s*), 1.73 (3H, *br s*), 1.94 (3H, *s*), 2.88 (1H, *dd*, $J=4.5$, 10 Hz), 3.32 (1H, *d*, $J=3$ Hz), 4.69 (1H, *t*, $J=3$ Hz), 4.97 (1H, *m*), 5.06 (1H, *d*, $J=16$ Hz), 5.44 (1H, *m*), 5.56 (1H, *dd*, $J=10$, 16 Hz), 5.65 (1H, *br d*, $J=10.5$ Hz), 7.41–7.54 (3H, *m*), 8.07 (2H, *m*); MS *m/z*: 542.2871 $[M]^+$ (calc. for $C_{31}H_{42}O_8$ *m/z*: 542.2877). Compound **66**: colourless oil: IR ν_{max}^{film} cm^{-1}: 3400 *br*, 1710, 1690, 1580; ^1H NMR ($CDCl_3$): δ0.81 (3H, *s*), 0.98 (3H, *d*, $J=6$ Hz), 1.02 (3H, *s*), 1.13 (3H, *d*, $J=7$ Hz), 1.63 (2H, *br s*), 2.87 (1H, *dd*, $J=5$, 10.5 Hz), 3.24 (2H, complex), 4.12 (1H, *br d*, $J=5$ Hz), 5.02 (1H, *d*, $J=15.5$ Hz), 5.32–5.64 (3H, complex), 7.39–7.63 (3H, *m*), 8.03 (2H, *m*); MS *m/z*: 458.2671 $[M]^+$ (calc. for $C_{27}H_{38}O_6$ *m/z* S 458.2671).

Ketal formation of monodeacetyleuphornin (**30**). To a soln of **30** (37 mg) in Me_2CO (2 ml) containing *p*-TsOH (6.5 mg) was added 5 drops of 2,2-dimethoxypropane with stirring. The reaction mixt. was further stirred at room temp for 7 hr and then partitioned between EtOAc and H_2O. The EtOAc soln was successively washed with satd aq NaCl, dried (Na_2SO_4) and concd under red. pres. to give an oil which was sepd by prep. TLC (Kieselgel 60 PF_{254}, 1 mm) using hexane–EtOAc (3:1) to afford a colourless oil of the acetonide (**29**, 40.6 mg): IR ν_{max}^{film} cm^{-1}: 1740, 1725, 1600, 1590; ^1H NMR ($CDCl_3$): δ0.89 (3H, *s*), 0.94 (3H, *s*), 0.98 (3H, *d*, $J=7$ Hz), 1.11 (3H, *d*, $J=7$ Hz), 1.28 (3H, *s*), 1.54 (3H, *br s*), 1.66 (6H, *s*), 1.96 (3H, *s*), 2.91 (1H, *dd*, $J=5$, 8 Hz), 4.08 (1H, *br s*), 4.8–4.98 (2H, complex), 4.98 (1H, *d*, $J=16$ Hz), 5.56 (1H, *t*, $J=4.5$ Hz), 5.69 (1H, *dd*, $J=8$, 16 Hz), 5.73 (1H, *br d*, $J=9$ Hz), 7.36–7.64 (3H, *m*), 8.08 (2H, *m*); MS *m/z*: 582.3235 $[M]^+$ (calc. for $C_{34}H_{46}O_8$ *m/z*: 582.3190).

Formation of p-bromobenzoate (**32**) *from acetonide* (**29**). A soln of **29** (115 mg) in K_2CO_3 (54.7 mg) in MeOH (5 ml) was stirred at room temp. overnight and then worked-up as usual to give an oil which was subjected to prep. TLC (Kieselgel 60 PF_{254}, 1 mm) using hexane–EtOAc (5:2) to afford a colourless oil of diol (**31**, 70.3 mg): IR ν_{max}^{film} cm^{-1}: 3480, 1710, 1600, 1580; ^1H NMR ($CDCl_3$): δ0.86 (3H, *s*), 0.97 (3H, *d*, $J=6$ Hz), 1.06 (3H, *s*), 1.10 (3H, *d*, $J=7$ Hz), 1.56 (9H, *br s*), 2.97 (1H, *dd*, $J=4.5$, 9 Hz), 3.51 (1H, *dd*, $J=3$, 4 Hz), 4.04 (1H, *br s*), 4.11 (1H, *br t*, $J=4$ Hz), 4.95 (1H, *d*, $J=16$ Hz), 5.49 (1H, *br d*, $J=4.5$ Hz), 5.58 (1H, *dd*, $J=7.5$, 16 Hz), 5.68 (1H, *br d*, $J=9$ Hz), 7.3–7.7 (3H, *m*), 8.08 (2H, *m*).

A soln of **31** (40 mg) and *p*-bromobenzoyl chloride (40 mg) in pyridine (1.5 ml) was stirred at room temp for 16 hr and then worked-up in the usual way to give an oil, which was sepd by prep. TLC (Kieselgel 60 PF_{254}, 1 mm) using hexane–EtOAc (2:1) to afford colourless plates of *p*-bromobenzoate (**32**, 17 mg), mp 159–161° (from hexane); IR ν_{max}^{film} cm^{-1}: 3450, 1705, 1600, 1580; ^1H NMR ($CDCl_3$): δ0.88 (3H, *s*), 0.90 (3H, *d*, $J=7$ Hz), 1.08 (3H, *s*), 1.19 (3H, *d*, $J=7$ Hz), 1.52 (3H, *s*), 1.55 (3H, *s*), 1.70 (3H, *br s*), 2.92 (1H, *dd*, $J=4.5$, 8 Hz), 3.57 (1H, *t*, $J=4$ Hz), 4.06 (1H, *br s*), 5.01 (1H, *d*, $J=16$ Hz), 5.21 (1H, *m*), 5.45–5.75 (3H, complex), 7.0–7.88 (9H, complex); MS *m/z*: 665.2109 $[M-Me]^+$ (calc. for $C_{36}H_{42}O_7Br$ *m/z*: 665.2112).

Acetylation of euphornin A (**33**). A soln of **33** (10 mg) in Ac_2O–pyridine (0.5 ml) was allowed to stand at room temp. overnight and then worked-up as usual to give euphornin (**28**, 6 mg) (IR and ^1H NMR).

Acetylation of euphornin B (**34**). A solution of **34** (4.28 mg) in Ac_2O (0.2 ml)–pyridine (0.2 ml) was allowed to stand at room temp for 3 days and then at 60° for 1 hr. The reaction soln was worked-up in the usual way and then purified by prep. TLC (Kieselgel 60 PF_{254}, 0.25 mm) using hexane–EtOAc (2:1) to afford euphornin (**28**, 2.1 mg) (IR and ^1H NMR).

Oxidation of euphornin A (**33**). A mixt of **33** (290 mg), PPC (255 mg) and Celite (766 mg) in CH_2Cl_2 (15 ml) was stirred at room temp for 23 hr. After filtration of insol material, the filtrate was concd under red. pres. to give a brown oil which was purified by prep. TLC (Kieselgel 60 PF_{254}, 1 mm) using hexane–EtOAc (5:2) to afford euphornin C (**35**, 268 mg) (TLC, IR and ^1H NMR).

Dehydration of euphornin (**28**). To a soln of **28** (138 mg) and DMAP (10 mg) in pyridine was added $SOCl_2$ (0.5 ml) under ice cooling. The reaction mixt was stirred at room temp for 100 min and then poured onto ice-H_2O and extracted with EtOAc. The EtOAc soln was washed with satd aq NaCl and then dried (Na_2SO_4). Removal of solvent under red. pres. gave an oil which was sepd by prep. TLC (Kieselgel 60 PF_{254}, 1 mm) using hexane–EtOAc (4:1) to afford euphornin E (**37**, 52.6 mg) (TLC, IR and ^1H NMR).

Acetylation of euphornin F (**38**), *euphornin I* (**45**) *and euphornin K* (**50**). A soln of **38** (8.3 mg) in Ac_2O (0.4 ml)–pyridine (0.4 ml) was allowed to stand at room temp for 16 hr and then worked-up as usual to give an oil which was purified by prep. TLC (Kieselgel 60 PF_{254}, 0.25 mm) using hexane–EtOAc (2:1) to afford a colourless oil of euphornin G (**39**, 6.0 mg) (TLC), IR and ^1H NMR). Using the same procedure, **45** (4.5 mg) and **50** (8.3 mg) were converted into **44** (3.8 mg) and **49** (8.3 mg), respectively.

Acetylation of acetonide (**29**) *derived from euphornin* (**28**). A soln of **29** (30.2 mg) in Ac_2O (11 μg)–pyridine (3 ml) was allowed to

stand at room temp for 6 days and then worked-up as usual to give an oil which was subjected to prep. TLC (Kieselgel 60 PF_{254}, 0.25 mm) using C_6H_6–EtOAc (5:1) to afford two monoacetates (**40**, 5.3 mg; **41**, 12 mg) in addition to the starting material (14.2 mg): **40** colourless oil; IR ν_{max}^{film} cm^{-1}: 3500, 1720, 1600, 1580; ^1H NMR ($CDCl_3$): δ0.93 (3H, *s*), 0.98 (3H, *d*, *J* = 6 Hz), 1.09 (3H, *s*), 1.12 (3H, *d*, *J* = 6 Hz), 1.38 (3H, *s*), 1.56 (3H, *s*), 1.60 (3H, *s*), 1.62 (3H, *d*, *J* = 1 Hz), 2.87 (1H, *dd*, *J* = 4.5, 8 Hz), 3.43 (1H, *t*, *J* = 4 Hz), 4.03 (1H, *br s*), 4.93 (1H, *d*, *J* = 15.5 Hz), 4.96 (1H, *t*, *J* = 3 Hz), 5.62 (1H, *br d*, *J* = 8 Hz), 5.77 (1H, *dd*, *J* = 8.5, 15.5 Hz), 7.3–7.6 (3H, *m*), 8.06 (2H, *m*); MS *m/z*: 525.3589 [M − 15]$^+$ (calc. for $C_{31}H_{41}O_7$ *m/z*: 525.3579). **41** colourless oil: IR ν_{max}^{film} cm $^{-1}$: 3500, 1720, 1600, 1580; ^1H NMR ($CDCl_3$): δ0.97 (3H, *s*), 1.00 (3H, *d*, *J* = 6 Hz), 1.01 (3H, *s*), 1.13 (3H, *d*, *J* = 7 Hz), 1.54 (3H, *br s*), 1.63 (6H, *s*), 2.06 (3H, *s*), 2.99 (1H, *dd*, *J* = 4.5, 8 Hz), 4.01 (1H, *br t*, *J* = 4 Hz), 4.06 (1H, *br s*), 4.64 (1H, *dd*, *J* = 1.5, 4.5 Hz), 4.97 (1H, *d*, *J* = 16 Hz), 5.55 (1H, *m*), 5.61 (1H, *dd*, *J* = 8, 16 Hz), 5.82 (1H, *dq*, *J* = 8, 1 Hz), 7.45–7.56 (3H, *m*), 8.06 (2H, *m*); MS *m/z*: 526.2889 [M − 14]$^+$ (calc. for $C_{31}H_{42}O_7$ *m/z*: 526.2918).

Oxidation of monoacetate (**41**). To a soln of **41** (2 mg) in CH_2Cl_2 (1 ml) was added PCC (2.5 mg) and Celite (7 mg) and the reaction mixt. stirred at room temp. for 3 days and then filtered. The filtrate was concd under red pres. and then purified by prep. TLC (Kiesel-gel 60 PF_{254}, 0.25 mm) using C_6H_6–EtOAc (5:1) to give a colourless oil of ketone (**42**, 1.3 mg): IR ν_{max}^{film} cm^{-1}: 1740, 1720, 1710, 1600, 1580; ^1H NMR ($CDCl_3$): δ0.97 (3H, *d*, *J* = 6 Hz), 1.03 (3H, *s*), 1.10 (3H, *s*), 1.11 (3H, *d*, *J* = 6 Hz), 1.21 (3H, *d*, *J* = 1 Hz), 1.63 (9H, *s*), 2.36 (1H, *dd*, *J* = 7.5, 13 Hz), 2.63 (1H, *t*, *J* = 4 Hz), 3.03 (1H, *dd*, *J* = 4, 11 Hz), 4.09 (1H, *br s*), 4.93 (1H, *d*, *J* = 15.5 Hz), 5.01 (1H, *dd*, *J* = 4, 11 Hz), 5.60 (1H, *m*), 5.63 (1H, *dd*, *J* = 9, 15.5 Hz), 7.3–7.6 (3H, *m*), 8.05 (2H, *m*); MS *m/z*: 538.2942 [M]$^+$ (calc. for $C_{32}H_{40}O_7$ *m/z*: 538.2928).

Hydrolysis of euphornin G (**39**). A soln of **39** (45 mg) and K_2CO_3 (11.5 mg) in MeOH (5 ml) was stirred at room temp for 2 hr and then worked-up in the usual way to give a pale yellow oil which was sepd by prep. TLC (Kieselgel 60 PF_{254}, 1 mm) using hexane–EtOAc (2:1) to afford a colourless oil of deacetyleuphornin G (**43**, 11 mg) in addition to starting material (11.4 mg). **43**: IR ν_{max}^{film} cm^{-1}: 3430, 1720, 1600, 1580; ^1H NMR ($CDCl_3$): δ0.98 (3H, *d*, *J* = 7 Hz), 1.18 (3H, *s*), 1.19 (3H, *s*), 1.20 (3H, *d*, *J* = 7 Hz), 1.28 (3H, *s*), 1.68 (3H, *d*, *J* = 1 Hz), 2.7–3.0 (3H, complex), 3.35 (1H, *br s*), 5.04 (1H, *dd*, *J* = 7, 12 Hz), 5.21 (1H, *d*, *J* = 15.5 Hz), 5.44 (1H, *t*, *J* = 4.5 Hz), 5.60 (1H, *d*, *J* = 9 Hz), 5.68 (1H, *dd*, *J* = 9, 15.5 Hz), 7.40–7.62 (3H, *m*), 8.07 (2H, *m*); MS *m/z*: 498.2620 [M]$^+$ (calc. for $C_{29}H_{38}O_7$ *m/z*: 498.2616).

Ketal formation of deacetyleuphornin G (**43**). A soln of **43** (10.7 mg) and 2,2-dimethoxypropane (0.5 ml) in Me_2CO (2 ml) containing *p*-TsOH (2 mg) was stirred at room temp for 18 hr and then worked-up as usual to give an oil which was subjected to prep. TLC (Kieselgel 60 PF_{254}, 0.25 mm) to afford a colourless oil of acetonide (7.2 mg) in addition to starting material (2.3 mg). The former was identical with compound (**42**) derived from euphornin (TLC, IR and ^1H NMR).

Silylation of euphornin F (**38**). A soln of **38** (12.5 mg), ^{t}BuMe$_2$SiCl (15.8 mg) and imidazole (7.1 mg) in DMF (2 ml) was stirred at room temp for 20 min and then worked-up in the usual way to give an oil which was purified by prep. TLC (Kieselgel 60 PF_{254}, 0.4 mm) using hexane–EtOAc (5:1) to afford a colourless oil of euphornin F silyl ether (12.7 mg): IR ν_{max}^{film} cm^{-1}: 1720, 1600, 1580; ^1H NMR ($CDCl_3$): δ −0.38 (3H, *s*), −0.16 (3H, *s*), 0.63 (9H, *s*), 0.96 (3H, *d*, *J* = 7 Hz), 1.08 (3H, *d*, *J* = 7 Hz), 1.10 (3H, *s*), 1.22 (3H, *s*), 1.66 (3H, *d*, *J* = 1 Hz), 2.18 (3H, *s*), 2.82 (1H, *dd*, *J* = 4, 11 Hz), 2.88 (1H, *dd*, *J* = 9, 14.5 Hz), 4.32 (1H, *dd*, *J* = 2, 9 Hz), 4.99 (1H, *d*, *J* = 2 Hz), 5.18 (1H, *d*, *J* = 15.5 Hz), 5.48 (1H, *t*, *J* = 4 Hz), 5.73 (1H, *dd*, *J* = 8, 15.5 Hz), 5.83 (1H, *br d*, *J* = 11 Hz), 7.4–7.56 (3H, *m*), 8.10 (2H, *m*); MS *m/z*: 612.3510 [M]$^+$ (calc. for $C_{35}H_{52}O_7Si$ *m/z*: 612.3479).

Hydrolysis of euphornin F silyl ether. A soln of the silyl ether (12.7 mg) and K_2CO_3 (*ca* 1 mg) in MeOH (1.5 ml) was allowed to stand at room temp. for 18 hr with stirring and then worked up as usual to give an oil which was purified by prep. TLC (Kieselgel 60 PF_{254}, 1 mm) using hexane–EtOAc (5:1) to afford a colourless oil of diol (**46**, 9.3 mg): IR ν_{max}^{film} cm^{-1}: 3530, 1710, 1600, 1580; ^1H NMR ($CDCl_3$): δ −0.45 (3H, *s*), −0.17 (3H, *s*), 0.63 (9H, *s*), 0.94 (3H, *d*, *J* = 6 Hz), 1.08 (3H, *s*), 1.13 (3H, *d*, *J* = 7 Hz), 1.18 (3H, *s*), 1.66 (3H, *d*, *J* = 1.5 Hz), 2.42 (1H, *dd*, *J* = 4, 8 Hz), 2.85 (1H, *dd*, *J* = 4, 10 Hz), 3.35 (1H, *d*, *J* = 2 Hz), 4.23 (1H, *dd*, *J* = 4, 8 Hz), 5.17 (1H, *d*, *J* = 16 Hz), 5.48 (1H, *t*, *J* = 4 Hz), 5.67 (1H, *dd*, *J* = 8, 16 Hz), 5.75 (1H, *br d*, *J* = 10 Hz), 7.4–7.9 (3H, *m*), 8.01 (2H, *m*); MS *m/z*: 570.3397 [M]$^+$ (calc. for $C_{33}H_{50}O_6Si$ *m/z*: 570.3374).

Silylation of euphornin I (**45**). Using the same procedure as described for **38** silylation of **45** (10.2 mg) afforded a colourless oil of euphornin silyl ether (**47**, 4.5 mg) in addition to starting material (6.2 mg). **47**: IR ν_{max}^{film} cm^{-1}: 1740, 1720, 1600, 1580; ^1H NMR ($CDCl_3$): δ −0.40 (3H, *s*), −0.15 (3H, *s*), 0.62 (9H, *s*), 0.87 (3H, *d*, *J* = 5.5 Hz), 0.99 (3H, *d*, *J* = 7 Hz), 1.07 (3H, *s*), 1.15 (3H, *s*), 1.69 (3H, *d*, *J* = 1.5 Hz), 2.12 (3H, *s*), 2.16 (3H, *s*), 3.22 (1H, *dd*, *J* = 4.5, 9 Hz), 4.23 (1H, *dd*, *J* = 3, 7.5 Hz), 5.21 (1H, *dd*, *J* = 5.5, 16.5 Hz), 5.38 (1H, *d*, *J* = 16.5 Hz), 5.52 (1H, *m*), 5.87 (1H, *br d*, *J* = 9,5 Hz), 7.36–7.57 (3H, *m*), 7.96 (2H, *m*), MS *m/z*: 597.2901 [M − ^{t}Bu]$^+$ (calc. for $C_{33}H_{45}O_8Si$ *m/z*: 597.2881).

Oxidation of silyl ethers (**46** and **47**). A soln of **46** (11.4 mg) in DMSO (1.5 ml)–Ac_2O (8 μl) was allowed to stand at room temp. for 3 days and then worked-up as usual to give an oil which was purified by prep. TLC (Kieselgel 60 PF_{254}, 1 mm) to afford a colourless oil of diketone (**48**, 9.6 mg), IR ν_{max}^{film} cm^{-1}: 3550, 1710, 1700, 1600, 1580; ^1H NMR ($CDCl_3$): δ −0.38 (3H, *s*), −0.17 (3H, *s*), 0.66 (9H, *s*), 1.06 (3H, *d*, *J* = 7 Hz), 1.20 (3H, *s*), 1.35 (3H, *d*, *J* = 7 Hz), 1.47 (3H, *d*, *J* = 1.5 Hz), 2.81 (1H, *dd*, *J* = 10.5, 14.5 Hz), 3.29 (1H, *dd*, *J* = 4.5, 10.5 Hz), 4.33 (1H, *dd*, *J* = 4.5, 9.5 Hz), 5.19 (1H, *d*, *J* = 16.5 Hz), 5.58 (1H, *dd*, *J* = 6.5, 10.5 Hz), 5.70 (1H, *t*, *J* = 4 Hz), 5.70 (1H, *m*), 7.42–7.57 (3H, *m*), 8.10 (2H, *m*); MS *m/z*: 568.3181 [M]$^+$ (calc. for $C_{33}H_{46}O_6Si$ *m/z*: 568.3216). Using the same procedure described above, **47** (5.0 mg) was converted into the same diketone (**48**, 3.8 mg) (IR and ^1H NMR).

Acetylation of euphornin K (**50**). A soln of **50** (8.3 mg) in Ac_2O (0.1 ml) was allowed to stand at room temp. for 16 hr and then worked-up in the usual way to give an oil which was purified by prep. TLC (Kieselgel 60 PF_{254}, 0.25 mm) using hexane–EtOAc (2:1) to afford a colourless oil of euphornin *J* (**49**, 6 mg) (TLC, IR and ^1H NMR).

Silylation of euphornin K (**50**) *followed by hydrolysis*. Using the procedure described for **38**, **50** (12.5 mg) in DMF (2 ml) was treated with ^{t}BuMe$_2$SiCl (16 mg)-imidazole (7 mg) to afford a colourless oil of euphornin K silyl ether (10.8 mg), IR ν_{max}^{film} cm^{-1}: 1740, 1720, 1600, 1580; ^1H NMR ($CDCl_3$): δ −0.43 (3H, *s*), −0.15 (3H, *s*), 0.63 (9H, *s*), 0.87 (3H, *d*, *J* = 6.5 Hz), 0.95 (3H, *d*, *J* = 6.5 Hz), 1.11 (3H, *s*), 1.16 (3H, *s*), 1.69 (3H, *d*, *J* = 1.5 Hz), 2.16 (3H, *s*), 2.33 (3H, *s*), 2.96 (1H, *dd*, *J* = 10, 14.5 Hz), 3.24 (1H, *dd*, *J* = 4, 8 Hz), 4.37 (1H, *dd*, *J* = 4 Hz), 5.19 (1H, *dd*, *J* = 8, 16.5 Hz), 5.43 (1H, *d*, *J* = 16.5 Hz), 5.57 (1H, *br t*, *J* = 4 Hz), 5.87 (1H, *br d*, *J* = 8 Hz), 7.33–7.66 (3H, *m*), 7.97 (2H, *m*); MS *m/z*: 654.3603 [M]$^+$ (calc. for $C_{37}H_{54}O_8Si$ *m/z*: 654.3585). This silyl ether (10 mg) was hydrolysed with excess K_2CO_3 in MeOH (1.5 ml) to afford a colourless oil of **51** (7 mg), IR ν_{max}^{film} cm^{-1}: 3530, 1700, 1680, 1600, 1580; ^1H NMR ($CDCl_3$): δ −0.41 (3H, *s*), −0.12 (3H, *s*), 0.63 (9H, *s*), 0.94 (3H, *d*, *J* = 6 Hz), 1.09 (3H, *s*), 1.10 (3H, *d*, *J* = 7 Hz), 1.15 (3H, *s*), 1.71 (3H, *br s*), 3.10 (1H, *dd*, *J* = 3, 6 Hz), 3.71 (1H, *br s*), 4.36 (1H, *dd*, *J* = 5, 13 Hz), 5.30 (1H, *dd*, *J* = 7.5, 16.5 Hz), 5.55 (1H, *d*, *J* = 16.5 Hz), 5.68 (1H, *m*), 5.75 (1H, *br d*, *J* = 6.5 Hz),

7.35–7.60 (3H, *m*), 7.95 (2H, *m*); MS *m/z*: 570.3404 $[M]^+$ (calc. for $C_{33}H_{50}O_6Si$ *m/z*: 570.3374).

Oxidation of **51**. A soln of **51** (7 mg) in DMSO (1.5 ml)–Ac_2O (8 μl) was allowed to stand at room temp for 3 days and then worked-up as usual to give an oil which was purified by prep. TLC (Kieselgel 60 PF_{254}, 0.25 mm) using hexane–EtOAc (5:1) to afford a colourless oil of ketone (**52**, 5.4 mg), IR ν_{max}^{film} cm^{-1}: 3550, 1720, 1700, 1600, 1580; ^1H NMR ($CDCl_3$): $\delta -0.22$ (3H, *s*), -0.11 (3H, *s*), 0.66 (9H, *s*), 0.98 (1H, *d*, $J=6$ Hz), 1.09 (3H, *s*), 1.13 (3H, *d*, $J=6$ Hz), 1.22 (3H, *s*), 1.45 (3H, *d*, $J=1$ Hz), 2.85 (1H, *dd*, $J=10$, 15 Hz), 3.48 (1H, *dd*, $J=4$, 10.5 Hz), 4.14 (1H, *quint*, $J=6$ Hz), 4.39 (1H, *dd*, $J=4.5$, 10.5 Hz), 5.23 (1H, *dd*, $J=8$, 15.5 Hz), 5.51 (1H, *d*, $J=15.5$ Hz), 5.58 (1H, *dd*, $J=3$, 4.5 Hz), 5.72 (1H, *br d*, $J=10.5$ Hz), 7.35–7.65 (3H, *m*), 8.05 (2H, *m*); MS *m/z*; 568.3211 $[M]^+$ (calc. for $C_{33}H_{48}O_6Si$ *m/z*: 568.3217).

Epimerization of ketone (**48**). A soln of **48** (4.5 mg) and excess NaOAc in DMF (1 ml) was heated at 80° for 2 days and then diluted with EtOAc. The EtOAc soln was washed with satd aq NaCl and dried (Na_2SO_4). Removal of solvent under red pres. gave an oil which was sepd by prep. TLC (Kieselgel 60 PF_{254}, 0.25 mm) using hexane–EtOAc (5:1) to afford a colourless oil of **52** (1.2 mg) (TLC, IR and ^1H NMR).

Hydrolysis of euphohelioscopin A (**53**). A soln of **53** (1.5 g) and K_2CO_3 (404 mg) in MeOH (20 ml) was stirred at room temp. for 18 hr and then worked-up in the usual way to give an oil, which was sepd by a Harrison Research Chromatotron (Kieselgel 60 GF_{254}, 4 mm) using hexane–EtOAc (1:4) to afford colourless crystals of triol (**55**, 730 mg) and methyl 2E,4Z-octadienoate (**56**, *ca* 40 mg) as a colourless oil: **55**, mp 139–140.5° (from hexane–EtOAc); IR ν_{max}^{Nujol} cm^{-1}: 3350, 3200, 1630, 1610; ^1H NMR (CD_3COCD_3): δ1.00 (3H, *d*, $J=7$ Hz), 1.08 (3H, *s*), 1.18 (3H, *s*), 1.46 (3H, *d*, $J=1.5$ Hz), 1.76 (3H, *d*, $J=1.5$ Hz), 1.88–2.58 (5H, complex), 3.72–4.08 (3H, complex), 6.14 (1H, *dd*, $J=1.5$, 11 Hz), 7.41 (1H, *dd*, $J=1.5$, 11 Hz), MS *m/z*: 334.2128 $[M]^+$ (calc. for $C_{20}H_{30}O_4$ *m/z*: 334.2147). Compound **56**: IR ν_{max}^{film} cm^{-1}: 1720, 1635, 1600; ^1H NMR ($CDCl_3$): δ0.93 (3H, *t*, $J=7$ Hz), 1.45 (2H, *tq*, $J=7$, 7 Hz), 2.29 (2H, *tt*, $J=7$, 7 Hz), 3.75 (3H, *s*), 5.84 (1H, *dt*, $J=10.5$, 7 Hz), 5.87 (1H, *d*, $J=15$ Hz), 6.14 (1H, *dd*, $J=10.5$, 11 Hz), 7.64 (1H, *dd*, $J=11$, 15 Hz); MS *m/z*: 154.0976 $[M]^+$ (calc. for $C_9H_{14}O_2$ *m/z*: 154.0992). Hydrolysis of **54** was also carried out under the same condition as described above to give the same triol (**55**). In this case, however, an ester corresponding to **56** has not yet been obtained.

Epoxidation of 2E,4Z-octadienoate (**56**). A soln of **56** (38 mg) and mCPBA (212 mg) in CH_2Cl_2 was allowed to stand at room temp for 1.5 hr with stirring, and then partitioned between CH_2Cl_2 and H_2O. The organic layer was washed with satd aq NaCl and then dried (Na_2SO_4). Removal of solvent afforded a colourless oil of epoxide (**57**, 9 mg), IR ν_{max}^{film} cm^{-1}: 1725, 1655; ^1H NMR ($CDCl_3$): δ0.95 (3H, *t*, $J=6.5$ Hz), 1.2–1.7 (4H, complex), 3.20 (1H, *dt*, $J=4.5$, 5 Hz), 3.51 (1H, *dd*, $J=4.5$, 7 Hz), 3.78 (3H, *s*), 6.13 (1H, *d*, $J=15.5$ Hz), 6.84 (1H, *dd*, $J=7$, 15.5 Hz); MS *m/z*: 139.0758 $[M-OMe]^+$ (calc. for $C_8H_{11}O_2$ *m/z*: 139.0759).

Acetylation of triol (**55**). A soln of **55** (27 mg) in pyridine (1 ml) and Ac_2O (15.2 μl) was allowed to stand at room temp for 10 hr and then concd under red. pres. to give an oil which was sepd by prep. TLC (Kieselgel 60 PF_{254}, 0.4 mm) using Me_2CO–$CHCl_3$ (1:3) to afford colourless needles of diacetate (**58**, 2.0 mg) and two monoacetates (**59**, 4.2 mg; **60**, 10.7 mg), **58**, mp 153–154° (from hexane–EtOAc); IR ν_{max}^{film} cm^{-1}: 3460, 1735, 1720 *sh*, 1640, 1610 *br*; ^1H NMR (C_6D_6): δ0.55–0.9 (1H, *m*), 0.97 (6H, *s*), 1.03 (3H, *d*, $J=6$ Hz), 1.18 (1H, *dd*, $J=8$, 11.5 Hz), 1.53 (3H, *d*, $J=1.5$ Hz), 1.74 (3H, *s*), 1.80 (3H, *s*), 1.84 (3H, *d*, $J=1$ Hz), 1.4–2.6 (5H, complex), 2.78 (1H, *dd*, $J=8.5$, 11 Hz), 3.03 (1H, *br s*), 4.80 (1H, *dd*, $J=6$, 8.5 Hz), 4.86 (1H, *dd*, $J=3$, 11.5 Hz), 5.92 (1H, *dd*, $J=1.5$, 11 Hz), 7.29 (1H, *dd*, $J=1$, 11.5 Hz); MS *m/z*: 418.2371 $[M]^+$ (calc. for $C_{24}H_{34}O_6$ *m/z*: 418.2354). Compound **59**: IR ν_{max}^{film} cm^{-1}: 3450, 1720 *br*, 1610 *br*; ^1H NMR ($CDCl_3$): δ1.03 (3H, *d*, $J=7$ Hz), 1.12 (3H, *s*), 1.21 (3H, *s*), 1.52 (3H, *s*), 1.81 (3H, *s*), 2.01 (3H, *s*), 2.06–2.73 (4H, complex), 2.90 (1H, *br s*), 3.71 (1H, *br s*), 3.83 (1H, *dd*, $J=2$, 6 Hz), 4.81 (1H, *dd*, $J=3$, 11 Hz), 6.07 (1H, *br d*, $J=11$ Hz), 7.37 (1H, *br d*, $J=11$ Hz); MS *m/z*: 376.2275 $[M]^+$ (calc. for $C_{22}H_{32}O_5$ *m/z*: 376.2248). Compound **60**, mp 196–201° (from hexane–EtOAc); IR ν_{max}^{film} cm^{-1}: 3400, 1715 *br*, 1610 *br*; ^1H NMR ($CDCl_3$): δ1.07 (3H, *s*), 1.08 (3H, *d*, $J=7$ Hz), 1.47 (3H, *d*, $J=1.5$ Hz), 1.77 (3H, *s*), 2.03 (3H, *s*), 2.17–2.53 (3H, complex), 2.71 (1H, *dd*, $J=8$, 10.5 Hz), 3.11 (1H, *br s*), 3.96 (1H, *dd*, $J=3.5$, 10 Hz), 4.80 (1H, *dd*, $J=6$, 8 Hz), 5.82 (1H, *br*, *d*, $J=10.5$ Hz), 7.26 (1H, *br d*, $J=11$ Hz); MS *m/z*: 376.2275 $[M]^+$ (calc. for $C_{22}H_{32}O_5$ *m/z*: 376.2248).

Oxidation of euphohelioscopin A (**53**). A soln of **53** (20 mg) and excess PCC (66 mg) in CH_2Cl_2 (2 ml) was stirred at room temp. for 10 hr and then filtered. The filtrate was concd under red pres. and then purified by prep. TLC (Kieselgel 60 PF_{254}, *ca* 1 mm) using hexane–EtOAc (3:1) to afford a pale yellow oil of conjugated dione (**61**, 12 mg), IR ν_{max}^{film} cm^{-1}: 1745, 1710, 1665, 1635, 1610; ^1H NMR ($CDCl_3$) δ0.92 (3H, *t*, $J=7$ Hz), 1.10 (3H, *s*), 1.17 (3H, *s*), 1.23 (3H, *d*, $J=7$ Hz), 1.58 (3H, *br s*), 1.86 (3H, *br s*), 2.01–2.65 (8H, complex), 5.24 (1H, *br d*, $J=9$ Hz), 5.67–6.20 (5H, complex), 7.61 (1H, *dd*, $J=11$, 15 Hz); MS *m/z*: 436.2606 $[M]^+$ (calc. for $C_{28}H_{36}O_4$ *m/z*: 436.2611).

Benzoylation of monoacetates (**59** *and* **60**). To a soln of **59** (14.8 mg) in pyridine (0.5 ml) was added benzoyl chloride (30 μl) under ice cooling. The reaction mixt was stirred at the same temp for 9 hr and then worked-up as usual to give a pale brown oil which was purified by prep. TLC (Kieselgel 60 PF_{254}, 1 mm) using hexane–EtOAc (2:1) to afford a colourless oil of benzoate (**62**, 16.6 mg), IR ν_{max}^{film} cm^{-1}: 3470, 1720, 1610 *br*; ^1H NMR ($CDCl_3$): δ1.06 (3H, *s*), 1.16 (3H, *d*, $J=7$ Hz), 1.19 (3H, *s*), 1.28 (3H, *s*), 1.56 (3H, *d*, $J=1.5$ Hz), 1.83 (3H, *s*), 2.88 (1H, *dd*, $J=8.5$, 11 Hz), 4.74 (1H, *dd*, $J=3$, 11 Hz), 5.02 (1H, *dd*, $J=6$, 8.5 Hz), 5.80 (1H, *dd*, $J=1.5$, 11 Hz), 7.26 (1H, *br d*, $J=11$ Hz), 7.41–7.56 (3H, *m*), 8.06 (2H, *m*); MS *m/z*: 480.2524 $[M]^+$ (calc. for $C_{29}H_{36}O_6$ *m/z*: 480.2510). Using the same procedure as described above, **60** (8.9 mg) was readily converted into the corresponding benzoate (**63**, 10.5 mg) as a colourless oil, IR ν_{max}^{film} cm^{-1}: 3430, 1715, 1605; ^1H NMR ($CDCl_3$): δ1.05 (3H, *d*, $J=6$ Hz), 1.11 (3H, *s*), 1.21 (3H,), 1.56 (3H, *s*), 1.62 (3H, *d*, $J=1.5$ Hz), 1.83 (3H, *s*), 2.00–2.61 (6H, complex), 2.77 (1H, *dd*, $J=8.5$, 11 Hz), 4.74 (1H, *dd*, $J=6$, 8.5 Hz), 5.06 (1H, *dd*, $J=3$, 11 Hz), 5.85 (1H, *dd*, $J=1.5$, 11 Hz), 7.32 (1H, *br d*, $J=11$ Hz), 7.44–7.56 (3H, *m*), 8.06 (2H, *m*), 8.06 (2H, *m*); MS *m/z*: 480.2538 $[M]^+$ (calc. for $C_{29}H_{36}O_6$ *m/z*: 480.2510).

Formation of carbonate ester (**64**) *from monoacetate* (**59**). A soln of **59** (31 mg) and 1,1-carbonyldiimidazole (133 mg) in CH_2Cl_2 (2 ml) was stirred at room temp. for 10 hr. The reaction mixt. was concd, heated at 140° for 3 days and then directly sepd by prep. TLC (Kieselgel 60 PF_{254}, 1 mm) using hexane–Me_2CO (1:8) to afford a pale green solid of carbonate ester (**64**, 1.8 mg), IR ν_{max}^{film} cm^{-1}: 1770 *br*, 1735, 1630, 1610; ^1H NMR ($CDCl_3$): δ1.17 (3H, *s*), 1.22 (3H, *d*, $J=6$ Hz), 1.23 (3H, *s*), 1.52 (3H, *br s*), 1.87 (3H, *br s*), 2.03 (3H, *s*), 2.91 (1H, *dd*, $J=2$, 9 Hz), 4.44 (1H, *d*, $J=2$ Hz), 4.78 (1H, *br dd*, $J=3$, 11 Hz), 5.77 (1H, *br d*, $J=9$ Hz), 6.77 (1H, *br d*, $J=11$ Hz); MS *m/z*: 402.2043 $[M]^+$ (calc. for $C_{23}H_{30}O_6$ *m/z*: 402.2040).

Transannular reaction of deacetyleuphornin (**66**). A soln of **66** (98 mg) and *p*-TsOH (67 mg) in Me_2CO (8 ml) was stirred at room temp for 5.5 hr. After addition of 2 drops of Et_2NH, the reaction mixt. was concd under red pres. and then directly subjected to prep. TLC (Kieselgel 60 PF_{254}, 1 mm) using hexane–EtOAc (5:4) to afford a colourless oil of tricyclic compound (**67**, 72.4 mg), IR ν_{max}^{film} cm^{-1}: 3450, 1705, 1600, 1580;

^{1}H NMR ($CDCl_3$): δ −0.16 (1H, *t*, J = 5.5 Hz), 0.84 (1H, *dd*, J = 5.5, 11 Hz), 0.95 (3H, *s*), 1.00 (3H, *s*), 1.05 (3H, *d*, J = 7 Hz), 1.09 (3H, *d*, J = 7 Hz), 1.59 (3H, *d*, J = 1 Hz), 2.39 (1H, *dd*, J = 5.5, 12 Hz), 2.96 (1H, *dd*, J = 5.5, 12 Hz), 3.54 (1H, *t*, J = 5.5 Hz), 4.00 (1H, *t*, J = 6.5 Hz), 4.18 (1H, *t*, J = 2 Hz), 5.45 (1H, *t*, J = 5.5 Hz), 5.74 (1H, *dq*, J = 12, 1 Hz), 7.4–7.6 (3H, *m*), 8.09 (2H, *m*); MS *m/z*: 440.2581 $[M]^+$ (calc. for $C_{27}H_{36}O_5$ *m/z*: 440.2509).

Benzoylation of **67**. A soln of **67** (22.5 mg) and excess benzoyl chloride in pyridine (2 ml) was stirred at room temp for 37 hr. The reaction mixt. was concd under red pres. to give a brown oil which was sepd by prep. TLC (Kieselgel 60 PF_{254}, 0.4 mm) using hexane–EtOAc (4:1) to afford euphohelionone (**65**, 5.8 mg) (TLC, IR and ^{1}H NMR).

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