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SESQUI-, SESTER- AND TRILIGNANS FROM STEMS OF *CERBERA MANGHAS* AND *C. ODOLLAM**

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Key Word Index—*Cerbera manghas*, *C. odollam*, Apocynaceae, stem, lignan; olivil, olivil–guaiacylglycerol ether; olivil dimer, guaiacylglycerol ether, oliviltrimer, cerberaliganan

Abstract—Sesqui-, sester- and tri-lignans principally composed of olivil were isolated from the stems of *Cerbera manghas* and *C. odollam* and named cerberalignans D–I. The structures were determined from spectral evidence.

INTRODUCTION

The genus *Cerbera* belongs to Apocynaceae and is distributed throughout Oceanian and Indian Ocean regions. Recently we reported the isolation of novel cardenolides including cerleasides A and B (oleagenin thevetoside and glucosylthevetoside [1]), 17β- and 17α-cerdollasides (8β-hydroxy-17β- and 17α-digitoxigenin thevetoside) [2, 3], 17β-digitoxigenin gentiotriosylthevetoside [3], 17α-digitoxigenin apiosylglucosylthevetoside [4], along with the normal 17β- and 17α-digitoxigenin and tanghinigenin glycosides [5]. In the preceding paper of this series, we described lignans including olivil, cycloolivil, two olivil glucosides and three dimers of olivil, cerberalignans A, B, and C [6]. This paper describes the isolation and structure determination of four sesquilignans (**1**–**4**), one sesterlignan (**5**), and one trilignan (**6**), composed of olivil units and phenylpropanoids, from the stems of *Cerbera manghas* and *C. odollam*.

RESULT AND DISCUSSION

Compound **1** has the molecular formula, $C_{30}H_{34}O_{10}$, based on its FAB mass spectrum, and afforded a tetraacetate (**1a**) upon acetylation. In the ^{1}H NMR spectrum of **1a**, four 3H singlet peaks due to two alcoholic acetoxyl and two phenolic acetoxyl groups were observed along with three methoxyl and eight aromatic proton signals. The ^{13}C NMR spectrum of **1** revealed the presence of 18 aromatic carbons and nine aliphatic carbons besides methoxyl carbons; **1** was considered to be a sesquilignan.

In the ^{1}H NMR spectrum of **1a**, the peaks at δ 5.09 and 5.80 were assignable to the protons attached to the benzyl carbons having an oxygen function, the ^{1}H COSY of **1a** showed the cross peaks between the peaks at δ 5.09 and 3.05, and also between the peak at δ 3.05 and a pair of peaks at 4.74 and 4.54. The chemical shifts and coupling constants of these four peaks as well as two pairs of methylene protons at C-7′(δ 3.31 and 3.13) and C-9′ (δ 4.24 and 4.20) were similar to those of the aliphatic portion in olivil acetate. Similar connections were observed between the peaks at δ 5.80 (H-7″), δ 3.93 (H-8″), and δ 4.61 and 4.48 (H-9″a, b), suggesting the presence of a benzofuran portion in the dehydrodiconiferylalcohol [7].

All the carbons due to an olivil framework were assignable in the ^{13}C NMR spectrum with the downfield shift (+13.8 ppm) and the transformation of C-5′ from a doublet to a singlet in DEPT, in comparison with those of olivil. Therefore, the extra phenylpropanoid is concluded to be linked to 4′-hydroxyl and C-5′ of ring B in olivil to form the dehydrodiconiferyl moiety. The orientations of the benzene ring (ring C) and the primary carbinol at C-8″ are considered to be *trans*, based on the cross peaks between H-8″/H-2″, and H-7″/H-9″a, b, respectively, in the NOESY of **1a**. Three methoxyl groups were allocated to C-3, 3′ and 3″, as cross peaks between H-2 (2′, 2″) and –OMe, respectively, are observed. Compound **1** is named cerberalignan D.

Compound **2** has the same molecular formula as **1** (FAB mass spectrum). In the ^{1}H and ^{13}C NMR spectra, the signals due to the aliphatic portion can be superimposed on those of **1**. Only two protons were assignable in ring A as *m*-coupled doublets. C-5 was shifted downfield and transformed into a singlet, so that the additional phenylpropanoid is located in ring A, instead of ring B as in **1**. Compound **2** is named cerberalignan E.

Compounds **3** and **4** had the same molecular formula, $C_{30}H_{36}O_{11}$. Upon acetylation, pentaacetates (**3a**, **4a**) were formed and the presence of three alcoholic and two phenolic acetoxyl groups was observed in their ^{1}H NMR spectra. In **3** and **4**, three aromatic protons and one extra methoxyl group were assignable as well as all the proton signals due to the olivil moiety in the ^{1}H NMR. Besides these, the presence of one primary and two secondary carbinols forming a glycerol structure was detected in the ^{1}H COSY. In the FD mass spectrum of **3** and **4**, the major peak was observed at *m/z* 180 ($C_{10}H_{12}O_3$) as well as a $[M]^+$ at *m/z* 572, suggesting **3** and **4** to be sesquilignans composed of olivil and guaiacylglycerol. The linkage of these two components was assigned to be at the 4′-hydroxyl of ring B and the β-hydroxyl of guaiacylglycerol, based on the downfield shifts of C-1′ and C-4′, and

* Part 7 in the series '*Cerbera*'. For Part 6, see ref [6].

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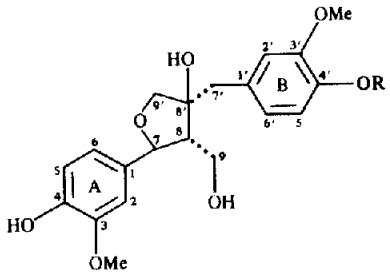
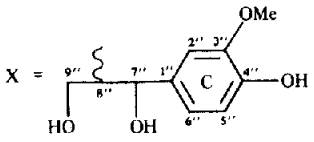
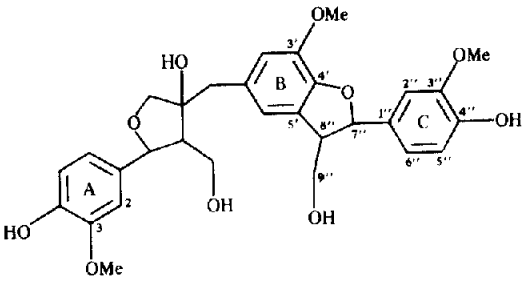


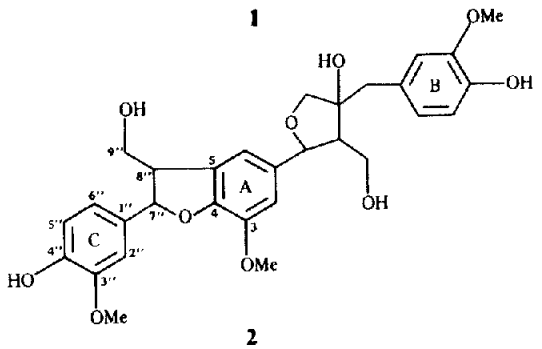
Olivil: R = H

3 R = X (*erythro*)
4 R = X (*threo*)





1



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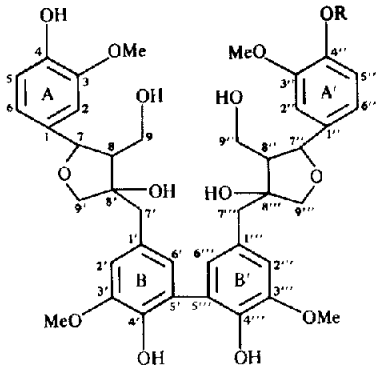
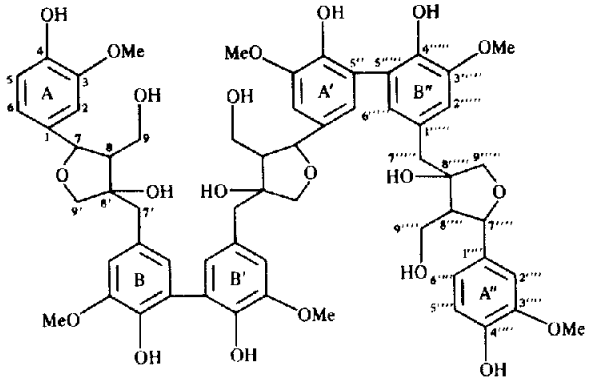


Cerberalignan A: R = H

5 R = X (*erythro*)

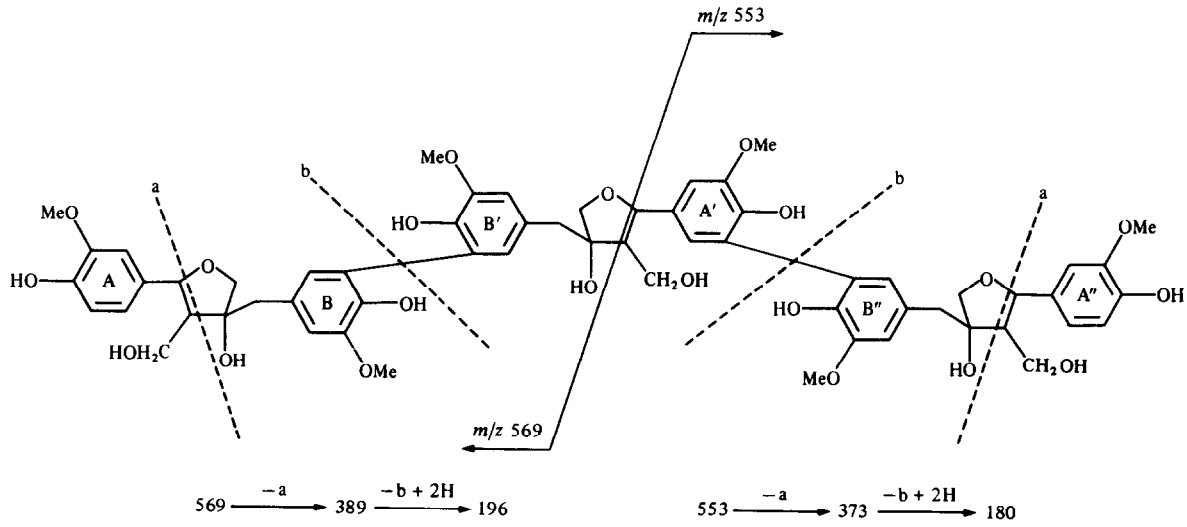


6

acetylation shifts of C-7″ and C-9″. In a comparison of the chemical shift and the coupling constant of H-7″ with those of guaiacylglycerol β-arylether [8], the guaiacylglycerols in **3** and **4** were determined to be *erythro* and *threo*-isomers, and **3** and **4** are named cerberalignans F and G, respectively.

The negative FAB mass spectrum of **5** afforded an $[M-1]^-$ peak at *m/z* 945 and the molecular formula was suggested to be $C_{50}H_{58}O_{18}$. Based on the fragment peaks at *m/z* 749 $[C_{40}H_{46}O_{14}-1]$, **5** seemed to be a sesterlignan composed of a dilignan and a guaiacylglycerol. The peaks due to *erythro*-guaiacylglycerol were observed in the ^1H and ^{13}C NMR spectra, and the remaining signals were in good agreement with those of cerberalignan A, one of the olivil-dimers previously isolated [6], except for the downfield shifts of C-1″ and C-4″. As in the case of **3** and **4**, the β-hydroxyl group of *erythro*-guaiacylglycerol is considered to be linked to the 4″-hydroxyl group of ring A′ in cerberalignan A: **5** is named cerberalignan H.

In the negative FAB mass spectrum of **6**, an $[M-1]^-$ peak was observed at *m/z* 1123, indicating the molecular formula to be $C_{60}H_{68}O_{21}$. In the FD mass specturm, **6** was cleaved into two moieties (*m/z* 569 and 553) at the centre of the molecule, and then the two decomposed in the same way (*m/z* 569, 389, 196 and *m/z* 553, 373, 180), suggesting the presence of the same terminal fragment in each moiety (Scheme 1). While the ^{13}C NMR signals in the aliphatic region were duplicated as those of olivil, three units of the proton signals corresponding to H-7, H-8, H-9, H-7′ and H-9′ of olivil were observed in the ^1H NMR spectrum. In the aromatic region, two units of H-2, H-5 and H-6 arising from ring A of the olivil moieties were assignable. All the other aromatic protons were observed as *m*-coupled peaks so that the two rings A were



Scheme 1

both located in the terminal position. **6** is named cerberalignan I

In the two *Cerbera* species, several sesterlignans and trilignans are present as mixtures, which show one spot on TLC but several peaks by HPLC. Compounds **5** and **6** were isolated by successive HPLC from the front peak of each fraction Isolation and structure determinations of other complex lignan components are under investigation

EXPERIMENTAL

General NMR 400 and 100 MHz, pyridine, TMS int std For TLC and silica gel CC, the following solvent systems were used. 1 $CHCl_3$–MeOH–H_2O (7 2.2, 7 3 1, bottom layer), 2· EtOAc–MeOH–H_2O (4 1 5, top layer) HPLC radial pack C_{18} column, MeCN–H_2O (25–28%) at 0 6–1 0 ml/min

Extraction and isolation of cerberalignans [6] Air-dried stems of *C manghas* L (6 kg), cultivated in the greenhouse of Fukuoka University and harvested in Sept 1986, were extracted with MeOH The MeOH extract was concd *in vacuo* and dil with H_2O The mixt was filtered and the filtrate extracted with C_6H_6 and then with $CHCl_3$(17 g) The H_2O layer was concd *in vacuo* and extracted with *n*-BuOH (128 1 g) The $CHCl_3$ and BuOH exts were combined and passed through an MCI-gel column (CHP-20P, Mitsubishi Chem Co) The 40–50%MeOH eluate was subjected to silica gel CC with solvent 1 to afford (−)-olivil (1 8 g) The 60–90% MeOH eluate was chromatographed on silica gel columns with solvent 1 and then solvent 2 Fractions containing each lignan were subjected to a further reversed phase CC (RQ-1, Fuji-gel, MeCN–H_2O) to give (−)-olivil (1 41 g) and (+)-cycloolivil (110 mg) Fractions containing sesqui-, di-, sester- and trilignans were subjected to prep HPLC to isolate **1** (162 mg), **2** (33 mg), **3** (67 mg), **4** (150 mg), **5** (30 mg) and **6** (24 mg) in addition to cerberalignans A (70 mg), B (230 mg), and C (90 mg) (described as lignans 5, 6 and 7 in the preceding paper [6])

Air-dried stems of *C odollam*, planted in Kent Ridge, Singapore, and collected in January 1987 (1 1 kg), were percolated as described above. The following lignans were obtained **1** (7 mg), **2** (3 mg), **3** (4 mg), **4** (9 mg), **5** (3 mg) and **6** (4 mg) in addition to (−)-olivil (126 mg), (+)-cycloolivil (4 mg), cerberalignan A (8 mg), cerberalignan B (14 mg) and cerberalignan C (4 mg)

Cerberalignan D (**1**) Solid, $[\alpha]_D^{25}$ −50 6° (MeOH, *c* 0 98), FABMS *m/z*· 577 205, $C_{30}H_{34}O_{10}Na$ requires 577 205. UV λ_{max}^{MeOH} nm (log ε) 228 (4.37), 280 (3 99), 286 (3 96) ^1H and ^{13}C NMR see Tables 1 and 2 Tetraacetate of **1** (**1a**) Formed on acetylation of **1** with pyridine and Ac_2O FDMS *m/z*: 722 $[M]^+$, 451, 43 ^1H NMR see Table 1

Cerberalignan E (**2**) Solid, $[\alpha]_D^{24}$ −35 9° (MeOH; *c* 0 40) FABMS *m/z* 577 205, $C_{30}H_{34}O_{10}Na$ requires 577 205, FDMS *m/z* 554 $[M]^+$, 536, 524, 494, 476, 328, 196 UV λ_{max}^{MeOH} nm (log ε)· 228(4 35), 280(3 96), 286(3 92). ^1H and ^{13}C NMR see Tables 1 and 2

Cerberalignan F (**3**). Solid, $[\alpha]_D^{28}$ −49 0° (MeOH· *c* 0 40), FABMS *m/z* 595 217, $C_{30}H_{36}O_{11}Na$ requires 595 216 UV λ_{max}^{MeOH}nm (log ε) 228 (4 34), 279 (3 94). ^1H and ^{13}C NMR see Tables 1 and 2 Pentaacetate of **3** (**3a**) formed on acetylation of **3** with pyridine and Ac_2O FDMS *m/z* 782 $[M]^+$ ^1H NMR see Table 1

Cerberalignan G (**4**) Solid, $[\alpha]_D^{28}$ −68 4°(MeOH, *c* 0.50), FABMS *m/z*· 595 213, $C_{30}H_{36}O_{11}Na$ requires 595 216 UV λ_{max}^{MeOH} nm(log ε) 230 (4 33), 2780 90 ^1H and ^{13}C NMR see Tables 1 and 2 Pentaacetate of **4** (**4a**)· formed on acetylation of **4** with pyridine and Ac_2O. FDMS *m/z* 782 $[M]^+$ ^1H NMR: see Table 1 ^{13}C NMR δ 84 7 (C-7), 81 3 (C-8′), 80 3 (C-8″), 77 6 (C-9′) 75 0 (C-7″), 63 2, 63 1 (C-9, 9″), 58 5 (C-8), 40 4 (C-7′)

Cerberalignan H (**5**). Solid, $[\alpha]_D^{25}$ −62 0° (MeOH, *c* 0.39), FABMS (negative) *m/z* 945 $[M-1]^-$ ($C_{50}H_{58}O_{18}-1$), 749, 553, 275 UV λ_{max}^{MeOH} nm (log ε) 222 (4 76), 281 (4 16) ^1H NMR δ. 5 62 (1H, *d*, *J* = 4 4 Hz, H-7‴), 5.31, 5 30 (1H each, *d*, *J* = 7 Hz, H-7,7″), 4 99 (1H, *m*, H-8‴), 4 54 (1H, *dd*, *J* = 11,5 Hz, H-9‴a), 4 38 (1H, *dd*, *J* = 11, 5 Hz, H-9‴b), 3 67 (6H, *s*, –OMe), 3.73, 3.71, 3 68 (3H each *s*, –OMe) ^{13}C NMR see Table 2

Cerberalignan I (**6**) Solid, $[\alpha]_D^{25}$ −76 7° (MeOH, *c* 0 72), FABMS (negative) *m/z*. 1123 $[M-1]^-$ ($C_{60}H_{68}O_{21}-1$), 695, 533, 373, 275. FDMS *m/z* 569, 553, 389, 373, 196, 180 UV λ_{max}^{MeOH} nm (log ε) 220 (4 88), 283 (4 18) ^1H NMR δ 7 67 (1H, *d*, *J* = 1 Hz), 7 63 (2H, *d*, *J* = 1 Hz, H-2, 2‴), 7 61 (1H, *d*, *J* = 1 Hz), 7 53(2H, *d*, *J* = 1 Hz), 7 48 (1H, *d*, *J* = 1 Hz), 7 36 (2H, *dd*, *J* = 8, 2 Hz, H-6, 6‴), 7 28 (3 H, *d*, *J* = 1 Hz), 7 21 (2H, *d*, *J* = 8 Hz, H-5, 5‴), 5 34, 5 31, 5 30 (1H each, *d*, *J* = 7 Hz, H-7, 7″, 7‴), 3 60, 3.56, 3 52 (1H each, *d*, *J* = 14 Hz, H-7′a, 7″a, 7‴a), 3 45, 3.43, 3.40 (1H each, *d*, *J* = 14 Hz, H-7′b, 7″b, 7‴b), 3.70 (9H, *s*, –OMe), 3 66

Table 1 ^{1}H chemical shifts of lignans, δ(ppm) in pyridine (400 MHz)

	Olivil	1	1a	2	3	3a	4	4a
aromatic H	H-2 7.62 *d*(2) H-5 7.22 *d*(8) H-6 7.36 *dd*(8,2) H-2′ 7.32 *d*(2) H-5′ 7.22 *d*(8) H-6′ 7.19 *dd*(8, 2)	H-2 7.61 *d*(2) H-5 7.22 *d*(8) H-6 7.35 *dd*(8,2) H-2′, 6′ 7.35 *d*(1, 2H) H-2″ 7.32 *d*(1) H-5″ 7.21 *d*(8) H-6″ 7.26 *dd*(8, 1)	H-2 7.55 *d*(2) H-5 7.26 *d*(8) H-6 7.31 *dd*(8,2) H-2′, 6′ 7.28 *d*(1) 7.18 *d*(1) H-2″ 7.33 *d*(2) H-5″ 7.23 *d*(8) H-6″ 7.21 *dd*(8, 2)	H-2, 6 7.60 *d*(1) 7.56 *d*(1) H-2′ 7.32 *d*(2) H-5′ 7.22 *d*(8) H-6′ 7.19 *dd*(8, 2) H-2″ 7.33 *d*(2) H-5″ 7.22 *d*(8) H-6″ 7.24 *dd*(8, 2)	H-2, 2′, 2″ 7.61 *d*(2) 7.60 *d*(2) 7.29 *s*(*br*) H-5, 5′5″ 7.36 *d*(8) 7.24 *d*(8) 7.21 *d*(8) H-6, 6′, 6″ 7.36 *dd* (8, 2, 2H) 7.15 *dd*(8, 2)	H-2, 2′, 2′ 7.53 *d*(2) 7.49 *d*(2) 7.27 *d*(2) H-5, 5′5′ 7.26 *d*(8) 7.25 *d*(8) 7.22 *d*(8) H-6, 6′, 6″ 7.32 *dd*(8, 2) 7.26 *dd*(8, 2) 7.14 *dd*(8, 2)	H-2, 2′, 2″ 7.62 *d*(2) 7.59 *d*(2) 7.32 *d*(2) H-5, 5′, 5″ 7.51 *d*(8) 7.26 *d*(8) 7.22 *d*(8) H-6, 6′, 6″ 7.42 *dd*(8, 2) 7.36 *dd*(8, 2) 7.16 *dd*(8, 2)	H-2, 2′, 2″ 7.53 *d*(2) 7.46 *d*(2) 7.27 *d*(2) H-5 5′, 5″ 7.28 *d*(8) 7.26 *d*(8) 7.22 *d*(8) H-6, 6′, 6″ 7.30 *dd*(8, 2) 7.28 *dd*(8, 2) 7.15 *dd*(8, 2)
aliphatic H	H-7 5.33 *d*(7) H-8 3.02 *m* H-7′a, b 3.57 *d*(14) 3.41 *d*(14) H-9′a, b 4.35 *d*(9) 4.24 *d*(9)	H-7 5.33 *d*(7) H-8 3.02 *m* H-7′a, b 3.59 *d*(14) 3.42 *d*(14) H-9′a, b 4.35 *d*(9) 4.24 *d*(9) H-7″ 6.08 *d*(6) H-8″ 4.01 *m*	H-7 5.09 *d*(7) H-8 3.05 *m* H-9a, b 4.74 *dd*(11, 6) 4.54 *dd*(11, 8) H-7′a, b 3.31 *d*(14) 3.13 *d*(14) H-9′a, b 4.24 *d*(9) 4.20 *d*(9) H-7″ 5.80 *d*(7) H-8″ 3.93 *m* H-9″a, b 4.61 *dd*(11, 5) 4.48 *dd*(11, 8)	H-7 5.36 *d*(7) H-8 3.03 *m* H-7′a, b 3.56 *d*(14) 3.41 *d*(14) H-9′a, b 4.36 *d*(9) 4.26 *d*(9) H-7″ 6.09 *d*(7) H-8″ 3.95 *m*	H-7 5.31 *d*(7) H-8 3.00 *m* H-9a, b 4.31 *dd*(11, 6) 4.23 *dd*(11, 6) H-7′a, b 3.53 *d*(14) 3.37 *d*(14) H-9′a, b 4.29 *d*(9) 4.19 *d*(9) H-7″ 5.62 *d*(4.9) H-8″ 4.99 *m* H-9″a, b 4.55 *dd*(12, 5) 4.39 *dd*(12, 4)	H-7 5.05 *d*(7) H-8 3.03 *m* H-9a, b 4.70 *dd*(11, 5) 4.50 *dd*(11, 8) H-7′a, b 3.26 *d*(14) 3.07 *d*(14) H-9′a, b 4.18 *d*(9) 4.15 *d*(9) H-7″ 6.56 *d*(5.4) H-8″ 5.13 *m* H-9″a, b 4.74 *dd* (12, 6) 4.54 *dd*(12, 3)	H-7 5.31 *d*(7) H-8 3.00 *m* H-9a, b 4.31 *dd*(12, 6) 4.23 *dd*(12, 6) H-7′a, b 3.55 *d*(14) 3.39 *d*(14) H-9′a, b 4.29 *d*(9) 4.19 *d*(9) H-7″ 5.59 *d*(5.9) H-8″ 4.92 *m* H-9″a, b 4.38 *dd*(12, 4) 4.07 *dd*(12, 5)	H-7 5.06 *d*(7) H-8 3.03 *m* H9a, b 4.71 *dd*(12, 6) 4.51 *dd*(12, 8) H-7′a b 3.28 *d*(14) 3.09 *d*(14) H-9′a b 4.19 *d*(9) 4.19 *d*(9) H-7″ 6.60 *d*(6.4) H-8″ 5.09 *m* H-9″a, b 4.62 *dd*(12, 4) 4.31 *dd*(12, 5)
–OMe	3.72, 3.67	3.81, 3.66 3.64	3.84, 3.68 3.66	3.76, 3.71 3.64	3.74, 3.68 3.67	3.73, 3.71 3.65	3.73 3.72 3.67	3.73 3.72 3.65
–OAc			2.27, 2.25 2.00, 1.99			2.25, 2.24 2.08, 1.98 1.97		2.25(6H) 2.05, 1.98 1.96

Coupling constants (J in Hz) are given in parentheses

Table 2. ^{13}C chemical shifts of lignans, δ(ppm) in pyridine (100 MHz)

C	Olivil	1	2	3	4	C	Cer A*	5
1	135 6	135 5	137 8	135.4	135 5	1 (1″)	135 6	135 5, 138.3
2	111 6	111.6	112.5	111 6	111.6	2 (2″)	111.7	111 7
3	148 7	148 7[a]	148 5[a]	148.7	148 7	3 (3″)	148 7[a]	148 7[a]
4	147 6	147 6	144 8	147 6	147.6	4 (4″)	147.5	147 5 a, 150 7
5	116 1[a]	116.1[b]	129.8[b]	116.1[a]	116.1[a]	5 (5″)	116 0	116 1b, 117.7
6	120 5	120 4	116 5[c]	120.4[b]	120 4[b]	6 (6″)	120 4	120 4[c]
7	84.8	84.8	84 9	84 7	84.7	7 (7″)	84.7	84.7
8	62.1	62 1	62 0	62 1	62 1	8 (8″)	62 1	62 0
9	60 5	60 4	60.4	60 4	60 4	9 (9″)	60 5	60 5
1′	130 1	132 2	130 0[b]	132.9	133.0	1′ (1‴)	129.5	129.2
2′	115 4	116 5[b]	115 4	116 0[a]	116 0[a]	2′ (2‴)	114 1	114 0
3′	148 2	148 1[a]	148 2	147 4[c]	147.5[c]	3′ (3‴)	148 6[a]	148 6[a]
4′	146 7	144.0	146 7	150 3	150.6	4′ (4‴)	144 0	144 3
5′	116 0[a]	129.8	116.4[c]	117.6	117 9	5′ (5‴)	127.2	127.2
6′	123 7	119 7	123.8	123.5	123 5	6′ (6‴)	126 6	126 4
7′	40 7	40 8	40.6	40.6	40 7	7′ (7‴)	40 8	40 8
8′	82.0	81.9	82 0	81.8	81 8	8′ (8‴)	82.0	82 0
9′	78 1	78.5	78 1	77.9	77 9	9′ (9‴)	78.1	78 0
1″	—	133.9	133 8	134 6	134 0	1⁗	—	134.6
2″	—	110 9	110.9	112.0	112.0	2⁗	—	112 0
3″	—	148 8[a]	148 7[a]	148 4[c]	148 4[c]	3⁗	—	148.4[a]
4″	—	148.1[a]	148 1[a]	147 6[c]	148 1[c]	4⁗	—	147.5
5″	—	116.0[b]	116.1[c]	116 0[a]	116.0[a]	5⁗	—	116 0[b]
6″	—	119.7	119 7	120.6[b]	120 7[b]	6⁗	—	120.6[c]
7″	—	88.5	88.6	73 6	73 5	7⁗	—	73.6
8″	—	54 9	54 9	86 2	87 5	8⁗	—	86 2
9″	—	64 5	64 3	61 6	61 7	9⁗	—	61 8
–OMe	55 8	55 8(× 2)	55 8(× 2)	55 7	55 8(× 2)	–OMe	55.8(× 2)	55 8(× 3)
	55 9	56 2	55 9	55.8	55 9		56 0 (× 2)	55 7 (× 2)
				55 9				

* Cer A = ceberalignan A.
[a–c] Signal assignments in each cloumn may be reversed.

(6H, *s*, –OMe), 3 65 (3H, *s*, –OMe) ^{13}C NMR δ 148 7, 148.6, 147.5 (C-3, 3′, 3″, 3‴, 3⁗, 3⁗′ C-4, 4″. 4‴. 4⁗, 4⁗′), 144.9 (C-4′, 4‴), 135.8 (C-11″, 1‴), 129 4 (C-1′, 1‴, 1⁗′), 127.2 (C-5′, 5‴, 5⁗′), 126.4, 126 5 (C-5″, C-6′, 6‴, 6⁗), 122 9 (C-6″), 120.4 (C-6, 6‴), 116.0 (C-5, 5⁗′), 114.0 (C-2′, 2‴, 2⁗′), 111 7 (C-2, 2⁗′), 110.0 (C-2″), 84.7 (C-7, 7″, 7⁗′), 82.0 (C-8′, 8‴, 8⁗′), 78.0 (C-9′, 9‴, 9⁗′), 62 0 (C-8, 8″, 8⁗′), 60.5 (C-9, 9″, 9⁗′), 40 8 (C-7′, 7‴, 7⁗′), 56.0 55 8, 55 7 (–OMe)

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