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DITERPENES FROM THE SEED OF *SCIADOPITYS VERTICILLATA*

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Key Word Index—*Sciadopitys verticillata*; Sciadopityaceae; seed; chemotaxonomy; diterpenes; labdane.

Abstract—Thirteen new labdane-type diterpenes have been isolated from the seeds of *Sciadopitys verticillata* together with six known ones, sciadin, sciadinone, dimethyl sciadinonate, lambertianic acid and its methyl ester and *trans*-communic acid. Their structures have been determined by chemical and spectral methods.

INTRODUCTION

Sciadopitys verticillata Sieb. et Zucc., endemic to Japan, is a sole species belonging to the family Sciadopityaceae. In earlier studies on the terpenoid constituents of this species, sciadin (**1**) [1], methyl sciadopate (**2**) [2], sciadinone (**3**), dimethyl sciadinonate (**4**) [3] and verticillol (**5**) [4] were isolated from the leaves or heartwood. Our present examination of the seed extract led to the isolation of a number of diterpenes, including **1**, **3** and **4**. This paper describes the structural elucidation of these diterpenes. In addition, the configurations at C-12 and C-20 of sciadin which had been proposed by Sumimoto [5] are discussed.

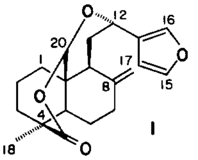
RESULTS AND DISCUSSION

The hexane extract of the seed which had been shown to contain no detectable amount of mono- and sesquiterpenes by GC analysis was treated with methanol to remove triacylglycerols and the methanol soluble portion was further fractionated into an acidic and a neutral parts.

Two diterpenes isolated from the acidic part after chromatographic separation were readily identified as *trans*-communic (**6**) and lambertianic acids. Four of the 17 diterpenes isolated from the neutral part were identified as **1**, **3**, **4** and methyl lambertianate (**7**) by comparison of their physical and spectral data with the published data.

The remaining 13 neutral compounds were new labdane-type diterpenes and their structures, now represented by the chemical formulae **8**–**13**, **17**–**19**, **21a**, **22a**, **23a** and **24a**, were established as follows.

The new diterpenes, except for **23a** and **24a**, showed common spectral features with those of **4** and **7**; that is, IR absorption bands at about 1725, 1160 and 900 cm^{-1} and proton resonances due to two methyl groups [*ca* δ1.2 and 3.6 (each *s*)] and an exocyclic methylene group [δ4.3–5.0 (2H, two *s*, *br*)] (Table 1). Hence, these compounds each have a labdane skeleton with an exocyclic methylene at C-8, and 4α-methyl and 4β-methoxycarbonyl groups.



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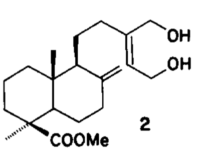

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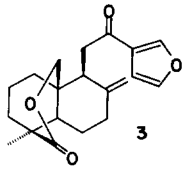

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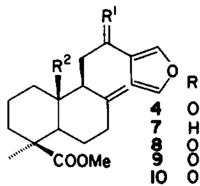
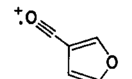
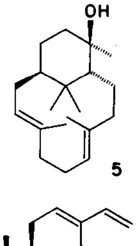


	R¹	R²
4	O	COOMe
7	H_2	Me
8	O	Me
9	O	CHO
10	O	CH_2OAc
11	H_2	CHO
12	H_2	COOMe
13	OAc H	Me
15	OH H	Me
16	H OH	Me



A



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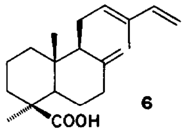

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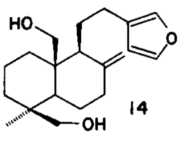

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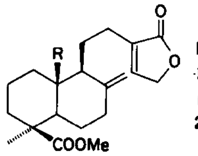


	R
17	CHO
18	COOMe
19	CH_2OAc
20	Me

Among them, compounds **8** ($C_{21}H_{28}O_4$, mp 81–82°, $[\alpha]_D$ −6.5°), **9** ($C_{21}H_{26}O_5$, mp 108–109°, $[\alpha]_D$ −12.0°) and **10** ($C_{23}H_{30}O_6$, an oil, $[\alpha]_D$ −6.5°), also in common with **4**, each contained a furan ring conjugated with a carbonyl group as shown by UV absorption maxima at 203 and 250 nm, an IR carbonyl absorption band at 1660–1675 cm^{-1}, an intense mass spectral ion at *m/z* 95 arising from fragment A and three aromatic proton signals at δ6.7, 7.4 and 8.0 in the ^{1}H NMR spectra. Further comparison of their IR and ^{1}H NMR spectra with those of **4** indicated that the methoxycarbonyl group at C-10 in **4** was replaced by a methyl group (δ0.59) in **8**, by an aldehyde group [ν_{max} 2752, 1710 cm^{-1}; δ9.73 (1H)] in **9** and by an acetoxymethyl group [ν_{max} 1745, 1240 cm^{-1}; δ3.99 (2H, ABq), 2.08 (3H, *s*)] in **10**. Thus **8**–**10** were methyl 12-oxo-lambertianate, methyl 12,20-dioxo-lambertianate and methyl 20-acetoxy-12-oxo-lambertianate, respectively. The former two compounds were isolated for the first time from a natural source, although **8** had been known as an intermediate in the synthesis of **7** by Bell *et al.* [6], and **9** as one of the compounds derived from **1** by Sumimoto [1].

Compounds **11** ($C_{21}H_{28}O_4$, an oil, $[\alpha]_D$ +36.2°) [7], **12** ($C_{22}H_{30}O_5$, an oil, $[\alpha]_D$ +0.4°) and **13** ($C_{23}H_{32}O_5$, mp

Table 1. ^{1}H NMR spectral data (100 MHz, in $CDCl_3$)

H	4*	7*	8	9	10	11	12	13	17	18
12								5.74 *dd* (1.5, 10)		
14	6.73 *dd* (0.9, 1.9)	6.21 *dd* (0.9, 1.9)	6.73 *dd* (1, 2)	6.71 *dd* (1, 2)	6.70 *dd* (1, 2)	6.19 *dd* (0.9, 1.9)	6.22 *dd* (0.9, 1.9)	6.35 *dd* (0.9, 1.9)	7.06 *t* (2.5)	7.07 *t* (2.5)
15	7.40 *dd* (1.3, 1.9)	7.29 *t* (1.9)	7.39 *dd* (1.5, 2)	7.38 *dd* (1.5, 2)	7.39 *dd* (1.5, 2)	7.29 *t* (1.9)	7.31 *t* (1.9)	7.31 *t* (1.9)	4.73 *dd* (2.5, 4.9)	4.75 *dd* (2.5, 4.9)
16	8.03 *dd* (0.9, 1.3)	7.14 *m* †	8.03 *dd* (1, 1.5)	8.02 *dd* (1, 1.5)	7.99 *dd* (1, 1.5)	7.12 *m* †	7.14 *m* †	7.36 *m* †		
17	4.69 *s* 4.32 *s*	4.84 *s* 4.54 *s*	4.71 *s* 4.35 *s*	4.79 *s* 4.39 *s*	4.76 *s* 4.42 *s*	4.96 *s* 4.65 *s*	4.86 *s* 4.53 *s*	4.86 *s* 4.44 *s*	4.96 *s* 4.64 *s*	4.86 *s* 4.54 *s*
18	1.26 *s*	1.17 *s*	1.20 *s*	1.27 *s*	1.24 *s*	1.23 *s*	1.22 *s*	1.19 *s*	1.24 *s*	1.24 *s*
20		0.51 *s*	0.59 *s*	9.73 *d* (1.7)	3.99 ABq ‡	9.65 *d* (1.7)		0.52 *s*	9.65 *d* (1.7)	
OMe	3.60 *s* 3.59 *s*	3.60 *s*	3.62 *s*	3.59 *s*	3.67 *s*	3.56 *s*	3.52 *s* 3.57 *s*	3.61 *s*	3.57 *s*	3.52 *s* 3.57 *s*
OAc					2.08 *s*			2.03 *s*		

H	19	21b	22b	1*	23a	23b	23b′	24a	24b	24b′
12				4.99 *dd* (4, 10)	4.83 *d* (*br*) (12)	4.87 *d* (*br*) (12)	4.84 *d* (*br*) (12)	5.00 *m*	4.89 *m*	4.89 *m*
14	7.03 *t* (2.5)	6.84 §	5.93 *m* ‖	6.43 *dd* (0.9, 1.9)	7.19 *t* (1)	7.24 *t* (1)	7.21 *t* (1.6)	6.08 *m* **	6.22 *dd* (1, 1.9)	6.16 *dd* (1, 1.8)
15	4.75 *dd* (2.5, 4.9)	6.84 §		7.35 *t* (1.9)	6.16 *m* ¶	6.92 *t* (1)	6.90 *dd* (1.6, 2)			
16			6.77 *m* ‖	7.41 *m* †				6.16– 6.26 *m*	6.97 *d* (1)	7.02 *d* (1)
17	4.92 *s* 4.64 *s*	4.85 *s* 4.52 *s*	4.87 *s* 4.40 *s*	5.02 *s* 4.76 *s*	5.07 *s* 4.95 *s*	5.06 *s* 4.94 *s*	5.06 *s* 4.94 *s*	5.06 *s* 4.79 *s*	5.05 *s* 4.64 *s*	5.05 *s* 4.69 *s*
18	1.21 *s*	1.24 *s*	1.25 *s*	1.24 *s*	1.23 *s*	1.24 *s*	1.24 *s*	1.24 *s*	1.24 *s*	1.24 *s*
20	3.92 *s*			5.50 *s*	5.45 *s*	5.46 *s*	5.45 *s*	5.45 *s*	5.43 *s*	5.43 *s*
OMe	3.65 *s*	3.53 *s* 3.58 *s*	3.55 *s* 3.59 *s*							
OAc	1.99 *s*	2.15 *s*	2.16 *s*			2.15 *s*	2.17 *s*		2.19 *s*	2.16 *s*

*Listed for comparison.

†$W_{1/2} = 3$ Hz.

‡$\Delta\nu = 10.6$ Hz, $J = 12$ Hz.

§Overlapped, $W_{1/2} = 2$ Hz.

‖$W_{1/2} = 4$ Hz.

¶$W_{1/2} = 7$ Hz.

**$W_{1/2} = 5$ Hz.

81–83°, $[\alpha]_D$ +79.4°) each contained a furan ring as shown by a positive Ehrlich's test and three aromatic proton signals in their ^{1}H NMR spectra, but the furan ring was not conjugated with a carbonyl group because of the UV absorption maximum at 200 nm and the lack of an enone carbonyl absorption in the IR spectra. The ^{1}H NMR spectra of **11** and **12** indicated the presence of an aldehyde group (δ9.65) and a methoxy carbonyl group (δ3.52), respectively, suggesting **11** and **12** were methyl 20-oxolambertianate and dimethyl 12-deoxo-sciadinonate. This was confirmed by the conversion of **11** and **12** into an identical diol (**14**) [7] on reduction with lithium aluminium hydride. On the other hand, **13** showed the presence of an additional tertiary methyl group (δ0.51) to that at C-4 (δ1.19) and a secondary acetoxyl group [ν_{max} 1740, 1240 cm^{-1}; δ5.74 (1H, *dd*), 2.03 (3H, *s*)]. This suggested that **13** was an acetoxyl derivative of **7**. The acetoxyl group was shown to be located at C-12 by the significant downfield shift of the signals of the two protons on the furan ring, H-14 and H-16, by 0.14 and 0.22 ppm each, as compared with those of **7**. On mild hydrolysis, **13** gave an alcohol which was identical to one of two epimeric alcohols (**15** and **16**) obtained from **8** by reduction with sodium borohydride. Bell *et al.* reported the synthesis of the two alcohols and determined the configurations of the hydroxyl groups mainly on the basis of a consideration of the ^{1}H NMR spectra [6]. The alcohol obtained from **13** was identical with the 12*R*-hydroxyl derivative, **15**, in all respects. Thus, **13** was established as methyl 12*R*-acetoxylambertianate.

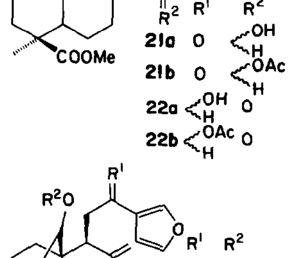
Compounds **17** ($C_{21}H_{32}O_5$, mp 120–121°, $[\alpha]_D$ +45.3°), **18** ($C_{22}H_{30}O_6$, an oil, $[\alpha]_D$ +16.7°) and **19** ($C_{23}H_{32}O_6$, an oil, $[\alpha]_D$ +34.1°), had no furan ring absorption bands in their spectra. Instead, their IR and ^{1}H NMR spectra displayed a carbonyl stretching band about 1750 cm^{-1} and two mutually coupled proton resonances about δ7.0 (1H) and 4.7 (2H), in common. These spectral features coupled with a positive Legal test suggested that each of the three compounds contained an α-substituted butenolide moiety in the side chain of the molecule, as in pinusolide (**20**) [8]. Furthermore, their ^{1}H NMR spectra indicated the presence of an aldehyde group (δ9.65) in **17**, an additional methoxycarbonyl group (δ3.52) to that at C-4 (δ3.57) in **18** and an acetoxymethyl group [δ3.92 (2H, *s*), 1.99 (3H, *s*)] in **19**. These compounds were, therefore, deduced to be C-20 oxygenated derivatives of **20**, and the structures were represented by formulae **17**–**19**, respectively.

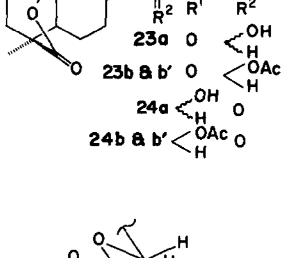
As compounds **21a** and **22a** were not separated from each other by chromatography on silica gel, they were isolated as the corresponding monoacetates, **21b** and **22b**. Both the acetates had the same molecular formula, $C_{24}H_{32}O_8$, and the same structure as **12** except for the furan ring, as shown by their mass and ^{1}H NMR spectra. The presence of an α-substituted γ-acetoxybutenolide moiety [9] in **21b** and of a β-substituted one [10] in **22b** was revealed by the IR absorption band at 1780 cm^{-1} (butenolide) and two proton signals ascribed to oxygen atom-bearing olefinic and methine groups [**21b**: δ6.84 (2H); **22b**: δ6.77, 5.93 (each 1H)]. Their ^{13}C NMR spectra (Table 2) revealed that **21b** and **22b** were a mixture of the 15- and 16-epimers, respectively, because several carbon signals of the acetates appeared as double lines. Verification of the structures was provided by the fact that when **12** in methanol was exposed to sunlight for 20 days it gave a mixture of **21a** and **22a**, as was expected [11].

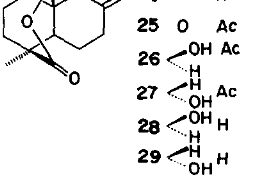
The last two compounds, **23a** (an oil, $[\alpha]_D$ −27.6°) and **24a** (an oil, $[\alpha]_D$ −7.8°), each having a molecular formula of $C_{20}H_{24}O_6$, were shown by their ^{1}H and ^{13}C NMR spectra to have the same partial structure as **1** except for the furan ring. Upon acetylation, **23a** and **24a** each gave two monoacetates (**23b** and **23b′**; **24b** and **24b′**), which were presumed to be mixtures of epimers concerning the acetoxyl group because of the close similarities of the ^{1}H NMR spectra between **23b** and **23b′** and between **24b** and **24b′**. Similarly as in the case of **21a** and **22a**, the presence of a α-substituted γ-hydroxy-butenolide in **23a** and of a β-substituted one in **24a** was also suggested by the IR spectra (**23a**: 3350, 1770 cm^{-1}; **24a**: 3300, 1770 cm^{-1}) and chemical shifts of two proton signals (**23a**: δ7.19, 6.16; **24a**: δ6.20, 6.08) as well as the effects of acetylation on the chemical shifts. In contrast with the case of **12**, **1** did not give any products by photolytic oxidation under the same condition, but this fact showed that, at least, **23a** and **24a** were not artifacts formed from **1** during the isolation procedure.

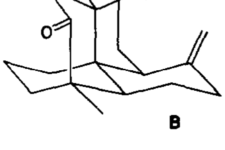
As for the configurations at C-12 and C-20 of **1**, Sumimoto demonstrated them to be 12*S* and 20*S* on the basis of the fact that, in the ^{1}H NMR spectra of **1** and its 8(17)-dihydro and 8-oxo derivatives, the chemical shifts of both H-12 and H-20 were largely effected by functional groups at C-8, supporting the stereostructure, **B** [5]. On the other hand, Bell reported an effect of a hydroxyl group at C-12 of labdane-type diterpenes on the chemical shift of exocyclic methylene protons at C-17 [12], and thus we attempted to establish the configurations according to Bell's consideration.

Sodium borohydride reduction of a lactol acetate, **25**, prepared from **1** in the manner described by Sumimoto [1], afforded two epimeric alcohols, **26** and **27**, in a ratio of 6:7. On the basis of the arguments of Bell, **27** was deduced to be 12*S*-hydroxyl derivative, because one of the exocyclic methylene protons underwent a downfield shift by 0.25 ppm as compared with that of **26** in the ^{1}H NMR spectra. Upon hydrolysis, **27** gave **1** together with sciadinic acid (**29**) [1] which gradually changed to **1** on standing, while **26** gave a stable lactol, **28**, as a sole product. Thus, the configuration of C-12 was confirmed as 12*S*. The *cis* relationship between H-12 and H-20 of **1** was established by the NOE measurement in the ^{1}H NMR:









B

Table 2. ^{13}C NMR spectral data (25.15 MHz, in CDCl$_3$)

C	7*	13	20*	17	18	19	8	10	4*	12	21b	22b	3*	1*	23a	24a
1	39.1	39.2	39.2	31.8	36.0	33.7	39.3	33.6	36.1	35.9	36.0	36.1	38.1	33.1	32.8	32.8
2	20.0	19.9	19.9	20.5	20.5	19.8	19.9	19.8	20.9	21.0	21.0	21.0	21.1	20.8	20.8	20.7
3	38.2	38.2	38.2	38.8	38.1	38.0	38.2	38.0	38.1	38.1	38.1	38.0	39.7	40.9	40.9	40.8
4	44.3	44.3	44.3	45.6	44.8	44.6	44.3	44.6	44.7	44.8	44.8	44.8	43.6	44.9	45.1	45.1
5	56.3	56.2	56.3	54.9	55.0	55.8	56.0	55.8	54.7	55.0	55.0	55.1	49.0	48.4	48.1	48.1
6	26.3	26.1	26.2	24.7	26.2	25.8	25.7	25.4	25.7	26.2	26.1	26.2	26.5	25.1	25.0	25.0
7	38.7	38.5	38.7	38.0	37.6	38.5	38.0	37.8	37.0	37.7	37.6	37.6	36.0†	35.6	35.4	35.4
8	147.9	147.6	147.4	145.4	146.1	146.3	148.7	147.8	147.7	146.5	146.0	146.1	146.6	145.1	144.0	144.1
9	55.2	52.0	55.7	53.2	53.7	56.1	50.4	49.8	48.1	53.0	53.7	53.5	45.3	44.9	44.7	44.6
10	40.2	39.8	40.3	53.0	53.3	43.0	39.6	42.3	52.5	53.1	53.2	53.3	37.9	37.9	37.7	37.7
11	23.6†	30.1	21.8	22.4	23.0	23.0	36.5	37.3	37.2	23.5†	22.2‡ 22.7	22.0‡ 22.1	35.8†	28.5	26.7‡ 27.1	25.2‡ 26.5
12	24.3†	67.4	24.7	24.0	24.7	25.1	194.1	194.1	193.4	25.1†	24.0‡ 24.6	26.4‡ 26.5	192.6	69.3	69.7	69.5‡ 70.6
13	125.4	125.8	134.8	134.2	134.3	134.6	128.0	128.1	127.8	124.8	138.8	167.1	127.6	125.8	137.3‡ 137.5	166.1 166.7
14	110.9	108.7	143.8	144.1	144.1	143.9	108.7	108.7	108.6	110.8	141.0‡ 141.1	118.4	108.6	108.8	144.4‡ 144.6	117.4‡ 118.4
15	142.6	143.0	70.1	70.2	70.1	70.1	144.0	144.2	144.1	142.7	92.5	169.0	144.3	143.1	97.3‡ 97.8	170.7
16	138.7	139.8	174.3	174.1	174.1	174.2	146.6	146.5	146.8	138.8	169.0	94.2‡ 94.6	146.9	139.2	169.6	97.3‡ 97.8
17	106.3	106.7	106.7	108.1	107.0	107.6	106.4	107.2	106.4	106.8	107.0	106.9	109.0	110.3	111.3	111.0‡ 111.3
18	28.8	28.7	28.8	27.0	28.3	29.1	28.8	29.0	28.2	28.2	28.3	28.3	23.2	22.3	22.1	22.1
19	177.7	177.5	177.6	176.4	176.1	177.1	177.5	177.1	176.1	176.1	175.7‡ 176.0	176.0	176.0	174.3	174.8	174.8‡ 175.1
20	12.6	12.6	12.6	205.0	172.7	62.4	13.1	62.8	173.0	172.7	172.5	172.3	73.0	100.3	100.6	100.3‡ 100.6
19-OMe	51.1	51.1	51.2	51.4	51.1	51.5	51.1	51.5	51.1	51.1	51.1‡ 51.4	51.1				
20-OMe					50.6				50.7	50.5	50.6	50.7				
OAc		170.4 21.2				170.6 21.1		170.3 21.1			170.4 20.7‡ 20.4	169.7 20.6				

^{13}C NMR spectral data for compounds **9** and **11**: see ref. [7].

*Listed for comparison.

†Assignments may be interchanged.

‡The signals appear as double lines because the compounds existed as C-15 or C-16 epimeric mixtures.

irradiation at H-20 (δ5.50) revealed an NOE enhancement (26%) on H-12 (δ5.02). Consequently, the stereostructure **B** for **1** as well as **23a** and **24a** was confirmed.

Finally, the proposed structures for the above compounds were also confirmed by their ^{13}C NMR spectra (Table 2), in which shift assignments were based on the multiplicities in the off-resonance spectra at single frequencies and recognition of proper substituent effects [13, 14].

EXPERIMENTAL

Mps: uncorr; ^{1}H NMR (100 MHz) and ^{13}C NMR (25.15 MHz): $CDCl_3$ containing TMS as an internal standard; GC: 5% OV-17 on Uniport KS (2 m × 3 mm), temp. 80–330° at 5°/min, N_2 60 ml/min.

Extraction. Seeds (900 g), collected in Wakayama prefecture, Japan, in 1979, were ground and extracted with hexane (2.5 l. × 2) and MeOH. The hexane extract (328 g) was treated with MeOH (150 ml × 3) in order to remove acylglycerols and the MeOH soluble part (29 g) was further fractionated into an acidic (1.5 g) and a neutral (27 g) part by treatment with 5% Na_2CO_3.

Trans-communic (**6**) *and lambertianic acids from the acidic part.* The acidic part was chromatographed on a silica gel column eluting with EtOAc–C_6H_6 (1:8). The least polar fraction (35 mg) was further purified by prep. TLC (layer thickness: 0.75 mm; Et_2O–hexane, 1:4) to give **6** (10 mg, R_f 0.65), an oil, $[\alpha]_D$ +38.0° (*c* 0.6, EtOH) and lambertianic acid (16 mg, R_f 0.60), mp 127–128° (from pentane), $[\alpha]_D$ +44.5° (*c* 0.97, $CHCl_3$).

Fractionation of the neutral part. The neutral part (6.4 g) was chromatographed on a silica gel column (33 × 4 cm) eluting with increasing amounts of EtOAc in hexane and fractions of 500 ml each were collected. The first fraction eluted with 10% EtOAc (630 mg) was further chromatographed on a silica gel column (Et_2O–hexane, 1:10) to give **7** (11 mg) as an oil, identical to the Me ester of lambertianic acid in all respects (TLC, MS and ^{1}H NMR), and triacylglycerols.

Isolation of methyl 12-*oxo-lambertianate* (**8**), *methyl* 12R-*acetoxy-lambertianate* (**13**), *methyl* 20-*oxo-lambertianate* (**11**) *and dimethyl* 12-*deoxo-sciadinonate* (**12**). The second fraction (947 mg) eluted with 15% EtOAc was subjected to repeated silica gel column chromatography (Et_2O–hexane, 1:3; EtOAc–C_6H_6, 1:20; $CHCl_3$) to afford **8** (40 mg), **13** (280 mg), **11** (47 mg) and **12** (520 mg). **8**: mp 81–82° (pentane), $[\alpha]_D$ −6.5° (*c* 0.61, $CHCl_3$); UV λ_{max}^{EtOH} nm (log ε): 203 (4.15), 250 (3.61); IR ν_{max}^{KBr} cm^{-1}: 3125, 1563, 1515, 873 (furan), 1660 (C=O), 890 (>C=CH_2), 1720, 1156 (ester); MS *m/z* (rel. int.): 344 $[M]^+$ (48), 285 (14), 284 (16), 235 (60), 234 (100), 175 (45), 121 (77), 95 (97). **13**: mp 81–83° (pentane), $[\alpha]_D$ +79.4° (*c* 0.63, $CHCl_3$); UV λ_{max}^{EtOH} nm (log ε): 202 (4.07); IR ν_{max}^{KBr} cm^{-1}: 3130, 1501, 874 (furan), 3085, 894 (>C=CH_2), 1740, 1240 (acetate), 1725, 1150 (ester); MS *m/z* (rel. int.): 388 $[M]^+$ (3), 329 (92), 323 (100), 269 (32), 121 (43), 81 (15), 43 (22). **11**: an oil, $[\alpha]_D$ +36.2° (*c* 0.58, $CHCl_3$); UV λ_{max}^{EtOH} nm (log ε): 202 (4.20); IR ν_{max}^{neat} cm^{-1}: 3135, 1503, 874 (furan), 3080, 1640, 894 (>C=CH_2), 2750, 1705 (CHO), 1720, 1160 (ester); MS *m/z* (rel. int.): 344 $[M]^+$ (98), 316 (30), 313 (23), 255 (20), 175 (60), 161 (66), 81 (100). **12**: an oil, $[\alpha]_D$ +0.4° (*c* 0.53, $CHCl_3$); UV λ_{max}^{EtOH} nm (log ε): 202 (4.00); IR ν_{max}^{neat} cm^{-1}: 3135, 1503, 874 (furan), 3080, 1644, 894 (>C=CH_2), 1730, 1200 (ester); MS *m/z* (rel. int.): 374 $[M]^+$ (80), 324 (43), 314 (100), 255 (47), 173 (27), 161 (38), 81 (34).

Isolation of methyl 12,20-*dioxo-lambertianate* (**9**), *sciadin* (**1**), *dimethyl sciadinonate* (**4**) *and methyl* 20-*acetoxy*-12-*oxo-lambertianate* (**10**). The third fraction eluted with 20% EtOAc (2.9 g) was recrystallized from $CHCl_3$–hexane to give **1** [530 mg, mp 162–163°, $[\alpha]_D$ +8.3° (*c* 3.03, $CHCl_3$)]. The mother liquor was subjected to repeated silica gel column chromatography (Et_2O–hexane, 1:1; EtOAc–C_6H_6, 1:10; Me_2CO–$CHCl_3$, 1:20) to give **9** (178 mg), **4** (356 mg), mp 124–125° (Et_2O–hexane), $[\alpha]_D$ −33.8° (*c* 0.45, $CHCl_3$), **10** (1.1 g) and **1** (360 mg). **9**: mp 108–109° (pentane); $[\alpha]_D$ −12° (*c* 1.67, EtOH); UV λ_{max}^{EtOH} nm (log ε): 203 (4.09), 250 (3.53); IR ν_{max}^{KBr} cm^{-1}: 3130, 1563, 1518, 873 (furan), 2725, 1710 (CHO), 1670 (C=O), 1725, 1160 (ester), 895 (>C=CH_2); MS *m/z* (rel. int.): 358 $[M]^+$ (6), 221 (21), 220 (14), 161 (24), 160 (27), 95 (100). **10**: an oil, $[\alpha]_D$ −6.5° (*c* 14.1, EtOH); UV λ_{max}^{EtOH} nm (log ε): 203 (4.12), 250 (3.49); IR ν_{max}^{neat} cm^{-1}: 3135, 1563, 1510, 875, 745 (furan), 1745, 1240 (acetate), 1675 (C=O), 1725, 1160 (ester), 897 (>C=CH_2); MS *m/z* (rel. int.): 402 $[M]^+$ (1), 342 (5), 329 (9), 311 (18), 251 (21), 173 (27), 159 (53), 95 (100), 43 (43). The fourth fraction (480 mg) eluted with 30% EtOAc gave the same compounds as above, after chromatography.

Isolation of sciadinone (**3**), 20-*oxo-pinusolide* (**17**), *dimethyl* 15,16-*epoxy*-16-*oxo-labda*-8(17),13-*diene*-19,20-*dioate* (**18**) *and* 20-*acetoxy-pinusolide* (**19**). The fifth fraction (542 mg) eluted with 50% EtOAc was subjected to repeated silica gel column chromatography (Et_2O–hexane, 1:1; EtOAc–C_6H_6, 1:8; Me_2CO–$CHCl_3$, 1:80) to give **3** (64 mg): mp 214–215° ($CHCl_3$–hexane), $[\alpha]_D$ −68.8° (*c* 0.32, $CHCl_3$). **17** (52 mg): mp 120–121° (Et_2O–hexane), $[\alpha]_D$ +45.3° (*c* 0.38, $CHCl_3$); UV λ_{max}^{EtOH} nm (log ε): 200 (4.17); IR ν_{max}^{KBr} cm^{-1}: 1745 (butenolide), 1700 (CHO), 1725, 1160 (ester), 1640, 905 (>C=CH_2); MS *m/z* (rel. int.): 360 $[M]^+$ (10), 300 (19), 272 (100), 208 (83), 175 (54). **18** (10 mg); an oil, $[\alpha]_D$ +16.7° (*c* 1.02, EtOH); UV λ_{max}^{EtOH} nm (log ε): 200 (4.10); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1755 (butenolide), 1725, 1200 (ester), 1640, 895 (>C=CH_2); MS *m/z* (rel. int.): 390 $[M]^+$ (19), 330 (48), 298 (96), 271 (80), 173 (100), 159 (78), 105 (82), 90 (74). **19** (34 mg): an oil, $[\alpha]_D$ +34.1° (*c* 0.40, EtOH); UV λ_{max}^{EtOH} nm (log ε): 200 (4.20); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1755–1720, 1645, 1240, 1160, 915; MS *m/z* (rel. int.): 404 $[M]^+$ (1), 344 (18), 331 (39), 285 (37), 284 (42), 271 (69), 105 (46), 43 (100).

Isolation of compounds **21b**, **22b**, **23a** *and* **24a**. The sixth fraction (739 mg) eluted with EtOAc was purified by prep. TLC on silica gel (Et_2O–hexane, 5:1). Elution of bands at R_f 0.43, 0.26 and 0.17 with EtOAc gave a mixture of **21a** and **22a** (209 mg) [in the ^{1}H NMR spectrum, two pairs of two proton signals (δ6.83, 6.07; δ5.97, 5.81) with a relative intensity of 9:4 were observed], **23a** (193 mg) and **24a** (154 mg), respectively. After acetylation with Ac_2O–pyridine, the mixture was separated by prep. TLC on silica gel developed three times with $CHCl_3$ to give **21b** (130 mg, R_f 0.55) and **22b** (60 mg, R_f 0.47). **21b**: an oil, $[\alpha]_D$ +7.6° (*c* 1.84, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1780, 1725, 1160, 990, 900; MS *m/z* (rel. int.): 448 $[M]^+$ (18), 389 (54), 388 (30), 356 (31), 329 (42), 328 (38), 296 (77), 268 (99), 267 (100), 173 (73), 172 (45), 159 (58). **22b**: an oil, $[\alpha]_D$ +13.3° (*c* 0.83, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1780, 1725, 1160, 990, 900; MS *m/z* (rel. int.): 448 $[M]^+$ (18), 389 (54), 388 (29), 356 (31); 329 (42), 328 (38), 296 (77), 268 (98), 267 (100), 173 (73), 172 (45), 159 (58), 105 (31). **23a**: an oil, $[\alpha]_D$ −27.6° (*c* 2.72, $CHCl_3$); UV λ_{max}^{EtOH} nm (log ε): 203 (3.91); IR ν_{max}^{neat} cm^{-1}: 3350, 1770–1730 (broad), 1140, 1080, 1010, 910, 760; MS *m/z* (rel. int.): 360 $[M]^+$ (23), 332 (13), 314 (14), 286 (30), 268 (21), 175 (80), 159 (100), 147 (68), 105 (80), 91 (72). **24a**: an oil, $[\alpha]_D$ −7.8° (*c* 1.29, $CHCl_3$); UV λ_{max}^{EtOH} nm (log ε): 203 (4.18); IR ν_{max}^{neat} cm^{-1}: 3300, 1770–1720, 1640, 1130, 1080, 960, 900, 740; MS *m/z* (rel. int.): 360 $[M]^+$ (21), 332 (18), 314 (26), 286 (27), 268 (30), 175 (57), 173 (60), 161 (84), 159 (81), 147 (71), 105 (100), 91 (93). After acetylation with Ac_2O–pyridine followed by chromatography by prep. TLC on silica gel, **23a** and **24a** each gave two acetates (epimers of an acetoxyl group), **23b** and **23b′** (2:3) and **24b** and **24b′** (2:1), as oils.

$NaBH_4$ *reduction of* **8**. To a soln of **8** (37 mg) in MeOH (10 ml) was added $NaBH_4$ (4 mg) at room temp. The mixture was stirred for 30 min and diluted with H_2O. After extraction with Et_2O, the product was purified by prep. TLC on silica gel (EtOAc–C_6H_6, 1:10) to yield **15** (15 mg, R_f 0.50), an oil, and **16** (17 mg, R_f 0.28), mp 134–135°. Their IR and ^{1}H NMR spectral data were in good agreement with those reported [6].

Hydrolysis of **13**. A soln of **13** (20 mg) in 2 M ethanolic KOH (5 ml) was stirred for 3 hr at room temp. After dilution with H_2O, the soln was extracted with Et_2O. Upon usual work-up, the product was purified on a silica gel column and an alcohol (13 mg) obtained which was identical to **15** in all respects (TLC, IR and ^{1}H NMR).

Photolytic oxidation of **12**. An MeOH soln of **12** (30 mg) in a pyrex flask was exposed to sunlight and the reaction was monitored by TLC. After the disappearance of **12** (20 days), removal of the solvent gave a mixture of **21a** and **22a** (3:2), identical to natural ones in all respects (TLC, ^{1}H NMR).

$NaBH_4$ *reduction of* **25**. To a soln of **25** (118 mg) in MeOH (10 ml) was added $NaBH_4$ (50 mg) at 0° and the mixture was stirred for 1 hr. Upon work-up, the product was purified on a silica gel column (EtOAc–$CHCl_3$, 1:4) to give **26** (38 mg) [IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500, 1730; ^{1}H NMR: δ7.33, 7.28, 6.31 (each 1H, furan), 6.48, 5.07, 4.63 (each 1H, *s*), 4.58 (1H, *d* (*br*), J = 10 Hz), 2.04, 1.21 (each 3H, *s*)] and **27** (42 mg) [IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500, 1740; ^{1}H NMR: δ7.37, 7.27, 6.37 (each 1H, furan), 6.48, 5.09, 4.88 (each 1H, *s*), 4.64 (1H, *dd*, J = 4 and 11 Hz), 2.14, 1.16 (each 3H, *s*)].

Hydrolysis of **26** *and* **27**. A soln of **26** (30 mg) in 1 M ethanolic KOH (5 ml) was stirred for 5 hr at room temp. After neutralization with 5% HCl, the product was extracted with Et_2O and chromatographed on a silica gel column (EtOAc–$CHCl_3$, 1:3) to give **28** (25 mg) [an oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600–3250, 1720; ^{1}H NMR: δ7.33 (2H, narrow *m*), 6.37 (1H, narrow *m*), 5.89 (1H, *br s*), 4.99, 4.64 (each 1H, *s*), 4.62 (1H, *dd*, J = 2 and 10 Hz), 1.20 (3H, *s*)]. By the same treatment as above, **27** gave **1** and sciadinic acid (**29**), mp 110–112° (monohydrate from aq. MeOH) [1], the latter of which gradually changed into **1** in the $CHCl_3$ soln.

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