Pergamon 0031-9422(95)00399-1 Phytochemistry, Vol. 40, No. 4, pp. 1175–1181, 1995

0031-9422/95 $9.50 + 0.00

LINDERANOLIDES AND *ISO*LINDERANOLIDES, TEN BUTANOLIDES FROM *LINDERA GLAUCA*

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(*Received in revised form* 3 *April* 1995)

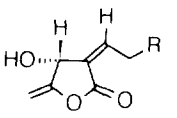
Key Word Index— *Lindera glauca*; Lauraceae; leaves; (+)-hydroxybutanolides; linderanolides A–E; *iso*linderanolides A–E.

Abstract—Ten new (+)-hydroxybutanolides, linderanolides A–E and *iso*linderanolides A–E, along with one known one have been isolated from the leaves of *Lindera glauca*. On the basis of spectroscopic methods and chemical evidence, linderanolides A–E were shown to be (3*R*,2*Z*)-3-hydroxy-4-methylenebutanolides having 2-((11*E*)-11-tetradecenylidene), 2-tetradecylidene, 2-((7*Z*,10*Z*)-7,10-hexadecadienylidene), 2-((7*Z*)-7-hexadecenylidene) and 2-hexadecylidene side-chains, respectively, while *iso*linderanolides A–E were their corresponding (2*E*)-isomers.

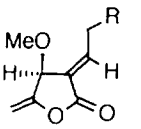
INTRODUCTION

Various (3*S*)-2-alkylidene-3-hydroxy-4-methylenebutanolides having cytotoxic activity [1] have been found in several members of the Lauraceae, e.g. *Lindera obtusiloba* [1–3], *Actinodaphne lancifolia* [4], *A. longifolia* [5] and *Machilus thunbergii* [6]. The isolation of their (3*R*)-isomers were, however, limited to five lactones, i.e. mahubenolide (**1**) and its related compounds, from the trunk wood of *Clinostemon mahuba* [7, 8]. Recently, we reported on the structures of two (3*S*)-methoxybutanolides (**2**, **3**) from the roots of *Lindera glauca* (Japanese name, 'Yamakobashi') which is a deciduous shrub distributed widely in the mountainous regions of Japan [9].

Further search for lactonic compounds in the leaves of the same species has led to the isolation of 10 new (+)-hydroxybutanolides, named linderanolides A–E (**4a–e**) and *iso*linderanolides A–E (**5a–e**), together with one known one (**5f**). This paper describes the isolation and structural elucidation of these compounds.



1 R= -$(CH_2)_{12}CH{=}CH_2$



2: R= -$(CH_2)_8CH{=}CH_2$
3: R= -$(CH_2)_8C{\equiv}CH$

RESULTS AND DISCUSSION

Benzene extracts of the fresh leaves, which after removal of essential oils and methanol-insoluble terpenoids, were fractionated by column chromatography on silica gel to yield lactones, showing 11 peaks (**4a**, 0.3%; **4b**, 1.2%; **5a**, 1.3%; **5b**, 4.3%; **4c**, 4.6%; **4d**, 2.0%; **4e**, 12.8%; **5c**, 25.8%; **5d**, 6.6%; **5e**, 40.0%; **5f**, 1.1%) on capillary GC. The lactonic fraction showed two spots on TLC, suggesting the presence of two groups, and the ratio was found to be *ca* 1:4 (R_f 0.40:0.45) by ^{1}H NMR analysis. After separation of the groups by Lober column chromatography on silica gel, each fraction was mainly fractionated on reverse-phase silica gel to afford **4a–e** and **5a–f**.

The compounds were classified into six groups according to molecular formula: $C_{19}H_{30}O_3$ ($[M]^+$ *m/z* 306): **4a** ($[\alpha]_D^{20}$ + 34.9°), **5a** ($[\alpha]_D^{20}$ + 45.7°); $C_{19}H_{32}O_3$ ($[M]^+$ *m/z* 308): **4b** ($[\alpha]_D^{20}$ + 39.7°), **5b** ($[\alpha]_D^{20}$ + 40.8°); $C_{21}H_{32}O_3$ ($[M]^+$ *m/z* 332): **4c** ($[\alpha]_D^{20}$ + 51.0°), **5c** ($[\alpha]_D^{20}$ + 40.8°); $C_{21}H_{34}O_3$ ($[M]^+$ *m/z* 334): **4d** ($[\alpha]_D^{20}$ + 49.0°), **5d** ($[\alpha]_D^{20}$ + 48.2°); $C_{21}H_{36}O_3$ ($[M]^+$ *m/z* 336): **4e** ($[\alpha]_D^{20}$ + 48.5°, mp 53–53.5°), **5e** ($[\alpha]_D^{20}$ + 37.7° mp 40.5–41°); and $C_{23}H_{40}O_3$ ($[M]^+$ *m/z* 364): **5f**. Their UV and IR spectra were similar to one another and contained UV absorption maxima (λ_{max}^{EtOH} 224 nm (log ε 4.02–4.12) and IR absorption bands 3450–3400 (OH), 1780–1750 (C=O), 1690 1660 cm^{-1} (C=C)) characteristic of α,β'-unsaturated-γ-lactones having a hydroxyl group. The ^{1}H and ^{13}C NMR data of **4a–e** and **5a–f** are summarized in Tables 1 and 2.

The spectral data of **4b**, **4d**, **5b** and **5d** showed a resemblance to those reported for obtusilactone A, obtusilactone B, *iso*obtusilactone A and *iso*obtusilactone B, respectively, from the leaves of *L. obtusiloba* [1, 3]. However, they were dextrorotatory in analogy with mahubenolide (**1**, $[\alpha]_D^{24}$ + 6.2°) [8] having a (3*R*)-hydroxyl

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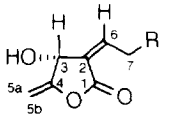
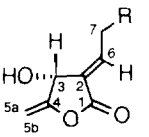


Linderanolides



Isolinderanolides

4a: R= -$(CH_2)_8\overset{trans}{CH{=}CH}CH_2Me$ (A: 0.3%)

4b: R= -$(CH_2)_{11}Me$ (B: 1.2%)

4c: R= -$(CH_2)_4\overset{cis}{CH{=}CH}CH_2CH\overset{cis}{=}CH(CH_2)_4Me$ (C: 4.6%)

4d: R= -$(CH_2)_4\overset{cis}{CH{=}CH}(CH_2)_7Me$ (D: 2.0%)

4e: R= -$(CH_2)_{13}Me$ (E: 12.8%)

5a: R= -$(CH_2)_8\overset{trans}{CH{=}CH}CH_2Me$ (A: 1.3%)

5b: R= -$(CH_2)_{11}Me$ (B: 4.3%)

5c: R= -$(CH_2)_4\overset{cis}{CH{=}CH}CH_2CH\overset{cis}{=}CH(CH_2)_4Me$ (C: 25.8%)

5d: R= -$(CH_2)_4\overset{cis}{CH{=}CH}(CH_2)_7Me$ (D: 6.6%)

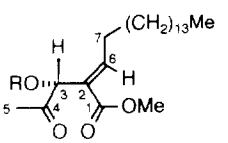
5e: R= -$(CH_2)_{13}Me$ (E: 40.0%)

5f: R= -$(CH_2)_{15}Me$ (1.1%)

group. These lactones (**4b**, **4d**, **5b**, **5d**) must therefore be the enantiomers of the above corresponding (3*S*)-lactones. The lactone **5f**, although it could not be obtained in a pure form, was identical to *iso*mahubanolide-23 [8] from the Amazonian Lauraceae. Hence, the structures for **4b**, **4d**, **5b**, **5d** and **5f** could be represented as shown in the formulae.

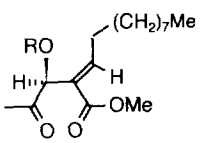
The remaining six compounds were divided into two groups, depending on the geometry of the exocyclic trisubstituted double bond to the lactonic carbonyl: linderanolides A (**4a**), C (**4c**), E (**4e**); *iso*linderanolides: A (**5a**), C (**5c**), E (**5e**). The former group had the same geometry (2*Z*) as **4b** and **4d**, while the latter were their geometrical isomers. This geometry was confirmed not only by the chemical shifts in and around the lactonic ring (H-3, 7; C-1–7) but also from the following observations. In the NOESY spectrum of **4e**, ring proton H-3 (δ5.11) showed a correlation with H-6 (δ6.69), as well as its geminal hydroxyl proton (δ2.26) and H-5a (δ4.68), so that H-3 and H-6 must possess a *syn*-relationship to each other with regard to the trisubstituted double bond. In the case of its geometrical isomer **5e**, H-3 (δ5.26) exhibited a NOE with H-7 (δ2.47) instead of H-6 (δ7.09).

On the other hand, the above six lactones could be classified into three types according to the structure of their side-chains: monoenylidene group (A: **4a**, **5a**), dienylidene group (C: **4c**, **5c**) and saturated alkylidene group (E: **4e**, **5e**). The ^{1}H NMR spectrum of **4a** in type A revealed vinylene signals (δ5.41 (2H, *m*, H-16, 17)) characteristic of a *trans*-double bond, which was also supported by an IR band at 965 cm^{-1}. This double bond must therefore be in the *E*-configuration and its position was determined to be ω-3 in the tetradecenylidene side-chain, because its ^{13}C NMR data showed a typical signal pattern (C-15 ~ 19) for a *trans*-ω-3 alkenyl group [10]. In addition, irradiation of the vinylene protons at δ5.41 sharpened the allylic methylene signals at δ1.97 (4H, *m*, H-15, 18), while irradiation of the methylene protons changed the above vinylene signals to two doublets (δ5.36, 5.45 (each 1H, J = 16.4 Hz)) and the terminal methyl signal at δ0.96 (3H, *t*, J = 7.4 Hz, H-19) to a singlet. Therefore, linderanolide A (**4a**) and *iso*linderanolide



10: R= -H

11: R= -Ac



12: R= -H

13: R= -Ac

A (**5a**) are (3*R*,2*Z*)- and (3*R*,2*E*)-3-hydroxy-4-methylene-2-((11*E*)-11-tetradecenylidene)butanolide, respectively.

The NMR spectra of **4e** (type E) showed a striking resemblance to those of **4b**, suggesting that **4e** was a homologue of **4b** which differed only in the chain length of the alkylidene moiety. This side-chain was found to be a hexadecylidene group from its molecular formula, while **5e** was the geometrical isomer of **4e**. Both side-chains in **4c** and **5c** (type C) were characteristic of a (*Z*,*Z*)-hexadecadienylidene group having a 1,4-diene structure [10] in their ^{13}C NMR spectra. The positions of the two double bonds were then determined by the following mass spectral data. Epoxidation of **5c** with *m*-chloroperbenzoic acid (MCPBA) gave two monoepoxides **7** and **8** ($C_{21}H_{32}O_4$, $[M]^+$ *m/z* 348). The mass spectra (Table 3) of the epoxides revealed significant peaks at *m/z* 277 and 237, respectively, resulting from cleavage α to the epoxy rings [11, 12]. Hence, these double bonds must occupy the 7- and 10-positions in the side-chain. The structures of other alkenylidene side-chains were also confirmed by the mass spectral data of the epoxides **6** (from **5a**) and **9** (from **5d**).

On methanolysis with 0.01% methanolic KOH, **5e** gave a ring-opening methyl ester (**10**) ($[\alpha]_D^{20}$ − 88.1°, mp 45.5–46.5°) with the unchanged secondary hydroxyl group (3500, 3450 cm^{-1}) and an oxo group (1720 cm^{-1}), while acetylation of **10**, although difficult to obtain the acetate of **5e**, yielded an acetate (**11**) ($[\alpha]_D^{20}$ − 54.7°, mp 50.5–51.5°). The derivatives **10** and **11** corresponded to the optical isomers of homologues of *secoiso*lancifolide (**12**) ($[\alpha]_D$ + 103°) and its acetate (**13**) ($[\alpha]_D$ + 33.2°) [5], respectively. However, the reported values ($[\alpha]_D^{24}$

Table 1. ^{1}H NMR data of compounds **4a**–**e** and **5a**–**f** (300 MHz, $CDCl_3$ with TMS as internal standard)*

H	4a	4b	4c	4d	4e	5a	5b	5c	5d	5e	5f
3	5.12 *br d* (6.6)	5.11 *br s*	5.11 *dd* (8.4, 1.6)	5.11 *br s*	5.11 *br d* (8.1)	5.26 *br d* (8.1)	5.28 *br d* (8.4)	5.26 *br d* (8.4)	5.26 *br d* (8.3)	5.26 *br d* (8.4)	5.27 *br d* (8.2)
5a	4.68 *dd* (2.8, 1.6)	4.68 *dd* (2.8, 1.6)	4.68 *dd* (2.8, 1.6)	4.68 *dd* (2.8, 1.6)	4.68 *dd* (2.8, 1.6)	4.73 *dd* (2.8, 1.4)	4.73 *dd* (2.8, 1.4)	4.73 *dd* (2.8, 1.4)	4.72 *dd* (2.8, 1.4)	4.73 *dd* (2.8, 1.4)	4.73 *dd* (2.8, 1.4)
5b	4.89 *dd* (2.8, 2.0)	4.89 *dd* (2.8, 2.0)	4.89 *dd* (2.8, 2.0)	4.89 *dd* (2.8, 2.0)	4.89 *dd* (2.8, 2.0)	4.96 *dd* (2.8, 1.7)	4.95 *dd* (2.8, 1.7)	4.95 *dd* (2.8, 1.7)	4.96 *dd* (2.8, 1.7)	4.96 *dd* (2.8, 1.7)	4.96 *dd* (2.8, 1.7)
6	6.69 *td* (7.8, 1.9)	6.69 *td* (7.8, 2.0)	6.68 *td* (7.9, 2.0)	6.68 *td* (7.9, 2.0)	6.69 *td* (7.9, 2.0)	7.09 *td* (7.9, 2.2)	7.08 *td* (7.9, 2.2)	7.08 *td* (7.9, 2.2)	7.08 *td* (7.9, 2.2)	7.09 *td* (7.9, 2.2)	7.09 *td* (7.9, 2.2)
7	2.78 *m*	2.77 *m*	2.77 *m*	2.78 *m*	2.77 *m*	2.47 *m*	2.47 *m*	2.48 *m*	2.47 *m*	2.47 *m*	2.47 *m*
8	1.49 *qui* (7.5)	1.49 *qui* (7.2)	1.50 *qui* (7.2)	1.50 *qui* (7.1)	1.49 *qui* (7.2)	1.53 *qui* (7.5)	1.53 *qui* (7.1)	1.54 *qui* (7.1)	1.54 *qui* (7.0)	1.53 *qui* (7.3)	1.53 *qui* (7.2)
9	1.26 *br s*	1.26 *br s*	1.38 *m*	1.37 *m*	1.26 *br s*	1.27 *br s*	1.26 *br s*	1.38 *m*	1.37 *m*	1.26 *br s*	1.26 *br s*
10	1.26 *br s*	1.26 *br s*	1.38 *m*	1.27 *br s*	1.26 *br s*	1.27 *br s*	1.26 *br s*	1.38 *m*	1.27 *br s*	1.26 *br s*	1.26 *br s*
11	1.26 *br s*	1.26 *br s*	2.05 *m*	2.01 *m*	1.26 *br s*	1.27 *br s*	1.26 *br s*	2.05 *m*	2.01 *m*	1.26 *br s*	1.26 *br s*
12	1.26 *br s*	1.26 *br s*	5.35 *m*	5.35 *m*	1.26 *br s*	1.27 *br s*	1.26 *br s*	5.35 *m*	5.35 *m*	1.26 *br s*	1.26 *br s*
13	1.26 *br s*	1.26 *br s*	5.35 *m*	5.35 *m*	1.26 *br s*	1.27 *br s*	1.26 *br s*	5.35 *m*	5.35 *m*	1.26 *br s*	1.26 *br s*
14	1.26 *br s*	1.26 *br s*	2.77 *m*	2.01 *m*	1.26 *br s*	1.27 *br s*	1.26 *br s*	2.77 *m*	2.01 *m*	1.26 *br s*	1.26 *br s*
15	1.97 *m*	1.26 *br s*	5.35 *m*	1.27 *br s*	1.26 *br s*	1.97 *m*	1.26 *br s*	5.35 *m*	1.27 *br s*	1.26 *br s*	1.26 *br s*
16	5.41 *m*	1.26 *br s*	5.35 *m*	1.27 *br s*	1.26 *br s*	5.41 *m*	1.26 *br s*	5.35 *m*	1.27 *br s*	1.26 *br s*	1.26 *br s*
17	5.41 *m*	1.26 *br s*	2.05 *m*	1.27 *br s*	1.26 *br s*	5.41 *m*	1.26 *br s*	2.05 *m*	1.27 *br s*	1.26 *br s*	1.26 *br s*
18	1.97 *m*	1.26 *br s*	1.30 *m*	1.27 *br s*	1.26 *br s*	1.97 *m*	1.26 *br s*	1.30 *m*	1.27 *br s*	1.26 *br s*	1.26 *br s*
19	0.96 *t* (7.4)	0.88 *br t* (6.8)	1.30 *m*	1.27 *br s*	1.26 *br s*	0.96 *t* (7.4)	0.88 *br t* (6.8)	1.30 *m*	1.27 *br s*	1.26 *br s*	1.26 *br s*
20	–		1.30 *m*	1.27 *br s*	1.26 *br s*			1.30 *m*	1.27 *br s*	1.26 *br s*	1.26 *br s*
21			0.89 *br t* (6.8)	0.88 *br t* (6.8)	0.88 *br t* (6.8)			0.89 *br t* (6.8)	0.88 *br t* (6.7)	0.88 *br t* (6.8)	1.26 *br s*
22											1.26 *br s*
23											0.88 *br t* (6.8)
OH	2.19 *d* (6.6)	2.19 *d* (6.6)	2.26 *d* (8.4)	2.19 *d* (6.6)	2.26 *br d* (8.1)	2.05 *d* (8.1)	2.31 *d* (8.4)	2.31 *d* (8.4)	2.19 *d* (8.3)	2.15 *d* (8.4)	1.96 *d* (8.2)

*Coupling constants (J in Hz) are given in parentheses. Assignments were based on ^{1}H–^{1}H COSY and ^{1}H–^{13}C COSY experiments.

Table 2. ^{13}C NMR data of compounds **4a–e** and **5a–f** (75 MHz, $CDCl_3$ with TMS as internal standard)*

C	4a	4b	4c	4d	4e	5a	5b	5c	5d	5e	5f
1	165.1	165.2	165.2	165.1	165.2	166.6	166.8	166.7	166.6	166.7	166.6
2	126.8	126.8	126.9	126.9	126.8	127.3	127.3	127.4	127.3	127.3	127.3
3	68.9	68.9	68.9	68.9	68.9	66.5	66.4	66.4	66.4	66.5	66.5
4	157.5	157.5	157.5	157.5	157.5	157.7	157.7	157.7	157.6	157.7	157.7
5	90.3	90.3	90.3	90.3	90.3	91.4	91.4	91.4	91.4	91.4	91.4
6	151.4	151.4	151.2	151.2	151.4	150.2	150.3	150.0	150.1	150.3	150.3
7	28.7	28.7	28.6	28.6	28.7	29.7	29.7	29.7	29.7	29.7	29.7
8	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.2	28.2	28.3	28.3
9	29.1	29.3	28.9	28.9	29.3	29.1	29.4	29.0	29.0	29.4	29.4
10	29.4	29.4	29.3	29.5	29.4	29.4	29.4	29.3	29.4	29.4	29.4
11	29.5	29.5	27.0	27.0	29.5	29.5	29.5	27.0	27.0	29.5	29.5
12	29.5	29.7	129.8	129.5	29.6	29.5	29.7	129.6	129.3	29.6	29.6
13	29.3	29.7	127.8	130.2	29.7	29.3	29.7	127.8	130.3	29.7	29.7
14	29.6	29.7	25.6	27.2	29.7	29.7	29.7	25.6	27.2	29.7	29.7
15	32.6	29.6	128.3	29.8	29.7	32.6	29.6	128.4	29.7	29.7	29.7
16	129.4	29.4	130.3	29.3	29.7	129.3	29.4	130.4	29.3	29.7	29.7
17	131.9	31.9	27.2	29.5	29.7	131.9	31.9	27.2	29.5	29.7	29.7
18	25.6	22.7	29.3	29.3	29.4	25.6	22.7	29.3	29.3	29.4	29.7
19	14.0	14.1	31.5	31.9	31.9	14.0	14.1	31.5	31.9	31.9	29.7
20	—	—	22.6	22.7	22.7	—	—	22.6	22.7	22.7	29.4
21	—	—	14.1	14.1	14.1	—	—	14.1	14.1	14.1	31.9
22	—	—	—	—	—	—	—	—	—	—	22.7
23	—	—	—	—	—	—	—	—	—	—	14.1

*Assignments were based on DEPT, ^1H–^{13}C COSY and ^1H–^{13}C long range COSY experiments. A few signals may be interchangeable within the same column.

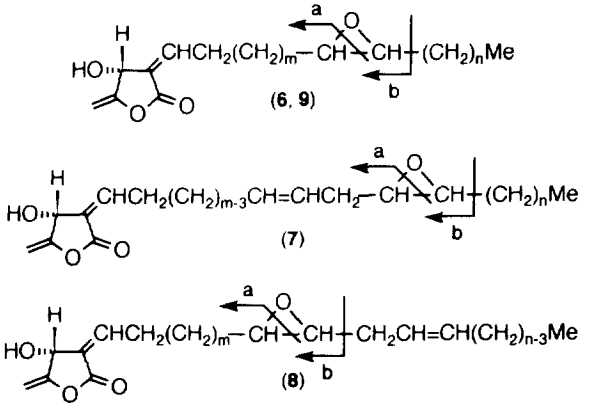


Table 3. Characteristic peaks in mass spectra of compounds **6–9**

		m/z (rel. int.)				
Epoxide	m/n	$[M]^+$	$[b]^+$	$[b-H_2O]^+$	$[a+H]^+$	$[a]^+$
6	8/1	322 (2)	293 (3)	275 (7)	265 (8)	264 (5)
7	7/4	348 (3)	277 (4)	259 (7)	249 (2)	248 (2)
8	4/7	348 (2)	237 (2)	219 (8)	209 (4)	208 (7)
9	4/7	350 (2)	237 (12)	219 (6)	209 (13)	208 (42)

+ 6.2°– + 23.1°) of the specific rotation for the Amazonian (3*R*)-lactones [7, 8] were extremely small, so that they seem to be considerably racemized. In practice, HPLC analysis of **5e**, having a comparatively small value ($[\alpha]_D^{20}$ + 37.7) among the specific rotations of **4a–e** and **5a–e**, revealed that **5e** is a mixture of (3*R*)- and (3*S*)-forms (83:17).

From these results, linderanolides A–E and *iso*linderanolides A–E were concluded to be **4a–e** and **5a–e** as shown in the formulae. It is interesting to note that the

leaves of *L. glauca* contained various (+)-hydroxybutanolides in contrast to its roots containing (−)-methoxybutanolides [9]; no lactonic compounds could be detected in the corresponding seed oil. This is the first report of the isolation of 4-methylenebutanolides having a dienylidene group and a (*E*)-monenylidene group.

EXPERIMENTAL

General. Mps: uncorr. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz): $CDCl_3$ with TMS as an int. standard. EIMS (probe): 70 eV. GC: FID, N_2 at 0.44 ml min^{-1}, fused silica capillary column (Hicap-CBP1-M50-025, 50 m × 0.2 mm, Shimadzu), temp. programmed 240–300° at 2° min^{-1}. CC: Kieselgel 60 (70–230 mesh, Merck) and $AgNO_3$–Kieselgel (1:4). Lober CC: LiChroprep RP-18 and Si60 (each 40–63 μm, Merck). HPLC: Chiralcel OD (25 cm × 4.6 mm, Daicel), *n*-hexane–*iso*-PrOH (49:1). TLC: silica gel (Wako), *n*-hexane–EtOAc (5:1).

Extraction and separation. Leaves of *L. glauca* Blume were collected at Utsunomiya, Tochigi Prefecture, in June 1990. The fresh leaves (4.4 kg) were cut into small pieces and extracted with benzene at room temp. for 4 days. Evapn of the solvent gave a dark green viscous oil (55 g), which after removal of essential oils and MeOH-insol. terpenoids, was treated with *n*-hexane. The *n*-hexane-sol. materials (16.3 g) were fractionated by CC on silica gel to afford lactones (2.4 g), showing 11 peaks (**4a**, 0.3%; **4b**, 1.2%; **5a**, 1.3%; **5b**, 4.3%; **4c**, 4.6%; **4d**, 2.0%; **4e**, 12.8%; **5c**, 25.8%; **5d**, 6.6%; **5e**, 40.0%; **5f**, 1.1%) on GC and two spots (R_f 0.40 and 0.45) on TLC. Repeated Lober CC on silica gel (benzene–EtOAc, 5:1) yielded two lactonic frs (*X*: (R_f 0.40, 0.5 g), *Y*: (R_f 0.45, 1.9 g)), which on Lober CC over reverse-phase silica gel using MeOH, were divided into 3 (*X*-1–3) and 4 frs (*Y*-1–4), respectively. Further CC on $AgNO_3$–silica gel followed by Lober CC on silica gel of these frs afforded the following lactones: **4a** (3 mg), **4c** (33 mg) (from fr. *X*-1); **4b** (5 mg), **4d** (8 mg) (fr. *X*-2); **5a** (8 mg), **5c** (102 mg) (fr. *Y*-1); **5b** (24 mg) and **5d** (16 mg) (fr. *Y*-2). Recrystallization of fr. *X*-3 yielded **4e** (95 mg), while Lober CC on silica gel of the frs *Y*-3 and 4, and subsequent recrystallization, gave **5e** (207 mg) and **5f** (2 mg), respectively. **5f** could not be obtained in a pure form.

Linderanolide A (**4a**). Oil. $[\alpha]_D^{20}$ + 34.9° ($CHCl_3$; *c* 0.10). UV λ_{max}^{EtOH} nm (log ε): 224 (4.05). IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 3025, 965 (*trans*-CH=CH–), 1780 (>C=O), 1680, 850 (>C=CH–). EIMS *m/z* (rel. int.): 307 $[M + H]^+$ (2), 306 $[M]^+$ (5), 289 $[M + H - H_2O]^+$ (5), 263 $[M - 43]^+$ (23), 151 $[M - 155]^+$ (11), 149 $[M - 157]^+$ (13), 140 $[C_7H_8O_3]^+$ (18), 135 (23), 126 (40), 123 (27), 109 (26), 97 (23), 95 (39), 83 (34), 81 (44), 79 (20), 70 $[MeCH{=}CHCHO]^+$ (68), 69 $[MeCH{=}CHC{\equiv}O]^+$ (57), 67 $[MeC{\equiv}CC{\equiv}O]^+$ (46), 57 (22), 55 $[CH_2{=}CHC{\equiv}O]^+$ (100), 43 $[MeC{\equiv}O]^+$ (55), 41 (94). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Linderanolide B (**4b**). Oil. $[\alpha]_D^{20}$ + 39.7° ($CHCl_3$, *c* 0.11). UV λ_{max}^{EtOH} nm (log ε): 224 (4.02). IR ν_{max}^{neat} cm^{-1}: 3400 (OH), 1780, 1750 (>C=O), 1660, 850 (>C=CH–). EIMS *m/z* (rel. int.): 309 $[M + H]^+$ (26), 308 $[M]^+$ (11), 291 $[M + H - H_2O]^+$ (12), 265 $[M - 43]^+$ (100), 153 $[M - 155]^+$ (17), 151 $[M - 157]^+$ (6), 140 $[C_7H_8O_3]^+$ (29), 135 (15), 126 (46), 123 (15), 109 (13), 97 (21), 95 (17), 83 (28), 81 (18), 79 (11), 70 $[MeCH{=}CHCHO]^+$ (92), 69 $[MeCH{=}CHC{\equiv}O]^+$ (27), 67 $[MeC{\equiv}CC{\equiv}O]^+$ (17), 57 (26), 55 $[CH_2{=}CHC{\equiv}O]^+$ (50), 43 $[MeC{\equiv}O]^+$ (84), 41 (53). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Iso*linderanolide A* (**5a**). Oil. $[\alpha]_D^{20}$ + 45.7° ($CHCl_3$; *c* 0.11). UV λ_{max}^{EtOH} nm (log ε): 224 (4.10). IR ν_{max}^{neat} cm^{-1}: 3425 (OH), 3025, 965 (*trans*-CH=CH–), 1780 (sh), 1770 (>C=O), 1680, 1670, 885 (>C=CH–). EIMS *m/z* (rel. int.): 307 $[M + H]^+$ (4), 306 $[M]^+$ (11), 289 $[M + H - H_2O]^+$ (4), 263 $[M - 43]^+$ (51), 151 $[M - 155]^+$ (11), 149 $[M - 157]^+$ (12), 140 $[C_7H_8O_3]^+$ (13), 135 (20), 126 (42), 123 (30), 109 (30), 97 (23), 95 (43), 83 (32), 81 (47), 79 (16), 70 $[MeCH{=}CHCHO]^+$ (81), 69 $[MeCH{=}CHC{\equiv}O]^+$ (60), 67 $[MeC{\equiv}CC{\equiv}O]^+$ (45), 57 (18), 55 $[CH_2{=}CHC{\equiv}O]^+$ (95), 43 $[MeC{\equiv}O]^+$ (48), 41 (100). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Iso*linderanolide B* (**5b**). Oil. $[\alpha]_D^{20}$ + 40.8° ($CHCl_3$; *c* 0.12). UV λ_{max}^{EtOH} nm (log ε): 224 (4.08). IR ν_{max}^{neat} cm^{-1}: 3425 (OH), 1780 (sh), 1760 (>C=O), 1680, 1665, 850 (>C=CH–). EIMS *m/z* (rel. int.): 309 $[M + H]^+$ (4), 308 $[M]^+$ (5), 291 $[M + H - H_2O]^+$ (2), 265 $[M - 43]^+$ (100), 153 $[M - 155]^+$ (8), 151 $[M - 157]^+$ (5), 140 $[C_7H_8O_3]^+$ (22), 135 (9), 126 (33), 123 (12), 109 (10), 97 (20), 95 (15), 83 (22), 81 (16), 79 (8), 70 $[MeCH{=}CHCHO]^+$ (93), 69 $[MeCH{=}CHC{\equiv}O]^+$ (24), 67 $[MeC{\equiv}CC{\equiv}O]^+$ (15), 57 (21), 55 $[CH_2{=}CHC{\equiv}O]^+$ (42), 43 $[MeC{\equiv}O]^+$ (66), 41 (39). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Linderanolide C (**4c**). Oil. $[\alpha]_D^{20}$ + 51.0° ($CHCl_3$; *c* 0.15). UV λ_{max}^{EtOH} nm (log ε): 224 (4.08); IR ν_{max}^{neat} cm^{-1}: 3425 (OH), 3000 (*cis*-CH=CH–), 1780, 1760 (sh) (>C=O), 1680, 850 (>C=CH–). EIMS *m/z* (rel. int.): 333 $[M + H]^+$ (1), 332 $[M]^+$ (2), 315 $[M + H - H_2O]^+$ (2), 289 $[M - 43]^+$ (10), 177 $[M - 155]^+$ (8), 175 $[M - 157]^+$ (6), 140 $[C_7H_8O_3]^+$ (17), 135 (15), 126 (7), 123 (22), 109 (25), 97 (12), 95 (51), 83 (20), 81 (70), 79 (45), 70 $[MeCH{=}CHCHO]^+$ (19), 69 $[MeCH{=}CHC{\equiv}O]^+$ (29), 67 $[MeC{\equiv}CC{\equiv}O]^+$ (100), 57 (11), 55 $[CH_2{=}CHC{\equiv}O]^+$ (74), 43 $[MeC{\equiv}O]^+$ (41), 41 (62). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Linderanolide D (**4d**). Oil. $[\alpha]_D^{20}$ + 49.0° ($CHCl_3$; *c* 0.13). UV λ_{max}^{EtOH} nm (log ε): 224 (4.12). IR ν_{max}^{neat} cm^{-1}: 3425 (OH), 3000 (*cis*-CH=CH–), 1780 (>C=O), 1680, 850 (>C=CH–). EIMS *m/z* (rel. int.): 335 $[M + H]^+$ (2), 334 $[M]^+$ (6), 317 $[M + H - H_2O]^+$ (7), 291 $[M - 43]^+$ (19), 179 $[M - 155]^+$ (7), 177 $[M - 157]^+$ (7), 140 $[C_7H_8O_3]^+$ (25), 135 (20), 126 (19), 123 (25), 109 (20), 97 (21), 95 (36), 83 (30), 81 (41), 79 (21), 70 $[MeCH{=}CHCHO]^+$ (45), 69 $[MeCH{=}CHC{\equiv}O]^+$ (44), 67 $[MeC{\equiv}CC{\equiv}O]^+$ (52), 57 (27), 55 $[CH_2{=}CHC{\equiv}O]^+$ (100), 43 $[MeC{\equiv}O]^+$ (90), 41 (52). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Linderanolide E (**4e**). Crystals, mp 53–53.5° (from *n*-hexane). $[\alpha]_D^{20}$ + 48.5° ($CHCl_3$; *c* 0.14). UV λ_{max}^{EtOH} nm (log

ε): 224 (4.06). IR ν_{max}^{KBr} cm^{-1}: 3425 (OH), 1770, 1750 (>C=O), 1660, 850 (>C=CH–). EIMS *m/z* (rel. int.): 337 $[M+H]^+$ (5), 336 $[M]^+$ (9), 319 $[M+H-H_2O]^+$ (4), 293 $[M-43]^+$ (96), 140 $[C_7H_8O_3]^+$ (25), 135 (13), 126 (49), 123 (17), 109 (15), 97 (23), 95 (19), 83 (34), 81 (20), 79 (12), 70 $[MeCH=CHCHO]^+$ (95), 69 $[MeCH=CHC\equiv O]^+$ (32), 67 $[MeC\equiv CC\equiv O]^+$ (19), 57 (34), 55 $[CH_2=CHC\equiv O]^+$ (57), 43 $[MeC\equiv O]^+$ (100), 41 (52). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Iso*linderanolide C* (**5c**). Oil. $[\alpha]_D^{20}$ +40.8° ($CHCl_3$; *c* 0.19). UV λ_{max}^{EtOH} nm (log ε): 224 (4.06). IR ν_{max}^{neat} cm^{-1}: 3425 (OH), 3000 (*cis*-CH=CH–), 1770 (>C=O), 1680, 1665, 855 (>C=CH–). EIMS *m/z* (rel. int.): 333 $[M+H]^+$ (2), 332 $[M]^+$ (6), 315 $[M+H-H_2O]^+$ (6), 289 $[M-43]^+$ (19), 177 $[M-155]^+$ (9), 175 $[M-157]^+$ (8), 140 $[C_7H_8O_3]^+$ (7), 135 (19), 126 (9), 123 (22), 109 (28), 97 (12), 95 (49), 83 (18), 81 (73), 79 (45), 70 $[MeCH=CHCHO]^+$ (18), 69 $[MeCH=CHC\equiv O]^+$ (28), 67 $[MeC\equiv CC\equiv O]^+$ (100), 57 (11), 55 $[CH_2=CHC\equiv O]^+$ (72), 43 $[MeC\equiv O]^+$ (41), 41 (61). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Iso*linderanolide D* (**5d**). Oil. $[\alpha]_D^{20}$ +48.2° ($CHCl_3$; *c* 0.14). UV λ_{max}^{EtOH} nm (log ε): 224 (4.06). IR ν_{max}^{neat} cm^{-1}: 3425 (OH), 3000 (*cis*-CH=CH–), 1765 (>C=O), 1680, 1665, 850 (>C=CH–). EIMS *m/z* (rel. int.): 335 $[M+H]^+$ (3), 334 $[M]^+$ (10), 317 $[M+H-H_2O]^+$ (7), 291 $[M-43]^+$ (42), 179 $[M-155]^+$ (8), 177 $[M-157]^+$ (11), 140 $[C_7H_8O_3]^+$ (16), 135 (19), 126 (27), 123 (34), 109 (31), 97 (24), 95 (52), 83 (40), 81 (52), 79 (20), 70 $[MeCH=CHCHO]^+$ (50), 69 $[MeCH=CHC\equiv O]^+$ (48), 67 $[MeC\equiv CC\equiv O]^+$ (59), 57 (33), 55 $[CH_2=CHC\equiv O]^+$ (100), 43 $[MeC\equiv O]^+$ (91), 41 (79). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Iso*linderanolide E* (**5e**). Crystals, mp 40.5–41 (from *n*-hexane). $[\alpha]_D^{20}$ +37.7° ($CHCl_3$; *c* 0.17). UV λ_{max}^{EtOH} nm (log ε): 224 (4.11). IR ν_{max}^{KBr} cm^{-1}: 3425 (OH), 1780, 1750 (>C=O), 1690, 1670, 885 (>C=CH–). EIMS *m/z* (rel. int.): 337 $[M+H]^+$ (3), 336 $[M]^+$ (5), 319 $[M+H-H_2O]^+$ (2), 293 $[M-43]^+$ (100), 140 $[C_7H_8O_3]^+$ (15), 135 (7), 126 (26), 123 (12), 109 (9), 97 (15), 95 (13), 83 (19), 81 (13), 79 (7), 70 $[MeCH=CHCHO]^+$ (62), 69 $[MeCH=CHC\equiv O]^+$ (19), 67 $[MeC\equiv CC\equiv O]^+$ (12), 57 (20), 55 $[CH_2=CHC\equiv O]^+$ (33), 43 $[MeC\equiv O]^+$ (59), 41 (27). ^{1}H and ^{13}C NMR: Tables 1 and 2. HPLC analysis of **5e** showed two peaks in a ratio of 83:17, of which the minor peak was identified as (3*S*,2*E*)-2-hexadecylidene-3-hydroxy-4-methylenebutanolide by comparison of its R_f on HPLC with that of an authentic sample [Seki, unpublished] isolated from *L. obtusiloba*. Thus, the ratio of (3*R*)- and (3*S*)-forms in **5e** is 83:17.

Iso*mahubanolide-23* (**5f**). Solid. IR ν_{max}^{KBr} cm^{-1}: 3425 (OH), 1780 (>C=O), 1680, 1665, 850 (>C=CH–). EIMS *m/z* (rel. int.): 365 $[M+H]^+$ (5), 364 $[M]^+$ (5), 347 $[M+H-H_2O]^+$ (2), 321 $[M-43]^+$ (68), 140 $[C_7H_8O_3]^+$ (11), 135 (22), 126 (19), 123 (19), 109 (23), 97 (20), 95 (26), 83 (31), 81 (25), 79 (13), 70 $[MeCH=CHCHO]^+$ (48), 69 $[MeCH=CHC\equiv O]^+$ (46), 67 $[MeC\equiv CC\equiv O]^+$ (22), 57 (34), 55 $[CH_2=CHC\equiv O]^+$ (73), 43 $[MeC\equiv O]^+$ (100), 41 (51). ^{1}H and ^{13}C NMR: Tables 1 and 2. The above data of **5f** are in agreement with those of *iso*mahubanolide-23 [8] from *C. mahuba*.

Epoxidation of iso*linderanolide A* (**5a**). To a soln of **5a** (5 mg) in CH_2Cl_2 (2 ml) was added MCPBA (4 mg) and the mixt. stirred at room temp. for 8 hr. After usual work-up, a 16,17-epoxide (**6**, 4 mg) was obtained as an oil by CC on silica gel using benzene–Et_2O (10:1). $[\alpha]_D^{20}$ +45.0° ($CHCl_3$; *c* 0.07). IR ν_{max}^{neat} cm^{-1}: 3400 (OH), 1780 (>C=O), 1680, 1665, 850 (>C=CH–), 880 (oxirane). ^{1}H NMR: δ0.99 (3H, *t*, *J* = 7.5 Hz, H-19), 1.29 (12H, *br s*, H-9 ~ 14), 1.53 (2H, *m*, H-8), 1.54 (4H, *m*, H-15, 18), 2.23 (1H, *d*, *J* = 8.8 Hz, OH), 2.47 (2H, *m*, H-7), 2.67 (2H, *m*, H-16, 17), 4.72 (1H, *dd*, *J* = 2.9, 1.3 Hz, H-5a), 4.96 (1H, *dd*, *J* = 2.9, 1.7 Hz, H-5b), 5.26 (1H, *br s*, H-3), 7.09 (1H, *td*, *J* = 7.9, 2.2 Hz, H-6); ^{13}C NMR: δ9.9 (C-19), 25.2 (C-14), 26.0 (C-18), 28.2 (C-8), 29.1 (C-9), 29.2 (C-10), 29.3 (2C) (C-11, 12), 29.4 (C-13), 29.6 (C-7), 32.1 (C-15), 58.8 (C-16), 60.0 (C-17), 66.5 (C-3), 91.3 (C-5), 127.3 (C-2), 150.1 (C-6), 157.7 (C-4), 166.5 (C-1). EIMS *m/z* (rel. int.): 322 $[M]^+$ (2), 305 $[M+H-H_2O]^+$ (5), 294 (2), 293 $[M-MeCH_2]^+$ (3), 279 $[M-43]^+$ (6), 275 $[M-MeCH_2-H_2O]^+$ (7), 265 (8), 264 $[M-MeCH_2CHO]^+$ (5), 140 $[C_7H_8O_3]^+$ (21), 126 (66), 99 (26), 95 (52), 81 (47), 70 (100), 69 (42), 55 (64), 43 (38), 41 (40).

Epoxidation of iso*linderanolide C* (**5c**). A soln of **5c** (44 mg) and MCPBA (46 mg) in CH_2Cl_2 (2 ml) was stirred at room temp. for 3 hr. Usual work-up afforded two monoepoxides, which were sepd by CC on silica gel. The fr. eluted with *n*-hexane–benzene (1:20) gave an 15,16-epoxide (**7**, 7 mg) and the fr. eluted with benzene yielded an 12,13-epoxide (**8**, 6 mg).

Epoxide **7**. Oil. $[\alpha]_D^{20}$ +30.7° ($CHCl_3$; *c* 0.12). IR ν_{max}^{neat} cm^{-1}: 3425 (OH), 3000 (*cis*-CH=CH–), 1780 (>C=O), 1680, 1665, 850 (>C=CH–), 820 (oxirane). ^{1}H NMR: δ0.91 (3H, *br t*, *J* = 7.1 Hz, H-21), 1.34 (10H, *m*, H-9, 10, 18 ~ 20), 1.53 (2H, *m*, H-8), 1.56 (2H, *m*, H-17), 2.06 (2H, *m*, H-11), 2.26 (2H, *m*, H-14), 2.48 (2H, *m*, H-7), 2.87 (1H, *d*, *J* = 8.3 Hz, OH), 2.93 (2H, *m*, H-15, 16), 4.72 (1H, *dd*, *J* = 2.8, 1.4 Hz, H-5a), 4.95 (1H, *dd*, *J* = 2.8, 1.7 Hz, H-5b), 5.25 (1H, *br d*, *J* = 8.3 Hz, H-3), 5.49 (2H, *m*, H-12, 13), 7.06 (1H, *td*, *J* = 7.2, 2.8 Hz, H-6). EIMS *m/z* (rel. int.): 349 $[M+H]^+$ (2), 348 $[M]^+$ (3), 331 $[M+H-H_2O]^+$ (6), 305 $[M-43]^+$ (5), 277 $[M-Me(CH_2)_4]^+$ (4), 259 $[M-Me(CH_2)_4-H_2O]^+$ (7), 249 (2), 248 $[M-Me(CH_2)_4CHO]^+$ (2), 140 $[C_7H_8O_3]^+$ (16), 126 (28), 99 (100), 95 (73), 81 (74), 70 (31), 69 (37), 55 (72), 43 (61), 41 (41).

Epoxide **8**. Oil. $[\alpha]_D^{20}$ +38.9° ($CHCl_3$; *c* 0.11). IR ν_{max}^{neat} cm^{-1}: 3425 (OH), 3000 (*cis*-CH=CH–), 1780 (>C=O), 1680, 1665, 850 (>C=CH–), 825 (oxirane). ^{1}H NMR: δ0.89 (3H, *br t*, *J* = 6.9 Hz, H-21), 1.30 (10H, *m*, H-9, 10, 18 ~ 20), 1.48 (2H, *m*, H-11), 1.53 (2H, *m*, H-8), 2.04 (2H, *m*, H-17), 2.25 (2H, *m*, H-14), 2.41 (1H, *s*, OH), 2.47 (2H, *m*, H-7), 2.93 (2H, *m*, H-12, 13), 4.72 (1H, *dd*, *J* = 2.8, 1.4 Hz, H-5a), 4.96 (1H, *dd*, *J* = 2.8, 1.6 Hz, H-5b), 5.26 (1H, *br s*, H-3), 5.46 (2H, *m*, H-15, 16), 7.08 (1H, *td*, *J* = 7.7, 2.1 Hz, H-6); EIMS *m/z* (rel. int.): 349 $[M+H]^+$ (2), 348 $[M]^+$ (2), 331 $[M+H-H_2O]^+$ (24), 237 $[M-Me(CH_2)_4CH=CHCH_2]^+$ (2), 219

$[M - Me(CH_2)_4CH=CHCH_2 H_2O]^+$ (8), 209 (4), 208 $[M - Me(CH_2)_4CH=CHCH_2CHO]^+$ (7), 140 $[C_7H_8O_3]^+$ (11), 126 (24), 99 (15), 95 (70), 81 (100), 70 (35), 69 (54), 55 (86), 43 (44), 41 (54).

Epoxidation of isolinderanolide D (**5d**). The lactone **5d** (8 mg) in CH_2Cl_2 (2 ml) was epoxidized with MCPBA (6 mg) at room temp. for 8 hr. Usual work-up and subsequent CC on silica gel using benzene Et_2O (10:1) gave an 12,13-epoxide (**9**, 5 mg) as an oil. $[\alpha]_D^{20}$ + 31.8 ($CHCl_3$; *c* 0.07). IR ν_{max}^{neat} cm^{-1}: 3425 (OH), 1780 (>C=O), 1680, 1665, 850 (>C=CH–), 825 (oxirane). ^{1}H NMR: δ0.88 (3H, *br t*, *J* = 6.7 Hz, H-21), 1.27 (16H, *br s*, H-9, 10, 15 ~ 20), 1.48 (4H, *m*, H-11, 14), 1.53 (2H, *m*, H-8), 2.34 (1H, *d*, *J* = 7.3 Hz, OH), 2.47 (2H, *m*, H-7), 2.91 (2H, *m*, H-12, 13), 4.72 (1H, *dd*, *J* = 2.7, 1.5 Hz, H-5a), 4.96 (1H, *dd*, *J* = 2.7, 1.7 Hz, H-5b), 5.26 (1H, *br s*, H-3), 7.08 (1H, *td*, *J* = 7.8, 2.2 Hz, H-6); ^{13}C NMR: δ14.1 (C-21), 22.7 (C-20), 26.3 (C-10), 26.6 (C-15), 27.5 (C-11), 27.8 (C-14), 28.1 (C-8), 29.0 (C-9), 29.2 (C-18), 29.4 (C-17), 29.5 (C-7), 29.6 (C-16), 31.9 (C-19), 57.1 (C-12), 57.4 (C-13), 66.5 (C-3), 91.3 (C-5), 127.3 (C-2), 149.7 (C-6), 157.7 (C-4), 166.6 (C-1). EIMS *m/z* (rel. int.): 351 $[M + H]^+$ (2), 350 $[M]^+$ (2), 307 $[M - 43]^+$ (5), 237 $[M - Me(CH_2)_7]^+$ (12), 219 $[M - Me(CH_2)_7-H_2O]^+$ (6), 209 (13), 208 $[M - Me(CH_2)_7CHO]^+$ (42), 140 $[C_7H_8O_3]^+$ (25), 126 (62), 99 (10), 95 (49), 81 (69), 70 (61), 69 (67), 55 (100), 43 (85), 41 (58).

Methanolysis of isoinderanolide E (**5e**). To **5e** (148 mg) was added 0.01% KOH in MeOH (12 ml) and the mixt. stirred at room temp. for 4 hr. Usual work-up and Lober CC on silica gel using benzene–EtOAc (5:1) afforded an ester (**10**, 148 mg). Colourless crystals, mp 45.5–46.5° (from *n*-hexane). $[\alpha]_D^{20}$ – 88.1 ($CHCl_3$; *c* 0.24). UV λ_{max}^{EtOH} nm (log ε): 230 (3.57); IR ν_{max}^{KBr} cm^{-1}: 3500, 3450 (OH), 1720 (>C=O), 1700 (CO_2Me), 1640 (>C=CH–). ^{1}H NMR: δ0.88 (3H, *br t*, *J* = 6.7 Hz, H-21), 1.26 (24H, *br s*, H-9–20), 1.52 (2H, *qui*, *J* = 7.4 Hz, H-8), 2.16 (3H, *s*, H-5), 2.36 (2H, *td*, *J* = 7.6, 7.4 Hz, H-7), 3.73 (3H, *s*, OMe), 4.02 (1H, *d*, *J* = 4.9 Hz, OH), 4.90 (1H, *d*, *J* = 4.9 Hz, H-3), 7.08 (1H, *t*, *J* = 7.6 Hz, H-6); ^{13}C NMR: δ14.1 (C-21), 22.7 (C-20), 24.8 (C-5), 28.7 (2C) (C-7, 8), 29.3 (C-18), 29.4 (2C) (C-9, 10), 29.5 (C-11), 29.6 (C-12), 29.7 (5C) (C-13–17), 31.9 (C-19), 52.0 (OMe), 73.4 (C-3), 129.8 (C-2), 149.0 (C-6), 166.6 (C-1), 206.3 (C-4). EIMS *m/z* (rel. int.): 369 $[M + H]^+$ (6), 326 $[M + H - Ac]^+$ (23), 325 $[M - Ac]^+$ (100), 294 $[M - 74]^+$ (8), 293 $[M - 75]^+$ (42), 140 (3), 125 (3), 115 (10), 111 (4), 109 (4), 97 (5), 95 (5), 83 (6), 70 (2), 69 (5), 57 (6), 55 (7), 43 $[MeC \equiv O]^+$ (68).

Acetylation of **10**. The ester **10** (30 mg) was treated with Ac_2O (1 ml) and pyridine (2 ml) at room temp. for 3 hr. After usual work-up, Lober CC on silica gel (benzene–EtOAc, 5:1) gave a monoacetate (**12**, 32 mg). Colourless crystals, mp 50.5–51.5° (from *n*-hexane). $[\alpha]_D^{20}$ – 54.7 ($CHCl_3$; *c* 0.13). UV λ_{max}^{EtOH} nm (log ε): 228 (3.63). IR ν_{max}^{KBr} cm^{-1}: 1760, 1230 (OAc), 1730 (>C=O), 1710 (CO_2Me), 1640 (>C=CH–). ^{1}H NMR: δ0.88 (3H, *br t*, *J* = 6.6 Hz, H-21), 1.26 (24H, *br s*, H-9–20), 1.47 (2H, *qui*, *J* = 6.7 Hz, H-8), 2.16 (3H, *s*, H-5), 2.20 (3H, *s*, OAc), 2.35 (2H, *td*, *J* = 7.8, 6.7 Hz, H-7), 3.77 (3H, *s*, OMe), 6.10 (1H, *s*, H-3), 7.14 (1H, *t*, *J* = 7.8 Hz, H-6); ^{13}C NMR: δ14.1 (C-21), 20.8 (OCOMe), 22.7 (C-20), 26.1 (C-5), 28.5 (C-8), 29.0 (C-7), 29.4 (3C) (C-9, 10, 18), 29.5 (C-11), 29.6 (C-12), 29.7 (5C) (C-13–17), 32.0 (C-19), 52.1 (OMe), 73.6 (C-3), 127.3 (C-2), 151.5 (C-6), 166.1 (C-1), 169.8 (OCOMe), 202.4 (C-4). EIMS *m/z* (rel. int.): 411 $[M + H]^+$ (32), 368 $[M + H - Ac]^+$ (4), 367 $[M - Ac]^+$ (9), 350 $[M - 60]^+$ (34), 325 $[M + H - 2Ac]^+$ (100), 293 $[M - 117]^+$ (36), 200 (7), 154 (15), 83 (6), 43 $[MeC \equiv O]^+$ (68).

Acknowledgements—Thanks are due to Prof. T. Uyehara of Utsunomiya University for his encouragement and to Daicel Chemical Industry Co. Ltd for HPLC measurements.

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