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PHENOLS AND A DIOXOTETRAHYDRODIBENZOFURAN FROM SEEDS OF *IRIS PALLASII*

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Key Word Index—*Iris pallasii*; Iridaceae; seeds; phenols; dioxotetrahydrodibenzofuran; belamcandaphenol P; belamcandone P.

Abstract—Three new compounds, along with four known ones, have been isolated from the seeds of *Iris pallasii*. On the basis of spectroscopic methods and chemical evidence, the new compounds were shown to be 2-[(*Z*)-10-heptadecenyl]-4,6-dimethoxyphenol, 3,5-dimethoxy-[(*Z*)-10-heptadecenyl]benzene and 9,9b-di[(*Z*)-10-heptadecenyl]-4a,8-dihydroxy-2,7-dimethoxy-1,4-dioxo-1,4,4a,9b-tetrahydrodibenzofuran. The biogenetic relationships between these compounds are also discussed.

INTRODUCTION

In the course of studies on biologically active substances in species of the Iridaceae, we have recently reported on the structures of 1,4-dioxotetrahydrodibenzofurans, belamcandones A–D (**1**–**4**), obtained from the seeds of *Belamcanda chinensis* Leman. *f. vulgaris* Makino [1]. The unique skeleton of belamcandones was of interest from a biogenetic point of view and the search for their homologues in other Iridaceae was then carried out. *Iris pallasii* Fisch. var. *chinensis* Fisch. is a perennial herb which is native to China. Its seeds are called 'Barinshi' and have been used in folk medicine as an antidote and a haemostatic in China. As far as the authors are aware, there is no report on its phytochemical constituents except for irisquinone (**5**) [2, 3], dihydroirisquinone (**6**) [2, 4], and pallasone C (**7**) [4], although 'Barinshi', as well as irisquinone **5**, are used in cancer chemotherapy [5].

Further research on the chemical constituents of the above seed oil resulted in the isolation of a new homologue (**13**) of the belamcandones, together with two new compounds (**9** and **11**) and known ones (**8**, **10** and **12**) having the same side-chain. This paper describes the structural elucidation of the new compounds and their biogenetic pathway is also discussed.

RESULTS AND DISCUSSION

The *n*-hexane seed oil of *I. pallasii* was fractionated by column chromatography and preparative TLC on silica gel to obtain various fractions. Finally, recrystallization or Lober column chromatography on reverse-phase silica gel afforded **5** and **8**–**13**, of which the known compounds (**8**, **10** and **12**) were identified by direct comparision with authentic samples [6–8]. The ^{1}H and ^{13}C NMR data of **5**, **8**–**13** and their related compounds are summarized in Tables 1–4.

Compound **8** was 3-hydroxyirisquinone [6], i.e. 3-[(*Z*)-10-heptadecenyl]-2-hydroxy-5-methoxy-*p*-benzo-quinone. It was isolated as orange yellow needles of mp 67–67.5° and assumed a violet colour on silica gel. Its NMR spectra (Tables 1 and 2) revealed the presence of a quinoic proton (δ5.84, *s*) showing a strong NOE with methoxyl protons (δ3.86, *s*) and a (*Z*)-10-heptadecenyl group which was the same side-chain as that of **5**.

Compound **9**, $C_{25}H_{42}O_3$ ($[M]^+$ m/z 390), exhibited UV and IR absorption bands characteristic of a polysubstituted phenol, viz., λ_{max}^{EtOH} 288 nm (log ε 3.63); ν_{max}^{neat} 3550 (sharp), 3450 (sh) (OH), 1610, 1500 (aromatic C=C), 825 cm^{-1} (ring C–H). Its ^{13}C NMR spectrum showed a typical signal pattern for a *cis*-ω-7 monoenyl group [9], so that **9** must have the same side-chain as **5** and **8**. The ^{1}H NMR spectrum revealed two *meta*-coupled aromatic protons [δ6.28, 6.35 (each 1H, *d*, $J = 3$ Hz)], two methoxyl groups [δ3.76, 3.85 (each 3H, *s*)] and a hydroxyl proton [δ5.25 (1H, *s*)]. The sharp signal at δ5.25 and sharp band at 3550 cm^{-1} suggested that this hydroxyl proton formed an intramolecular hydrogen bond to an adjacent methoxyl oxygen. In the NOESY spectrum of **9**, one (δ6.35) of the ring protons exhibited NOE correlations with two methoxyl groups, while the other (δ6.28) showed NOEs not only with the methoxyl group at δ3.76 but also with an α-methylene group at δ2.60. Thus, **9** is 2-[(*Z*)-10-heptadecenyl]-4,6-dimethoxyphenol, named belamcandaphenol P, corresponding to a homologue of

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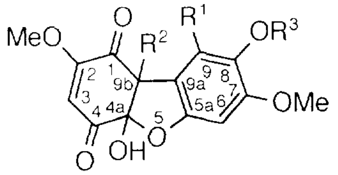


1: $R^1=R^2= -(CH_2)_9CH\overset{cis}{=}CH(CH_2)_3Me$; $R^3= -H$

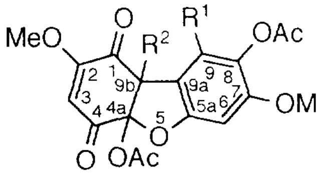
2: R^1, $R^2= -(CH_2)_9CH\overset{cis}{=}CH(CH_2)_3Me$, $-(CH_2)_{11}CH\overset{cis}{=}CH(CH_2)_3Me$; $R^3= -H$

3: R^1, $R^2= -(CH_2)_9CH\overset{cis}{=}CH(CH_2)_3Me$, $-(CH_2)_{16}Me$; $R^3= -H$

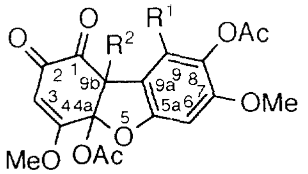
4: R^1, $R^2= -(CH_2)_{11}CH\overset{cis}{=}CH(CH_2)_3Me$, $-(CH_2)_{16}Me$; $R^3= -H$

13: $R^1=R^2= -(CH_2)_9CH\overset{cis}{=}CH(CH_2)_5Me$; $R^3= -H$

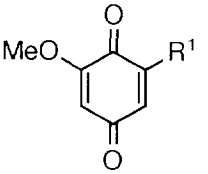
19: $R^1=R^2= -(CH_2)_9CH\overset{cis}{=}CH(CH_2)_5Me$; $R^3= -Ac$



20: $R^1=R^2= -(CH_2)_9CH\overset{cis}{=}CH(CH_2)_5Me$

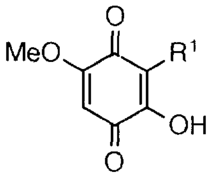


21: $R^1=R^2= -(CH_2)_9CH\overset{cis}{=}CH(CH_2)_5Me$



5: $R^1= -(CH_2)_9CH\overset{cis}{=}CH(CH_2)_5Me$

6: $R^1= -(CH_2)_{16}Me$



7: $R^1= -(CH_2)_9CH\overset{cis}{=}CH(CH_2)_7Me$

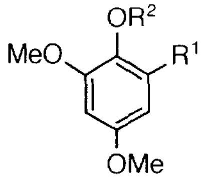
8: $R^1= -(CH_2)_9CH\overset{cis}{=}CH(CH_2)_5Me$

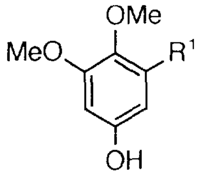
belamcandaphenol (**14**) obtained from species of *Belamcanda* [10, 11] and *I. tectorum* [12], and **15** found in the green alga, *Botryococcus braunii* [13].

The nature of the side-chain was further confirmed by the following chemical evidence. Methylation of **9** with dimethyl sulphate afforded a methyl ether **16** which was identical with the quinol dimethyl ether of irisquinone (**5**) [2]. Furthermore, ozonolysis of **16** gave 2,3,5-trimethoxyphenyldecanal (**17**).

Compound **10** having the same formula as **9** was irisphenol [7], i.e. 3-[(*Z*)-10-heptadecenyl]-4,5-dimethoxyphenol. The ^{1}H NMR spectrum revealed that **10** had the same substituents as **9** and two ring protons also occupied *meta*-positions to each other. However, its hydroxyl proton formed an intermolecular hydrogen bond in contrast to that of **9**.

Compound **11** showed a $[M]^+$ at m/z 374, corresponding to the formula $C_{25}H_{42}O_2$. Its UV and IR spectra were characteristic of a 1,3,5-trisubstituted benzene, viz., λ_{max}^{EtOH} 274, 280 nm (log ε 3.31, 3.31); ν_{max}^{neat} 1605, 1595 (aromatic C=C), 830, 690 cm^{-1} (ring C–H). In addition, the ^{1}H NMR spectrum exhibited the presence of two equivalent methoxyl groups [δ3.78 (6H, *s*)], three aromatic protons [δ6.29 (1H, *t*, $J = 2$ Hz), 6.34 (2H, *d*, $J = 2$ Hz)]





9: $R^1 = -(CH_2)_9CH\overset{cis}{=}CH(CH_2)_5Me$; $R^2 = -H$

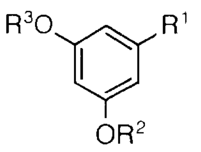
10: $R^1 = -(CH_2)_9CH\overset{cis}{=}CH(CH_2)_5Me$

14: $R^1 = -(CH_2)_9CH\overset{cis}{=}CH(CH_2)_3Me$; $R^2 = -H$

15: $R^1 = -(CH_2)_nCH\overset{cis}{=}CH(CH_2)_7Me$ (n=15, 17 and 19); $R^2 = -H$

16: $R^1 = -(CH_2)_9CH\overset{cis}{=}CH(CH_2)_5Me$; $R^2 = -Me$

17: $R^1 = -(CH_2)_9CHO$; $R^2 = -Me$



11: $R^1 = -(CH_2)_9CH\overset{cis}{=}CH(CH_2)_5Me$; $R^2 = R^3 = -Me$

12: $R^1 = -(CH_2)_9CH\overset{cis}{=}CH(CH_2)_5Me$; $R^2 = -H$, $R^3 = -Me$

18: $R^1 = -(CH_2)_9CH\overset{cis}{=}CH(CH_2)_5Me$; $R^2 = R^3 = -H$

Table 1. ^1H NMR data of **5** and related compounds (300 MHz, $CDCl_3$ with TMS as internal standard)

H	**5**	**8***	**9**†	**16**†	**17**†	**10**†	**11**†	**12**†
2			6.35 *d* (3)	6.35 *d* (3)	6.35 *d* (3)	6.29 *d* (3)	6.29 *t* (2)	6.23 *dd* (2, 2)
3	6.48 *td* (2, 2)							
4							6.34 *d* (2)	6.26 *dd* (2, 2)
5	5.88 *d* (2)	5.84 *s*						
6			6.28 *d* (3)	3.28 *d* (3)	6.28 *d* (3)	6.21 *d* (3)	6.34 *d* (2)	6.33 *dd* (2, 2)
HO–1						4.86 *br* s		4.71 *s*
HO–3		7.24 *s*						
HO–4			5.25 *s*					
MeO-1			3.76 *s*	3.77 *s*	3.77 *s*		3.78 *s*	
MeO-3			3.85 *s*	3.83 *s*	3.83 *s*	3.80 *s*	3.78 *s*	3.77 *s*
MeO-4				3.75 *s*	3.75 *s*	3.74 *s*		
MeO-6	3.82 *s*	3.86 *s*						
1′	2.43 *td* (7, 2)	2.44 *t* (8)	2.60 *t* (8)	2.59 *t* (8)	2.59 *t* (8)	2.55 *t* (8)	2.54 *t* (7)	2.51 *t* (8)
2′	1.50 *qui* (7)	1.45 *qui* (8)	1.60 *qui* (8)	1.58 *qui* (8)	1.58 *qui* (8)	1.55 *qui* (8)	1.60 *qui* (7)	1.58 *qui* (8)
3′–7′	1.28 *br s*	1.27 *br s*	1.28 *br s*	1.28 *br s*	1.30 *br s*	1.28 *br s*	1.28 *br s*	1.28 *br s*
8′	1.28 *br s*	1.27 *br s*	1.28 *br s*	1.28 *br s*	1.62 *qui* (7)	1.28 *br s*	1.28 *br s*	1.28 *br s*
9′	2.01 *qu* (6)	2.01 *qu* (6)	2.01 *qu* (6)	2.01 *qu* (6)	2.41 *td* (7, 2)	2.01 *qu* (6)	2.01 *qu* (6)	2.01 *qu* (6)
10′	5.35 *m*	5.35 *m*	5.35 *m*	5.35 *m*	9.76 *t* (2)	5.35 *m*	5.35 *m*	5.35 *m*
11′	5.35 *m*	5.35 *m*	5.35 *m*	5.35 *m*		5.35 *m*	5.35 *m*	5.35 *m*
12′	2.01 *qu* (6)	2.01 *qu* (6)	2.01 *qu* (6)	2.01 *qu* (6)		2.01 *qu* (6)	2.01 *qu* (6)	2.01 *qu* (6)
13′–16′	1.28 *br s*	1.27 *br s*	1.28 *br s*	1.28 *br s*		1.28 *br s*	1.28 *br s*	1.28 *br s*
17′	0.88 *t* (7)	0.88 *t* (6)	0.88 *t* (7)	0.88 *t* (7)		0.88 *t* (6)	0.88 *t* (7)	0.88 *t* (7)

*·†Carbon skeletons of **8** and phenols are numbered as derivatives of **5** and 5-alkenylresorcinol, respectively. Coupling constants (*J* in Hz) are given in parentheses.

Assignments based on ^1H–^1H COSY and ^1H–^{13}C COSY experiments.

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

C	**5**	**8***	**9†**	**16†**	**17†**	**10†**	**11†**	**12†**
1	182.1	182.8	152.7	155.8	155.8	151.8	160.7	156.4
2	147.6	119.3	96.6	97.7	97.7	98.1	97.5	98.6
3	132.9	151.5	146.7	153.3	153.3	153.3	160.7	160.8
4	187.7	181.7	137.5	141.1	141.1	140.8	106.5	106.8
5	107.1	102.2	128.7	136.9	136.8	137.2	145.4	145.8
6	158.8	161.1	105.7	105.0	105.0	107.3	106.5	107.8
MeO-1			55.7	55.5	55.5		55.2	
MeO-3			56.0	55.7	55.7	55.7	55.2	55.2
MeO-4				60.8	60.8	60.8		
MeO-6	56.3	56.8						
1′	28.7	22.6	30.0	30.1	30.1	29.8	36.3	36.0
2′	27.7	28.0	29.9	30.9	30.8	30.7	31.3	31.2
3′	29.2	29.4	29.6	29.6	29.6	29.5	29.4	29.5
4′	29.3	29.5	29.6	29.6	29.4	29.6	29.5	29.6
5′	29.5	29.5	29.6	29.6	29.3	29.6	29.6	29.6
6′	29.5	29.6	29.6	29.7	29.3	29.6	29.6	29.6
7′	29.3	29.3	29.3	29.3	29.1	29.3	29.3	29.3
8′	29.7	29.8	29.8	29.8	22.1	29.8	29.8	29.8
9′	27.2	27.2	27.2	27.2	43.9	27.2	27.2	27.2
10′	129.8	129.9	129.9	129.9	202.9	129.9	129.9	129.9
11′	129.9	129.9	129.9	129.9		129.9	129.9	129.9
12′	27.2	27.2	27.2	27.2		27.2	27.2	27.2
13′	29.7	29.8	29.8	29.8		29.8	29.8	29.8
14′	29.0	29.0	29.0	29.0		29.0	29.0	29.0
15′	31.8	31.8	31.8	31.8		31.8	31.8	31.8
16′	22.7	22.7	22.7	22.7		22.7	22.7	22.7
17′	14.1	14.1	14.1	14.1		14.1	14.1	14.1

*†Carbon skeletons of **8** and phenols are numbered as derivatives of **5** and 5-alkenylresorcinol, respectively.

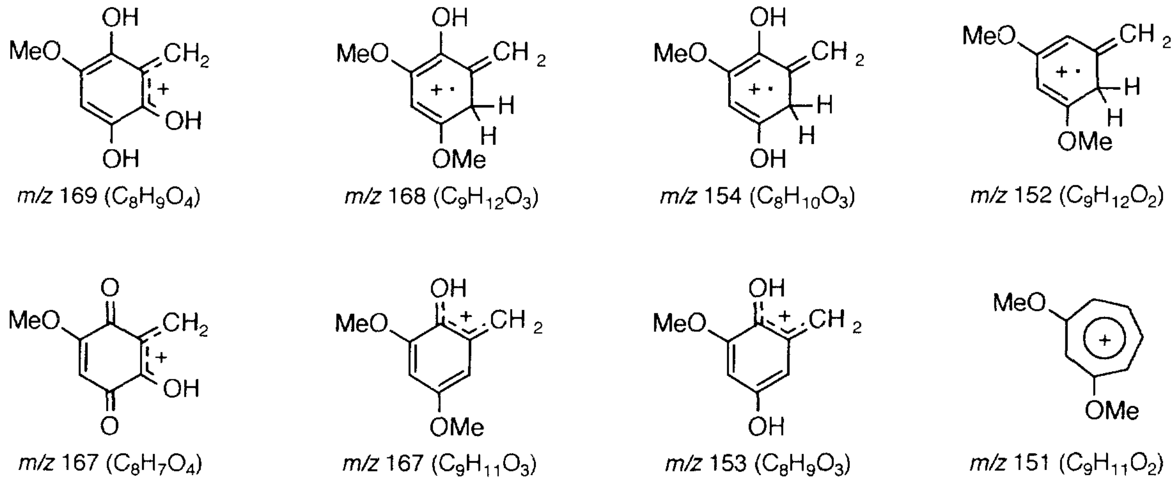
Assignments based on DEPT, ^{1}H–^{13} COSY, and ^{1}H–^{13}C long-range COSY experiments.

on positions *meta* to each other and the same side-chain as those of **5**–**10**. Therefore, **11** is 3,5-dimethoxy-[(*Z*)-10-heptadecenyl]benzene, i.e. the dimethyl derivative of irisresorcinol (**18**) [14] isolated from the seeds of *I. pseudacorus*.

Compound **12** was 3-[(*Z*)]-10-heptadecenyl]-5-methoxyphenol [8]. Its NMR spectra were similar to those of **11**, but in **12** one of the methoxyl groups present in **11** was replaced by a hydroxyl group. Methylation of **12** gave **11**, which also supported the structure of **11**.

The structures for **8**–**12** were also supported by their mass spectra (Fig. 1) and 2D NMR experiments.

Compound **13** has the molecular formula $C_{48}H_{76}O_7$ ($[M]^+$ *m/z* 764) and showed UV absorption maxima



m/z 169 ($C_8H_9O_4$) *m/z* 168 ($C_9H_{12}O_3$) *m/z* 154 ($C_8H_{10}O_3$) *m/z* 152 ($C_9H_{12}O_2$)

m/z 167 ($C_8H_7O_4$) *m/z* 167 ($C_9H_{11}O_3$) *m/z* 153 ($C_8H_9O_3$) *m/z* 151 ($C_9H_{11}O_2$)

Fig. 1. Representative peaks in the mass spectra of compounds **5**, **8**–**11** and **13**.

Table 3. ^1H NMR data of **13** and related compounds (300 MHz, $CDCl_3$ with TMS as internal standard)

H	**1**	**13**	**19**	**20**	**21**
3	6.18 *s*	6.17 *s*	6.18 *s*	5.99 *s*	5.85 *s*
MeO-2	3.82 *s*	3.82 *s*	3.83 *s*	3.77 *s*	
MeO-4					3.82 *s*
HO-4a	5.16 *s*	5.16 *s*	5.21 *s*		
AcO-4a				2.21 *s*	2.22 *s*
1″	2.23 *ddd*	2.23 *ddd*	2.22 *ddd*	1.53 *m*	1.55 *m*
	(13, 12, 5);	(13, 12, 4);	(13, 12, 4);		
	2.57 *ddd*	2.57 *ddd*	2.56 *m*	2.42 *ddd*	2.30 *m*
	(13, 11, 5)	(13, 12, 5)		(15, 13, 5)	
2″	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*	1.27–1.30 *br*	1.27–1.30 *br*	1.20–1.28 *br*	1.20–1.28 *br*
9″	2.02 *br*	2.01 *br*	2.01 *br*	2.01 *br*	2.01 *br*
10″, 11″	5.35 *m*	5.35 *m*	5.35 *m*	5.35 *m*	5.35 *m*
12″	2.02 *br*	2.01 *br*	2.01 *br*	2.01 *br*	2.01 *br*
13″, 14″	1.22–1.30 *br*	1.27–1.30 *br*	1.27–1.30 *br*	1.20–1.28 *br*	1.20–1.28 *br*
15″	0.90 *m*	1.27–1.30 *br*	1.27–1.30 *br*	1.20–1.28 *br*	1.20–1.28 *br*
16″		1.27–1.30 *br*	1.27–1.30 *br*	1.20–1.28 *br*	1.20–1.28 *br*
17″		0.88 *t* (6)	0.88 *t* (7)	0.88 *t* (7)	0.88 *t* (7)
6	6.29 *s*	6.28 *s*	6.34 *s*	6.45 *s*	6.45 *s*
MeO-7	3.81 *s*	3.81 *s*	3.74 *s*	3.77 *s*	3.79 *s*
HO-8	5.33 *s*	5.33 *s*			
AcO-8			2.29 *s*	2.28 *s*	2.26 *s*
1′	2.76 *ddd*	2.76 *ddd*	2.52 *m*	2.22 *m*	2.22 *m*
	(13, 11, 5);	(13, 12, 5);			
	3.06 *ddd*	3.06 *ddd*	3.05 *m*		
	(13, 11, 4)	(13, 12, ,3)			
2′	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*	1.27–1.30 *br*	1.27–1.30 *br*	1.20–1.28 *br*	1.20–1.28 *br*
9′	2.02 *br*	2.01 *br*	2.01 *br*	2.01 *br*	2.01 *br*
10′, 11′	5.35 *m*	5.35 *m*	5.35 *m*	5.35 *m*	5.35 *m*
12′	2.02 *br*	2.01 *br*	2.01 *br*	2.01 *br*	2.01 *br*
13′, 14′	1.22–1.30 *br*	1.27–1.30 *br*	1.27–1.30 *br*	1.20–1.28 *br*	1.20–1.28 *br*
15′	0.90 *m*	1.27–1.30 *br*	1.27–1.30 *br*	1.20–1.28 *br*	1.20–1.28 *br*
16′		1.27–1.30 *br*	1.27–1.30 *br*	1.20–1.28 *br*	1.20–1.28 *br*
17′		0.88 *t* (6)	0.88 *t* (7)	0.88 *t* (7)	0.88 *t* (7)

Coupling constants (*J* in Hz) are given in parentheses.
Assignments based on ^1H–^1H COSY and ^1H–^{13}C COSY experiments.

λ_{max}^{EtOH} 271, 408 nm (log ε 4.04, 3.03). It had IR bands for conjugated carbonyls (1700, 1670 cm^{-1}) and C=C bonds (1630, 1605 cm^{-1}) characteristic of an enedione. The ^1H NMR spectrum (Table 3) revealed the presence of two methoxyl groups [δ3.81, 3.82 (each 3H, *s*)], two ring protons [δ6.17, 6.28 (each 1H, *s*)], two hydroxyl protons [δ5.16, 5.33 (each 1H, *s*)] and two unsaturated side-chains [δ5.35 (4H, *m*)]. The UV, IR and ^1H NMR spectra showed a striking resemblance to those of belamcandone A (**1**) [1]. Hence, **13**, named belamcandone P, was a homologue of belamcandone A and differed only in the chain length of two alkenyl groups. In addition, carbon signals (Table 4) for two side-chains in **13** were characteristic of (*Z*)-10-heptadecenyl groups by analogy with all the above compounds (**5**, **8**–**12**).

Therefore, the structure of belamcandone P (**13**) can be represented as shown in the formula and its relative stereochemistry was then determined by NOE experiments (Fig. 2). In addition, the specific rotation of **13** was zero, so that **13** must also be a racemate of (4a*R*, 9b *S*) and

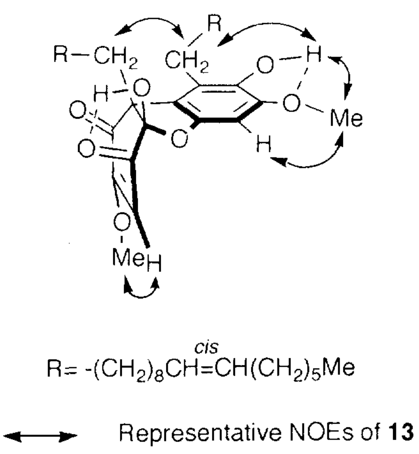


Fig. 2. Relative stereochemistry of **13**.

Table 4. ^{13}C NMR data of **13** and related compounds (75 MHz, $CDCl_3$ with TMS as internal standard)

C	**1**	**13**	**19**	**20**	**21**
1	190.7	190.7	190.4	189.5	191.8
2	165.7	165.7	165.6	164.6	182.9
3	108.3	108.4	108.4	109.1	105.5
4	190.1	190.1	189.6	186.9	168.6
4a	102.5	102.6	102.9	109.3	111.2
9b	65.2	65.2	64.8	64.6	64.5
MeO-2	56.9	56.9	57.0	56.7	
MeO-4					57.2
$Me\underline{C}O_2$-4a				170.0	168.7
$\underline{Me}CO_2$-4a				20.3	20.4
1″	32.8	32.8	33.0	30.4	30.2
2″	25.8	25.8	25.8	23.7	23.4
3″	30.2	30.1	30.3	29.9	29.6
4″	29.1	29.1	29.1	29.3	29.2
5″	29.5	29.5	29.5	29.5	29.5
6″	29.5	29.6	29.5	29.5	29.5
7″	29.3	29.3	29.3	29.3	29.3
8″	29.8	29.8	29.8	29.8	29.8
9″	27.2	27.2	27.2	27.2	27.2
10″	129.9	129.9	129.9	129.8	129.9
11″	129.9	129.9	129.9	129.9	129.9
12″	26.9	27.2	27.2	27.2	27.2
13″	32.0	29.8	29.7	29.8	29.8
14″	22.4	29.0	29.0	29.0	29.0
15″	14.0	31.8	31.9	31.9	31.8
16″		22.7	22.7	22.7	22.7
17″		14.1	14.1	14.1	14.1
5a	149.8	149.8	155.1	153.9	153.1
6	92.2	92.2	93.4	93.3	93.4
7	147.4	147.4	152.7	153.0	153.3
8	139.8	139.8	134.3	133.9	134.1
9	128.1	128.1	135.5	134.5	134.8
9a	115.4	115.5	115.3	114.8	113.5
MeO-7	56.1	56.1	56.0	56.1	56.1
$Me\underline{C}O_2$-8			169.0	168.8	168.7
$\underline{Me}CO_2$-8			20.5	20.5	20.4
1′	26.3	26.3	26.8	25.8	25.8
2′	30.3	30.3	30.6	30.0	30.0
3′	30.2	30.1	30.1	30.0	30.0
4′	29.5	29.5	29.4	29.4	29.4
5′	29.6	29.6	29.6	29.6	29.6
6′	29.7	29.7	29.6	29.6	29.6
7′	29.3	29.3	29.3	29.3	29.3
8′	29.8	29.8	29.8	29.8	29.8
9′	27.2	27.2	27.2	27.2	27.2
10′	129.8	129.9	129.9	129.8	129.8
11′	129.9	129.9	129.9	129.9	129.9
12′	26.9	27.2	27.2	27.2	27.2
13′	32.0	29.8	29.8	29.8	29.8
14′	22.4	29.0	29.0	29.0	29.0
15′	14.0	31.8	31.8	31.8	31.8
16′		22.7	22.7	22.7	22.7
17′		14.1	14.1	14.1	14.1

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

A few signals may be interchangeable within the same column.

4a*S*,9b*R* in Fig. 2) by analogy with belamcandones A–D [1]. This structure was also supported by the mass spectrum and chemical evidence. Its mass spectrum showed two significant peaks at *m*/*z* 390 ($C_{24}H_{38}O_4$) and 376 ($C_{24}H_{40}O_3$) corresponding to **8** and the quinol of **5** respectively. Cleavage β to the quinone ring in the former afforded *m*/*z* 167 ($C_8H_7O_4$), while the latter gave *m*/*z* 153 ($C_8H_9O_3$) accompanied by McLafferty rearrangement and subsequent loss of a proton (Fig. 1). Acetylation of **13** first afforded a monoacetate **19** [pale yellow solid, $C_{50}H_{78}O_8$ ($[M]^+$ *m*/*z* 806)], which on further acetylation gave two diacetates **20** and **21** (*ca* 9:2) according to the mechanism described in the previous paper [1].

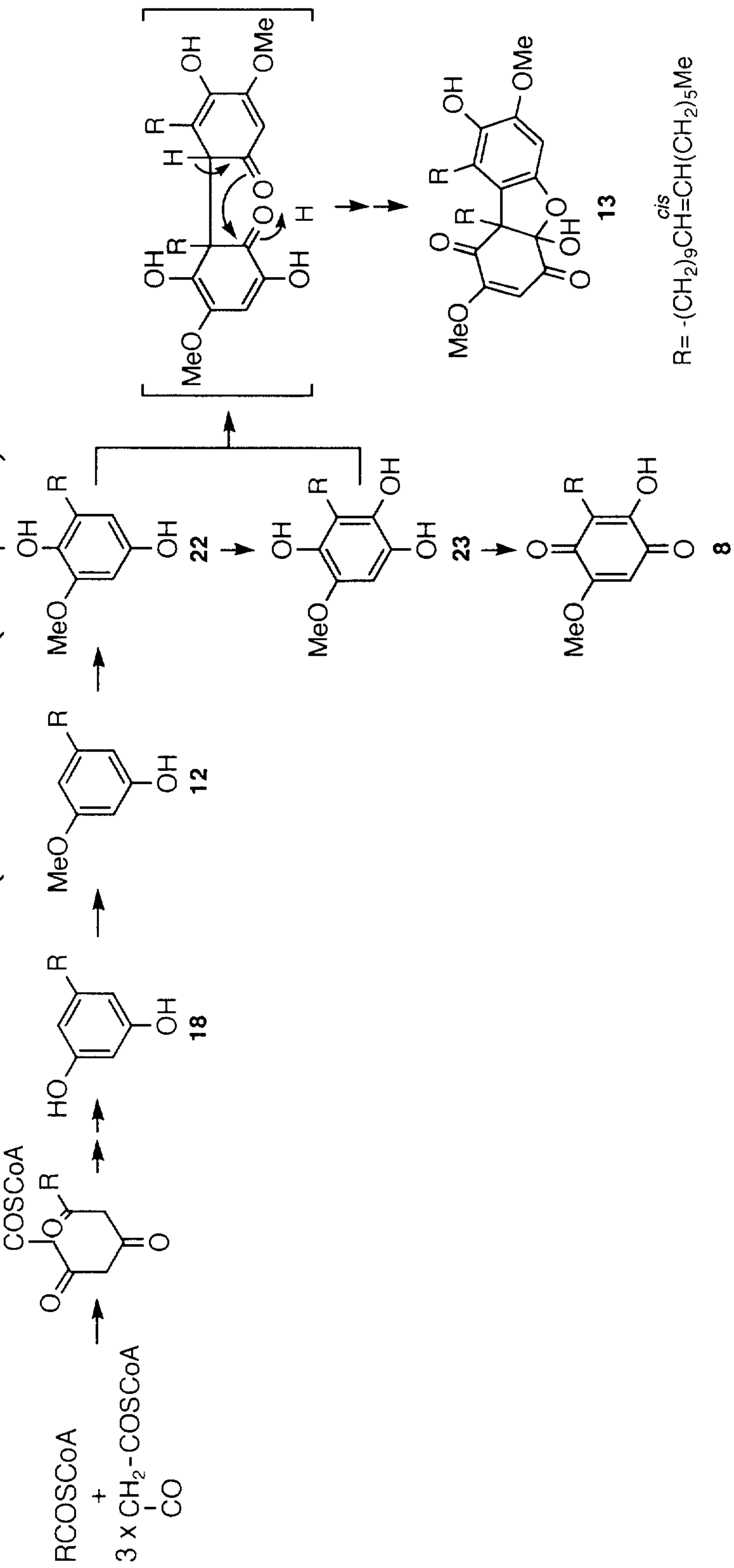
Dibenzofuran derivatives usually have UV absorption maxima at 250 and 280 nm of almost equal intensity and bathochromic displacement of these bands occurs in the hydroxy derivatives [15]. However, belamcandone P (**13**), although changing to a pale yellow colour on acetylation, assumed a dull red colour. This extremely bathochromic shift could be explained by considering internal charge transfer from the aromatic ring as an electron donor to the enedione ring as an electron acceptor, because both rings appear to be close enough to each other (Fig. 2).

Thus, all the side-chains of **8**–**13** isolated newly from *I. pallasii* were (*Z*)-10-heptadecenyl group and no homologue **7** [4] with a (*Z*)-10-nonadecenyl side-chain was detected; **9**, **11** and **13** are new compounds, although **8** [6], **10** [7] and **12** [8] have already been isolated from seeds of *I. pseudacorus*.

From a biogenetic point of view, belamcandone P (**13**) must be closely related to the other compounds (**5**, **8**–**12**) and all the compounds are considered to be biosynthesized by a polyketide pathway (Scheme 1). That is, irisresorcinol **18** [14] is first derived from (*Z*)-10-octadecenoate and three units of malonyl-SCoA and subsequent methylation proceeds to afford a biosynthetic key intermediate **12** in species of the Iridaceae, together with **11**. Belamcandaphenol P (**9**) and irisphenol **10** are biosynthesized via **22**, while oxidation of **22** and **23** yields mainly irisquinone (**5**) and 3-hydroxyirisquinone (**8**), respectively. Oxidative coupling of **22** with **23** (or **8**) and subsequent cyclization must partly occur to afford **13**. Although **23** seems to be too labile to exist, its homologue, sorgolenone having a (8*Z*,11*Z*,14)-8,11,14-pentadecatrienyl side-chain, has already been isolated as a germinative stimulator of its parasitic plant from the roots of sorgo [16].

It is noteworthy from the viewpoint of chemotaxonomy that the phenols **9** and **10** coexist in the same seed oil and have the same side-chain, (*Z*)-10-heptadecenyl group. The former type of phenol in the Iridaceae has been isolated from only two species [10, 11] of *Belamcanda*, except for *I. tectorum* [12], but its side-chain was a (*Z*)-10-pentadecenyl group. On the other hand, the latter-type phenols were found only in species of *Iris* and **10** was the main component of the phenols [7, 8].

I. pallasii is the first example including both types of phenol **9** and **10**. In addition, one of the belamcandones and many related compounds have been found in the same seed oil. It is interesting to note that the presence of



Scheme 1. Possible pathway for biosynthesis of **13** and related compounds.

belamcandones is limited to species [1] of *Belamcanda* and *I. pallasii*, although the reason is still uncertain.

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: Kieselgel 60 (70–230 mesh, Merck). Prep. TLC: Kieselgel 60 F_{254} (2 mm × 20 cm × 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 (450 g) of *I. pallasii* collected at Fujun, China in October 1982 were milled and extracted with *n*-hexane at room temp. The seed oil (23.6 g) was fractionated by CC on silica gel deactivated by the addition of H_2O (40%) using *n*-hexane, *n*-hexane–C_6H_6, C_6H_6, C_6H_6–Et_2O and Et_2O as eluents, successively. Saponification of the frs eluted with *n*-hexane and *n*-hexane–C_6H_6 (20:1–5:1) gave crude **11** and **9**, which were further purified by Lober CC on silica gel and RP-18 to afford **11** (7 mg) and **9** (28 mg). Frs from *n*-hexane-C_6H_6 (2:1–1:1) were treated with MeOH to remove insol. glycerides and the MeOH-sol. part was then recrystallized from MeOH, followed by *n*-hexane, to afford **5** (1.76 g) as pale yellow fine needles. The next frs (*n*-hexane–C_6H_6, 1:1), on repeated recrystallization from *n*-hexane gave **8** (832 mg). The frs eluted with *n*-hexane–C_6H_6 (1:1–1:2), containing **12**, **10** and **13** together with a small quantity of **8**, were further sepd by CC and subsequent prep. TLC on silica gel to give enediones and phenols. Finally, Lober CC on RP-18 using MeOH afforded **10** (25 mg), **12** (7 mg) and **13** (88 mg), respectively.

Irisquinone (**5**). Pale yellow fine needles, mp 42.5–43°. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 268, 364 (4.18, 2.98). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1675, 1650 (quinoic C=O), 1625, 1595 (quinoic C=C), 1230, 1065 (OMe), 3070, 900 (ring C–H). EIMS *m/z* (rel. int.): 376 $[M + 2H]^+$ (12), 375 $[M + H]^+$ (27), 374 $[M]^+$ (100), 154 $[C_8H_{10}O_3]^+$ (96), 153 $[C_8H_9O_3]^+$ (98), 152 $[C_8H_8O_3]^+$ (10), 95 (18), 81 (25), 69 $[O{\equiv}C{-}CH{=}C{=}O]^+$ (34), 67 (31), 55 (57), 53 (14), 43 (42), 41 (61). ^{1}H and ^{13}C NMR: Tables 1 and 2.

3-Hydroxyirisquinone (**8**). Orange yellow needles, mp 67–67.5°. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 288, 420 (4.32, 2.74). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3350 (sharp) (OH), 1660, 1635 (quinoic C=O), 1595 (quinoic C=C), 1205, 1065 (OMe), 840 (ring C–H). EIMS *m/z* (rel. int.): 392 $[M + 2H]^+$ (10), 391 $[M + H]^+$ (27), 390 $[M]^+$ (100), 169 $[C_8H_9O_4]^+$ (59), 168 $[C_8H_8O_4]^+$ (74), 167 $[C_8H_7O_4]^+$ (23), 153 (13), 139 (22), 69 $[O{\equiv}C{-}CH{=}C{=}O]^+$ (18), 67 (12), 55 (31), 43 (24), 41 (29). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Belamcandaphenol P (**9**). Oil. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 288 (3.63). IR $\nu_{\max}^{\mathrm{neat}}$ cm^{-1}: 3550 (sharp), 3450 (sh) (OH), 1610, 1500 (aromatic C=C), 1225, 1055 (OMe), 825 (ring C–H). EIMS *m/z* (rel. int.): 391 $[M + 1]^+$ (25), 390 $[M]^+$ (100), 168 $[C_9H_{12}O_3]^+$ (65), 167 $[C_9H_{11}O_3]^+$ (48), 154 $[C_8H_{10}O_3]^+$ (5), 153 $[C_8H_9O_3]^+$ (17), 139 $[C_7H_7O_3]^+$ (20), 69 (10), 67 (9), 55 (39), 43 (17), 41 (43). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Methylation of belamcandaphenol P (**9**). Me_2SO_4 (0.5 ml) was added dropwise to a refluxed mixt. of **9** (25 mg) and K_2CO_3 (1.5 g) in Me_2CO (5 ml). After refluxing for 3 hr, usual work-up and subsequent Lober CC on RP-18 using MeOH afforded **16** (23 mg), which was identified as 2,3,5-trimethoxy[(*Z*)-10-heptadecenyl]benzene by comparison of spectral data with those of an authentic sample derived from irisquinone (**5**) [2] in *I. pseudacorus.*

Compound **16**. Oil. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 283 (3.44). IR $\nu_{\max}^{\mathrm{neat}}$ cm^{-1}: 1600, 1490 (aromatic C=C), 1225, 1200, 1060 (OMe), 830 (ring C–H). EIMS *m/z* (rel. int.): 405 $[M + 1]^+$ (31), 404 $[M]^+$ (100), 182 $[C_{10}H_{14}O_3]^+$ (11), 181 $[C_{10}H_{13}O_3]^+$ (8), 168 $[C_9H_{12}O_3]^+$ (5), 167 $[C_9H_{11}O_3]^+$ (29), 166 $[C_9H_{10}O_3]^+$ (10), 153 $[C_8H_9O_3]^+$ (4), 152 $[C_8H_8O_3]^+$ (13), 139 $[C_7H_7O_3]^+$ (5), 69 (4), 55 (7), 43 (7), 41 (4). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Ozonolysis of **16**. Oxygen containing O_3 was bubbled through a soln of **16** (20 mg) in EtOAc (5 ml) at −50° for 1 hr. Me_2S (0.5 ml) was then added and the mixt. allowed to stand at room temp. for 1 hr. After evapn of solvent, the residue was purified by Lober CC on RP-18 using MeOH to afford **17** (6 mg), which was identified as 2,3,5-trimethoxyphenyldecanal.

Compound **17**. Oil. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 283 (3.42). IR $\nu_{\max}^{\mathrm{neat}}$ cm^{-1}: 2720, 1725 (CHO), 1600, 1490 (aromatic C=C), 1225, 1200, 1060 (OMe), 830 (aromatic C–H). EIMS *m/z* (rel. int.): 323 $[M + 1]^+$ (21), 322 $[M]^+$ (100), 182 $[C_{10}H_{14}O_3]^+$ (14), 181 $[C_{10}H_{13}O_3]^+$ (7), 168 $[C_9H_{12}O_3]^+$ (10), 167 $[C_9H_{11}O_3]^+$ (58), 166 $[C_9H_{10}O_3]^+$ (19), 153 $[C_8H_9O_3]^+$ (6), 139 $[C_7H_7O_3]^+$ (10), 55 (8), 44 (20), 43 (7), 41 (10). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Irisphenol **10**. Viscous oil. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 283 (3.39), $\lambda_{\max}^{\mathrm{EtOH+KOH}}$ nm (log ε): 294 (3.49). IR $\nu_{\max}^{\mathrm{neat}}$ cm^{-1}: 3400 (br) (OH), 1610, 1595, 1495 (aromatic C=C), 1225, 1010 (O Me), 835 (ring C–H). EIMS *m/z* (rel. int.): 391 $[M + 1]^+$ (27), 390 $[M]^+$ (100), 168 $[C_9H_{12}O_3]^+$ (21), 167 $[C_9H_{11}O_3]^+$ (19), 154 $[C_8H_{10}O_3]^+$ (7), 153 $[C_8H_9O_3]^+$ (45), 152 $[C_8H_8O_3]^+$ (30), 69 (10), 55 (15), 43 (16), 41 (16). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Compound **11**. Oil. UV $\lambda_{\max}^{\mathrm{EtOH}}$ (log ε): 274, 280 (3.31, 3.31). IR $\nu_{\max}^{\mathrm{neat}}$ cm^{-1}: 1605, 1595 (aromatic C=C), 1205, 1060 (O Me), 830, 690 (ring C–H). EIMS *m/z* (rel. int.): 375 $[M + 1]^+$ (13), 374 $[M]^+$ (40), 194 $[M - 180]^+$ (4), 165 $[M - 209]^+$ (13), 153 (10), 152 $[C_9H_{12}O_2]^+$ (100), 151 $[C_9H_{11}O_2]^+$ (13), 138 $[C_8H_{10}O_2]^+$ (2), 137 $[C_8H_9O_2]^+$ (2), 91 (5), 69 (4), 67 (3), 55 (7), 43 (18), 41 (8). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Compound **12**. Viscous oil. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 274, 280 (3.32, 3.32). IR $\nu_{\max}^{\mathrm{neat}}$ cm^{-1}: 3400 (OH), 1620, 1600, 1500 (aromatic C=C), 1195, 1060 (OMe), 835, 690 (ring C–H). EIMS *m/z* (rel. int.): 361 $[M + 1]^+$ (13), 360 $[M]^+$ (41), 180 $[M - 180]^+$ (4), 151 $[M - 209]^+$ (11), 139 (9), 138 $[C_8H_{10}O_2]^+$ (100), 137 $[C_8H_9O_2]^+$ (19), 69 (5), 67 (5), 55 (13), 43 (10), 41 (17). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Methylation of **12**. Compound **12** (5 mg) in Me_2CO (3 ml) was methylated with Me_2SO_4 (0.3 ml) and K_2CO_3 (0.6 g) for 3 hr. Usual work-up, followed by Lober CC on RP-18 using MeOH, gave **11** (4 mg).

Belamcandone P (**13**). Dull red semi-solid. $[\alpha]_D^{20}$ 0° ($CHCl_3$; *c* 0.13). UV λ_{max}^{EtOH} nm (log ε): 271, 408 (4.04, 3.03). IR ν_{max}^{neat} cm^{-1}: 3550 (sh), 3450 (OH), 1700, 1670 (C=O), 1630, 1605 (C=C), 1240, 1080, 1040 (OMe), 3070, 855, 820 (ring C–H). EIMS *m/z* (rel. int.): 766 $[M + 2H]^+$ (30), 765 $[M + H]^+$ (54), 764 $[M]^+$ (100), 738 $[M + 2H - 28]^+$ (37), 737 $[M + H - 28]^+$ (46), 736 $[M - 28]^+$ (82), 710 $[M - 54]^+$ (14), 692 $[M - 72]^+$ (12), 680 $[M - 84]^+$ (5), 390 $[C_{24}H_{38}O_4]^+$ (5), 389 $[C_{24}H_{37}O_4]^+$ (3), 376 $[C_{24}H_{40}O_3]^+$ (4), 247 (17), 233 (10), 167 $[C_8H_7O_4]^+$ (8), 154 $[C_8H_{10}O_3]^+$ (6), 153 $[C_8H_9O_3]^+$ (13), 95 (12), 83 (21), 81 (17), 69 $[O{\equiv}C{-}CH{=}C{=}O]^+$ (39), 67 (17), 57 (22), 56 (18), 55 (47), 43 (43), 41 (28). ^{1}H and ^{13}C NMR: Tables 3 and 4.

Monoacetylation of belamcandone P (**13**). To a soln of **13** (27 mg) in pyridine (1 ml), Ac_2O (0.5 ml) was added and the mixt. stirred at room temp. for 20 min. Usual work-up and subsequent CC on silica gel using C_6H_6 afforded a monoacetate **19** (24 mg).

Monoacetate **19**. Pale yellow solid. UV λ_{max}^{EtOH} nm (log ε): 275, 377 (4.02, 3.00). IR ν_{max}^{KBr} cm^{-1}: 3550 (sh), 3400 (OH), 1765, 1195 (OAc), 1700, 1675 (C=O), 1610, 1580 (C=C), 1240, 1080, 1040 (OMe), 3070, 855, 815 (C–H). EIMS *m/z* (rel. int.): 808 $[M + 2H]^+$ (4), 807 $[M + H]^+$ (9), 806 $[M]^+$ (16), 766 $[M + 3H - Ac]^+$ (25), 765 $[M + 2H - Ac]^+$ (53), 764 $[M + H - Ac]^+$ (100), 738 $[M + 3H - Ac - 28]^+$ (24), 737 $[M + 2H - Ac - 28]^+$ (20), 736 $[M + H - Ac - 28]^+$ (40), 390 $[C_{24}H_{38}O_4]^+$ (1), 389 $[C_{24}H_{37}O_4]^+$ (2), 376 $[C_{24}H_{40}O_3]^+$ (2), 167 $[C_8H_7O_4]^+$ (6), 154 $[C_8H_{10}O_3]^+$ (3), 153 $[C_8H_9O_3]^+$ (7), 95 (11), 83 (16), 81 (12), 69 $[O{\equiv}C{-}CH{=}C{=}O]^+$ (28), 67 (13), 57 (18), 56 (13), 55 (32), 43 (48), 41 (20). ^{1}H and ^{13}C NMR: Tables 3 and 4.

Diacetylation of belamcandone P (**13**). Compound **13** (48 mg) was acetylated with Ac_2O (1 ml) and pyridine (1 ml) at room temp. for 24 hr, observing its production with HPLC. The monoacetate **19** first formed and mainly converted into a diacetate **20**, together with a small quantity of **21**. The ratio of **21** increased accompanied by a decrease of **19** and **20** with the passage of time and the diacetate **20** and **21** were finally obtained in a ratio of *ca* 9:2. Usual work-up and Lober CC on RP-18 using MeOH, gave two diacetates **20** (31 mg) and **21** (7 mg).

Diacetate **20**. Pale yellow semi-solid. UV λ_{max}^{EtOH} nm (log ε): 270, 375 (3.93, 3.16). IR ν_{max}^{neat} cm^{-1}: 1765, 1750, 1195 (OAc), 1715, 1680 (C=O), 1610, 1585 (C=C), 1240, 1080, 1040 (OMe), 3070, 850, 820 (ring C–H). EIMS *m/z* (rel. int.): 850 $[M + 2H]^+$ (4), 849 $[M + H]^+$ (11), 848 $[M]^+$ (20), 808 $[M + 3H - Ac]^+$ (17), 807 $[M + 2H - Ac]^+$ (44), 806 $[M + H - Ac]^+$ (78), 766 $[M + 4H - 2Ac]^+$ (22), 765 $[M + 3H - 2Ac]^+$ (52), 764 $[M + 2H - 2Ac]^+$ (100), 738 $[M + 4H - 2Ac - 28]^+$ (21), 737 $[M + 3H - 2Ac - 28]^+$ (21), 736 $[M + 2H - 2Ac - 28]^+$ (38), 390 $[C_{24}H_{38}O_4]^+$ (2), 389 $[C_{24}H_{37}O_4]^+$ (8), 376 $[C_{24}H_{40}O_3]^+$ (3), 167 $[C_8H_7O_4]^+$ (10), 154 $[C_8H_{10}O_3]^+$ (5), 153 $[C_8H_9O_3]^+$ (11), 95 (17), 83 (28), 81 (23), 69 $[O{\equiv}C{-}CH{=}C{=}O]^+$ (45), 67 (22), 57 (27), 56 (18), 55 (49), 43 (87), 41 (33). ^{1}H and ^{13}C NMR: Tables 3 and 4.

Diacetate **21**. Pale yellow viscous oil. UV λ_{max}^{EtOH} nm (log ε): 276, 404 (4.03, 2.54). IR ν_{max}^{neat} cm^{-1}: 1765, 1735, 1195 (O Ac), 1680, 1660 (sh) (C=O), 1620, 1590 (C=C), 1245, 1090, 1030 (OMe), 845, 820 (ring C–H). EIMS *m/z* (rel. int.): 850 $[M + 2H]^+$ (1), 849 $[M + H]^+$ (3), 848 $[M]^+$ (7), 808 $[M + 3H - Ac]^+$ (5), 807 $[M + 2H - Ac]^+$ (13), 806 $[M + H - Ac]^+$ (19), 766 $[M + 4H - 2Ac]^+$ (20), 765 $[M + 3H - 2Ac]^+$ (49), 764 $[M + 2H - 2Ac]^+$ (100), 738 $[M + 4H - 2Ac - 28]^+$ (29), 737 $[M + 3H - 2Ac - 28]^+$ (32), 736 $[M + 2H - 2Ac - 28]^+$ (63), 389 $[C_{24}H_{37}O_4]^+$ (5), 376 $[C_{24}H_{40}O_3]^+$ (5), 374 $[C_{24}H_{38}O_3]^+$ (10), 167 $[C_8H_7O_4]^+$ (9), 154 $[C_8H_{10}O_3]^+$ (6), 153 $[C_8H_9O_3]^+$ (14), 95 (19), 83 (19), 81 (10), 69 $[O{\equiv}C{-}CH{=}C{=}O]^+$ (31), 67 (26), 57 (19), 56 (15), 55 (42), 43 (54), 41 (24). ^{1}H and ^{13}C NMR: Tables 3 and 4.

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