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DITERPENOIDS FROM *RABDOSIA INFLEXA*

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Key Word Index—*Rabdosia inflexa*; Labiatae; inflexarabdonins C–F; *ent*-kaurenoid.

Abstract—Four new diterpenoids, inflexarabdonins C, D, E, and F were isolated from the aerial parts of *Rabdosia inflexa* and their structure established on the basis of spectroscopic and chemical evidence.

INTRODUCTION

Six *ent*-kaurenoid diterpenoids, inflexin (**12**), inflexinol (**13**), inflexanins A (**3**) and B (**14**), and inflexarabdonins A (**8**) and B (**9**) were isolated from *Rabdosia inflexa* (Thunb.) HARA [1] and the structures determined [2–6]. Some of these compounds showed cytotoxic activity against cultured cancer cells *in vitro* [2, 3]. We have examined the minor diterpenoid constituents of *R. inflexa* collected in Hiroshima Prefecture, Japan and isolated additional new diterpenoids, inflexarabdonins C (**1**), D (**5**), E (**6**) and F (**7**). This paper deals with the structure determination of these new compounds.

RESULTS AND DISCUSSION

Inflexarabdonin C (**1**), mp 179–181°, $[\alpha]_D$ −55.2° (*c* 0.87, MeOH) has the molecular formula, $C_{22}H_{30}O_5$ based on the results of HRMS. This compound contains a five-membered ketone conjugated with an *exo*-methylene group [λ_{max} 239 nm (ε 6560); ν_{max} 1710 and 1645 cm^{-1}; ^1H NMR (pyridine-d_5): δ 6.05 (H_a) and 5.31 (H_b) (each 1H, *br s*); ^{13}C NMR (pyridine-d_5): δ 205.0 (*s*), 150.0 (s), 112.9 (*t*)], a secondary acetoxy group [ν_{max} 1730 and 1260–1200 cm^{-1}; δ 1.92 (3H, *s*) and 4.68 (1H, *t*, *J* = 2.5 Hz, H_c); δ 20.8 (*q*), 169.8 (*s*) and 77.7 (*d*)], a secondary hydroxyl group [ν_{max} 3600 and 3450 cm^{-1}; δ 4.33 (1H, *br d*, *J* = 4.5 Hz, H_d); δ 63.6 (*d*)] and an isolated ketone group [ν_{max} 1710 cm^{-1}; δ210.8 (*s*)], three tertiary methyl groups [δ 1.06, 1.08 and 1.40 (each 3H, *s*); δ 18.8, 21.9 and 26.9 (each *q*)] as partial structures. The ^{13}C NMR spectrum of **1** (Table 1) showed, in addition to the above mentioned signals, signals due to five methylene groups, three methine groups and three quaternary carbon atoms. Acetylation of **1** gave the monoacetate (**2**) [δ 5.21 (1H, *br d*, *J* = 4.5 Hz, H_d)].These spectral data, together with a consideration of the structures of diterpenoids isolated from the genus *Rabdosia* [7], suggested that inflexarabdonin C has a structure which acetoxy, hydroxyl and ketone groups were introduced to the basic skeleton, *ent*-kaur-16-en-15-one. An acetoxy group was suggested to be located between a methylene group and a quaternary carbon atom with an axial arrangement judged from the coupling pattern of the proton on the carbon having an acetoxy group. The position was determined to be C-3 on the basis of the results from NOE experiments. On irradiation at δ 1.08 (H_3-18) and 1.40 (H_3-19), respectively, NOE (5.9%) and difference NOE for H_c were observed. A secondary hydroxyl group must be located at C-11 from the following considerations. On irradiation at the frequency of H_d, the signal at δ 2.04 (1H, *m*, H-12α, H_k) changed to a doublet of doublet (*J* = 14 and 4 Hz) and that at δ 2.26 (1H, *br d*, *J* = 14 Hz, H-12β, H_i) became sharp. The signal due to H_k changed to a doublet of doublet (*J* = 14 and 4.5 Hz) and the signal due to H_i became sharp on irradiation at δ 3.00 (1H, *m*, H-13, H_f). An NOE (5.4%) was observed for H_d on irradiation at δ 1.06 (H_3-20). An isolated ketone might be located between a methine group and a methylene group based on the findings that signals due to a methylene group [δ_H 3.55 (1H, *d*, *J* = 13.5 Hz), H_e and 2.07 (1H, *d*, *J* = 13.5 Hz), H_j] and a methine group [δ_H 2.96 (1H, *s*), H_g] adjacent to a carbonyl group were observed. The possible position is C-6. On irradiation at δ 1.08 (H_3-18) and 2.96 (H_g), respectively, an NOE for H_g (10.5%) and that for H_e (6.8%) were observed, confirming the location of a ketone group at C-6. On the basis of the findings, inflexarabdonin C was elucidated as *ent*-3α,11α-dihydroxy-kaur-16-en-6,15-dione 3-acetate (**1**). The structure was chemically confirmed from the following chemical correlation with inflexanin A (**3**) [4]. Acetylation of **3** gave the monoacetate (**4**) which was oxidized by Jones reagent to give inflexarabdonin C monoacetate (**2**). Thus, the structure of inflexarabdonin C is represented as **1**.

Inflexarabdonin D (**5**), mp 210–212°, $C_{24}H_{36}O_7$, $[\alpha]_D$ −17.1° (MeOH; *c* 0.82) showed very similar spectral data (see Experimental) to those of inflexarabdonin A (**8**) [6] and was presumed to be an isomer concerning the position of an acetyl group. Acetylation of **5** gave inflexarabdonin A diacetate (**11**). Comparison of the ^1H NMR spectra (in $CDCl_3$) of **5** and **8** led to the conclusion that two acetoxy groups were located at C-3 and C-15, and three hydroxyl groups were located at C-1, C-6 and C-11. The signal due to H-11 resonated at δ 5.05, *ca* 1.2 ppm upfield compared to that (δ 6.23) of **8**. On the other hand, the signal due to H-15 resonated at δ 5.33, *ca* 1.5

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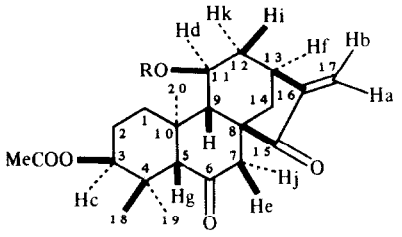

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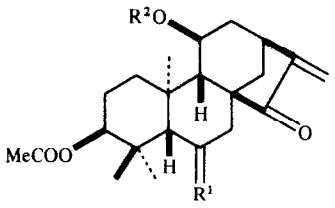

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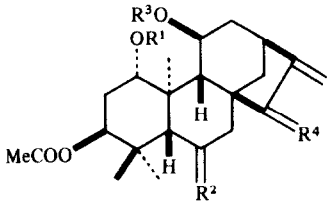
4 R^1 = α-OH, β-H, R^2 = COMe



5 R^1 = R^3 = H, R^2 = α-OH, β-H, R^4 = α-H, β-OCOMe
6 R^1 = R^3 = H, R^2 = R^4 = O
7 R^1 = R^3 = H, R^2 = α-OH, β-H, R^4 = α-H, β-OH
8 R^1 = H, R^2 = α-OH, β-H, R^3 = COMe, R^4 = α-H, β-OH
9 R^1 = H, R^2 = O, R^3 = COMe, R^4 = α-H, β-OH
10 R^1 = R^3 = COMe, R^2 = R^4 = O
11 R^1 = R^3 = COMe, R^2 = α-OH, β-H, R^4 = α-H, β-OCOMe
12 R^1 = H, R^2 = R^4 = O, R^3 = COMe
13 R^1 = H, R^2 = α-OH, β-H, R^3 = COMe, R^4 = O
14 R^1 = R^3 = H, R^2 = α-OH, β-H, R^4 = O

ppm downfield compared to that (δ 3.83) of **8**. Thus, the structure of inflexarabdonin D was determined as *ent*-1β,3α,6β,11α,15α-pentahydroxy-kaur-16-ene 3, 15-diacetate (**5**).

Table 1. ^{13}C NMR data* of inflexarabdonins C (**1**), D (**5**), E (**6**) and F (**7**)

C	1	5	6	7
1	33.4	77.3	74.7	77.9
2	22.5	34.3	33.4	34.5
3	77.7	80.1	78.9	80.2
4	36.0	37.9	36.1	37.9
5	60.1	49.1	59.4	49.6
6	210.8	66.6	211.2	67.6
7	50.5	47.4	51.0	48.5
8	55.0	44.1[a]	54.8	44.4[b]
9	64.6	58.5	64.9	57.3
10	45.3	43.8[a]	50.9	44.0[b]
11	63.6	66.8	65.9	67.0
12	41.2	43.6	40.8	42.9
13	37.3	39.8	37.6	40.8
14	37.2	38.4	37.6	38.7
15	205.0	83.3	205.3	84.0
16	150.0	154.1	150.8	159.5
17	112.9	107.3	111.8	104.8
18	26.9	28.2	26.5	28.4
19	21.9	24.2	21.9	24.0
20	18.8	14.1	15.3	14.7
MeCO	20.8	20.88	20.7	20.9
		20.94		
MeCO	169.8	169.9	170.0	170.2
		170.4		

*The spectra were measured in C_5D_5N and the shifts are given in ppm(δ) relative to the internal TMS.
[a,b]The assignments may be interchanged.

Inflexarabdonin E (**6**), mp 234–237°, $C_{22}H_{30}O_6$, $[\alpha]_D$ −42.8° (MeOH; *c* 0.80) showed similar spectroscopic data (see Experimental) to those of inflexanin B (**14**) [4, 5] and the M_r is two mass units less than that of **14**. In the ^{1}H NMR spectrum (pyridine-d_5), inflexarabdonin E did not show any signals due to H-6 which was observed at δ4.72 in the spectrum of 14. Instead, signals due to a methylene group [δ3.62 and 2.12 (each 1H, *d*, *J* = 13 Hz), H_2-7] and a methine group [δ3.11 (1H, *s*), H-5] which are adjacent to a ketone group, were observed in the ^{1}H NMR spectrum of **6**. Acetylation of **6** gave the diacetate (**10**) which was identical with inflexin monoacetate. Thus, the structure of inflexarabdonin E was determined as *ent*-1β,3α,11α-trihydroxy-kaur-16-en-6,15-dione 3-acetate (**6**).

Inflexarabdonin F (**7**), mp 263–266°, $C_{22}H_{34}O_6$, $[\alpha]_D$ +13.4° (MeOH; *c* 1.10) showed similar spectral data (see Experimental) to those of inflexanin B (**14**) [4, 5]. This compound did not show any absorption maxima above 220 nm and the molecular formula has two mass units more than that of **14**. This fact suggests that inflexarabdonin F must have a structure corresponding to dihydroinflexanin B in which the ketone group at C-15 was reduced to an allylic alcohol. Acetylation of **7** gave inflexarabdonin A diacetate (**11**) and sodium borohydride reduction of inflexanin B (**14**) gave inflexarabdonin F (**7**). Thus, the structure of inflexarabdonin F was determined as *ent*-1β,3α,6β,11α,15α-pentahydroxy-kaur-16-ene 3-acetate (**7**).

EXPERIMENTAL

General. Mps: uncorr. NMR: ^{1}H (200 MHz) and ^{13}C (50.1 MHz). EIMS: 70 eV. CC Kiesel gel 60 (Merck). Prep. TLC (Kiesel gel 60 F_{254}).

Plant material. The same plant material was used as in the previous report [6].

Isolation of diterpenoids. The residue (233 mg) from the fractions 59–92 of column II in the previous report [6] was

further purified by a silica gel CC (EtOAc–hexane with increasing amount of EtOAc content) followed by prep. TLC ($CHCl_3$–Me_2CO 19:1, developed × 4) to give inflexarabdonin C (**1**) (35.3 mg). The residue (2.40 g) from the fraction 47–63 of column I in the previous report [6] was subjected to a silica gel CC (Et_2O and then Me_2CO). The residue (550 mg) from the Me_2CO eluate was further subjected to a silica gel CC ($CHCl_3$–MeOH with increasing MeOH content). The residue (64 mg) from the faster eluate was purified by prep. TLC ($CHCl_3$–MeOH 9:1, developed × 2) to give inflexarabdonin D (**5**) (36.5 mg). The residue (110 mg) from the slower eluate was purified repeatedly by prep. TLC ($CHCl_3$–Me_2CO 8:2, developed × 4; Et_2O, developed × 5) to give inflexarabdonin E (**6**) (28.6 mg) and inflexarabdonin F (**7**) (4.2 mg). The physical properties of the isolated compounds were as follows.

Inflexarabdonin C (**1**). Mp 179–181° (from MeOH), $[\alpha]_D^{24}$ −55.2° (MeOH; *c* 0.87); UV λ_{max}^{MeOH}: 239 nm (ε 6560); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3450, 1730, 1710, 1645, 1375, 1260–1200, 1060, 1035 and 985; ^1H NMR (pyridine-d_5): δ1.06, 1.08 and 1.40 (each 3H, *s*, 3× tert. Me), 1.46 (1H, *br dd*, *J* = 12 and 4 Hz, H-14β), 1.92 (3H, *s*, OAc), 2.04 (1H, *m*, H-12α), 2.07 (1H, *d*, *J* = 13.5 Hz, H-7α), 2.26 (1H, *br d*, *J* = 14 Hz, H-12β), 2.35 (1H, *d*, *J* = 12 Hz, H-14α), 2.50 (1H, *br s*, H-9), 2.96 (1H, *s*, H-5), 3.00 (1H, *m*, H-13), 3.55 (1H, *d*, *J* = 13.5 Hz, H-7β), 4.33 (1H, *br d*, *J* = 4.5 Hz, H-11), 4.68 (1H, *t*, *J* = 2.5 Hz, H-3), 5.31 (1H, *br s*, H-17), 6.05 (1H, *br s*, H-17); ^{13}C NMR: see Table 1; MS *m/z*: 374.2105 $[M]^+$. $C_{22}H_{30}O_5$ requires 374.2094.

Inflexarabdonin D (**5**). Mp 210–212° (from MeOH), $[\alpha]_D^{24}$ −17.1° (MeOH; *c* 0.82); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3575, 3400, 1730, 1375, 1260–1200, and 1030; ^1H NMR ($CDCl_3$): δ 0.92, 1.29, and 1.39 (each 3H, *s*, 3× tert. Me), 2.07 and 2.23 (each 3H, *s*, 2× OAc), 2.36 (1H, *d*, *J* = 12.5 Hz, H-14α), 2.71 (1H, *m*, H-13), 3.86 (1H, *dd*, *J* = 11.5 and 4.5 Hz, H-1), 4.35 (1H, *m*, H-6), 4.68 (1H, *t*, *J* = 3 Hz, H-3), 4.95 (1H, *dd*, *J* = 2 and 1 Hz, H-17), 5.05 (1H, *br d*, *J* = 5 Hz, H-11), 5.18 (1H, *dd*, *J* = 2.5 and 1 Hz, H-17), 5.33 (1H, *t*, *J* = 2.5 Hz, H-15); ^{13}C NMR: see Table 1; MS *m/z*: 436.2474 $[M]^+$. $C_{24}H_{36}O_7$ requires 436.2462.

Inflexarabdonin E (**6**). Mp 234–237° (from MeOH), $[\alpha]_D^{25.5}$ −42.8° (MeOH; *c* 0.80); UV λ_{max}^{MeOH}: 240 nm (ε 6290); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3590, 3550–3250, 1720, 1640, 1250–1190, 1030 and 985; ^1H NMR ($CDCl_3$): δ 0.98, 1.13 and 1.33 (each 3H, *s*, 3× tert. Me), 1.50 (1H, *br dd*, *J* = 12.5 and 4.5 Hz, H-14β), 1.89 (1H, *d*, *J* = 13.5 Hz, H-7α), 2.13 (3H, *s*, OAc), 2.32 (1H, *d*, *J* = 12.5 Hz, H-14α), 2.80 (1H, *br s*, H-5), 3.09 (1H, *m*, H-13), 3.21 (1H, *br d*, *J* = 13.5 Hz, H-7β), 4.08 (1H, *dd*, *J* = 10.5 and 6 Hz, H-1), 4.60 (1H, *t*, *J* = 3 Hz, H-3), 5.24 (1H, *br d*, *J* = 4.5 Hz, H-11), 5.37 (1H, *br s*, H-17), 5.96 (1H, *br s*, H-17); ^1H NMR (pyridine-d_5): δ 1.09, 1.43, and 1.48 (each 3H, *s*, 3× tert. Me), 1.88 (3H, *s*, OAc), 2.12 (1H, *d*, *J* = 13 Hz, H-7α), 2.49 (1H, *d*, *J* = 12 Hz, H-14α), 3.02 (1H, *m*, H-13), 3.11 (1H, *s*, H-5), 3.62 (1H, *d*, *J* = 13 Hz, H-7β), 4.43 (1H, *m*, changed to *dd*, *J* = 10.5 and 6 Hz, H-1), 4.81 (1H, *t*, *J* = 3 Hz, H-3), 5.28 (1H, *br s*, H-17), 6.03 (1H, *br s*, H-17), 6,09 (1H, *t*, *J* = 3 Hz, H-11), 6.21 and 6.55 (each 1H, *m*, 2× OH); ^{13}C NMR: see Table 1; MS *m/z*: 390.2052 $[M]^+$. $C_{22}H_{30}O_6$ requires 390.2043.

Inflexarabdonin F (**7**). Mp 263–266° (from a mixture of MeOH and Et_2O), $[\alpha]_D^{27}$ +13.4° (MeOH; *c* 1.10); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3400, 1720, 1370, 1250–1190, and 1030; ^1H NMR ($CDCl_3$): δ0.92, 1.29, and 1.41 (each 3H, *s*, 3× tert. Me), 2.08 (3H, *s*, OAc), 2.36 (1H, *d*, *J* = 12.5 Hz, H-14α), 2.64 (1H, *m*, H-13), 3.80 (1H, *t*, *J* = 2.5 Hz, H-15), 3.84 (1H, *dd*, *J* = 11.5 and 4.5 Hz, H-1), 4.08 (1H, *m*, OH), 4.39 (1H, *m*, H-6), 4.67 (1H, *t*, *J* = 3 Hz, H-3), 5.05 (1H, *br d*, *J* = 3 Hz, H-17), 5.12 (1H, *br s*, H-17), 5.26 (1H, *br d*, *J* = 5 Hz, H-11); ^1H NMR (pyridine-d_5): δ 1.11 and 1.60 (each 3H, *s*, 2× tert. Me), 1.94 (3H, *s*, OAc), 1.99 (3H, *s*, tert. Me), 2.73 (1H, *m*, H-13), 2.91 (1H, *d*, *J* = 12.5 Hz, H-14α), 4.16 (1H, *m*, changed to *t*, *J* = 2 Hz on addition of D_2O, H-15), 4.36 (1H, *dd*, *J* = 11.5 and 4.5 Hz, H-1), 4.70 (1H, *m*, H-6), 4.99 (1H, *t*, *J* = 3 Hz, H-3), 5.21 (1H, *br s*, H-17), 5.43 (1H, *br s*, H-17), 5.74 (1H, *d*, *J* = 3 Hz, OH), 6.06 (1H, *br d*, *J* = 10 Hz, OH), 6.21 (1H, *br d*, *J* = 4 Hz, H-11), 6.48 (1H, *m*, OH); ^{13}C NMR: see Table 1; MS *m/z*: 394.2352 $[M]^+$. $C_{22}H_{34}O_6$ requires 394.2356.

Acetylation of inflexarabdonin C (**1**). Usual acetylation of inflexarabdonin C (**1**) (8.0 mg) with a mixture of Ac_2O and pyridine gave a residue (9.4 mg) which was purified by prep. TLC ($CHCl_3$–Me_2CO, 19:1; developed × 2) to give the monoacetate (**2**) (3.8 mg) as colourless needles, mp 197–199°, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725, 1640, 1370, 1250–1190, 1055, 1030 and 980; ^1H NMR ($CDCl_3$): δ 0.93 and 1.10 and 1.32 (each 3H, *s*, 3 × tert. Me), 1.89 (1H, *d*, *J* = 13.5 Hz, H-7α), 1.90 and 2.11 (each 3H, *s*, 2 × OAc), 2.37 (1H, *d*, *J* = 12 Hz, H-14α), 2.76 (1H, *br s*, H-5), 3.09 (1H, *m*, H-13), 3.21 (1H, *br d*, *J* = 13.5 Hz, H-7β), 4.55 (1H, *t*, *J* = 2.5 Hz, H-3), 5.21 (1H, *br d*, *J* = 4.5 Hz, H-11), 5.36 (1H, *br s*, H-17), 6.01 (1H, *br s*, H-17), MS *m/z*: 416.2174 $[M]^+$. $C_{24}H_{32}O_6$ requires 416.2200.

Acetylation of inflexanin A (**3**). Acetylation of inflexanin A (**3**) (31.6 mg) in the usual manner gave a residue (33 mg) which was purified by prep. TLC ($CHCl_3$–Me_2CO, 19:1; developed × 2) to give the monoacetate (**4**) (15.8 mg) as an amorphous powder. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1640, 1370, 1250–1190, 1045, 1015; ^1H NMR ($CDCl_3$): δ 0.95, 1.28 and 1.46 (each 3H, *s*, 3 × tert. Me), 1.86 and 2.06 (each 3H, *s*, 2 × OAc), 2.27 (1H, *dd*, *J* = 15 and 3 Hz, H-7β), 2.83 (1H, *d*, *J* = 12.5 Hz, H-14α), 3.07 (1H, *m*, H-13), 4.48 (1H, *m*, H-6), 4.62 (1H, *t*, *J* = 3 Hz, H-3), 5.17 (1H, *br d*, *J* = 4.5 Hz, H-11), 5.27 (1H, *br s*, H-17), 5.92 (1H, *br s*, H-17); MS *m/z*: 358.2128 $[M-AcOH]^+$. Calc. for $C_{22}H_{30}O_4$: 358.2145.

Jones oxidation of inflexanin A monoacetate (**4**). Inflexanin A monoacetate (**4**) (11.6 mg) was dissolved in Me_2CO (5 ml). Jones reagent (1 drop) was added to the soln with stirring and ice cooling. The mixture was stirred for 5 min at 0°, and then, neutralized with a small amount of 5% aq. $NaHCO_3$ soln and concd *in vacuo*. H_2O (30 ml) was added to the residue and the mixture extracted with EtOAc (30 ml × 3). After being washed with satd NaCl aq. soln, the EtOAc extract was dried and evapd *in vacuo* to give a residue (10.5 mg) which was purified by prep. TLC ($CHCl_3$–Me_2CO, 19:1; developed × 2) to give the inflexarabdonin C monoacetate (**2**) (6.1 mg) as colourless needles, mp 201–203°; MS *m/z*: 416.2224 $[M]^+$. Calc. for $C_{24}H_{32}O_6$: 416.2200. This compound was identical to the compound derived from inflexarabdonin C (**1**) (mmp, IR and ^1H NMR).

Acetylation of inflexarabdonin D (**5**). Inflexarabdonin D (**5**) (4.2 mg) gave the inflexarabdonin A diacetate (**11**) (3.9 mg) as an amorphous powder on acetylation. MS *m/z*: 520.2677 $[M]^+$. Calc. for $C_{28}H_{40}O_9$: 520.2673. This compound was identical to the compound derived from inflexarabdonin A (**8**) (IR and ^1H NMR).

Acetylation of inflexarabdonin E (**6**). Inflexarabdonin E (**6**) (3 mg) gave the inflexin monoacetate (**10**) (3.6 mg) as an amorphous powder on acetylation. MS *m/z*: 474.2238 $[M]^+$. Calc. for $C_{26}H_{34}O_8$: 474.2254. This compound was identical to the compound derived from inflexin (**12**) (IR and ^1H NMR).

Acetylation of inflexarabdonin F (**7**). Inflexarabdonin F (**7**) (4.7 mg) gave the inflexarabdonin A diacetate (**11**) (3.1 mg) as an amorphous powder on acetylation. MS *m/z*: 520.2639 $[M]^+$. Calc. for $C_{28}H_{40}O_9$: 520.2673. This compound was identical to the compound derived from inflexarabdonin A (**8**) (IR and ^1H NMR).

Reduction of inflexanin B (**14**) *by* $NaBH_4$. To the soln of inflexanin B (**14**) (20.5 mg) in MeOH (5 ml), the soln of $NaBH_4$ (20 mg) in MeOH (1 ml) was added dropwise under ice-cooling and stirring. The reaction mixture was kept at 0° for 1 hr with stirring. After addition of H_2O (30 ml), the reaction mixture was extracted with EtOAc (30 ml × 3). After being washed with satd

NaCl aq. soln, the EtOAc extract was dried and evapd *in vacuo* to give a residue (20.6 mg) which was purified by prep. TLC ($CHCl_3$–Me_2CO, 7:3; developed ×3; silica gel impregnated with $AgNO_3$) to give the inflexarabdonin F (7) (12.0 mg) as colourless needles on addition of MeOH–Et_2O, mp 263–266°, MS *m/z*: 394.2386 $[M]^+$. Calc. for $C_{22}H_{34}O_6$: 394.2356. This compound was identical to inflexarabdonin F of natural origin (mmp, IR and ^1H NMR).

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REFERENCES

1. Hara, H. (1972) *J. Jap. Botany* **47**, 193.
2. Kubo, I., Nakanishi, K., Kamikawa, T., Isobe, T. and Kubota, T. (1977) *Chemistry Letters* 99.
3. Fujita, T., Takeda, Y., Yuasa, E., Okamura, A., Shingu, T. and Yokoi, T. (1982) *Phytochemistry* **21**, 903.
4. Takeda, Y., Ichihara, T., Fujita, T., Kida, K. and Ueno, A. (1987) *Chem. Pharm. Bull.* **35**, 3490.
5. Takeda, Y., Shingu, T., Ichihara, T., Fujita, T., Yokoi, T., Kida, K. and Ueno, A. (1988) *Chem. Pharm. Bull.* **36**, 4576.
6. Takeda, Y., Ichihara, T., Yamasaki, K. and Otsuka, H. *Phytochemistry* **28**, 851.
7. Fujita, E. and Node, M. (1984) in *Progress in the Chemistry of Organic Natural Products* Vol. 46 (Herz, W., Grisebach, H., Kirby, G.W. and Tamm, Ch. eds), p. 77. Springer, Vienna.