Pergamon

0031-9422(93)E0167-D

Phytochemistry, Vol. 36, No 2, pp. 433 438, 1994

0031-9422/94 $7.00 + 0.00

IRISTECTORENE B, A MONOCYCLIC TRITERPENE ESTER FROM *IRIS TECTORUM*

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(*Received* 5 *October* 1993)

Key Word Index—*Iris tectorum*; Iridaceae; seeds; monocyclic triterpene ester; iristectorene B.

Abstract—A monocyclic triterpene ester, iristectorene B, has been isolated from the seeds of *Iris tectorum*. On the basis of spectroscopic methods and chemical evidence, the ester was shown 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 tetradecanoate and its stereochemistry was also clarified.

INTRODUCTION

Iris tectorum Maxim (Japanese name 'Ichihatsu') is a perennial herb which is native to China. Its rhizomes have been used in traditional Japanese medicine as an emetic and a laxative. We have already reported on the isolation of irisquinone [1], a compound having antitumour and immunostimulatory activities [2, 3], from the seeds of *Iris pseudacorus* L. and of sesquiterpene hydrocarbons [4] from the seeds of *I. tectorum*.

In the course of further investigations on the biologically active substances in Iridaceae plants, seven new monocyclic triterpene esters have been found in the latter plant. This paper describes the isolation and the structural elucidation of the major ester (**1**).

RESULTS AND DISCUSSION

Iristectorene B (**1**), $[\alpha]_D^{20}$ +34, was the main constituent of the triterpene ester fraction obtained from the seeds of *I. tectorum*. It exhibited a positive Cotton effect and its MS spectrum showed a molecular ion peak at *m/z* 684 corresponding to the formula $C_{44}H_{76}O_5$ and indicative of seven degrees of unsaturation. The ^{13}C NMR and DEPT spectra revealed that **1** possessed eight methyls, 22 methylenes, six methines and eight quaternary carbons. It showed UV absorption [λ_{max}^{EtOH} 255 nm (log ε 4.14)] and IR bands [1660 (>C=O), 1610 cm^{-1} (>C=C<)] characteristic of a conjugated enone chromophore. Signals at δ_C 189.9 (*d*, CHO), 133.3 (*s*, >C=), 162.6 (*s*, >C=), 11.0 [*q*, =C(Me)–], δ_H 10.16 [1H, *s*, >C=C(CHO)–] and 1.84 [3H, *s*, >C=C(Me)–] established that this chromophore corresponded to that of an α,β-unsaturated aldehyde skeleton containing an exocyclic tetrasubstituted double bond on a ring and a methyl substituent at the α-position. It showed three olefinic pair signals due to isolated trisubstituted double bonds: δ_C 120.0 (*d*) and 138.8 (*s*), 124.1 (*d*) and 131.7 (*s*), 125.3 (*d*) and 137.1 (*s*). The signal at δ_C 173.9 was attributed to an ester carbonyl carbon, which was confirmed by the IR bands at 1730 and 1180 cm^{-1}. The absence of any other sp^2 carbons indicated that **1** must have one ring in order to satisfy its unsaturation number. In addition, the IR band at 3500 cm^{-1} and fragment ion peaks (*m/z* 666 [M $-H_2O]^+$, 648 [M $-2H_2O]^+$) suggested the presence of two hydroxyl groups. The hydroxylic character was further confirmed by the formation of a monoacetate. Thus, on acetylation with Ac_2O and pyridine, **1** afforded monoacetate **2**, $C_{46}H_{78}O_6$ (M^+ 726), having a tertiary hydroxyl group [3500 cm^{-1} (OH); δ_C 74.9, *s*, >C(OH)–] and an allylic acetoxymethine group [1740, 1370, 1240, 1020 cm^{-1}; δ2.02 (3H, *s*), 4.97 (1H, *td*, J = 7.2, 1.2 Hz); δ_C 79.0 (*d*, >CHOAc)].

Hence, **1** was characterized as an ester having two hydroxyl groups, one of which was assigned to a secondary hydroxyl group and the other was attributed to a tertiary hydroxyl group. The ^{13}C NMR spectrum of **1** also exhibited three carbons at δ64.3 (*t*), 75.0 (*s*) and 76.6 (*d*), which were attributed to a methylene, a quaternary carbon and a methine each bearing an oxygen function. Its ^{1}H NMR spectrum showed two tertiary methyl groups at δ1.08 and 1.16 (each 3H, *s*), of which the latter was attributable to the methyl group geminal to the tertiary hydroxyl group. Furthermore, the ^{1}H NMR spectrum revealed the presence of four methyl groups [δ1.55, 1.60, 1.62, 1.68 (each 3H, *s*)] and three methine protons [δ5.05, 5.08 (each 1H, *m*), 5.25 (1H, *br t*, J = 7.1 Hz)] attached to the three trisubstituted double bonds described above. The double doublet signal at δ3.30 (1H, J = 11.4, 2.1 Hz) and the triplet signal at δ3.92 (1H, J = 6.3 Hz) were assigned to a methine proton at the γ-position of the α,β-unsaturated aldehyde moiety and the allylic methine proton geminal to the secondary hydroxyl group, respectively. Additional signals at δ0.88 (3H, *t*, J

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= 6.8 Hz, -Me), 1.25 (*br s*, $-CH_2-$) and 2.27 (2H, *t*, *J* = 7.6 Hz, $-CH_2CO_2-$) suggested the presence of a long aliphatic acyloxy group. A methylene group adjacent to the above acyloxy group was also observed at δ4.01 (2H, *t*, *J* = 6.7 Hz).

Methanolysis of **1** gave an alcohol **3** ($[\alpha]_D^{20}$ +55), which on acetylation afforded a diacetate (**4**) having a tertiary hydroxyl group [3520 cm^{-1} (OH); δ_C 74.9, *s*, >C(OH)-], and a methyl ester. The latter was identified as methyl tetradecanoate by comparison of the spectral data with those of an authentic sample.

Compound **3** had the molecular formula $C_{30}H_{50}O_4$ (M^+ 474), indicating six degrees of unsaturation. The ^{13}C NMR and DEPT spectra suggested that **3** was a triterpenoid made up of seven methyls, 10 methylenes, six methines and seven quaternary carbons. Its UV and IR spectra revealed that **3** had the same α-methyl-α,β-unsaturated aldehyde moiety as iristectorene B (**1**): λ_{max}^{EtOH} 255 nm (log ε 4.13); ν_{max}^{neat} 3400 (OH), 1660, 1610 cm^{-1} [>C=C(CHO)-]. The ^1H NMR spectrum of **3** was very similar to that of **1** except for replacement of the signals of the acyloxymethylene group in **1** with those of a hydroxymethylene group [δ3.61 (2H, *t*, *J* = 6.3 Hz)]. Therefore, **1** must be the ester formed on esterification of the primary hydroxyl group in **3** with tetradecanoic acid.

In addition to the above facts, the ^1H-^1H and ^1H-^{13}C COSY spectra of **1** and **3** showed the presence of six partial structures (Fig. 1). The relationship between these structures was examined as follows and the structure of **3** was determined to be as shown in Fig. 2. In the ^1H-^{13}C long range COSY spectrum (Fig. 2) of **3**, H-3 (δ3.31) exhibited long range correlations with C-1 (δ75.0) and C-2 (δ44.7) and H-5 (δ2.58) with C-1 and C-6 (δ37.0), so that units I and II must form a six-membered ring. Cross-peaks from H-3 to C-1″ (δ26.7) and C-2″ (δ32.7), and from H-11 (δ1.10) to C-1′ (δ36.9) were also observed. These facts indicate that unit III-3 must be linked to C-3 in unit I, and C-1′ of unit IV to C-2 in unit II. Moreover, correlations between H-6′ (δ2.22) and C-5′ (δ76.7), and between H-10′ (δ2.07) and C-9′ (δ39.8) suggested connections between units IV and V, and between units V and VI. In the NOESY spectrum (Fig. 3) of **3**, a strong correlation peak was observed not only between H-10 (δ1.83) and one H-5, but also between H-9 (δ10.18) and H-3. Consequently, both the groups have a *syn* relationship to each other with regard to the exocyclic tetrasubstituted double bond on the ring and H-3 must have equatorial configuration. NOEs between H-2′ and H-14′, H-3′ and H-5′, H-6′ and H-15′, and H-7′ and H-9′ indicated that the double bonds in the isoprenyl side chain had all *trans* configurations.

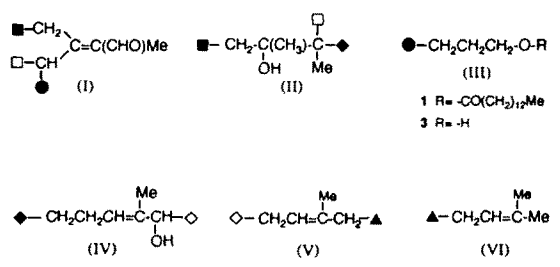


Fig. 1. Partical structures of **1** and **3**.

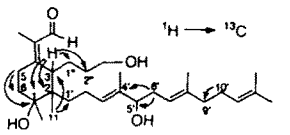


Fig. 2. Key correlations in ^1H-^{13}C long range COSY spectrum of **3**.

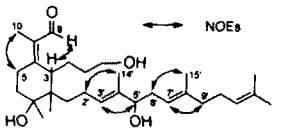
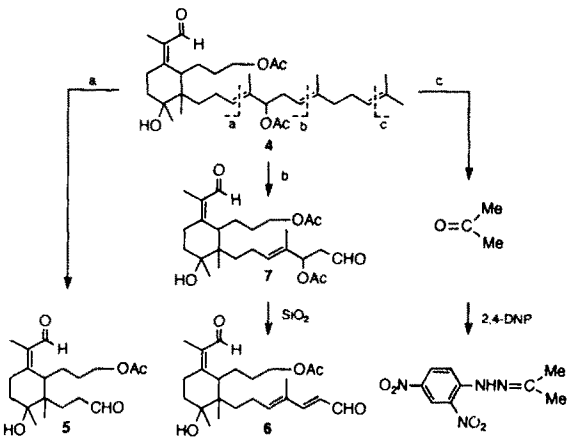


Fig. 3. Key correlations in NOESY spectrum of **3**.



Scheme 1. Ozonolysis of **4**.

The positions of the trisubstituted double bonds and the secondary hydroxyl group in the isoprenyl side chain were also confirmed by oxidative degradation (Scheme 1). Ozonization of the diacetate **4** followed by reduction with Me_2S yielded a volatile ketone, which was converted into acetone 2,4-dinitrophenylhydrazone, and non-volatile aldehydes. Chromatography of the latter part on silica gel afforded two aldehydes in a ratio of *ca* 4:1. The major product was the expected monocyclic α,β-unsaturated aldehyde **5** [$C_{19}H_{30}O_5$, $[\alpha]_D^{20}$ +66] having a formylethylene group [δ1.56 (2H, *dt*, *J* = 9.9, 5.7 Hz), 2.38 (2H, *m*), 9.74 (1H, *t*, *J* = 1.2 Hz)] and an acetoxytrimethylene group, while the minor product was a conjugated (*E*,*E*)-dienal (**6**) [$C_{24}H_{36}O_5$, $[\alpha]_D^{20}$ +44; δ5.85 (1H, *br t*, *J* = 7.4 Hz), 7.05 (1H, *d*, *J* = 15.3 Hz), 6.09 (1H, *dd*, *J* = 15.3, 7.8 Hz), 9.54 (1H, *d*, *J* = 7.8 Hz), 1.75 (3H, *d*, *J* = 0.9 Hz); -CH=C(Me)CH=CHCHO]. The ^1H and ^{13}C NMR spectra established that **5** had the same α,β-unsaturated aldehyde moiety as **4**, but signals due to the isoprenyl side chain were no longer observed. These facts indicate that in **5** the isoprenyl group present in **4** is replaced by a

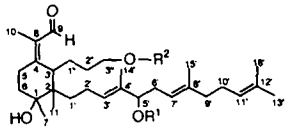
formylethylene group and that **6** is formed by elimination of acetic acid from **7** (Scheme 1). From these results, it is clear that the isoprenyl side chain attached to the six-membered ring in **1** is 5-hydroxy-4,8,12-trimethyl-(3*E*,7*E*)-3,7,11-tridecatrienyl group. Therefore, the structures of iristectorene B and its related compounds are as represented by formulae **1**–**4** (Fig. 4). The alcohol **3** may be isoiridogermanal [5] isolated from the rhizomes of *I. pallida* and *I. florentina*, although its stereochemistry has not been reported.

Finally, the stereochemistry of the ring system was determined by a NOESY experiment of the simplified compound **5**. As shown in Fig. 5, H-7 correlated with H-11 and H-1′. In addition, H-11 showed NOE correlations with H-1″ as well as H-3 and H-2′, but no correlation was observed between H-1′ and H-1″. Therefore, both H-7 and H-11 have to have equatorial configuration, while both the formylethylene group on C-2 and the acetyloxypropylene group on C-3 have *trans*-orientation with respect to each other and must be axial. These results indicate that iristectorene B and its related compound have the relative stereochemistry shown in Fig. 5.

As far as the authors are aware, this is the first report of the isolation of a natural monocyclic triterpene ester, though monocyclic triterpene alcohols, e.g. iridogermanal [6], isoiridogermanal [5] and iriversical [7], have already been reported in *Iris*.

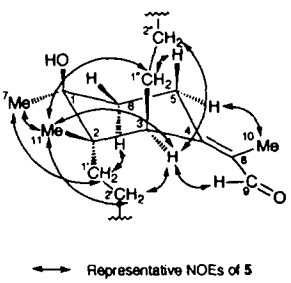
EXPERIMENTAL

General. Mp: uncorr.; ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz): $CDCl_3$ with TMS as int. standard; EIMS (probe): 70 eV; 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).



1 R^1 = -H, R^2 = -$CO(CH_2)_{12}Me$
2 R^1 = -Ac, R^2 = -$CO(CH_2)_{12}Me$
3 R^1 = R^2 = -H
4 R^1 = R^2 = -Ac

Fig. 4. Structures of **1**–**4**.



Representative NOEs of 5

Fig. 5. Relative stereochemistry of iristectorenes.

Extraction and isolation. The seeds of *I. tectorum* Maxim. cultivated at Utsunomiya University were collected in July 1987. Air-dried and milled seeds (2.43 kg) were extracted with *n*-hexane at room temp. After removal of the solvent, the extract (414 g) was fractionated by CC on alumina deactivated by the addition of H_2O [6%] using *n*-hexane, *n*-hexane–C_6H_6, C_6H_6, C_6H_6–Et_2O and Et_2O as eluents, successively. The frs eluted with C_6H_6–Et_2O (10:1 ~ 3:1) on Lober CC on silica gel using *n*-hexane–EtOAc (2:1) yielded a mixt. of triterpene esters (1.03 g), which gave rise to 7 peaks (A: 14%, B: 49%, C: 14%, D: 1%, E: 17%, F: 2%, G: 3%) on HPLC on reversed phase silica gel (93% MeOH). Repeated Lober CC and prep. HPLC on reversed phase silica gel using 90–95% MeOH afforded iristectorene B (**1**, 250 mg) as a main constituent.

Iristectorene B (**1**). Oil, $[\alpha]^{20}$ (λ): +34 (589), +35 (578), +41 (546), +65 (436), 0 (365) ($CHCl_3$; *c* 0.21); 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.): 684 $[M]^+$ (1), 666 $[M-H_2O]^+$ (10), 648 $[M-2H_2O]^+$ (5), 547 $[M-137]^+$ (41), 529 $[M-155]^+$ (26), 471 $[M-213]^+$ (15), 301 (36), 283 (21), 261 (20), 147 (43), 138 (37), 135 (41), 123 (44), 121 (30), 109 (28), 107 (33), 97 (20), 95 (64), 93 (28), 81 (37), 69 (100), 55 (34), 43 (38), 41 (22); ^{1}H and ^{13}C NMR: Tables 1 and 2.

Acetylation of iristectorene B (**1**). To a soln of **1** (14 mg) in pyridine (1 ml), Ac_2O (0.5 ml) was added and the mixt. was left overnight at room temp. Usual work-up, followed by Lober CC on silica gel using *n*-hexane–EtOAc (3:1), gave the monoacetate **2** (10 mg). Oil, $[\alpha]^{20}$: (λ) +33 (589), +35 (578), +38 (546), +59 (436), −6 (365) ($CHCl_3$; *c* 0.24); UV λ_{max}^{EtOH} nm (log ε): 255 (4.15); IR ν_{max}^{neat} cm^{-1}: 3500 (OH), 1740, 1370, 1240, 1020 (OAc), 1730, 1180 (CO_2R), 1660, 1610 [>C=C(CHO)–]; EIMS *m/z* (rel. int.): 726 $[M]^+$ (1), 708 $[M-H_2O]^+$ (1), 667 $[M-AcO]^+$ (17), 666 $[M-AcOH]^+$ (26), 649 $[M-H_2O-AcO]^+$ (2), 648 $[M-H_2O-AcOH]^+$ (3), 597 $[M-129]^+$ (11), 589 $[M-137]^+$ (7), 547 $[M-179]^+$ (9), 529 $[M-197]^+$ (13), 301 (15), 147 (36), 135 (29), 123 (29), 121 (24), 109 (22), 107 (28), 95 (25), 81 (31), 69 (100), 55 (22), 43 (72), 41 (27); ^{1}H and ^{13}C NMR: Tables 1 and 2.

Methanolysis of iristectorene B (**1**). A mixt. of **1** (230 mg) and 0.1% methanolic KOH (30 ml) was stirred at room temp. for 10 hr. Usual work-up and Lober CC on silica gel (*n*-hexane–EtOAc, 2:1) afforded a methyl ester (73 mg) and **3** (148 mg). The former ester was identified as methyl tetradecanoate by comparison of the following spectral data with those of an authentic sample. Oil, IR ν_{max}^{neat} cm^{-1}: 1740, 1245, 1195, 1170 (CO_2Me); ^{1}H NMR: δ0.88 (3H, *t*, *J* = 6.7 Hz, H-14), 1.26 (20H, *br s*, H-4 ~ 13), 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-14), 22.7 (C-13), 25.0 (C-3), 29.2 (C-4), 29.3 (2C) (C-5, 11), 29.5 (C-6), 29.6 (4C) (C-7 ~ 10), 31.9 (C-12), 34.1 (C-2), 51.4 (OMe), 174.2 (C-1); EIMS *m/z* (rel. int.): 242 $[M]^+$ (12), 211 $[M-OMe]^+$ (6), 199 $[M-43]^+$ (12), 149 (11), 143 (18), 87 $[CH_2=CHC(=OH)OMe]^+$ (66), 83 (11), 75 (16), 74 $[CH_2$

Table 1. ^{1}H NMR data of **1**–**6** (300 MHz, $CDCl_3$ with TMS as internal standard)

H	1	2	3	4	5	6
3	3.30 *dd* (11.4, 2.1)	3.28 *dd* (11.4, 2.2)	3.31 *dd* (11.0, 2.6)	3.29 *dd* (11.1, 2.7)	3.17 *dd* (11.0, 2.4)	3.31 *dd* (11.0, 2.3)
5	2.58 *m*	2.58 *m*	2.58 *m*	2.58 *m*	2.59 *m*	2.60 *m*
6	1.6–2.0 *m*	1.6–2.0 *m*	1.6–2.0 *m*	1.6–2.0 *m*	1.70, 1.90 *m*	1.6–2.0 *m*
7	1.16 *s*	1.15 *s*	1.16 *s*	1.15 *s*	1.21 *s*	1.81 *s*
9	10.17 *s*	10.17 *s*	10.18 *s*	10.17 *s*	10.13 *s*	10.20 *s*
10	1.84 *s*	1.84 *s*	1.83 *d* (0.9)	1.85 *s*	1.85 *d* (0.9)	1.86 *d* (0.9)
11	1.08 *s*	1.07 *s*	1.10 *s*	1.07 *s*	1.04 *s*	1.12 *s*
1′	1.1–1.4 *m*	1.1–1.4 *m*	1.1–1.4 *m*	1.1–1.4 *m*	1.56 *dt* (9.9, 5.7)	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*	2.38 *m*	2.0–2.2 *m*
3′	5.25 *br t* (7.1)	5.26 *br t* (6.9)	5.25 *br t* (6.9)	5.26 *br t* (7.0)	9.74 *t* (1.2)	5.85 *br t* (7.4)
5′	3.92 *br t* (6.3)	4.97 *td* (7.2, 1.2)	3.92 *td* (7.3, 1.2)	4.97 *td* (7.2, 1.2)		7.05 *d* (15.3)
6′	2.22 *m*	2.27 *m*	2.22 *m*	2.21, 2.34 *m*		6.09 *dd* (15.3, 7.8)
7′	5.08 *m*	5.08 *m*	5.08 *m*	5.08 *m*		9.54 *d* (7.8)
9′	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*		
11′	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*		
14′	1.55 *s*	1.53 *s*	1.55 *s*	1.53 *s*		
15′	1.62 *s*	1.60 *s*	1.62 *s*	1.60 *s*		
16′	1.60 *s*	1.59 *s*	1.60 *s*	1.59 *s*		
Me-4′						1.75 *d* (0.9)
OAc-5′		2.02 *s*		2.02 *s*		
1″	1.7–2.2 *m*	1.7–2.2 *m*	1.7–2.2 *m*	1.7–2.2 *m*	1.74, 2.10 *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*	1.33, 1.43 *m*	1.2–1.5 *m*
3″	4.01 *t* (6.7)	4.01 *t* (6.8)	3.61 *t* (6.3)	4.01 *t* (6.9)	4.01 *t* (6.8)	4.02 *t* (6.8)
5″	2.27 *t* (7.6)	2.27 *t* (7.5)		2.03 *s* (Ac)	2.04 *s* (Ac)	2.04 *s* (Ac)
6″	1.5–1.7 *br*	1.5–1.7 *br*				
7″	1.25 *br s*	1.26 *br s*				
8″	1.25 *br s*	1.26 *br s*				
9″	1.25 *br s*	1.26 *br s*				
10″	1.25 *br s*	1.26 *br s*				
11″	1.25 *br s*	1.26 *br s*				
12″	1.25 *br s*	1.26 *br s*				
13″	1.25 *br s*	1.26 *br s*				
14″	1.25 *br s*	1.26 *br s*				
15″	1.25 *br s*	1.26 *br s*				
16″	1.25 *br s*	1.26 *br s*				
17″	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.

=C(OH)OMe]$^+$ (100), 69 (15), 57 (18), 55 (33), 43 (42), 41 (22).

Compound **3**. Viscous oil, $[\alpha]^{20}$ (λ): +55 (589), +57 (578), +64 (546), +101 (436), +39 (365) ($CHCl_3$; *c* 0.27); UV λ_{max}^{EtOH} nm (log ε): 255 (4.13); IR ν_{max}^{neat} cm^{-1}: 3400 (OH), 1660, 1610 [>C=C(CHO)–]; EIMS *m/z* (rel. int.): 475 [M+H]$^+$ (1), 474 [M]$^+$ (1), 457 [M+H−H_2O]$^+$ (36), 456 [M−H_2O]$^+$ (3), 439 [M+H−2H_2O]$^+$ (24), 438 [M−2H_2O]$^+$ (1), 337 [M−137]$^+$ (25), 319 [M−155]$^+$ (60), 301 (31), 177 (17), 147 (15), 135 (19), 123 (30), 121 (18), 109 (36), 107 (21), 97 (29), 95 (58), 81 (25), 69 (100), 55 (23), 43 (53), 41 (37); ^{1}H and ^{13}C NMR: Tables 1 and 2.

Acetylation of compound **3**. Compound **3** (143 mg) was acetylated with Ac_2O (2.5 ml) and pyridine (5 ml) at room temp. for 1 day. After usual work-up, the diacetate **4** (164 mg) was obtained by Lober CC on silica gel using *n*-hexane–EtOAc (2:1). Oil, $[\alpha]^{20}$ (λ): +39 (589), +41 (578), +46 (546), +66 (436), −27 (365) ($CHCl_3$; *c* 0.42); UV λ_{max}^{EtOH} nm (log ε): 255 (4.15); IR ν_{max}^{neat} cm^{-1}: 3520 (OH), 1740, 1370, 1240, 1020 (OAc), 1660, 1610 [>C=C(CHO)–]; EIMS *m/z* (rel. int.): 558 [M]$^+$ (1), 500 [M+H−AcO]$^+$ (10), 499 [M−AcO]$^+$ (34), 498 [M−AcOH]$^+$ (36), 481 [M−H_2O−AcO]$^+$ (14), 480 [M−H_2O−AcOH]$^+$ (14), 429 [M−129]$^+$ (22), 411

Table 2. ^{13}C NMR data of **1**–**6** (75 MHz, $CDCl_3$ with TMS as internal standard)

C	1	2	3	4	5	6
1	75.0	74.9	75.0	74.9	74.9	74.8
2	44.7	44.7	44.7	44.7	44.2	44.8
3	43.3	43.3	43.4	43.3	43.6	43.4
4	162.6	162.4	162.9	162.4	161.5	162.1
5	23.8	23.8	23.9	23.8	23.8	23.8
6	37.0	37.0	37.0	37.0	37.1	37.1
7	26.3	26.3	26.3	26.3	26.4	26.3
8	133.3	133.3	133.2	133.3	133.6	133.8
9 (CHO)	189.9	189.7	190.0	189.7	189.6	189.7
10	11.0	11.0	11.0	11.0	11.2	11.1
11	17.9	17.9	17.9	17.9	17.8	17.9
1′	36.8	36.7	36.9	36.7	28.4	36.1
2′	21.8	21.8	21.8	21.8	38.7	23.4
3′	125.3	127.9	125.3	127.9	201.1	127.2
4′	137.1	133.3	137.1	133.3		133.5
5′	76.6	79.0	76.7	79.0		157.2
6′	34.2	31.5	34.2	31.5		143.2
7′	120.0	119.1	120.0	119.1		194.0
8′	138.8	137.7	138.8	137.7		
9′	39.8	39.7	39.8	39.7		
10′	26.6	26.6	26.6	26.6		
11′	124.1	124.1	124.1	124.1		
12′	131.7	131.4	131.6	131.4		
13′	25.7	25.7	25.7	25.7		
14′	11.9	11.8	11.9	11.8		
15′	16.3	16.2	16.3	16.2		
16′	17.7	17.7	17.7	17.7		
Me-4′						12.2
$MeCO_2$-5′		170.3		170.3		
$MeCO_2$-5′		21.3		21.3		
1″	26.6	26.7	26.7	26.7	26.5	26.6
2″	28.7	28.7	32.7	28.6	28.5	28.6
3″	64.3	64.2	63.0	64.5	64.4	64.5
4″ (C=O)	173.9	173.9		171.1	171.0	171.1
5″	34.4	34.4		21.0	21.0	21.0
6″	25.0	25.0				
7″	29.2	29.2				
8″	29.3	29.3				
9″	29.5	29.5				
10″	29.6	29.6				
11″	29.7	29.7				
12″	29.7	29.7				
13″	29.7	29.7				
14″	29.4	29.4				
15″	31.9	31.9				
16″	22.7	22.7				
17″	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.

$[M-147]^+$ (27), 361 $[M-197]^+$ (30), 343 $[M-215]^+$ (34), 301 (3), 177 (32), 147 (39), 135 (43), 123 (30), 122 (41), 121 (27), 109 (27), 107 (33), 95 (25), 81 (26), 69 (73), 43 (100), 41 (25); ^1H and ^{13}C NMR: Tables 1 and 2.

Ozonolysis of diacetate **4**. Oxygen containing O_3 was bubbled through a soln of **4** (160 mg) in MeOH (10 ml) at $-55°$ for 5 hr. Me_2S (0.5 ml) was then added and the mixt. was allowed to stand at room temp. for 3 hr. After evapn of the solvent, the residue was sepd by Lober CC on silica gel using *n*-hexane–EtOAc (1:1) to give **5** (41 mg) and **6** (12 mg). 2,4-Dinitrophenylhydrazine soln was added to the distillate and the mixt. was left overnight. Usual work-up afforded a 2,4-dinitrophenylhydrazone derivative (38 mg), as red crystals of mp 126–127°, which was identified as Me_2CO 2,4-dinitrophenylhydrazone by direct comparison with an authentic sample.

Compound **5**. Semi-solid, $[\alpha]^{20}$ (λ): +66 (589), +73 (578), +82 (546), +142 (436), +161 (365) ($CHCl_3$; *c* 0.17);

UV λ_{max}^{EtOH} nm (log ε): 255 (4.16); IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 2820, 2720, 1730 (CHO), 1740, 1370, 1240 (OAc), 1640, 1600 [>C=C(CHO)–]; EIMS *m/z* (rel. int.): 338 $[M]^+$ (2), 320 $[M-H_2O]^+$ (5), 279 $[M-AcO]^+$ (3), 278 $[M-AcOH]^+$ (3), 261 $[M-H_2O-AcO]^+$ (3), 260 $[M-H_2O-AcOH]^+$ (12), 219 (22), 195 (21), 163 (22), 136 (26), 135 (59), 109 (20), 107 (19), 43 (100); ^1H and ^{13}C NMR: Tables 1 and 2.

Compound **6**. Semi-solid, $[\alpha]^{20}$ (λ): +44 (589), +47 (578), +51 (546), +61 (436), −60 (365) ($CHCl_3$; *c* 0.13); UV λ_{max}^{EtOH} nm (log ε): 262 (4.36); IR ν_{max}^{KBr} cm^{-1}: 3500 (OH), 2720, 1680, 970 (*trans*–CH=CHCHO), 1730, 1370, 1240 (OAc), 1660, 1620 [>C=C(CHO)–]; EIMS *m/z* (rel. int.): 404 $[M]^+$ (30), 386 $[M-H_2O]^+$ (15), 264 (24), 163 (34), 159 (26), 136 (25), 135 (43), 123 (27), 121 (31), 110 (27), 109 (33), 95 (51), 55 (27), 43 (100); ^1H and ^{13}C NMR: Tables 1 and 2.

Acknowledgement—Thanks are due to Professor T. Uyehara of Utsunomiya University for his encouragement.

REFERENCES

1. Seki, K. and Kaneko, R. (1975) *Chem. Ind. (London)* 349.
2. Li, D.-H., Hao, X.-G., Zhang, S.-K., Wang, S.-X., Liu, R.-Y., Ma, K.-S., Yu, S.-P., Jiang, H. and Guan, J.-F. (1981) *Chung-kuo Yao Li Hsueh Pao* **2**, 131.
3. Li, W., Wang, S. and Li, D. (1981) *Yaoxue Tongbao* **16**, 19.
4. Seki, K., Ohe, Y. and Kaneko, R. (1986) *Yukagaku* **35**, 176.
5. Krick, W., Marner, F.-J. and Jaenicke, L. (1983) *Z. Naturforsch.* **38c**, 179.
6. Marner, F.-J., Krick, W., Gellrich, B. and Jaenicke, L. (1982) *J. Org. Chem.* **47**, 2531.
7. Krick, W., Marner, F.-J. and Jaenicke, L. (1983) *Z. Naturforsch.* **38c**, 689.