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BELAMCANDONES A–D, DIOXOTETRAHYDRODIBENZOFURANS FROM *BELAMCANDA CHINENSIS*

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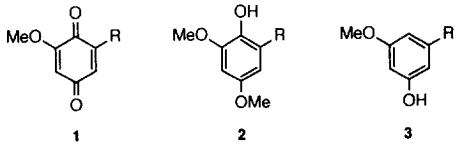
Key Word Index—*Belamcanda chinensis*; Iridaceae; seeds; dioxotetrahydrodibenzofurans; belamcandones A–D.

Abstract—Four new enediones, belamcandones A–D, have been isolated from the seeds of *Belamcanda chinensis*. On the basis of spectroscopic methods and chemical evidence, they are concluded to be 4a,8-dihydroxy-2,7-dimethoxy-1,4-dioxo-1,4,4a,9b-tetrahydrodibenzofurans having two alkyl side-chains at the C-9 and C-9b positions.

INTRODUCTION

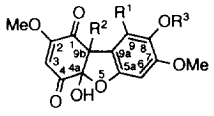
In the course of studies on biologically active substances in plants of the Iridaceae, irisquinone [1], a compound having antitumour and immunostimulatory activities [2, 3], has been isolated from the seeds of *Iris pseudacorus*. Recently, we reported on the structures of several kinds of triterpenoids obtained from the seeds of *I. tectorum*, viz. iristectorenes A–H [4, 5], higher fatty esters of a monocyclic triterpene alcohol, and iristectorones A–H [6], adducts of belamcandaquinone (**1**) with spirobicyclic triterpenes. *Belamcanda chinensis f. vulgaris* (Japanese name, 'Darumahiougi') is a perennial herb and the seeds contain considerable amounts of *p*-benzoquinones and related compounds, e.g. **1** [7], and its precursors **2** and **3** [8], in analogy with other species of the Iridaceae [1, 9–16].

Further investigation of the same seed oil has led to the isolation and characterization of four enediones, named belamcandones A–D (**4**–**7**), which were considered to be biogenetically related to belamcandaquinone (**1**) and belamcandaphenol (**2**).



1 **2** **3**

R= -(CH$_2$)$_9$CH=^{cis}CH(CH$_2$)$_3$Me



4: R^1=R^2= -(CH$_2$)$_9$CH=^{cis}CH(CH$_2$)$_3$Me; R^3= -H (A: 38%)

5: R^1, R^2= -(CH$_2$)$_9$CH=^{cis}CH(CH$_2$)$_3$Me, -(CH$_2$)$_{11}$CH=^{cis}CH(CH$_2$)$_3$Me; R^3= -H (B: 42%)

6: R^1, R^2= -(CH$_2$)$_9$CH=^{cis}CH(CH$_2$)$_3$Me, -(CH$_2$)$_{16}$Me; R^3= -H (C: 17%)

7: R^1, R^2= -(CH$_2$)$_{11}$CH=^{cis}CH(CH$_2$)$_3$Me, -(CH$_2$)$_{16}$Me; R^3= -H (D: 3%)

9: R^1=R^2= -(CH$_2$)$_9$CH=^{cis}CH(CH$_2$)$_3$Me; R^3= -Ac

10: R^1=R^2= -(CH$_2$)$_9$CH=^{cis}CH(CH$_2$)$_3$Me **11**: R^1=R^2= -(CH$_2$)$_9$CH=^{cis}CH(CH$_2$)$_3$Me

RESULTS AND DISCUSSION

The *n*-hexane-soluble seed oil of *B. chinensis*, which after removal of methanol-insoluble glycerides was fractionated by column chromatography and preparative TLC on silica gel to obtain enediones, which showed four major peaks (A: 38%, B: 42%, C: 17%, D: 3%) on reversed-phase HPLC. Lober column chromatography on reversed-phase silica gel afforded belamcandones A–D (**4**–**7**) as a dull red semi-solid. The ^{13}C and ^{1}H NMR data of belamcandones and their related compounds are summarized in Tables 1 and 2.

Belamcandone A (**4**) had the molecular formula $C_{44}H_{68}O_7$ ([M]$^+$ *m/z* 708), corresponding to 11 degrees of unsaturation, and showed UV absorption maxima [λ_{max}^{EtOH} 271, 408 nm (log ε 4.03, 3.03)]. Its IR spectrum contained characteristic bands for conjugated carbonyls (1700, 1670 cm^{-1}) and C=C bonds (1630, 1600 cm^{-1}). The ^{13}C NMR and DEPT spectra suggested that belamcandone A possessed four methyls, 24 methylenes, six methines and 10 quaternary carbons. Its ^{13}C NMR spectrum further revealed the presence of two carbonyl groups and six C=C bonds in the molecule, so that the compound must have three ring systems. The ^{13}C NMR

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Table 1. ^{13}C NMR spectral data of **1**, **2**, **4**–**7** and **9**–**11** (75 MHz, $CDCl_3$ with TMS as internal standard)

C	1	2*	4	5	6	7	9	10	11
1	182.1		190.7	190.7	190.7	190.7	190.4	189.5	191.8
2	158.9		165.7	165.7	165.7	165.7	165.5	164.6	182.9
3	107.1		108.3	108.3	108.3	108.3	108.4	109.1	105.5
4	187.7		190.1	190.1	190.1	190.1	189.6	186.9	168.6
4a	132.9		102.5	102.5	102.5	102.5	102.9	109.3	111.2
9b	147.6		65.2	65.2	65.2	65.2	64.8	64.6	64.5
MeO-2	56.3		56.9	56.9	56.9	56.9	57.0	56.7	
MeO-4									57.2
$MeCO_2$-4a								170.0	168.7
$MeCO_2$-4a								20.3	20.4
1″	28.7		32.8	32.8	32.8	32.8	33.0	30.4	30.2
2″	27.7		25.8	25.8	25.8	25.8	25.8	23.7	23.4
3″	29.3		30.2	30.2	30.2	30.2	30.3[a]	29.9[a]	29.6[a]
4″	29.3		29.1	29.1	29.1	29.1	29.1	29.3	29.2
5″	29.5		29.5	29.5	29.5	29.4	29.5	29.5	29.5
6″	29.5		29.5	29.5	29.5	29.6	29.5	29.5	29.6
7″	29.3		29.3	29.3	29.4	29.6	29.3	29.3	29.3
8″	29.8		29.8	29.8	29.8	29.7	29.8	29.8	29.8
9″	27.2		27.2	27.2	27.2	29.4	27.2	27.2	27.2
10″	129.9		129.9	129.8	129.8	29.7	129.9	129.8	129.8
11″	129.9		129.9	129.9	129.9	27.2	129.9	129.9	129.9
12″	26.9		26.9	26.9	26.9	129.8	26.9	26.9	26.9
13″	32.0		32.0	32.0	32.0	129.9	32.0	32.0	32.0
14″	22.4		22.4	22.4	22.4	26.9	22.4	22.4	22.4
15″	14.0		14.0	14.0	14.0	32.0	14.0	14.0	14.0
16″						22.4			
17″						14.0			
5a		152.7	149.8	149.8	149.8	149.8	155.1	153.9	153.1
6		96.6	92.2	92.2	92.2	92.2	93.4	93.3	93.4
7		146.7	147.4	147.4	147.4	147.4	152.7	153.0	153.3
8		137.5	139.8	139.8	139.8	139.8	134.2	133.9	134.1
9		128.7	128.1	128.1	128.1	128.1	135.5	134.5	134.8
9a		105.7	115.4	115.5	115.5	115.5	115.3	114.8	113.5
MeO-5a		55.8							
MeO-7		56.0	56.1	56.1	56.1	56.1	56.0	56.1	56.1
$MeCO_2$-8							169.0	168.7	168.7
$MeCO_2$-8							20.5	20.5	20.4
1′		30.0	26.3	26.3	26.3	26.3	26.8	25.8	25.8
2′		29.9	30.3	30.3	30.3	30.3	30.6	30.0	30.0
3′		29.6	30.2	30.2	30.2	30.2	30.1[a]	30.0[a]	30.0[a]
4′		29.6	29.5	29.5	29.6	29.6	29.4	29.4	29.4
5′		29.6	29.6	29.6	29.7	29.7	29.6	29.6	29.6
6′		29.6	29.7	29.6	29.7	29.7	29.6	29.6	29.6
7′		29.3	29.3	29.7	29.7	29.7	29.3	29.3	29.3
8′		29.8	29.8	29.7	29.7	29.7	29.8	29.8	29.8
9′		27.2	27.2	29.3	29.7	29.7	27.2	27.2	27.2
10′		129.8	129.8	29.8	29.7	29.7	129.9	129.8	129.8
11′		129.9	129.9	27.2	29.7	29.7	129.9	129.9	129.9
12′		26.9	26.9	129.8	29.7	29.7	26.9	26.9	26.9
13′		32.0	32.0	129.9	29.7	29.7	32.0	32.0	32.0
14′		22.4	22.4	26.9	29.4	29.4	22.4	22.4	22.4
15′		14.0	14.0	32.0	31.9	31.9	14.0	14.0	14.0
16′				22.4	22.7	22.7			
17′				14.0	14.1	14.1			

Assignments were based on DEPT, ^1H–^{13}C COSY and ^1H–^{13}C long range COSY experiments.

*Carbon skeleton of **2** is numbered in the same manner as that of **4**.

[a]Signals may be interchangeable within the same column.

Signals of C-*n* ($n \geq 5$) in **5**–**7** may be interchanged with those of C-*n*″ ($n \geq 5$).

Table 2. ^{1}H NMR spectral data of **4**–**7** and **9**–**11** (300 MHz, $CDCl_3$ with TMS as internal standard)

H	4	5	6	7	9	10	11
3	6.18 *s*	6.18 *s*	6.18 *s*	6.18 *s*	6.19 *s*	5.99 *s*	5.85 *s*
MeO-2	3.82 *s*	3.82 *s*	3.82 *s*	3.82 *s*	3.82 *s*	3.77 *s*	
MeO-4							3.82 *s*
HO-4a	5.16 *s*	5.16 *s*	5.16 *s*	5.15 *s*	5.22 *br s*		
AcO-4a						2.21 *s*	2.22 *s*
1″	2.23 *ddd* (13, 12, 5); 2.57 *ddd* (13, 11, 5)	2.23 *ddd* (13, 12, 5); 2.57 *ddd* (13, 11, 5)	2.23 *ddd* (13, 12, 5); 2.57 *ddd* (13, 11, 5)	2.23 *ddd* (13, 12, 5); 2.57 *ddd* (13, 11, 5)	2.23 *ddd* (13, 12, 4); 2.56 *m*	1.53 *ddd* (13, 12, 4); 2.42 *ddd* (13, 11, 5)	1.55 *ddd* (13, 12, 4); 2.30 *m*
2″	1.12 *m*	1.12 *m*	1.12 *m*	1.12 *m*	1.12 *m*	0.69, 1.38 *m*	0.69, 1.38 *m*
3″–8″	1.22–1.30 *br*	1.22–1.30 *br*	1.26 *br*	1.26 *br*	1.22–1.30 *br*	1.20–1.28 *br*	1.20–1.28 *br*
9″	2.02 *br*	2.02 *br*	2.02 *br*	1.26 *br*	2.02 *br*	2.02 *br*	2.02 *br*
10″	5.35 *m*	5.35 *m*	5.35 *m*	1.26 *br*	5.35 *m*	5.35 *m*	5.35 *m*
11″	5.35 *m*	5.35 *m*	5.35 *m*	2.02 *br*	5.35 *m*	5.35 *m*	5.35 *m*
12″	2.02 *br*	2.02 *br*	2.02 *br*	5.35 *m*	2.02 *br*	2.02 *br*	2.02 *br*
13″	1.22–1.30 *br*	1.22–1.30 *br*	1.26 *br*	5.35 *m*	1.22–1.30 *br*	1.20–1.28 *br*	1.20–1.28 *br*
14″	1.22–1.30 *br*	1.22–1.30 *br*	1.26 *br*	2.02 *br*	1.22–1.30 *br*	1.20–1.28 *br*	1.20–1.28 *br*
15″	0.90 *m*	0.90 *m*	0.90 *m*	1.26 *br*	0.90 *m*	0.90 *m*	0.90 *m*
16″				1.26 *br*			
17″				0.90 *m*			
6	6.29 *s*	6.28 *s*	6.29 *s*	6.29 *s*	6.34 *s*	6.45 *s*	6.45 *s*
MeO-7	3.81 *s*	3.81 *s*	3.81 *s*	3.81 *s*	3.74 *s*	3.77 *s*	3.79 *s*
HO-8	5.33 *s*	5.33 *s*	5.33 *s*	5.32 *s*			
AcO-8					2.29 *s*	2.28 *s*	2.26 *s*
1′	2.76 *ddd* (13, 11, 5); 3.06 *ddd* (13, 11, 4)	2.76 *ddd* (13, 11, 5); 3.06 *ddd* (13, 11, 4)	2.76 *ddd* (13, 12, 5); 3.06 *ddd* (13, 11, 4)	2.76 *ddd* (13, 11, 5); 3.06 *ddd* (13, 11, 4)	2.52 *m*; 3.05 *ddd* (13, 11, 4)	2.22 *m*	2.22 *m*
2′	1.47, 1.66 *m*	1.47, 1.66 *m*	1.47, 1.66 *m*	1.47, 1.66 *m*	1.45 *m*	1.26 *m*	1.26 *m*
3′-8′	1.22–1.30 *br*	1.22–1.30 *br*	1.26 *br*	1.26 *br*	1.22–1.30 *br*	1.20–1.28 *br*	1.20–1.28 *br*
9′	2.02 *br*	1.22–1.30 *br*	1.26 *br*	1.26 *br*	2.02 *br*	2.02 *br*	2.02 *br*
10′	5.35 *m*	1.22–1.30 *br*	1.26 *br*	1.26 *br*	5.35 *m*	5.35 *m*	5.35 *m*
11′	5.35 *m*	2.02 *br*	1.26 *br*	1.26 *br*	5.35 *m*	5.35 *m*	5.35 *m*
12′	2.02 *br*	5.35 *m*	1.26 *br*	1.26 *br*	2.02 *br*	2.02 *br*	2.02 *br*
13′	1.22–1.30 *br*	5.35 *m*	1.26 *br*	1.26 *br*	1.22–1.30 *br*	1.20–1.28 *br*	1.20–1.28 *br*
14′	1.22–1.30 *br*	2.02 *br*	1.26 *br*	1.26 *br*	1.22–1.30 *br*	1.20–1.28 *br*	1.20–1.28 *br*
15′	0.90 *m*	1.22–1.30*br*	1.26 *br*	1.26 *br*	0.90 *m*	0.90 *m*	0.90 *m*
16′		1.22–1.30 *br*	1.26 *br*	1.26 *br*			
17′		0.90 *m*	0.88 *t* (7)	0.88 *t* (7)			

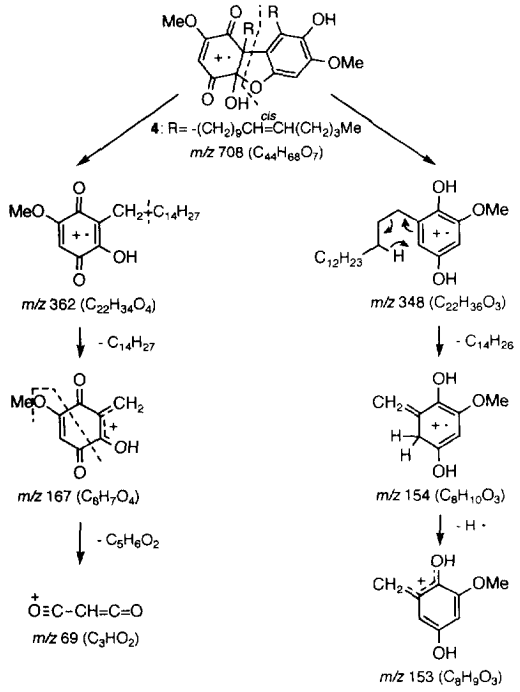
Coupling constants (J in Hz) are given in parentheses.
Assignments were based on ^{1}H–^{1}H COSY and ^{1}H–^{13}C COSY experiments.
Signals of H-n' ($n \geqq 9$) in **5**–**7** may be interchanged with those of H-n'' ($n \geqq 9$).

data (Table 1) showed a resemblance to the combined data of **1** and **2**, although several differences were observed. Furthermore, its mass spectrum (Scheme 1) exhibited two significant peaks at m/z 362 and 348, corresponding to the formulae, $C_{22}H_{34}O_4$ and $C_{22}H_{36}O_3$, respectively. These data suggested that **4** is a belamcandaquinone dimer with an additional oxygen function. The ^{1}H NMR spectrum (Table 2) revealed the presence of two ring protons [δ6.18, 6.29 (each 1H, *s*)], two hydroxyl protons [δ5.16, 5.33 (each 1H, *s*)] and two methoxyl groups [δ3.81, 3.82 (each 3H, *s*)]. One (δ6.29) of the ring protons was assigned to a pentasubstituted aromatic proton (820 cm^{-1}), while the other (δ6.18) was attributed to a pentasubstituted six-membered enedione proton (855 cm^{-1}). Additional signals at δ0.90 (6H, *m*, Me), 1.22–1.30 (32H, *br*, $-CH_2-$), 2.02 (8H, *br*, $-CH_2C{=}C-$) and 5.35 (4H, *m*, $-CH{=}CH-$) suggested the presence of two unsaturated aliphatic side-chains.

The orientation of the substituents on each of the rings was examined by the ^{1}H–^{13}C long range COSY spectrum and the two ring systems were then determined as I and II (Fig. 1). Hence, the structure of belamcandone A must be either **4** or **4a** (Fig. 2), in which units I and II form a dihydrofuran ring in opposite directions. It seems reasonable to speculate that the carbon signals at δ102.5 and 65.2 are the result of a quaternary carbon bearing two oxygen functions and a quaternary carbon situated in a position β to the oxygen functions, when comparing the chemical shifts of **4** with those of iristectorone A (**8**) [6]. As shown in Fig. 2, NOE correlations (3–6%) were also

observed between two unequivalent α-methylene groups on the aromatic and enedione rings. Therefore, the structure of **4** was best suited for belamcandaone A.

The side-chains of belamcandone A are inferred to be two (*Z*)-10-pentadecenyl groups by analogy with **1** and **2** in the ^{13}C NMR spectra (Table 1), in which signals of the side-chains in **4** are in good agreement with those in **1** and **2**, except for those of the α-(C-1′, C-1″), β-(C-2′, C-2″) and γ-carbons (C-3′, C-3″). In addition, carbon signals at δ26.9 (C-12′ and C-12″) and 27.2 (C-9′ and C-9″) are characteristic of methylenes adjacent to *cis*-double bonds [17].



Scheme 1. Characteristic peaks in the mass spectrum of **4**.

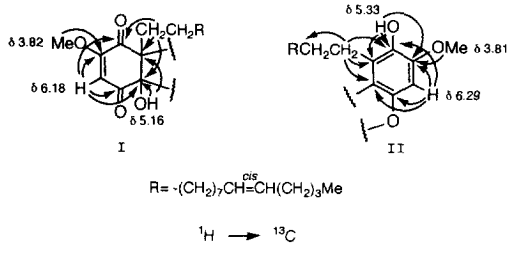


Fig. 1. Key correlations in ^{1}H–^{13}C long range COSY spectrum of belamcandone A.

The structure for belamcandone A was also supported by its mass spectral fragmentation pattern (Scheme 1) and the following chemical evidence. On acetylation with acetic anhydride and pyridine at room temperature for 20 min, **4** afforded a monoacetate **9** [pale yellow solid, $C_{46}H_{70}O_8$ ([M]$^+$ *m/z* 750)] having a tertiary hydroxyl group [3550 (sh), 3400 cm^{-1} (OH); δ_H 5.22 (1H, *br s*, OH); δ_C 102.9 (*s*), > C(OH)O–]. Although it is usually difficult to obtain the acetate of a tertiary hydroxyl group under the above conditions, acetylation of **4** and **9** for a long time gave two diacetates **10** [1765, 1750, 1195 cm^{-1} (OAc)] and **11** [1765, 1735, 1195 cm^{-1} (OAc)] with the same molecular formula [$C_{48}H_{72}O_9$ ([M]$^+$ *m/z* 792)] in a ratio of *ca* 9:2. Further treatment of **10** with acetic anhydride and pyridine yielded a mixture of **10** and **11** in the same ratio described above. It is noteworthy that the ratio of **10** and **11** was always *ca* 9:2. This equilibriun can be explained by assuming that the diacetates **10** and **11** were derived from the complex triones, **12a** and **b**, respectively (Scheme 2), although direct acetylation from **9** to **10** might occur with the aid of a neighbouring effect. That is, partial acetylation of **4** first occurs to form the monoacetate **9**, which is subsequently converted into the trione **12a** by further acetylation accompanied by cleavage of the furan ring. A part of **12a** converts into its rotational isomer **12b**. As a result of reformation of a furan ring, the diacetates **10** and **11** are finally obtained. In the case of the excluded structure **4a**, it is impossible to obtain the above diacetates.

As shown in Table 2, the chemical shifts of H-1″ and H-2″ showed higher field shifts from δ2.23 and 1.12 in the monoacetate **9** to δ1.53 and 0.69 in the diacetate **10**. This suggests that these protons are situated in the shielding region of the acetoxyl group on C-4a. In addition, all the specific rotations of **4**, **9** and **10** were zero. Hence, the hydroxyl group on C-4a and the side-chain on C-9b in **4** have a *syn* relationship to each other and **4** must be a racemate of (4a*R*,9b*S*) and (4a*S*,9b*R*).

The structures of the other constituents were elucidated as follows. The ^{1}H and ^{13}C NMR data of belamcandones A (**4**), B (**5**), C (**6**) and D (**7**) showed a striking

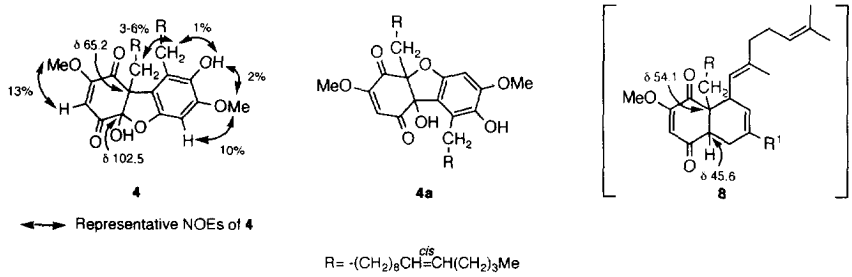
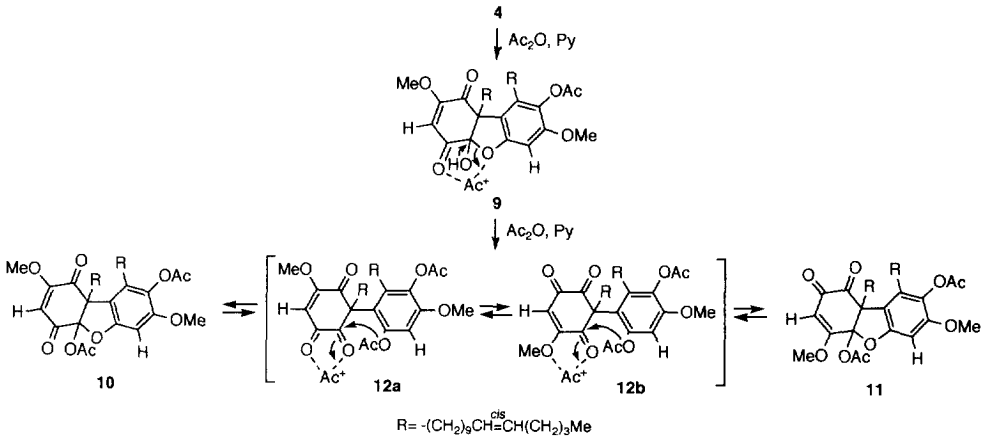


Fig. 2. Possible structures and NOEs of belamcandone A.



Scheme 2. Mechanism for acetylation of **4**.

resemblance to one another, suggesting that they are homologues differing in the structure of the side-chains. All unsaturated side-chains in **4**–**7** showed carbon signals characteristic of a *cis*-ω-5 monoene group [18], while the saturated side-chains in **6** and **7** exhibited typical carbon signals corresponding to a heptadecyl group. Furthermore, each one of the side-chains in **5** and **6** was shown to be a (*Z*)-10-pentadecenyl group, because the ^{13}C NMR data (Table 1) are in good agreement with those of **4**. The residual unsaturated side-chain in **5** and **7** must, therefore, be a (*Z*)-12-heptadecenyl group.

From these results, the structures for the belamcandones A–D are concluded to be **4**–**7** as shown. As far as we are aware, this is the first report of the isolation of natural dioxotetrahydrodibenzofuran derivatives.

EXPERIMENTAL

General. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz): $CDCl_3$ with TMS as int. standard. EI-MS (probe): 70 eV. mesh, Merck CC: Kieselgel 60 (70–230 mesh, Merck). Prep. TLC: Kieselgel 60 F_{254} (2 mm × 20 × 20 cm, Merck). Lober CC: LiChroprep RP-18 and Si60 (each 40–63 μm, Merck). HPLC: Shim-pack CLC-ODS (15 cm × 6 mm, Shimadzu).

Extraction and isolation. Seeds (410 g) of *B. chinensis* Leman. *f. vulgaris* Makino cultivated at Utsunomiya University were collected in September 1987. The seed oil (65 g) obtained by extraction with *n*-hexane at room temp. was treated with MeOH several times to remove MeOH-insol. triglycerides. The MeOH-sol. materials (41 g) were fractionated by CC on silica gel deactivated by the addition of H_2O (30%) 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 *n*-hexane and *n*-hexane–C_6H_6 (20:1–5:1) contained belamcandaphenol (**2**) [8, 13, 15], while belamcandaquinone (**1**) [7, 13, 19] and its precursor (**3**) [8, 15] was obtained mainly from the frs eluted with *n*-hexane–C_6H_6 (5:1–2:1) and *n*-hexane–C_6H_6 (2:1–1:1), respectively. The frs eluted with *n*-hexane–benzene (1:1–1:3) were further separated by CC followed by prep. TLC on silica gel to concentrate enedions (401 mg), which showed 4 peaks on reversed-phase HPLC using MeOH; A: 38%, B: 42%, C: 17% and D: 3%. Repeated Lober CC on RP-18 using MeOH afforded belamcandones A (**4**) (141 mg), B (**5**) (162 mg), C (**6**) (58 mg) and D (**7**) (10 mg) as dull red semi-solids.

Belamcandone A (**4**). $[\alpha]_D^{20}$ 0° ($CHCl_3$; *c* 0.17). UV λ_{max}^{EtOH} nm (log ε): 271, 408, (4.03, 3.03). IR ν_{max}^{neat} cm^{-1}: 3550 (sh), 3450 (OH), 3070, 860, 820 (ring C–H), 1700, 1670 (>C=O), 1630, 1600 (C=C), 1240, 1080, 1040 (OMe). EI-MS *m/z* (rel. int.): 710 $[M + 2H]^+$ (25), 709 $[M + H]^+$ (49), 708 $[M]^+$ (100), 682 $[M + 2H - 28]^+$ (14), 681 $[M + H - 28]^+$ (30), 680 $[M - 28]^+$ (64), 637 $[M - 71]^+$ (13), 636 $[M - 72]^+$ (27), 624 $[M - 84]^+$ (10), 362 $[C_{22}H_{34}O_4]^+$ (1), 348 $[C_{22}H_{36}O_3]^+$ (3), 247 (18), 233 (9), 191 (7), 167 $[C_8H_7O_4]^+$ (5), 154 $[C_8H_{10}O_3]^+$ (4), 153 $[C_8H_9O_3]^+$ (8), 95 (15), 85 (6), 83 (17), 81 (17), 69 $[C_3HO_2]^+$ (39), 67 (23), 57 (18), 56 (19), 55 (85), 43 (33), 41 (42). ^1H and ^{13}C NMR: Tables 1 and 2.

Belamcandone B (**5**). $[\alpha]_D^{20}$ 0° ($CHCl_3$; *c* 0.21). UV λ_{max}^{EtOH} nm (log ε): 271, 408 (4.04, 3.01). IR ν_{max}^{neat} cm^{-1}: 3550 (sh), 3450 (OH), 3070, 860, 820 (ring C–H), 1700, 1670 (>C=O), 1630, 1600 (C=C), 1240, 1080, 1040 (OMe). EI-MS *m/z* (rel. int.): 738 $[M + 2H]^+$ (15), 737 $[M + H]^+$ (44), 736 $[M]^+$ (89), 710 $[M + 2H - 28]^+$ (26), 709 $[M + H - 28]^+$ (57), 708 $[M - 28]^+$ (75), 683 $[M - 53]^+$ (19), 682 $[M - 54]^+$ (41), 664 $[M - 72)]^+$ (8), 247 (16), 233 (10), 191 (11), 167 $[C_8H_7O_4]^+$ (7), 153 $[C_8H_9O_3]^+$ (14), 95 (17), 85 (10), 83 (24), 81 (20), 69 $[C_3HO_2]^+$ (51), 67 (28), 57 (34), 56 (26), 55 (100), 44 (30), 43 (59), 42 (19), 41 (55). ^1H and ^{13}C NMR: Tables 1 and 2.

Belamcandone C (**6**). $[\alpha]_D^{20}$ 0° ($CHCl_3$; *c* 0.13). UV λ_{max}^{EtOH} nm (log ε): 271, 408 (4.01, 3.04). IR ν_{max}^{neat} cm^{-1}: 3550 (sh), 3450 (OH), 3070, 860, 820 (ring C–H), 1700, 1670 (>C=O), 1630, 1600 (C=C), 1240, 1080, 1040 (OMe). EI-MS *m/z* (rel. int.): 740 $[M + 2H]^+$ (22), 739 $[M + H]^+$ (46), 738 $[M]^+$ (91), 712 $[M + 2H - 28]^+$ (18), 711 $[M + H - 28]^+$ (33), 710 $[M - 28]^+$ (69), 692 $[M - 46]^+$ (10), 666 $[M - 72]^+$ (17), 654 $[M - 84]^+$ (10), 247 (21), 233 (12), 191 (10), 167 $[C_8H_7O_4]^+$ (10), 154 $[C_8H_{10}O_3]^+$ (8), 153 $[C_8H_9O_3]^+$ (14), 95 (17), 85 (12), 83 (27), 81 (20),

69 $[C_3HO_2]^+$ (55), 67 (27), 57 (50), 56 (31), 55 (100), 44 (32), 43 (78), 42 (21), 41 (62). ^1H and ^{13}C NMR: Tables 1 and 2.

Belamcandone D (**7**). UV λ_{max}^{EtOH} nm (log ε): 271, 408 (4.04, 3.03). IR ν_{max}^{neat} cm^{-1}: 3550 (sh), 3450 (OH), 3070, 860, 820 (ring C–H), 1700, 1670 (>C=O), 1630, 1600 (C=C), 1240, 1080, 1040 (OMe). EI-MS *m/z* (rel. int.): 767 $[M + H]^+$ (23), 766 $[M]^+$ (44), 740, $[M + 2H - 28]^+$ (22), 739 $[M + H - 28]^+$ (22), 738 $[M - 28]^+$ (45), 712 $[M - 54]^+$ (15), 694 $[M - 72]^+$ (10), 682 $[M - 84]^+$ (10), 247 (13), 167 $[C_8H_7O_4]^+$ (6), 153 $[C_8H_9O_3]^+$ (11), 95 (18), 85 (13), 83 (29), 81 (23), 69 $[C_3HO_2]^+$ (49), 67 (30), 57 (54), 56 (30), 55 (86), 44 (38), 43 (100), 42 (28), 41 (79). ^1H and ^{13}C NMR: Tables 1 and 2.

Monoacetylation of belamcandone A (**4**). To a soln of **4** (70 mg) in pyridine (1 ml), Ac_2O (0.5 m) was added and the mixt. stirred at room temp. for 20 min. After decomposition of excess Ac_2O and usual work-up, a monoacetate **9** (67 mg) was obtained by Lober CC on RP-18 using MeOH.

Monoacetate **9**. Pale yellow solid, $[\alpha]_D^{20}$ 0° ($CHCl_3$; *c* 0.18). UV λ_{max}^{EtOH} nm (log ε): 275, 378 (4.01, 3.00). IR ν_{max}^{KBr} cm^{-1}: 3550 (sh), 3400 (OH), 3070, 855, 815 (ring C–H), 1765, 1195 (OAc), 1700, 1675 (>C=O), 1610, 1580 (C=C), 1240, 1080, 1040 (OMe). EI-MS *m/z* (rel. int.): 752 $[M + 2H]^+$ (2), 751 $[M + H]^+$ (6), 750 $[M]^+$ (11), 710 $[M + 3H - Ac]^+$ (17), 709 $[M + 2H - Ac]^+$ (50), 708 $[M + H - Ac]^+$ (100), 682 $[M + 3H - Ac - 28]^+$ (6), 681 $[M + 2H - Ac - 28]^+$ (18), 680 $[M + H - Ac - 28]^+$ (39), 362 $[C_{22}H_{34}O_4]^+$ (1), 348 $[C_{22}H_{36}O_3]^+$ (2), 167 $[C_8H_7O_4]^+$ (3), 154 $[C_8H_{10}O_3]^+$ (2), 153 $[C_8H_9O_3]^+$ (4), 95 (12), 83 (17), 81 (14), 69 $[C_3HO_2]^+$ (36), 67 (20), 57 (17), 56 (25), 55 (84), 43 (87), 42 (20), 41 (52). ^1H and ^{31}C NMR: Tables 1 and 2.

Acetylation of monoacetate **9**. Compound **9** (40 mg) was further acetylated with Ac_2O (0.8 ml) and pyridine (1 ml) at room temp. for 13 hr to afford two diacetates **10** and **11**. The ratio of **10** and **11** was *ca* 9:2 by ^1H NMR and HPLC analyses. Lober CC on RP-18 using MeOH gave **10** (26 mg) and **11** (5 mg).

Diacetate **10**. Pale yellow semi-solid, $[\alpha]_D^{20}$ 0° ($CHCl_3$; *c* 0.10). UV λ_{max}^{EtOH} nm (log ε): 270, 375 (3.96, 3.26). IR ν_{max}^{neat} cm^{-1}: 3070, 850, 820 (ring C–H), 1765, 1750, 1195 (OAc), 1715, 1680 (>C=O), 1610, 1585 (C=C), 1240, 1080, 1040 (OMe). EI-MS *m/z* (rel. int.): 794 $[M + 2H]^+$ (2), 793 $[M + H]^+$ (5), 792 $[M]^+$ (10), 752 $[M + 3H - Ac]^+$ (5), 751 $[M + 2H - Ac]^+$ (16), 750 $[M + H - Ac]^+$ (34), 710 $[M + 4H - 2Ac]^+$ (6), 709 $[M + 3H - 2Ac]^+$ (19), 708 $[M + 2H - 2Ac]^+$ (37), 680 $[M + 2H - 2Ac - 28]^+$ (10), 362 $[C_{22}H_{34}O_4]^+$ (3), 348 $[C_{22}H_{36}O_3]^+$ (1), 167 $[C_8H_7O_4]^+$ (3), 154 $[C_8H_{10}O_3]^+$ (2), 153 $[C_8H_9O_3]^+$ (3), 95 (9), 83 (13), 81 (11), 69 $[C_3HO_2]^+$ (29), 67 (14), 57 (13), 56 (18), 55 (59), 43 (100), 42 (18), 41 (38). ^1H and ^{13}C NMR: Tables 1 and 2.

Diacetate **11**. Pale yellow viscous oil. UV λ_{max}^{EtOH} nm (log ε): 275, 404 (4.01, 2.58). IR ν_{max}^{neat} cm^{-1}: 1765, 1735, 1195 (OAc), 1680, 1660 (sh) (>C=O), 1620, 1590 (C=C), 1245, 1090, 1030 (OMe), 845, 820 (ring C–H). EI-MS *m/z* (rel. int.): 794 $[M + 2H]^+$ (1), 793 $[M + H]^+$ (2), 792 $[M]^+$ (3), 752 $[M + 3H - Ac]^+$ (2), 751 $[M + 2H - Ac]^+$ (7), 750 $[M + H - Ac]^+$ (14), 710 $[M + 4H - 2Ac]^+$ (3), 709 $[M + 3H - 2Ac]^+$ (10), 708 $[M + 2H - 2Ac]^+$ (21), 680 $[M + 2H - 2Ac - 28]^+$ (9), 362 $[C_{22}H_{34}O_4]^+$ (1), 348 $[C_{22}H_{36}O_3]^+$ (3), 346 $[C_{22}H_{34}O_3]^+$ (10), 167 $[C_8H_7O_4]^+$ (2), 154 $[C_8H_{10}O_3]^+$ (2), 153 $[C_8H_9O_3]^+$ (3), 95 (8), 83 (12), 81 (10), 69 $[C_3HO_2]^+$ (29), 67 (14), 57 (13), 56 (16), 55 (60), 43 (100), 42 (16), 41 (39). ^1H and ^{13}C NMR: Tables 1 and 2.

Diacetylation of belamcandone A (**4**). A soln of **4** (11 mg) in pyridine (0.3 ml) was acetylated with Ac_2O (0.3 ml) at room temp. for 24 hr. Its progress was followed by observing product ratios with HPLC. Usual work-up gave two diacetates **10** and **11** (11 mg) in a ratio of *ca* 9:2.

Isomerization of diacetate **10**. Compound **10** (10 mg) was further treated with Ac_2O (0.3 ml) and pyridine (0.5 ml) at room temp. for 18 hr. Usual work-up and subsequent ^1H NMR analysis revealed a mixt. (10 mg) of **10** and **11** (*ca* 9:2).

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