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IRISTECTORENES A AND C–G, MONOCYCLIC TRITERPENE ESTERS FROM *IRIS TECTORUM*

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Key Word Index—*Iris tectorum*; Iridaceae; seeds; monocyclic triterpene esters; iristectorenes A and C–G.

Abstract—Six new triterpene esters, iristectorenes A and C–G, along with one known one have been found in the seeds of *Iris tectorum*. On the basis of spectroscopic methods and chemical evidence, the esters were established to be 3-{3-hydroxy-2-[5-hydroxy-4,8,12-trimethyl-(3*E*,7*E*)-3,7,11-tridecatrienyl]-2,3-dimethyl-6-(1-methyl-2-oxoethylidene)-cyclohexyl}propyl (*Z*)-9-tetradecenoate, (*Z*)-11-hexadecenoate, (*Z*,*Z*)-9,12-octadecadienoate, hexadecanoate, (*Z*)-11-octadecenoate and octadecanoate, respectively.

INTRODUCTION

In the course of our search for biologically active substances in plants of the Iridaceae, irisquinone [1], a compound having antitumour and immunostimulatory activities [2, 3], was isolated from the seeds of *Iris pseudacorus* L. and the sesquiterpene hydrocarbons from the seeds of *Iris tectorum* Maxim [4]. Recently, we also reported on the isolation of iristectorene B (**1**), the tetradecanoate of a monocyclic triterpene alcohol, from the seeds of *I. tectorum* [5], a perennial herb whose rhizomes have been used as traditional crude drugs in Japan.

Further investigation of the triterpene esters in the same plant gave six additional esters, named iristectorenes A (**2**) and C–G (**3**–**7**), as minor constituents. Iristectorenes are the first monocyclic triterpene esters to be isolated from natural sources, although several monocyclic triterpene alcohols have already been reported [6–8]. This paper deals with the isolation and structural elucidation of these new esters.

RESULTS AND DISCUSSION

The seed oil was chromatographed on alumina followed by silica gel to give a triterpenoid ester fraction, which showed seven peaks (A: 14%, B: 48%, C: 14%, D: 1%, E: 17%, F: 2%, G: 4%) on HPLC. Separation of the esters was carried out by repeated Lober column chromatography and preparative HPLC on reversed phase silica gel to afford iristectorenes A (**2**), C (**3**), E (**5**), F (**6**) and G (**7**), together with the known B (**1**). Iristectorene D (**4**) could not be obtained in pure form.

All the compounds were obtained as oils and exhibited a positive Cotton effect. Their UV and IR spectra showed a striking resemblance to one another. The ^{1}H and ^{13}C NMR data of **1**–**3** and **5**–**8** are summarized in Tables 1 and 2.

Iristectorene A (**2**), $[\alpha]_D^{20}$ +33, had the molecular formula $C_{44}H_{74}O_5$ (M^+ 682), corresponding to eight degrees of unsaturation. The ^{13}C NMR and DEPT experiments revealed the presence of eight methyls, 20 methylenes, eight methines and eight quaternary carbons. The following spectral data suggested that **2** had an α-methyl-α,β-unsaturated aldehyde skeleton in the molecule: λ_{max}^{EtOH} 255 nm (log ε 4.13); ν_{max}^{neat} 1660 (>C=O), 1610 cm^{-1} (>C=C<); δ_H 1.84 (3H, *s*, Me), 10.17 (1H, *s*, CHO); δ_c 162.6 (*s*), 133.3 (*s*), 11.0 (*q*), 189.9 (*d*) [>C=C(Me)CHO]. The ^{13}C NMR spectrum showed the presence of three isolated trisubstituted double bonds [δ120.0 (*d*) and 138.8 (*s*); 124.1 (*d*) and 131.6 (*s*); 125.3 (*d*) and 137.1 (*s*)] and a vinylene group [δ129.8 (*d*) and 129.9 (*d*)]. Moreover, the IR and ^{13}C NMR spectra revealed the presence of an ester group [1730, 1180 cm^{-1}; δ173.9 (*s*, CO_2R) and two hydroxyl groups [3500 cm^{-1}; δ75.0, *s*, >C(Me)OH; 76.6, *d*, >CHOH], of which the latter were also confirmed by fragment ion peaks at *m/z* 664 [M $-H_2O$]$^+$ and 646 [M $-2H_2O$]$^+$. The absence of any other sp^2 carbons indicated that **2** must have a ring system.

In addition, **2** showed the following ^{1}H NMR signals: δ1.08 [3H, *s*, >C(Me)–], 1.16 [3H, *s*, >C(Me)OH], 1.55 (3H, *s*), 3.92 (1H, *br t*, J = 6.4 Hz), 5.25 (1H, *br t*, J = 6.9 Hz) [–CH=C(Me)CH(OH)–], 1.62 (3H, *s*), 5.08 (1H, *m*) [–CH=C(Me)–], 1.60, 1.68 (each 3H, *s*), 5.05 (1H, *m*) (–CH=CMe_2), 3.30 [1H, *dd*, J = 11.1, 2.3 Hz, >C=C(CH<)–], 0.90 (3H, *m*), 1.30 (*br s*), 2.02 (*br*), 2.27 (2H, *t*, J = 7.5 Hz), 4.01 (2H, *t*, J = 6.8 Hz) and 5.35 (2H, *m*) [$Me(CH_2)_nCH$=$CH(CH_2)_mCO_2CH_2$–]. These signals were very similar

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Table 1. ^{1}H NMR data of **1** **3** and **5–8** (300 MHz, $CDCl_3$ with TMS as internal standard)

H	1	2	3	5	6	7	8
3	3.30 *dd* (11.4, 2.1)	3.30 *dd* (11.1, 2.3)	3.30 *dd* (10.2, 2.2)	3.30 *dd* (11.1, 2.4)	3.30 *dd* (11.1, 2.4)	3.30 *dd* (11.6, 2.5)	3.28 *dd* (10.8, 1.8)
5	2.58 *m*	2.58 *m*	2.58 *m*	2.58 *m*	2.58 *m*	2.58 *m*	2.58 *m*
6	1.6–2.0 *m*	1.6–2.0 *m*	1.6–2.0 *m*	1.6–2.0 *m*	1.6–2.0 *m*	1.6–2.0 *m*	1.6–2.0 *m*
7	1.16 *s*	1.16 *s*	1.16 *s*	1.16 *s*	1.16 *s*	1.16 *s*	1.15 *s*
9	10.17 *s*	10.17 *s*	10.17 *s*	10.18 *s*	10.18 *s*	10.17 *s*	10.17 *s*
10	1.84 *s*	1.84 *s*	1.84 *s*	1.84 *s*	1.84 *s*	1.84 *s*	1.84 *s*
11	1.08 *s*	1.08 *s*	1.08 *s*	1.08 *s*	1.08 *s*	1.08 *s*	1.07 *s*
1′	1.1–1.4 *m*	1.1–1.4 *m*	1.1–1.4 *m*	1.1–1.4 *m*	1.1–1.4 *m*	1.1–1.4 *m*	1.1–1.4 *m*
2′	1.8–2.0 *m*	1.8–2.0 *m*	1.8–2.0 *m*	1.8–2.0 *m*	1.8–2.0 *m*	1.8–2.0 *m*	1.8–2.0 *m*
3′	5.25 *br t* (7.1)	5.25 *br t* (6.9)	5.25 *br t* (7.1)	5.25 *br t* (7.1)	5.25 *br t* (6.9)	5.25 *br t* (7.0)	5.26 *br t* (6.9)
5′	3.92 *br t* (6.3)	3.92 *br t* (6.4)	3.92 *br t* (6.5)	3.92 *br t* (6.5)	3.92 *br t* (6.5)	3.92 *br t* (6.5)	4.97 *td* (7.2, 1.2)
6′	2.22 *m*	2.22 *m*	2.22 *m*	2.22 *m*	2.22 *m*	2.22 *m*	2.27 *m*
7′	5.08 *m*	5.08 *m*	5.08 *m*	5.08 *m*	5.08 *m*	5.08 *m*	5.08 *m*
9′	2.03 *m*	2.03 *m*	2.03 *m*	2.03 *m*	2.03 *m*	2.03 *m*	2.03 *m*
10′	2.07 *m*	2.07 *m*	2.07 *m*	2.07 *m*	2.07 *m*	2.07 *m*	2.07 *m*
11′	5.05 *m*	5.05 *m*	5.05 *m*	5.05 *m*	5.05 *m*	5.05 *m*	5.05 *m*
13′	1.68 *s*	1.68 *s*	1.68 *s*	1.68 *s*	1.68 *s*	1.68 *s*	1.68 *s*
14′	1.55 *s*	1.55 *s*	1.55 *s*	1.55 *s*	1.55 *s*	1.55 *s*	1.53 *s*
15′	1.62 *s*	1.62 *s*	1.62 *s*	1.62 *s*	1.62 *s*	1.62 *s*	1.60 *s*
16′	1.60 *s*	1.60 *s*	1.60 *s*	1.60 *s*	1.60 *s*	1.60 *s*	1.59 *s*
OAc-5′							2.01 *s*
1″	1.7–2.2 *m*	1.7–2.2 *m*	1.7–2.2 *m*	1.7–2.2 *m*	1.7–2.2 *m*	1.7–2.2 *m*	1.7–2.2 *m*
2″	1.2–1.5 *m*	1.2–1.5 *m*	1.2–1.5 *m*	1.2–1.5 *m*	1.2–1.5 *m*	1.2–1.5 *m*	1.2–1.5 *m*
3″	4.01 *t* (6.7)	4.01 *t* (6.8)	4.01 *t* (6.7)	4.01 *t* (6.8)	4.01 *t* (6.8)	4.01 *t* (6.8)	4.01 *t* (6.6)
5″	2.27 *t* (7.6)	2.27 *t* (7.5)	2.27 *t* (7.6)	2.27 *t* (7.5)	2.27 *t* (7.5)	2.27 *t* (7.5)	2.27 *t* (7.7)
6″	1.5–1.7 *br*	1.5–1.7 *br*	1.5–1.7 *br*	1.5–1.7 *br*	1.5–1.7 *br*	1.5–1.7 *br*	1.5–1.7 *br*
7″	1.25 *br s*	1.30 *br s*	1.27 *br s*	1.25 *br s*	1.26 *br s*	1.25 *br s*	1.30 *br s*
8″	1.25 *br s*	1.30 *br s*	1.27 *br s*	1.25 *br s*	1.26 *br s*	1.25 *br s*	1.30 *br s*
9″	1.25 *br s*	1.30 *br s*	1.27 *br s*	1.25 *br s*	1.26 *br s*	1.25 *br s*	1.30 *br s*
10″	1.25 *br s*	1.30 *br s*	1.27 *br s*	1.25 *br s*	1.26 *br s*	1.25 *br s*	1.30 *br s*
11″	1.25 *br s*	2.02 *br*	1.27 *br s*	1.25 *br s*	1.26 *br s*	1.25 *br s*	2.02 *br*
12″	1.25 *br s*	5.35 *m*	1.27 *br s*	1.25 *br s*	1.26 *br s*	1.25 *br s*	5.35 *m*
13″	1.25 *br s*	5.35 *m*	2.02 *br*	1.25 *br s*	2.02 *br*	1.25 *br s*	5.35 *m*
14″	1.25 *br s*	2.02 *br*	5.35 *m*	1.25 *br s*	5.35 *m*	1.25 *br s*	2.02 *br*
15″	1.25 *br s*	1.30 *br s*	5.35 *m*	1.25 *br s*	5.35 *m*	1.25 *br s*	1.30 *br s*
16″	1.25 *br s*	1.30 *br s*	2.02 *br*	1.25 *br s*	2.02 *br*	1.25 *br s*	1.30 *br s*
17″	0.88 *t* (6.8)	0.90 *m*	1.27 *br s*	1.25 *br s*	1.26 *br s*	1.25 *br s*	0.90 *m*
18″			1.27 *br s*	1.25 *br s*	1.26 *br s*	1.25 *br s*	
19″			0.90 *m*	0.88 *t* (6.8)	1.26 *br s*	1.25 *br s*	
20″					1.26 *br s*	1.25 *br s*	
21″					0.88 *t* (6.8)	0.88 *t* (6.7)	

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.

to those of **1**, except for the signals at δ2.02 and 5.35. These results and the following facts suggest that iristectorene A (**2**) must be the compound in which the tetradecanoyl group in **1** is replaced by a tetradecenoyl group. Acetylation of **2** gave an oily monoacetate **8** having a tertiary hydroxyl group [3520 cm^{-1} (OH); δ_c 74.9, *s*, >C(Me)OH] and an allylic acetoxymethine group [1740, 1370, 1240, 1020 cm^{-1}; δ2.01 (3H, *s*), 4.97 (1H, *td*, J = 7.2, 1.2 Hz); δ_c 79.0, *d*, >CHOAc]. Methanolysis of **2** afforded an alcohol **9**, which was identical with isoiridogermanal [5, 7] obtained from iristectorene B, and a methyl tetradecenoate ($C_{15}H_{28}O_2$, M^+ 240). The ester showed two carbon signals at δ26.9 and 27.2 characteristic of methylene groups adjacent to a *cis* double bond [9], but no C–H absorption at 965 cm^{-1} was observed. This double bond must therefore have *Z*-configuration and its position can be determined from the following MS data. Epoxidation of the ester with *m*-chloroperbenzoic acid (MCPBA) yielded a monoepoxy derivative ($C_{15}H_{28}O_3$, M^+ 256). The MS spectrum (Table 3) of the epoxide revealed

Table 2. ^{13}C NMR data of **1–3** and **5–8** (75 MHz, $CDCl_3$ with TMS as internal standard)

C	1	2	3	5	6	7	8
1	75.0	75.0	75.0	75.0	75.0	75.0	74.9
2	44.7	44.7	44.7	44.7	44.7	44.7	44.7
3	43.3	43.3	43.3	43.3	43.3	43.3	43.3
4	162.6	162.6	162.6	162.5	162.6	162.5	162.4
5	23.8	23.8	23.8	23.8	23.8	23.8	23.8
6	37.0	37.0	37.0	37.0	37.0	37.0	37.0
7	26.3	26.3	26.3	26.3	26.3	26.3	26.3
8	133.3	133.3	133.3	133.3	133.3	133.3	133.3
9 (CHO)	189.9	189.9	189.9	189.9	189.9	189.9	189.7
10	11.0	11.0	11.0	11.0	11.0	11.0	11.0
11	17.9	17.9	17.9	17.9	17.9	17.9	17.9
1′	36.8	36.8	36.8	36.8	36.8	36.8	36.7
2′	21.8	21.8	21.8	21.8	21.8	21.8	21.8
3′	125.3	125.3	125.3	125.3	125.3	125.3	127.9
4′	137.1	137.1	137.1	137.1	137.1	137.1	133.3
5′	76.6	76.6	76.6	76.6	76.6	76.6	79.0
6′	34.2	34.2	34.2	34.2	34.2	34.3	31.5
7′	120.0	120.0	120.0	120.0	119.9	120.0	119.1
8′	138.8	138.8	138.8	138.8	138.8	138.8	137.7
9′	39.8	39.8	39.8	39.8	39.8	39.8	39.7
10′	26.6	26.6	26.6	26.6	26.5	26.6	26.6
11′	124.1	124.1	124.1	124.1	124.1	124.1	124.1
12′	131.7	131.6	131.7	131.7	131.7	131.7	131.4
13′	25.7	25.7	25.7	25.7	25.7	25.7	25.7
14′	11.9	11.9	11.9	11.9	11.9	11.9	11.8
15′	16.3	16.3	16.3	16.3	16.3	16.3	16.2
16′	17.7	17.7	17.7	17.7	17.7	17.7	17.7
$MeCO_2$-5′							170.3
$MeCO_2$-5′							21.3
1″	26.6	26.6	26.6	26.6	26.6	26.6	26.7
2″	28.7	28.7	28.7	28.7	28.7	28.7	28.7
3″	64.3	64.3	64.3	64.3	64.3	64.2	64.3
4″ (C=O)	173.9	173.9	173.9	173.9	173.9	173.9	173.9
5″	34.4	34.4	34.4	34.4	34.4	34.4	34.4
6″	25.0	25.0	25.0	25.0	25.0	25.0	25.0
7″	29.2	29.1*	29.2	29.2	29.2	29.2	29.2
8″	29.3	29.2*	29.3	29.3	29.3	29.3	29.2
9″	29.5	29.1	29.5	29.5	29.5	29.5	29.1
10″	29.7*	29.7	29.5	29.6*	29.5	29.6	29.7
11″	29.7	27.2	29.3	29.7	29.3	29.7	27.2
12″	29.7	129.8	29.8	29.7	29.7	29.7	129.8
13″	29.6*	129.9	27.2	29.7	27.2	29.7	129.9
14″	29.4	26.9	129.9	29.7	129.9	29.7	26.9
15″	31.9	32.0	129.9	29.7*	129.9	29.7	32.0
16″	22.7	22.4	26.9	29.4	27.2	29.7	22.4
17″	14.1	14.0	32.0	31.9	29.7	29.7	14.0
18″			22.4	22.7	29.1	29.4	
19″			14.0	14.1	31.9	31.9	
20″					22.7	22.7	
21″					14.1	14.1	

Assignments were based on DEPT, ^1H–^{13}C COSY and ^1H–^{13}C long range COSY experiments.
*Signals may be interchanged within each column.

significant peaks at *m/z* 199 and 99 resulting from cleavage α to the 9,10-epoxy ring [10, 11], so that the ester was identified as methyl (*Z*)-9-tetradecenoate. Therefore, the structure of iristectorene A can be represented as **2**, in which the relative stereochemistry of the ring has already been determined by NOESY experiments [5].

The structures of the other minor constituents were elucidated as follows. The ^1H and ^{13}C NMR data of iristectorenes B (**1**), E (**5**) and G (**7**) show a striking resemblance to one another, suggesting that the esters **5** and **7** are homologues of **1** which differ only in the chain length of the saturated acyl moiety. The acyl moieties of **3**

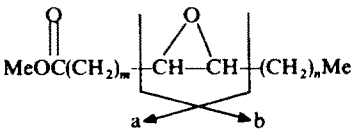


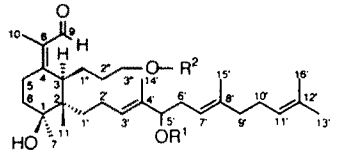
Table 3. Characteristic peaks in MS spectra of epoxy fatty esters

		m/z (rel. int.)				
$C_{x:y}$	m/n	$[M]^+$	$[a]^+$	$[a-28]^+$	$[b]^+$	$[M-a]^+$
$C_{14:1}$	7/3	256 (1)	199 (20)	171 (27)	99 (17)	57 (32)
$C_{16:1}$	9/3	284 (3)	227 (33)	199 (50)	99 (25)	57 (27)
$C_{18:1}$	9/5	312 (3)	227 (11)	199 (26)	127 (22)	85 (15)

and **6** must be monoenoic, because their NMR data are similar to those of **2**. Iristectorene D (**4**) could not be obtained pure. Its structure was determined as follows.

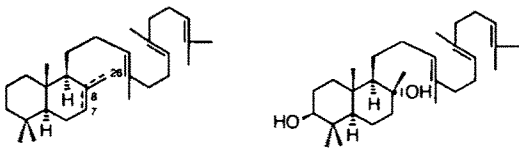
Methanolysis of the ester fraction gave, in addition to **9**, a mixture of methyl esters showing seven peaks ($C_{14:0}$: 49%, $C_{14:1}$: 13%, $C_{16:0}$: 18%, $C_{16:1}$: 14%, $C_{18:0}$: 3%, $C_{18:1}$: 2%, $C_{18:2}$: 1%) on capillary GC. These proportions were almost equal to those obtained by HPLC analysis of the ester fraction. Hence, the dienoate ($C_{18:2}$) must be derived from **4** and it was identified as methyl (*Z*,*Z*)-9,12-octadecadienoate by comparison of its R_t in GC with that of an authentic sample. This fact suggests that iristectorene D is the (*Z*,*Z*)-9,12-octadecadienoate of **9**. Consequently, iristectorenes A–G (**2**, **1**, **3**–**7**) were classified into three groups according to the degree of unsaturation in their component acids: saturated group (**1**, **5**, **7**), monoenoic group (**2**, **3**, **6**) and dienoic group (**4**). Methanolysis of **5** and **7** afforded methyl hexadecanoate ($C_{17}H_{34}O_2$, M^+ 270) and octadecanoate ($C_{19}H_{38}O_2$, M^+ 298), respectively, together with **9**. The same treatment of **3** and **6** yielded methyl (*Z*)-hexadecenoate ($C_{17}H_{32}O_2$, M^+ 268) and (*Z*)-octadecenoate ($C_{19}H_{36}O_2$, M^+ 296). The position of the double bond in each of the monoenoates was determined in the same manner as with (*Z*)-tetradecenoate. Table 3 shows that the esters derived from **3** and **6** correspond to methyl (*Z*)-11-hexadecenoate and (*Z*)-11-octadecenoate, respectively. Trace amounts of methyl (*Z*)-13-octadecenoate were also recognized along with the latter ester, suggesting the presence of (*Z*)-13-octadecenoate of **9** in iristectorenes. Therefore, iristectorenes C–G are represented as **3**–**7** (Fig. 1), respectively.

The component acids of iristectorenes were thus limited to C_{14}, C_{16} and C_{18}, the main components being C_{14}. It is interesting to note that the component acids clearly differed from those of the triglycerides coexisting in the same seed oil: the glycerides consisted of tetradecanoic (1%), hexadecanoic (11%), octadecanoic (4%), (*Z*)-9-octadecenoic (51%) and (*Z*,*Z*)-9,12-octadecadienoic acid (30%). ω-5 Monoenoates, e.g. iristectorenes A and C, accounted for *ca* 28% of the acid moieties present in the iristectorenes, even though ω-5 monoenoic acids are not present in the glycerides and are not widely distributed in



1 R^1= -H, R^2= $-CO(CH_2)_{12}Me$ (B 48%)
2 R^1= -H, R^2= $-CO(CH_2)_7CH^{cis}=CH(CH_2)_3Me$ (A 14%)
3 R^1= -H, R^2= $-CO(CH_2)_5CH^{cis}=CH(CH_2)_3Me$ (C 14%)
4 R^1= -H, R^2= $-CO(CH_2)_7CH^{cis}=CHCH_2CH^{cis}=CH(CH_2)_4Me$ (D 1%)
5 R^1= -H, R^2= $-CO(CH_2)_{14}Me$ (E 17%)
6 R^1= -H, R^2= $-CO(CH_2)_9CH^{cis}=CH(CH_2)_5Me$ (F 2%)
7 R^1= -H, R^2= $-CO(CH_2)_{18}Me$ (G 4%)
8 R^1= -Ac, R^2= $-CO(CH_2)_7CH^{cis}=CH(CH_2)_3Me$
9 R^1= R^2= -H

Fig. 1. Structures of **1**–**9**.

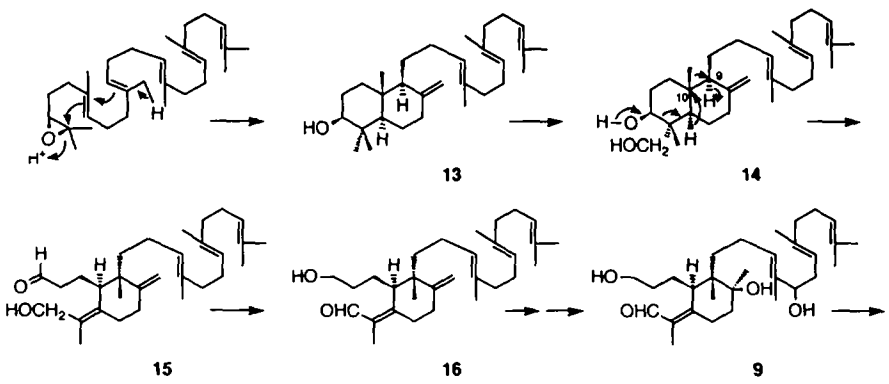


10 $\Delta^{7(8)}$
11 $\Delta^{7(26)}$
12

Fig. 2. Bicyclic triterpenoids **10**–**12**.

higher plants [12, 13]. Furthermore, no free alcohol **9** could be detected in any fractions of the *n*-hexane and methanol extracts. These facts also suggest that iristectorenes are not artefacts but natural products.

From a biogenetic point of view, **9**, although it is a monocyclic triterpene and has a different stereochemistry in its ring system, must be closely related to the onocerane-type triterpenoids. Many onocerane-type triterpenoids have already been found in Nature, but there have been few reports on the isolation of bicyclic compounds: i.e., α-polypodatetraene (**10**) and γ-polypodatetraene (**11**) from species of Polypodaceous and Aspidaceous ferns [14], and diol **12** from the resin of *Pistacia lentiscus* [15]. These compounds are regarded as products formed as a result of the interruption of the proton-initiated cyclization of squalene to furnish pentacyclic triterpenoids [14, 15] and biosynthetic intermediates of onocerane-type triterpenoids [16]. Thus, **9** can be assumed to be derived from cleavage of ring A of such a bicyclic triterpene (**13**) as shown in Scheme 1, in which partial cyclization at one end of the chair–chair conformation of (3*S*)-squalene 2,3-epoxide [15] affords **13** and subsequent oxidation gives **14**. As a result of a methyl shift accompanied by a hydride shift and subsequent cleavage of ring A, the diol **14** can be envisaged to give rise to **15**, having the same stereochemistry as **9**. Similar oxidations (**13**→**14**) and methyl shifts have already been reported in the literature [17, 18]. Transfer of hydride from the hydroxymethyl group to the formyl group in **15**



Scheme 1. Possible pathway for the biosynthesis of iristectorenes.

and further hydroxylation would afford **9**, though it is uncertain at which step additional hydroxyl groups are formed. Finally, **9** can be esterified to give iristectorenes A–G.

EXPERIMENTAL

General. Mps: uncorr.; ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz): $CDCl_3$ with TMS as int. standard; EIMS (probe): 70 eV; GC: FID, N_2 at 0.6 ml min^{-1}, fused silica capillary column (ULBON HR-SS-10, 50 m × 0.25 mm, Shinwa), temp. programmed 150° to 200° at 3° min^{-1}; CC: alumina 90 and Kieselgel 60 (each 70–230 mesh, Merck); Lober CC: LiChroprep RP-18 and Si60 (each 40–63 μm, Merck); HPLC: Shim-pack CLC-ODS (15 cm × 6 mm) and PREP-ODS (25 cm × 20 mm, Shimadzu).

Extraction and isolation. The seeds of *Iris tectorum* Maxim. cultivated at Utsunomiya University were collected in July 1988. Air-dried and milled seeds (1.89 g) were extracted with *n*-hexane at room temp. The extracts (323 g) were subjected to CC on alumina using *n*-hexane, *n*-hexane–C_6H_6, C_6H_6, C_6H_6–Et_2O and Et_2O, successively, as eluents. Frs eluted with C_6H_6–Et_2O (10:1 ~ 3:1) gave crude products, which were further sepd by Lober CC on silica gel using *n*-hexane–EtOAc (2:1) to obtain iristectorenes (811 mg). The ester fr. showed 7 peaks (A: 14%, B: 48%, C: 14%, D: 1%, E: 17%, F: 2%, G: 4%) on reversed-phase HPLC (RP-silica gel, 93% MeOH). Further purification was carried out by repeated Lober CC and prep. RP-HPLC (RP-silica gel, 90–95% MeOH) to afford **2** (36 mg), **3** (29 mg), **5** (38 mg), **6** (3 mg) and **7** (13 mg), respectively.

Iristectorene A (**2**). Oil, $[\alpha]^{20}$ (λ): +33 (589), +35 (578), 40 (546), +62 (436), +12 (365) ($CHCl_3$; *c* 0.22); UV λ_{max}^{EtOH} nm (log ε): 255 (4.13); IR ν_{max}^{neat} cm^{-1}: 3500 (OH), 1730, 1180 (CO_2R), 1660, 1610 [>C=C(CHO)–]; EIMS *m/z* (rel. int.): 682 [M]$^+$ (1), 664 [M − H_2O]$^+$ (14), 646 [M − 2H_2O]$^+$ (3), 546 [M − 136]$^+$ (25), 545 [M − 137]$^+$ (67), 527 [M − 155]$^+$ (30), 469 [M − 213]$^+$ (19), 301 (47), 283 (28), 261 (21), 147 (35), 138 (54), 135 (33), 123 (47), 121 (28), 109 (29), 107 (31), 97 (23), 95 (86), 93 (24), 81 (43), 69 (100), 55 (51), 43 (46), 41 (40); ^{1}H and ^{13}C NMR: Tables 1 and 2.

Iristectorene C (**3**). Oil, $[\alpha]^{20}$ (λ): +33 (589), +34 (578), +39 (546), +63 (436), +13 (365) ($CHCl_3$; *c* 0.27); UV λ_{max}^{EtOH} nm (log ε): 255 (4.14); IR ν_{max}^{neat} cm^{-1}: 3500 (OH), 1730, 1180 (CO_2R), 1660, 1610 [>C=C(CHO)–]; EIMS *m/z* (rel. int.): 710 [M]$^+$ (1), 692 [M − H_2O]$^+$ (2), 648 [M − 2H_2O]$^+$ (1), 573 [M − 137]$^+$ (45), 555 [M − 155]$^+$ (18), 497 [M − 213]$^+$ (13), 301 (39), 283 (23), 261 (21), 147 (19), 138 (42), 135 (26), 123 (41), 121 (24), 109 (27), 107 (25), 97 (28), 95 (93), 93 (23), 81 (46), 69 (100), 55 (51), 43 (50), 41 (26); ^{1}H and ^{13}C NMR: Tables 1 and 2.

Iristectorene E (**5**). Oil, $[\alpha]^{20}$ (λ): +31 (589), +33 (578), +35 (546), +56 (436), +7 (365) ($CHCl_3$; *c* 0.36); UV λ_{max}^{EtOH} nm (log ε): 255 (4.13); IR ν_{max}^{neat} cm^{-1}: 3500 (OH), 1730, 1180 (CO_2R), 1660, 1610 [>C=C(CHO)–]; EIMS *m/z* (rel. int.): 712 [M]$^+$ (1), 694 [M − H_2O]$^+$ (2), 676 [M − 2H_2O]$^+$ (1), 575 [M − 137]$^+$ (42), 557 [M − 155]$^+$ (34), 499 [M − 213]$^+$ (22), 301 (50), 283 (24), 261 (18), 147 (25), 138 (34), 135 (28), 123 (34), 121 (20), 109 (25), 107 (25), 97 (25), 95 (78), 93 (21), 81 (40), 69 (100), 55 (29), 43 (63), 41 (24); ^{1}H and ^{13}C NMR: Tables 1 and 2.

Iristectorene F (**6**). Oil, $[\alpha]^{20}$ (λ): +31 (589), +33 (578), +37 (546), +55 (436), +12 (365) ($CHCl_3$; *c* 0.20); UV λ_{max}^{EtOH} nm (log ε): 255 (4.14); IR ν_{max}^{neat} cm^{-1}: 3500 (OH), 1730, 1180 (CO_2R), 1660, 1610 [>C=C(CHO)–]; EIMS *m/z* (rel. int.): 738 [M]$^+$ (1), 720 [M − H_2O]$^+$ (8), 702 [M − 2H_2O]$^+$ (1), 601 [M − 137]$^+$ (10), 583 [M − 155]$^+$ (7), 525 [M − 213]$^+$ (3), 301 (13), 283 (5), 261 (17), 147 (16), 138 (9), 135 (18), 123 (43), 121 (33), 109 (41), 107 (48), 97 (34), 95 (73), 93 (30), 81 (19), 69 (100), 55 (54), 43 (85), 41 (71); ^{1}H and ^{13}C NMR: Tables 1 and 2.

Iristectorene G (**7**). Oil, $[\alpha]^{20}$ (λ): +34 (589), +35 (578), +39 (546), +64 (436), +17 (365) ($CHCl_3$; *c* 0.22); UV λ_{max}^{EtOH} nm (log ε): 255 (4.13); IR ν_{max}^{neat} cm^{-1}: 3500 (OH), 1730, 1180 (CO_2R), 1660, 1610 [>C=C(CHO)–]; EIMS *m/z* (rel. int.): 740 [M]$^+$ (1), 722 [M − H_2O]$^+$ (4), 704 [M − 2H_2O]$^+$ (1), 603 [M − 137]$^+$ (40), 585 [M − 155]$^+$ (24), 527 [M − 213]$^+$ (17), 301 (67), 283 (34), 261 (25), 147 (26), 138 (59), 135 (32), 123 (46), 121 (26), 109 (26), 107 (26), 97 (30), 95 (99), 93 (19), 81 (43), 69 (100), 55 (36), 43 (73), 41 (33); ^{1}H and ^{13}C NMR: Tables 1 and 2.

Acetylation of iristectorene A (**2**). Compound **2** (10 mg) was treated with Ac_2O (0.5 ml) in pyridine (1 ml) overnight at room temp. After usual work-up, Lober CC on

silica gel using *n*-hexane-EtOAc (3:1) afforded a monoacetate **8** (9 mg). Oil, $[\alpha]^{20}$ (λ) = +34 (589), +35 (578), +39 (546), +56 (436), −13 (365) ($CHCl_3$; *c* 0.18); UV λ_{max}^{EtOH} nm (log ε): 255 (4.15); IR ν_{max}^{neat} cm^{-1}: 3520 (OH), 1740, 1370, 1240, 1020 (OAc), 1730, 1180 (CO_2R), 1660, 1610 [>C=C(CHO)-]; EIMS *m/z* (rel. int.): 724 $[M]^+$ (1), 665 $[M-AcO]^+$ (36), 664 $[M-AcOH]^+$ (58), 647 $[M-H_2O-AcO]^+$ (5), 646 $[M-H_2O-AcOH]^+$ (6), 595 $[M-129]^+$ (18), 587 $[M-137]^+$ (16), 545 $[M-179]^+$ (18), 527 $[M-197]^+$ (25), 301 (27), 147 (46), 135 (38), 123 (42), 121 (31), 109 (30), 107 (31), 95 (31), 81 (38), 69 (100), 55 (37), 43 (79), 41 (21); ^1H and ^{13}C NMR: Tables 1 and 2.

Methanolysis of iristectorene A (**2**). A soln of **2** (23 mg) and 0.1% methanolic KOH (4 ml) was stirred at room temp. for 15 hr. Usual work-up and Lober CC on silica gel using *n*-hexane–EtOAc (2:1) gave **9** (12 mg), which was identical in all respects with the alcohol obtained from iristectorene B [5], and methyl (*Z*)-tetradecenoate (4 mg) having the following data: oil, IR ν_{max}^{neat} cm^{-1}: 3000 (*cis*-CH=CH-), 1740, 1245, 1195, 1170 (CO_2Me); ^1H NMR: δ0.90 (3H, *m*, H-14), 1.30 (12H, *br s*, H-4 ~ 7, 12, 13), 1.62 (2H, *qui*, *J* = 7.4 Hz, H-3), 2.02 (4H, *br*, H-8, 11), 2.30 (2H, *t*, *J* = 7.4 Hz, H-2), 3.67 (3H, *s*, OMe), 5.35 (2H, *m*, H-9, 10); ^{13}C NMR: δ14.0 (C-14), 22.4 (C-13), 25.0 (C-3), 26.9 (C-11), 27.2 (C-8), 29.1 (2C) (C-4, 6), 29.2 (C-5), 29.7 (C-7), 32.0 (C-12), 34.1 (C-2), 51.5 (OMe), 129.8 (C-9), 129.9 (C-10), 174.3 (C-1); EIMS *m/z* (rel. int.): 240 $[M]^+$ (15), 209 $[M-OMe]^+$ (25), 208 $[M-MeOH]^+$ (27), 166 $[M-74]^+$ (33), 110 (27), 98 (37), 97 (40), 96 (43), 87 $[CH_2=CHC(=OH)OMe]^+$ (69), 84 (45), 83 (47), 81 (38), 74 $[CH_2=C(OH)OMe]^+$ (86), 69 (61), 67 (40), 55 (100), 43 (53), 41 (62).

Methanolysis of iristectorene C (**3**). To **3** (25 mg) was added 0.1% methanolic KOH (3 ml). The mixture was then stirred at room temp. for 8 hr. Usual work-up and Lober CC on silica gel (*n*-hexane–EtOAc, 2:1) yielded **9** (16 mg) and methyl (*Z*)-hexadecenoate (7 mg): oil, IR ν_{max}^{neat} cm^{-1}: 3000 (*cis*-CH=CH-), 1740, 1245, 1195, 1170 (CO_2Me); ^1H NMR: δ0.90 (3H, *m*, H-16), 1.28 (16H, *br s*, H-4 ~ 9, 14, 15), 1.62 (2H, *qui*, *J* = 7.4 Hz, H-3), 2.02 (4H, *br*, H-10, 13), 2.30 (2H, *t*, *J* = 7.4 Hz, H-2), 3.67 (3H, *s*, OMe), 5.35 (2H, *m*, H-11, 12); ^{13}C NMR: δ14.0 (C-16), 22.4 (C-15), 25.0 (C-3), 26.9 (C-13), 27.2 (C-10), 29.2 (C-4), 29.3 (2C) (C-5, 8), 29.4 (C-6), 29.5 (C-7), 29.8 (C-9), 32.0 (C-14), 34.1 (C-2), 51.4 (OMe), 129.9 (2C) (C-11, 12), 174.3 (C-1); EIMS *m/z* (rel. int.): 268 $[M]^+$ (10), 237 $[M-OMe]^+$ (17), 236 $[M-MeOH]^+$ (28), 194 $[M-74]^+$ (18), 98 (26), 97 (39), 96 (31), 87 $[CH_2=CHC(=OH)OMe]^+$ (38), 84 (32), 83 (35), 74 $[CH_2=C(OH)OMe]^+$ (50), 70 (10), 69 (47), 67 (28), 55 (100), 43 (38), 41 (48).

Methanolysis of iristectorene E (**5**). A mixt. of **5** (34 mg) and 0.1% methanolic KOH (2 ml) was stirred at room temp. for 5 hr. Usual work-up followed by Lober CC on silica gel (*n*-hexane–EtOAc, 2:1) afforded **9** (18 mg) and methyl hexadecanoate (12 mg): solid, mp 29–30°; IR ν_{max}^{KBr} cm^{-1}: 1740, 1245, 1195, 1170 (CO_2Me); ^1H NMR: δ0.88 (3H, *t*, *J* = 6.7 Hz, H-16), 1.25 (24H, *br s*, H-4 ~ 15), 1.62 (2H, *qui*, *J* = 7.5 Hz, H-3), 2.30 (2H, *t*, *J* = 7.5 Hz, H-2), 3.67 (3H, *s*, OMe); ^{13}C NMR: δ14.1 (C-16), 22.7 (C-15), 25.0 (C-3), 29.2 (C-4), 29.3 (C-5), 29.4 (C-13), 29.5 (C-6), 29.6 (C-7), 29.7 (5C) (C-8 ~ 12), 31.9 (C-14), 34.1 (C-2), 51.4 (OMe), 174.4 (C-1); EIMS *m/z* (rel. int.): 270 $[M]^+$ (27), 239 $[M-OMe]^+$ (7), 227 $[M-43]^+$ (10), 196 $[M-74]^+$ (1), 143 (16), 87 $[CH_2=CHC(=OH)OMe]^+$ (71), 75 (21), 74 $[CH_2=C(OH)OMe]^+$ (100), 69 (13), 57 (14), 55 (29), 43 (45), 41 (21).

Methanolysis of iristectorene G (**7**). Compound **7** (11 mg) was treated with 0.1% methanolic KOH (2 ml) at room temp. for 6 hr. After usual work-up, methyl octadecanoate (5 mg) and **9** (6 mg) was obtained by Lober CC on silica gel using *n*-hexane–EtOAc (2:1). The ester was obtained as a solid of mp 38–39°; IR ν_{max}^{KBr} cm^{-1}: 1740, 1245, 1195, 1170 (CO_2Me); ^1H NMR: δ0.88 (3H, *t*, *J* = 6.7 Hz, H-18), 1.25 (28H, *br s*, H-4 ~ 17), 1.62 (2H, *qui*, *J* = 7.5 Hz, H-3), 2.30 (2H, *t*, *J* = 7.5 Hz, H-2), 3.67 (3H, *s*, OMe); ^{13}C NMR: δ14.1 (C-18), 22.7 (C-17), 25.0 (C-3), 29.2 (C-4), 29.3 (C-5), 29.4 (C-15), 29.5 (C-6), 29.6 (C-7), 29.7 (7C) (C-8 ~ 14), 31.9 (C-16), 34.1 (C-2), 51.5 (OMe), 174.4 (C-1); EIMS *m/z* (rel. int.): 298 $[M]^+$ (60), 267 $[M-OMe]^+$ (10), 255 $[M-43]^+$ (16), 143 (26), 89 (20), 87 $[CH_2=CHC(=OH)OMe]^+$ (73), 75 (28), 74 $[CH_2=C(OH)OMe]^+$ (100), 69 (15), 57 (16), 55 (23), 43 (36), 41 (20).

Methanolysis of iristectorenes (**1**–**7**). The ester fr. (124 mg) described above was stirred with 0.1% methanolic KOH (15 ml) at room temp. for 8 hr. Usual work-up and Lober CC on silica gel using *n*-hexane–EtOAc (2:1) gave, in addition to **9** (57 mg), a mixt. of methyl esters (43 mg) showing 7 peaks on GC: $C_{14:0}$ 49%, $C_{14:1}$ 13%, $C_{16:0}$ 18%, $C_{16:1}$ 14%, $C_{18:0}$ 3%, $C_{18:1}$ 2% and $C_{18:2}$ 1%. The dienoate ($C_{18:2}$) derived from **4** was identified as methyl (*Z*,*Z*)-9,12-octadecadienoate by comparison of its R_t in GC with that of an authentic sample.

Methanolysis of glycerides. Methanolysis of the glycerides (541 mg) which coexisted in the same seed oil and subsequent GC analysis revealed the following methyl esters (468 mg): tetradecanoate (1%), hexadecanoate (11%), octadecanoate (4%), (*Z*)-9-octadecenoate (51%) and (*Z*,*Z*)-9,12-octadecadienoate (30%).

Epoxidation of methyl (Z)-*tetradecenoate.* To a soln of the ester (3 mg) derived from **2** was added MCPBA (4 mg) in CH_2Cl_2 (2 ml). The mixt. was then stirred at room temp. for 6 hr. After usual work-up, methyl 9,10-epoxytetradecanoate (2 mg) was obtained as an oil by CC on silica gel using *n*-hexane–EtOAc (15:1). IR ν_{max}^{neat} cm^{-1}: 1740, 1245, 1195, 1170 (CO_2Me), 820 (oxirane); ^1H NMR: δ0.93 (3H, *t*, *J* = 7.1 Hz, H-14), 1.33 (12H, *br s*, H-4 ~ 7, 12, 13), 1.49 (4H, *br*, H-8, 11), 1.63 (2H, *qui*, *J* = 7.5 Hz, H-3), 2.31 (2H, *t*, *J* = 7.5 Hz, H-2), 2.90 (2H, *m*, H-9, 10), 3.70 (3H, *s*, OMe); ^{13}C NMR: δ14.0 (C-14), 22.6 (C-13), 24.9 (C-3), 26.6 (C-7), 27.5 (C-11), 27.8 (C-8), 28.8 (C-12), 29.0 (C-5), 29.2 (C-4), 29.3 (C-6), 34.1 (C-2), 51.7 (OMe), 57.2 (2C) (C-9, 10), 174.3 (C-1); EIMS *m/z* (rel. int.): 256 $[M]^+$ (1), 225 $[M-OMe]^+$ (15), 199 $[M-(CH_2)_3Me]^+$ (20), 171 $[(CH_2)_8CO_2Me]^+$ (27), 139 (26), 127 (28), 99 (17), 97 (39), 95 (23), 94 (24), 87 (54), 74 (100), 69 (49), 67 (20), 57 $[(CH_2)_3Me]^+$ (32), 55 (56), 43 (39), 41 (41).

Epoxidation of methyl (Z)-*hexadecenoate.* The ester

(6 mg) derived from **3** was epoxidized with MCPBA (7 mg) in CH_2Cl_2 (2 ml) at room temp. for 5 hr. Usual work-up followed by CC on silica gel using *n*-hexane–EtOAc (30:1) afforded methyl 11,12-epoxyhexadecanoate (5 mg). Oil; IR ν_{max}^{neat} cm^{-1}: 1740, 1245, 1195, 1170 (CO_2Me), 820 (oxirane); ^1H NMR: δ0.93 (3H, *t*, J = 7.1 Hz, H-16), 1.30 (16H, *br s*, H-4 ~ 9, 14, 15), 1.50 (4H, *br*, H-10, 13), 1.62 (2H, *qui*, J = 7.5 Hz, H-3), 2.30 (2H, *t*, J = 7.5 Hz, H-2), 2.90 (2H, *m*, H-11, 12), 3.67 (3H, *s*, OMe); ^{13}C NMR: δ14.0 (C-16), 22.6 (C-15), 25.0 (C-3), 26.6 (C-9), 27.5 (C-13), 27.8 (C-10), 28.8 (C-14), 29.1 (C-4), 29.2, 29.3, 29.5 (2C) (C-5 ~ 8), 34.1 (C-2), 51.5 (OMe), 57.2 (2C) (C-11, 12), 174.3 (C-1); EIMS *m/z* (rel. int.): 284 $[M]^+$ (3), 253 $[M-OMe]^+$ (15), 227 $[M-(CH_2)_3Me]^+$ (33), 199 $[(CH_2)_{10}CO_2Me]^+$ (50), 155 (28), 148 (26), 99 (25), 97 (28), 95 (30), 87 (94), 83 (34), 81 (36), 74 (100), 69 (57), 67 (28), 57 $[(CH_2)_3Me]^+$ (27), 55 (54), 43 (28), 41 (24).

Epoxidation of methyl (Z)-octadecenoate. To a soln of the esters (137 mg) derived from crude **6** was added MCPBA (28 mg) in CH_2Cl_2 (14 ml) and the mixt. was stirred at room temp. for 5 hr. After usual work-up, CC on silica gel using *n*-hexane–EtOAc (15:1) followed by prep. HPLC on reversed phase silica gel (90% MeOH) yielded methyl 11,12-epoxyoctadecanoate (4 mg). Oil; IR ν_{max}^{neat} cm^{-1}: 1740, 1245, 1195, 1170 (CO_2Me), 820 (oxirane); ^1H NMR: δ0.88 (3H, *t*, J = 7.1 Hz, H-18), 1.28 (20H, *br s*, H-4 ~ 9, 14 ~ 17), 1.49 (4H, *br*, H-10, 13), 1.63 (2H, *qui*, J = 7.5 Hz, H-3), 2.31 (2H, *t*, J = 7.5 Hz, H-2), 2.90 (2H, *m*, H-11, 12), 3.67 (3H, *s*, OMe); ^{13}C NMR: δ14.1 (C-18), 22.7 (C-17), 24.9 (C-3), 26.6 (2C) (C-9, 14), 27.8 (2C) (C-10, 13), 29.0 (C-15), 29.2 (2C), 29.4 (C-4 ~ 6), 29.5 (2C) (C-7, 8), 31.8 (C-16), 34.1 (C-2), 51.5 (OMe), 57.2 (C-11), 57.3 (C-12), 174.3 (C-1); EIMS *m/z* (rel. int.): 312 $[M]^+$ (3), 281 $[M-OMe]^+$ (5), 227 $[M-(CH_2)_5Me]^+$ (11), 199 $[(CH_2)_{10}CO_2Me]^+$ (26), 155 (31), 127 (22), 97 (34), 95 (31), 87 (49), 85 $[(CH_2)_5Me]^+$ (15), 83 (45), 74 (100), 69 (47), 67 (31), 55 (57), 43 (41), 41 (36).

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