PERGAMON

Phytochemistry 56 (2001) 759–767

PHYTOCHEMISTRY

www.elsevier.com/locate/phytochem

Phenolic constituents from the core of Kenaf (*Hibiscus cannabinus*)

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Received 14 July 2000; received in revised form 13 November 2000

Abstract

Four lignans, boehmenan H {2-(4-hydroxy-3-methoxyphenyl)-5-[3-(4-hydroxy-3-methoxycinnamoyloxy)propyl]-3-hydroxy methyl-7-methoxybenzodihydrofuran}, boehmenan K {2-(4-hydroxy-3-methoxyphenyl)-5-[3-(4-hydroxycinnamoyloxy)-1-propenyl] -3-(4-hydroxy-3-methoxycinnamoyloxymethyl)-7-methoxybenzodihydrofuran}, *threo*-carolignan H {*threo*-1-(4-hydroxy-3-methoxyphenyl)-2-{4-[3-(4-hydroxy-3-methoxycinnamoyloxy)propyl]-2-methoxyphenoxy}-1,3-propanodiol}, and *threo*-carolignan K {*threo*-1-(4-hydroxy-3-methoxyphenyl)-3-(4-hydroxy-3-methoxycinnamoyloxy)-2-{4-[3-(4-hydroxycinnamoyloxy)-1-propenyl]-2-methoxy phenoxy}-1-propanol} as well as several other lignans, aldehydes and a tyramine derivative were isolated from the acetone extract of core of kenaf (*Hibiscus cannabinus*). All the structures were established by spectroscopic methods. The hitherto unreported ^{13}C NMR spectra of some compounds are also presented and discussed. 2D NMR techniques have allowed the revision of certain previously reported ^{13}C NMR assignments of some scarce naturally occurring compounds.

Keywords: Kenaf (*Hibiscus cannabinus*); Malvaceae; Lignans; Boehmenan H; Boehmenan K; *threo*-Carolignan H; *threo*-Carolignan K

1. Introduction

Kenaf (*Hibiscus cannabinus*) is an annual dicotyledonous herbaceous African plant, but also well known in other geographical areas. In Portugal, the variety Salvador has been experimentally cultivated with good results. It has already been shown that this plant has good features to be used in several applications, such as antidotes to poisoning with chemicals (acids, alkali, pesticides) and venomous mushrooms in traditional medicine (Chifundera et al., 1994) and as source of fibres to pulp and paper industries (Pande and Roy, 1996). Our previous studies on the chemical composition of the light petroleum extract of bark and core of this plant resulted in the isolation of several sterols, a triterpene, and a long chain fatty ester (Sêca et al., 2001). In the present study we report on the isolation and structure elucidation of four new lignans, designated as boehmenan H **1**, boehmenan K **2**, *threo*-carolignan K **3** and *threo*-carolignan H **4**, as well as 16 other compounds from the acetone extract of the core of *Hibiscus cannabinus*. The detailed NMR studies of these compounds **5**–**20** allowed us to correct some literature ^{13}C NMR assignments for boehmenan **5**, *erythro*- and *threo*-carolignan E, **6** and **7**, and to come forward for the first time with the ^{13}C assignments for boehmenan D **8** and *erythro*-carolignan F **9**.

2. Results and discussion

The core of *Hibiscus cannabinus* was finely ground and extracted successively with light petroleum and acetone. The acetone extract was fractionated by its solubility in chloroform and acetone, but almost all the amount of this extract was soluble in chloroform. In this way, only the latter fraction was considered; it was successively submitted to column and preparative thin-layer silica gel chromatographies to give four new lignans **1**–**4** and 16 known compounds **5**–**20** (Fig. 1).

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0031-9422/01/$ - see front matter
PII: S0031-9422(00)00473-8

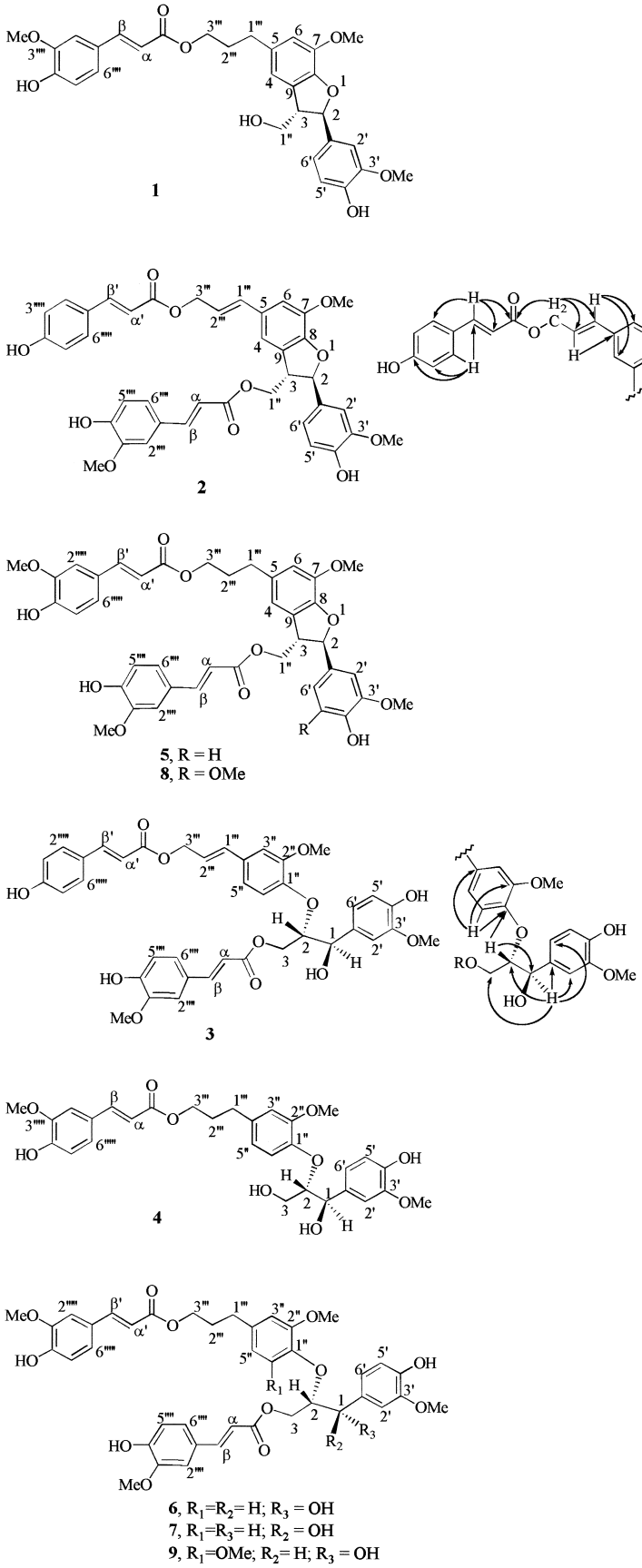


Fig. 1. Lignans **1**–**9** from *Hibiscus cannabinus* and major connectivities observed for **2** and **3**.

Due to the complexity and similarity of the ^1H and ^{13}C NMR spectra of compounds **1**, **2**, **5** and **8** and the available large amount of **5**, it was decided to start with **5** for the elucidation of these compounds. In the ^1H NMR spectrum of **5** four different spin systems can be found. One set of ABX signals corresponding to three methylene groups appear at δ_H 1.97–2.06 (2H, *m*), 2.71 (2H, *t*, $J=7.6$ Hz) and 4.23 (2H, *t*, $J=6.5$ Hz). In the HMBC spectrum of **5**, correlations between the proton resonance at δ 4.23 with that of the carbon at δ 167.3 and also between that at δ_H 2.71 with carbon resonances of an aromatic ring (δ_C 112.4, 116.1 and 134.9) were observed. From these results one can conclude that the referred three methylene groups (δ_C 30.7, 32.1 and 63.7) connect an aromatic ring to an ester group.

In the ^1H NMR spectrum of **5** an ABC set of signals can also be found. They are due to proton resonances of a methine group [δ_H 3.84–3.93 (*m*); δ_C 50.7], one benzylic methine group [δ_H 5.50 (*d*, $J=7.8$ Hz); δ_C 88.9] and also a methylene group [δ_H 4.42 (1H, *dd*, $J=7.7$ and 11.2 Hz) and 4.59 (1H, *dd*, $J=5.1$ and 11.2 Hz); δ_C 65.4]. The inequivalence of these two methylene protons and the multiplicity of their resonances indicate that this methylene group is attached to a chiral methine carbon. In the HMBC spectrum of **5** these methylene proton resonances showed connectivities with that of the carbon of another ester group (δ_C 167.0).

The aromatic region of the ^1H NMR spectrum of **5** showed two AB sets of signals at δ_H 6.23, 7.49 (2H, *2d*, $J=15.9$ Hz) and δ_H 6.30, 7.60 (2H, *2d*, $J=15.9$ Hz). The coupling constants of these two vinylic systems indicate that they have a *trans* configuration. Correlations between the proton resonances of these vinylic systems with the already referred carbon resonances of ester groups, indicate that compound **5** have two α,β-unsaturated ester moieties in their structure. The presence of these moieties was also confirmed by the presence of a band at 1700 cm^{-1} in the IR spectrum of **5**.

The ^1H NMR spectrum of **5** showed three singlets (δ_H 5.65, 5.91 and 5.92, one proton each) which disappear after shaking its $CDCl_3$ solution with D_2O, suggesting the presence of three phenolic protons involved in hydrogen bonds.

The presence of ester groups in the structure of compound **5** lead us to consider a transesterification reaction in order to aid its structure elucidation. The transesterification reaction of **5** with sodium methoxide in methanol lead to the formation of three products **21**–**23**. One of these compounds was identified as methyl ferulate **21**, suggesting the presence of esters of this acid in the structure of compound **5**. The ^1H NMR spectrum of the second compound **22** obtained in this reaction showed an aliphatic region similar to that already described for **5**. The analysis of the ^1H and ^{13}C NMR spectra of **22**, the connectivities found in their HMBC spectrum (Fig. 2) and the molecular ion (*m*/*z* 360) present in the EIMS

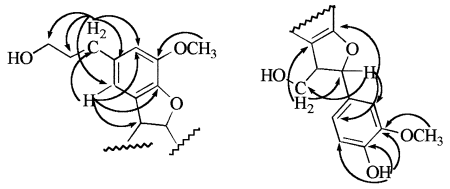
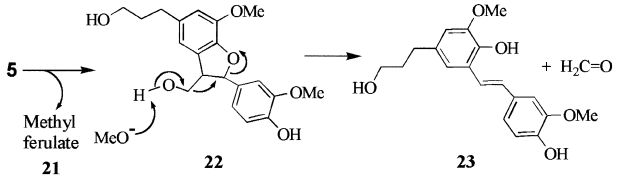


Fig. 2. Major HMBC connectivities observed for **22**.

allowed to establish its structure as 3-hydroxymethyl-5-(3-hydroxypropyl)-2-(4-hydroxy-3-methoxyphenyl)-7-methoxybenzodihydrofuran **22** (Takemoto et al., 1975). The coupling constant $J_{H2\text{-}H3}=7.8$ Hz indicates that these protons have a *trans* configuration. The structure of the third compound obtained in the transesterification of **5** was identified as 2,4′-dihydroxy-3,3′-dimethoxy-5-(3-hydroxypropyl)stilbene **23**. The formation of this compound **23** in the base-catalysed transesterification reaction of **5** can be envisaged by the elimination of formaldehyde, induced by sodium methoxide, and consequent ring opening of the dihydrofuran moiety of compound **22** (Scheme 1). The formation of formaldehyde in this reaction was confirmed by GC–MS (*m*/*z* 30).

All the discussed spectroscopic data and the results obtained in the transesterification reaction of **5** support the assignment of its structure to boehmenan (Takemoto et al., 1975; Paula et al., 1995). The analysis of the ^1H, ^{13}C, COSY, HETCOR and HMBC spectra of **5** permits to correct the literature assignment of the carbon resonances of C-5, C-7, C-1′, C-4′, C-4′′′′ and C-4′′′′′.

The ^1H and ^{13}C NMR spectral data of compound **8** were very similar to those of **5** except for one additional methoxyl group signal in the case of **8**. The presence of one extra methoxyl group at the aromatic nucleus attached to the dihydrofuran ring of **8** simplified its ^1H NMR spectrum, compared with that of boehmenan **5**. In the case of **8** the resonances of H-2′ and H-6′ appear as a singlet (δ_H 6.67), since these protons are chemically equivalents. In the HMBC spectrum that proton resonance correlates with the carbon signals at δ_C 89.3 (C-2), 131.7 (C-1′), 134.7 (C-4′) and 147.0 (C-3′,5′). These results confirm the assignment of structure **8** to boehmenan D (Paula et al., 1995). The ^1H NMR spectral data of **8** have been already reported, but its ^{13}C NMR data is now being added. The assignments of all carbon



Scheme 1.

resonances of boehmenan D **8** were made by analysis of its HMBC spectrum.

In the case of compound **1**, its HR–EIMS spectrum shows a molecular ion at *m/z* 536.2053 and this is consistent with the molecular formula $C_{30}H_{32}O_9$ (calculated mass: 536.2046) (corroborated by its ^{13}C NMR spectrum). The ^1H and ^{13}C NMR spectra of **1** are similar to those of boehmenan **5** although lacking the resonances of one feruloyl moiety. The attachment site of the feruloyl residue was determinated through the connectivities found in its HMBC spectrum. The correlation between the proton resonance of H-3‴ and that of the carbonyl ester carbon indicates that the feruloyl is attached to C-3‴ of the propyl chain. The presence of the ester group in **1** was also confirmed by the presence of the band at 1700 cm^{-1} in its IR spectrum. Structure **1** was fully characterised and named as boehmenan H.

For compound **2** the molecular formula $C_{39}H_{36}O_{11}$ (calculated mass: 680.2257) was assigned by HR–FABMS (*m/z* 680.2285). The major differences between the ^1H NMR spectrum of compound **2** in relation with that of boehmenan **5** were the presence of one additional double bond and the disappearance of one methoxyl group. The signals at δ_H 1.97–2.06 (*m*, 2H) and 2.71 (*t*, 2H) due to the proton resonances of H-2″ and H-1″ in boehmenan **5** are now for **2** being replaced by others at δ_H 6.18–6.30 (*m*, 1H) and 6.66 (*d*, $J=15.9$ Hz, 1H), which are due to the vinylic protons H-2″ and H-1″. The coupling constants of these two protons indicate that this double bond has a *trans* configuration. The ^1H NMR spectrum of **2** also showed an AB set of signals at δ_H 6.84 and 7.45 (2H each), which are due to the resonances of a *p*-substituted phenyl ring. The attachment position of the coumaroyl moiety was established by the connectivities found in its HMBC spectrum (Fig. 1). All these spectroscopic data of **2** support the assignment of the structure depicted in Fig. 1; this compound is named boehmenan K. The coupling constant $J_{H2\text{-}H3}\sim 8$ Hz in the case of compounds **1** and **2** indicates that these protons have a *trans* configuration like boehmenan **5** and boehmenan D **8**.

The ^1H NMR spectrum of **3** showed basically the same resonances and coupling constants of boehmenan K **2** (see Experimental), but with a few differences. The absence of the dihydrofuran ring was suggested by the following data: (a) the presence of a protonated carbon resonance at δ_C 120.0 assigned to C-6″, confirmed by ^{13}C DEPT NMR spectrum, in place of the signal at δ_C 127.7 due to the quaternary carbon C-9 of boehmenan K **2**. In the HETCOR spectrum this carbon resonance correlates with the proton resonance at δ_H 7.11 (d, $J=8.1$ Hz), which belongs to a trisubstituted aromatic ring, confirmed from their COSY spectrum; (b) some important connectivities found in the HMBC spectrum, as shown in Fig. 1. The HR-FABMS of **3** showed a $M+H^+$ ion at *m/z* 699.2445 consistent with the molecular formula of $C_{39}H_{39}O_{12}$ (calculated mass: 699.2442). All this spectral data are compatible with the structure of compound **3** shown in Fig. 1, which is called carolignan K.

Due to the presence of two chiral carbons in the 1,2,3-trioxygenated propane moiety of carolignan K **3**, two possible diastereomers, *erythro* and *threo*, can be present. The coupling constant $J_{H1\text{-}H2}=7.5$ Hz indicates the presence of the *threo* diastereomer, and so these protons have a *trans* diaxial orientation (Shimomura et al., 1987; Abraham et al., 1991).

The ^1H and ^{13}C spectra of compounds **6** and **7** are very similar to that of carolignan K **3**, except the presence of an additional methoxyl group signal and the disappearance of those due of one double bond ($C_{1''}=C_{2''}$) in both compounds and the multiplicity of the H-1 resonance in the case of **6**. Due to the presence of this methoxyl group in **6** and **7** a trisubstituted aromatic ring is in place of the *p*-substituted phenyl ring in the case of **3**. The signals at δ_H 6.24 and 7.49 (2H, 2d, $J=15.9$ Hz), due to the vinylic protons H-2″ and H-1″ in calolignan K **3** were replaced by others in the aliphatic region due to the proton resonances of H-2″ and H-1″ in the case of **6** and **7**. All these data and the connectivities found in the HMBC spectrum of these two compounds allowed us to assign their structures to carolignan E isomers. It was also possible to correct the literature assignments of some quaternary carbon resonances, C-1′, C-3′, C-4′, C-1″, C-2″, C-4″, C-4‴ and C-4⁗ in the case of **6** and those of C-1′ and C-4″ in the case of **7** (Paula et al., 1995). The proton resonance of H-1 appears in the case of **7** as a doublet and its coupling constant with H-2 ($J_{H1\text{-}H2}=8.1$ Hz) indicates these two protons have a *trans* diaxial orientation. Thus, the structure of **7** was assigned to *threo*-carolignan E. However, in the case of **6**, H-1 appears as a slightly broad singlet, suggesting a small coupling constant with H-2. The structure of **6** is then assigned to *erythro*-carolignan E.

Compound **9** has an additional methoxyl group in comparison with the carolignan E isomers **6** and **7** and in this case H-3″ and H-5″ appear as a singlet (δ_H 6.46), because they are chemically equivalent. An analysis of the spectroscopic data (^1H, ^{13}C, COSY, HETCOR and HMBC NMR spectra and MS) showed a good agreement to those assigned to carolignan F (Paula et al., 1995). In this case H-1 also appears as a singlet, indicating the presence of the *erythro* diastereomer.

The ^1H and ^{13}C NMR spectra of **4** are very similar to those of boehmenan H **1**. The absence of the dihydrofuran ring and the presence of the trioxygenated propane moiety in the structure of **4** were suggested by their spectral data as described above for carolignan K **3**. These facts and the assigned molecular formula of $C_{30}H_{34}O_{10}$ (calculated mass: 577.2049) by HR-FABMS (*m/z* 577.2041 $M+Na^+$) are only compatible with the structure of **4** (Fig. 1), which was designated as

carolignan H. The coupling constant $J_{H1\text{-}H2} = 7.5$ Hz indicates the presence of the *threo* isomer of carolignan H.

The known compounds **10**–**20**, were identified by comparisons of spectral data with the commercially available vanillin **10**, *trans*-coniferyl aldehyde **11**, syringaldehyde **12**, *trans*-sinapaldehyde **13** and *p*-hydroxy benzaldehyde **17**, and also with 3-hydroxy-3′-methoxy-4′-hydroxypropiophenone **19** (Achenbach et al., 1988), *N-trans*-feruloyl tyramine **20** (Fukuda et al., 1983; Lajide et al., 1995) and the six lignans, pinoresinol **14**, 4-ketopinoresinol **15** (Otsuka et al., 1989), medioresinol **16** (Tsukamoto et al., 1984; Deyama et al., 1987) and syringaresinol **18** (Ratnayake et al., 1992; Changzeng and Zhongjian, 1997).

3. Experimental

3.1. General

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AMX 300 at 300.13 and 75.47 MHz, respectively; the chemical shifts are expressed in δ (ppm) values relative to TMS as internal reference and the coupling constants J are expressed in Hz. ^{1}H assignments were made using 2D COSY and NOESY (mixing time of 800 ms) experiments, while ^{13}C assignments were made using 2D HETCOR and HMBC experiments (long range C/H coupling constants were optimised to 4 and 7 Hz). MS were obtained at 70 eV electron impact and positive FAB ionisation (nitrobenzyl alcohol as matrix) using a VG Autospect Q mass spectrometer. IR spectra were obtained with a MATTSON 7000 FTIR spectrometer. GC–MS analysis was performed using a HP 5890 chromatograph equipped with a mass selective detector MSD series II (electron-impact ionization). Injector and interface temperatures were 220 and 250°C, respectively. Initial oven temperature was 30°C (8 min), then 10°C/min up to 200°C (5 min), carrier gas helium (flow rate 0.9 ml/min^1), split ratio, 1:100, injections 1 μl. Fused silica capillary column DB-5 (30 m×0.25 mm×0.25 μm) was used. Prep TLC was carried out on silica gel plates (Merck silica gel 60 F_{254}); spots were detected under UV (at 254 and/or 366 nm). Phenolic compounds were detected by the appearance of a brown colour when the TLC plates was sprayed with a (3:2) $CHCl_3$:py solution of $FeCl_3$ (1%) (Browning, 1967). Column chromatography was also performed on silica gel (Merck silica gel 60, 70–230 mesh).

3.2. Plant material

Hibiscus cannabinus, variety Salvador, was harvested in Figueira da Foz, Portugal, in September 1995.

3.3. Extraction and isolation

The stems were separated from foliage and air-dried at room temperature. The core of stems was separated from bark and then finely ground (1470 g) and extracted successively with light petroleum and Me_2CO. The acetone extract (18.5 g) was fractionated by its solubility in $CHCl_3$ and Me_2CO. The residue obtained from the fraction soluble in $CHCl_3$ was defatted with hexane and then separated by silica gel CC. The column was eluted with $CHCl_3$ (fr I and II) and Me_2CO (fr III). Fr I was chromatographed on prep. silica gel TLC, eluting with $CHCl_3$-light petroleum (3:2), to give **5** (58.3 mg), **10** (5.7 mg), **11** (1.5 mg), **12** (10.1 mg), **13** (17.1 mg) **14** (12.1 mg), **15** (25.6 mg), and **16** (4.3 mg). Fr II on prep silica gel TLC, eluted with $CHCl_3$–EtOAc (4:1), yielded **5** (206.5 mg), **14** (2.1 mg), **17** (5.5 mg) and **18** (17.3 mg). Fr III on prep. TLC [silica gel, iso-PrOH–$CHCl_3$ (1:25)] gave **1** (13.9 mg), **2** (12.3 mg), **3** (33.5 mg), **4** (3.3 mg), **5** (64.5 mg), **6** (40.2 mg), **7** (48.5 mg), **8** (17.1 mg), **9** (25.2 mg), **18** (5.2 mg), **19** (5.8 mg) and **20** (47.1 mg).

3.3.1. 2-(4-Hydroxy-3-methoxyphenyl)-5-[3-(4-hydroxy-3-methoxycinnamoyloxy)propyl]-3-hydroxymethyl-7-methoxybenzodihydrofuran (boehmenan H) **1**

Yellowish oil, IR ν_{max} (KBr) cm^{-1}: 3412 (O–H), 2952, 1700 (C=O), 1604, 1516 (C=C), 1430, 1271, 1032. ^{1}H NMR: δ 1.99–2.06 (2H, *m*, H-2‴), 2.71 (2H, *t*, $J = 7.5$ Hz, H-1‴), 3.53–3.67 (1H, *m*, H-3), 3.86 (3H, *s*, 3′-OCH_3), 3.89 (3H, *s*, 3⁗-OCH_3), 3.93 (3H, *s*, 7-OCH_3), 3.86–4.00 (2H, *m*, H-1″), 4.17–4.24 (2H, *m*, H-3‴), 5.54 (1H, *d*, $J = 7.8$ Hz, H-2), 5.64 (1H, *s*, 4′-OH), 5.90 (1H, *s*, 4⁗-OH), 6.31 (1H, *d*, $J = 15.9$ Hz, H-α), 6.68 (2H, *s*, H-4,6), 6.87 (1H, *d*, $J = 8.1$ Hz, H-5′), 6.88–6.93 (2H, *m*, H-6′,5⁗), 6.94 (1H, *s*, H-2′), 7.04 (1H, d, $J = 1.8$ Hz, H-2⁗), 7.09 (1H, *dd*, $J = 1.8$ and 8.4 Hz, H-6⁗), 7.62 (1H, *d*, $J = 15.9$ Hz, H-β). ^{13}C NMR: δ 30.6 (C-2‴), 32.0 (C-1‴), 53.7 (C-3), 56.0 (7,3′,3⁗-OCH_3), 63.5 (C-3‴), 63.7 (C-1″), 87.8 (C-2), 108.8 (C-2′), 109.3 (C-2⁗), 112.3 (C-6), 114.2 (C-5′), 114.7 (C-5⁗), 115.3 (C-α), 116.0 (C-4), 119.4 (C-6′), 123.0 (C-6⁗), 126.9 (C-1⁗), 127.8 (C-9), 133.0 (C-1′), 134.6 (C-5), 144.2 (C-7), 145.0 (C-β), 145.6 (C-4′), 146.6 (C-8,3′), 146.7 (C-3⁗), 148.0 (C-4⁗), 167.4 (CO_2R on C-3‴). EIMS 70eV, *m*/*z* (rel. int.): 536 [M]$^+$ (70), 519 (100), 506 (89), 342 (19), 324 (30), 177 (93). HR–EIMS *m*/*z*: 536.2053, [M]$^+$ (calculated for $C_{30}H_{32}O_9$: 536.2046).

3.3.2. 2-(4-Hydroxy-3-methoxyphenyl)-5-[3-(4-hydroxy cinnamoyloxy)-1-propenyl]-3-(4-hydroxy-3-methoxy cinnamoyloxymethyl)-7-methoxybenzodihydrofuran (boehmenan K) **2**

Yellowish oil, IR ν_{max} (KBr) cm^{-1}: 3400 (O–H), 2940, 1693 (C=O), 1605, 1515 (C=C), 1268, 1168, 832. ^{1}H

NMR: δ 3.84–3.93 (1H, *m*, H-3), 3.84 (3H, *s*, 3′-OCH_3), 3.92 (3H, *s*, 7-OCH_3), 3.93 (3H, *s*, 3‴-OCH_3), 4.43 (1H, *dd*, *J* = 7.5 and 11.1 Hz, H-1″), 4.59 (1H, *dd*, *J* = 5.1 and 11.1 Hz, H-1″), 4.84 (2H, *d*, *J* = 6.3 Hz, H-3‴), 5.55 (1H, *d*, *J* = 7.5 Hz, H-2), 5.65 (1H, *s*, 4′-OH), 5.91 (1H, *s*, 4⁗-OH), 6.24 (1H, *d*, *J* = 15.9 Hz, H-α), 6.18–6.30 (1H, *m*, H-2‴), 6.33 (1H, *d*, *J* = 15.9 Hz, H-α′), 6.66 (1H, *d*, *J* = 15.9 Hz, H-1‴), 6.84 (2H, *d*, *J* = 8.4 Hz, H-3⁗′,5⁗′), 6.90–6.95 (6H, *m*, H-4,6,2′,5′,6′,5‴), 6.98 (1H, *d*, *J* = 1.8 Hz, H-2⁗), 7.04 (1H, *dd*, *J* = 1.8 and 8.4 Hz, H-6⁗), 7.45 (2H, *d*, *J* = 8.7 Hz, H-2⁗′,6⁗′), 7.51 (1H, *d*, *J* = 15.9 Hz, H-β), 7.66 (1H, *d*, *J* = 15.9 Hz, H-β′). ^{13}C NMR δ: 50.4 (C-3), 55.9 (7,3′,3⁗-OCH_3), 65.2 (C-3‴), 65.3 (C-1″), 89.1 (C-2), 108.7 (C-2′), 109.4 (C-2⁗), 110.5 (C-6), 114.3 (C-5′), 114.6 (C-α), 114.7 (C-5⁗), 115.3 (C-4,α′), 115.9 (C-3⁗′,5⁗′), 119.7 (C-6′), 121.4 (C-2‴), 123.2 (C-6⁗), 126.7 (C-1⁗), 127.1 (C-1⁗′), 127.7 (C-9), 130.0 (C-2⁗′,6⁗′), 130.6 (C-5), 132.3 (C-1′), 134.3 (C-1‴), 144.4 (C-7), 144.8 (C-β′), 145.7 (C-β), 145.8 (C-4′), 146.7 (C-3′), 146.8 (C-3⁗), 148.2 (C-8,4⁗), 157.8 (C-4⁗′), 167.1 (CO_2R on C-1″), 167.2 (CO_2R on C-3‴). FABMS *m*/*z* (rel. int.): 703 $[M+Na]^+$ (8), 680 $[M]^+$ (8). HR-FABMS *m*/*z*: 680.2285 $[M]^+$ (calculated for $C_{39}H_{36}O_{11}$: 680.2257).

3.3.3. *threo-1-(4-Hydroxy-3-methoxyphenyl)-3-(4-hydroxy-3-methoxycinnamoyloxy)-2-{4-[3-(4-hydroxycinnamoyloxy)-1-propenyl]-2-methoxyphenoxy}-1-propanol (threo-carolignan K)* **3**

Yellowish oil, IR ν_{max} (KBr) cm^{-1}: 3394 (O–H), 2917, 1702 (C=O), 1604, 1513 (C=C), 1428, 1166, 1031, 833. ^{1}H NMR: δ 3.83 (3H, s, 3⁗-OCH_3), 3.90 (3H, *s*, 2″-OCH_3), 3.92 (3H, *s*, 3′-OCH_3), 4.14–4.24 (1H, *m*, H-3), 4.30–4.37 (2H, *m*, H-2,3), 4.85 (1H, *d*, *J* = 5.7 Hz, H-3‴), 4.95 (1H, *d*, *J* = 7.5 Hz, H-1), 5.70 (1H, *s*, 4′-OH), 6.01 (1H, *s*, 4⁗-OH), 6.24 (1H, *d*, *J* = 15.9 Hz, H-α), 6.33 (1H, *d*, *J* = 15.9 Hz, H-α′), 6.22–6.34 (1H, *m*, H-2‴), 6.64 (1H, *d*, *J* = 15.9 Hz, H-1‴), 6.82 (2H, *d*, *J* = 8.7 Hz, H-3⁗′,5⁗′), 6.88–6.92 (3H, *m*, H-5′,6′,5‴), 6.91–6.93 (1H, *m*, H-2⁗), 6.70–6.95 (1H, *m*, H-3″), 6.94–7.00 (1H, *m*, H-5″), 7.01–7.04 (2H, *m*, H-2′,6⁗), 7.11 (1H, *d*, *J* = 8.1 Hz, H-6″), 7.41 (2H, *d*, *J* = 8.7 Hz, H-2⁗′,6⁗′), 7.49 (1H, *d*, *J* = 15.9 Hz, H-β), 7.67 (1H, *d*, *J* = 15.9 Hz, H-β′). ^{13}C NMR: δ 55.8 (2″-OCH_3), 55.9 (3′,3⁗-OCH_3), 63.1 (C-3), 65.0 (C-3‴), 74.3 (C-1), 85.8 (C-2), 109.2 (C-2⁗), 109.3 (C-2′), 109.8 (C-3″), 114.4 (C-α), 114.5 (C-5′), 114.8 (C-5⁗), 114.9 (C-α′), 115.9 (C-3⁗′,5⁗′), 120.0 (C-6″), 120.1 (C-5″), 120.3 (C-6′), 122.8 (C-2‴), 123.3 (C-6⁗), 126.6 (C-1⁗), 126.8 (C-1⁗′), 130.0 (C-2⁗′,6⁗′), 130.9 (C-1′), 132.3 (C-4″), 133.5 (C-1‴), 145.0 (C-β′), 145.7 (C-4′,β), 146.7 (C-3⁗), 146.8 (C-3′), 147.8 (C-1″), 148.2 (C-4⁗), 150.8 (C-2″), 158.2 (C-4⁗′), 166.9 (CO_2R on C-3), 167.3 (CO_2R on C-3‴). FABMS *m*/*z* (rel. int.): 721 $[M+Na]^+$ (5), 698 (3). HR–FABMS *m*/*z*: 699.2445 $[M+H]^+$ (calculated for $C_{39}H_{39}O_{12}$: 699.2442).

3.3.4. *threo-1-(4-Hydroxy-3-methoxyphenyl)-2-{4-[3-(4-hydroxy-3-methoxycinnamoyloxy)propyl]-2-methoxyphenoxy}-1,3-propanodiol (threo-carolignan H)* **4**

Yellowish oil, IR ν_{max} (KBr) cm^{-1}: 3413 (O–H), 2921, 1698 (C=O), 1600, 1515 (C=C), 1428, 1268, 1159, 1029. ^{1}H NMR: δ 1.98–2.06 (2H, *m*, H-2‴), 2.72 (2H, *t*, *J* = 7.5 Hz, H-1‴), 3.94 (1H, *dd*, *J* = 3.9 and 8.4 Hz, H-3), 3.58–3.65 (1H, *m*, H-3), 3.89 (3H, *s*, 3′-OCH_3), 3.92 (3H, *s*, 7-OCH_3), 3.94 (3H, *s*, 3‴-OCH_3), 3.86–3.99 (1H, *m*, H-2), 4.22 (2H, *t*, J = 6.5 Hz, H-3‴), 4.96 (1H, *d*, J = 7.5 Hz, H-1), 5.64 (1H, *s*, 4′-OH), 5.89 (1H, s, 4⁗-OH), 6.31 (1H, *d*, *J* = 15.9 Hz, H-α), 6.77 (1H, *dd*, *J* = 1.8 and 8.9 Hz, H-5″), 6.79 (1H, *s*, H-3″), 6.89 (1H, *d*, *J* = 8.1 Hz, H-5′), 6.93 (1H, *d*, *J* = 8.2 Hz, H-5⁗), 6.85–6.94 (1H, *m*, H-6′), 6.97 (1H, *s*, H-2′), 7.04 (1H, *d*, *J* = 1.8 Hz, H-2⁗), 7.06 (1H, *d*, *J* = 8.9 Hz, H-6″), 7.09 (1H, *dd*, *J* = 1.8 and 8.2 Hz, H-6⁗), 7.62 (1H, *d*, *J* = 15.9 Hz, H-β). ^{13}C NMR: δ 30.4 (C-2‴), 32.0 (C-1‴), 55.9 (3′-OCH_3), 56.0 (7,3⁗-OCH_3), 61.0 (C-3), 63.6 (C-3‴), 74.0 (C-1), 89.7 (C-2), 109.3 (C-2′,2⁗), 112.3 (C-3″), 114.3 (C-5′), 114.7 (C-5⁗), 115.3 (C-α), 120.3 (C-6′), 121.1 (C-6″), 121.3 (C-5″), 123.1 (C-6⁗), 126.9 (C-1⁗), 131.4 (C-1′), 137.6 (C-4″), 144.9 (C-β), 145.5 (C-4′), 145.7 (C-1″), 146.6 (C-3⁗), 146.8 (C-3′), 148.0 (C-4⁗), 151.1 (C-2″), 167.3 (CO_2R on C-3‴). EIMS 70 eV, *m*/*z* (rel. int.): 554 $[M]^+$ (3), 536 (6), 519 (10), 177 (30), 164 (100), 149 (30), 77 (26). HR–FABMS *m*/*z*: 577.2041 $[M+Na]^+$ (calculated for $C_{30}H_{34}O_{10}$ + Na: 577.2049).

3.3.5. *2-(4-Hydroxy-3-methoxyphenyl)-5-[3-(4-hydroxy-3-methoxycinnamoyloxy)propyl]-3-(4-hydroxy-3-methoxycinnamoyloxymethyl)-7-methoxybenzodihydrofuran (boehmenan)* **5**

Yellowish oil, IR ν_{max} (KBr) cm^{-1}: 3401 (O–H), 2940, 1700 (C=O), 1602, 1515 (C=C), 1430. ^{1}H NMR: δ 1.97–2.06 (2H, *m*, H-2‴), 2.71 (2H, *t*, *J* = 7.6 Hz, H-1‴), 3.84 (3H, *s*, 3′-OCH_3), 3.90 (3H, *s*, 7-OCH_3), 3.93 (6H, *s*, 3⁗,3⁗′-OCH_3), 3.84–3.93 (1H, *m*, H-3), 4.23 (2H, *t*, *J* = 6.5 Hz, H-3‴), 4.42 (1H, *dd*, *J* = 7.7 and 11.2 Hz, H-1″), 4.59 (1H, *dd*, *J* = 5.1 and 11.2 Hz, H-1″), 5.50 (1H, *d*, *J* = 7.8 Hz, H-2), 5.65 (1H, *s*, 4′-OH), 5.91 and 5.92 (2H, 2s, 4⁗-OH and 4⁗′-OH), 6.23 (1H, *d*, *J* = 15.9 Hz, H-α), 6.30 (1H, *d*, *J* = 15.9 Hz, H-α′), 6.69 (1H, *s*, H-6), 6.71 (1H, *s*, H-4), 6.91 (2H, *d*, *J* = 8.3 Hz, H-5⁗,5⁗′), 6.92 (1H, *d*, *J* = 8.1 Hz, H-5′), 6.90–6.94 (3H, m, H-2′,6′,2⁗′), 7.00 (1H, dd, *J* = 1.7 and 8.3 Hz, H-6⁗′), 7.05 (1H, *d*, *J* = 1.7 Hz, H-2⁗), 7.08 (1H, *dd*, *J* = 1.7 and 8.3 Hz, H-6⁗), 7.49 (1H, *d*, *J* = 15.9 Hz, H-β), 7.60 (1H, *d*, *J* = 15.9 Hz, H-β′). ^{13}C NMR: δ 30.7 (C-2‴), 32.1 (C-1‴), 50.7 (C-3), 55.9 and 56.0 (4×OCH_3), 63.7 (C-3‴), 65.4 (C-1″), 88.9 (C-2), 108.8 (C-2′), 109.3 (C-2⁗), 109.4 (C-2⁗′), 112.4 (C-6), 114.2 (C-5′), 114.7 (C-α,5⁗,5⁗′), 115.4 (C-α′), 116.1 (C-4), 119.7 (C-6′), 123.0 (C-6⁗), 123.1 (C-6⁗′), 126.7 (C-1⁗), 126.9 (C-1⁗′), 127.4 (C-9), 132.5 (C-1′), 134.9 (C-5), 144.1 (C-7), 144.9 (C-β′), 145.5 (C-β), 145.7 (C-4′), 146.2 (C-8), 146.6 (C-3′), 146.7 (C-

3‴″,3‴″″), 147.9 (C-4‴″), 148.1 (C-4′″″), 167.0 (CO_2R on C-1″), 167.3 (CO_2R on C-3‴). FABMS *m*/*z* (rel. int.): 735 $[M+Na]^+$ (4), 713 $[M+H]^+$ (4), 518 (6), 391 (8), 329 (12).

3.3.6. *erythro-1-(4-Hydroxy-3-methoxyphenyl)-3-(4-hydroxy-3-methoxycinnamoyloxy)-2-{4-[3-(4-hydroxy-3-methoxycinnamoyloxy)propyl]-2-methoxyphenoxy}-1-propanol (erythro-carolignan E)* **6**

Yellowish oil, IR ν_{max} (KBr) cm^{-1}: 3511 (O–H), 2938, 1700 (C=O), 1631, 1592, 1513 (C=C), 1430, 1031. ^1H NMR: δ 1.97–2.07 (2H, *m*, H-2‴), 2.71 (2H, *t*, $J=7.7$ Hz, H-1‴), 3.88 (6H, *s*, 3′,2″-OCH_3), 3.92 and 3.93 (2×3H, 2s, 2×OCH_3), 4.22 (2H, *t*, $J=6.5$ Hz, H-3‴), 4.22–4.30 (1H, *m*, H-3), 4.47–4.52 (2H, *m*, H-2,3), 4.92 (1H, *s*, H-1), 5.64 (1H, *s*, 4′-OH), 5.95 (2H, s, 4‴,4′″″-OH), 6.24 (1H, *d*, $J=15.9$ Hz, H-α), 6.30 (1H, *d*, $J=15.9$ Hz, H-α′), 6.73–6.77 (2H, *m*, H-3″,5″), 6.83 (1H, *dd*, $J=1.8$ and 8.1 Hz, H-6′), 6.88 (1H, d, $J=8.1$ Hz, H-5′), 6.91* (1H, *d*, $J=8.1$ Hz, H-5′″″), 6.92* (1H, *d*, $J=8.1$ Hz, H-5‴″), 6.67 (1H, *d*, $J=8.3$ Hz, H-6″), 7.05–6.96 (4H, m, H-2′,2‴″,2′″″,6‴″), 7.08 (1H, *dd*, $J=1.8$ and 8.1 Hz, H-6′″″), 7.51 (1H, *d*, $J=15.9$ Hz, H-β), 7.62 (1H, *d*, $J=15.9$ Hz, H-β′). *They can be interchanged. ^{13}C NMR: δ 30.3 (C-2‴), 32.0 (C-1‴), 55.8 (2″-OCH_3), 55.9 (3′,3‴″,3′″″-OCH_3), 62.6 (C-3), 63.6 (C-3‴), 72.0 (C-1), 84.5 (C-2), 108.8 (C-2′), 109.3 (C-2‴″,2′″″), 112.3 (C-3″), 114.1 (C-5′), 114.7 (C-5‴″,5′″″), 114.9 (C-α), 115.3 (C-α′), 119.2 (C-6′), 120.7 (C-6″), 121.1 (C-5″), 123.0 (C-6′″″), 123.2 (C-6‴″), 126.8 (C-1′″″), 126.9 (C-1‴″), 131.0 (C-1′), 137.4 (C-4″), 144.9 (C-β′), 145.0 (C-4′,1″), 145.2 (C-β), 146.6 (C-3′), 146.7 (C-3‴″,3′″″), 148.0 (C-4‴″,4′″″), 151.3 (C-2″), 167.1 (CO_2R on C-3), 167.3 (CO_2R on C-3‴). FABMS *m*/*z* (rel. int.): 753 $[M+Na]^+$ (35).

3.3.7. *threo-1-(4-Hydroxy-3-methoxyphenyl)-3-(4-hydroxy-3-methoxycinnamoyloxy)-2-{4-[3-(4-hydroxy-3-methoxycinnamoyloxy)propyl]-2-methoxyphenoxy}-1-propanol (threo-carolignan E)* **7**

Yellowish oil, IR ν_{max} (KBr) cm^{-1}: 3413 (O–H), 2940, 1700 (C=O), 1631, 1600, 1513 (C=C), 1430, 1172, 1031. ^1H NMR: δ 1.97–2.06 (2H, *m*, H-2‴), 2.71 (2H, *t*, $J=7.7$ Hz, H-1‴), 3.85, 3.93 and 3.94 (3×3H, 3s, 3×OCH_3), 3.90 (3H, *s*, 7-OCH_3), 4.12 (1H, *dd*, $J=4.7$ and 11.9 Hz, H-3), 4.22 (2H, *t*, $J=6.5$ Hz, H-3‴), 4.17–4.27 (1H, *m*, H-2), 4.36 (1H, *dd*, $J=3.3$ and 12.0 Hz, H-3), 4.94 (1H, *d*, $J=8.1$ Hz, H-1), 5.69 (1H, *s*, 4′-OH), 6.00 (2H, *s*, 4‴,4′″″-OH), 6.28 (1H, *d*, $J=15.9$ Hz, H-α), 6.31 (1H, *d*, $J=15.9$ Hz, H-α′), 6.74–6.78 (1H, *m*, H-5″), 6.78 (1H, *s*, H-3″), 6.85–6.94 (5H, *m*, H-2′,5′,6′,5‴″,5′″″), 7.02–7.07 (4H, *m*, H-6″,2‴″,6‴″,2′″″), 7.08 (1H, *dd*, $J=1.9$ and 8.1 Hz, H-6′″″), 7.51 (1H, *d*, $J=15.9$ Hz, H-β), 7.62 (1H, *d*, $J=15.9$ Hz, H-β′). ^{13}C NMR: δ 30.4 (C-2‴), 32.0 (C-1‴), 55.8 (7-OCH_3), 55.9 (3′,3‴″,3′″″-OCH_3), 63.0 (C-3), 63.6 (C-3‴), 74.4 (C-1), 86.3 (C-2), 109.2 (C-2′), 109.3 (C-2‴″,2′″″), 112.3 (C-3″), 114.3 (C-5′), 114.7 (C-5‴″,5′″″,α), 115.3 (C-α′), 120.4 (C-6′), 120.6 (C-6″), 121.0 (C-5″), 123.0 (C-6′″″), 123.2 (C-6‴″), 126.7 (C-1′″″), 126.9 (C-1‴″), 131.1 (C-1′), 137.4 (C-4″), 145.0 (C-β′), 145.5 (C-β), 145.6 (C-4′), 146.0 (C-1″), 146.7 (C-3′), 146.8 (C-3‴″,3′″″), 148.0 (C-4‴″), 148.1 (C-4′″″), 150.7 (C-2″), 166.8 (CO_2R on C-3), 167.3 (CO_2R on C-3‴). FABMS *m*/*z* (rel. int.): 753 $[M+Na]^+$ (12).

3.3.8. *2-(4-Hydroxy-3,5-dimethoxyphenyl)-5-[3-(4-hydroxy-3-methoxycinnamoyloxy)propyl]-3-(4-hydroxy-3-methoxycinnamoyloxymethyl)-7-methoxybenzodihydrofuran (boehmenan D)* **8**

Yellowish oil, IR ν_{max} (KBr) cm^{-1}: 3411 (O–H), 2939, 1701 (C=O), 1603, 1515 (C=C), 1429, 1269, 1159. ^1H NMR: δ 1.99–2.08 (2H, *m*, H-2‴), 2.72 (2H, *t*, $J=7.5$ Hz, H-1‴), 3.84 (6H, *s*, 3′,5′-OCH_3), 3.90 (3H, *s*, 7-OCH_3), 3.93 (6H, s, 3‴″,3′″″-OCH_3), 3.81–3.93 (1H, *m*, H-3), 4.23 (2H, *t*, $J=6.5$ Hz, H-3‴), 4.44 (1H, *dd*, $J=7.8$ and 11.1 Hz, H-1″), 4.61 (1H, *dd*, $J=5.1$ and 11.1 Hz, H-1″), 5.47 (1H, *d*, $J=8.1$ Hz, H-2), 5.52 (1H, *s*, 4′-OH), 5.90 (2H, *s*, 4‴″,4′″″-OH), 6.23 (1H, *d*, $J=15.9$ Hz, H-α), 6.30 (1H, *d*, $J=15.9$ Hz, H-α′), 6.67 (2H, *s*, H-2′,6′), 6.70 (1H, *s*, H-6), 6.71 (1H, *s*, H-4), 6.91* (1H, *d*, $J=8.1$ Hz, H-5′″″), 6.92* (1H, *d*, $J=8.1$ Hz, H-5‴″), 6.97 (1H, *d*, $J=1.8$ Hz, H-2‴″), 7.03 (1H, *d*, $J=1.8$ Hz, H-2′″″), 7.03** (1H, *dd*, $J=1.8$ and 8.1 Hz, H-6′″″), 7.08** (1H, *dd*, $J=1.8$ and 8.1 Hz, H-6‴″), 7.48 (1H, *d*, $J=15.9$ Hz, H-β), 7.60 (1H, *d*, $J=15.9$ Hz, H-β′). * And ** they can be interchanged. ^{13}C NMR: δ 30.7 (C-2‴), 32.1 (C-1‴), 50.8 (C-3), 55.9* (7-OCH_3), 56.0* (3‴″,3′″″-OCH_3), 56.3 (3′,5′-OCH_3), 63.7 (C-3‴), 65.4 (C-1″), 89.3 (C-2), 103.2 (C-2′.6′), 109.3 (C-2′″″), 109.4 (C-2‴″), 112.5 (C-6), 114.7 (C-α,5‴″,5′″″), 115.4 (C-α′), 116.1 (C-4), 123.0 (C-6‴″,6′″″), 126.6 (C-1′″″), 126.9 (C-1‴″), 127.3 (C-9), 131.7 (C-1′), 134.7 (C-4′), 135.0 (C-5), 144.2 (C-7), 144.9 (C-β′), 145.6 (C-β), 146.2 (C-8), 146.8 (C-3‴″,3′″″), 147.0 (C-3′,5′), 148.0 (C-4′″″), 148.2 (C-4‴″), 167.0 (CO_2R on C-1″), 167.3 (CO_2R on C-3‴). *They can be interchanged. FABMS *m*/*z* (rel. int.): 765 $[M+Na]^+$ (35), 743 $[M+H]^+$ (14), 742 $[M]^+$ (17), 549 (90).

3.3.9. *erythro-1-(4-Hydroxy-3-methoxyphenyl)-3-(4-hydroxy-3-methoxycinnamoyloxy)-2-{4-[3-(4-hydroxy-3-methoxycinnamoyloxy)propyl]-2,6-dimethoxyphenoxy}-1-propanol (erythro-carolignan F)* **9**

Yellowish oil, IR ν_{max} (KBr) cm^{-1}: 3416 (O–H), 2936, 1703 (C=O), 1592, 1515 (C=C), 1428, 1271, 1173, 1125. ^1H NMR: δ 1.96–2.09 (2H, *m*, H-2‴), 2.71 (2H, *t*, $J=7.5$ Hz, H-1‴), 3.85 (6H, *s*, 2″,6″-OCH_3), 3.89, 3.92 and 3.93 (3×3H, 3*s*, 3×OCH_3), 4.24 (2H, *t*, $J=6.5$ Hz, H-3‴), 4.32 (1H, *dd*, $J=3.6$ and 11.7 Hz, H-3), 4.45 (1H, *dd*, $J=7.7$ and 11.6 Hz, H-3), 4.55 (1H, *m*, $J=3.4$ Hz, H-2), 4.90 (1H, *s*, H-1), 5.61 (1H, *s*, 4′-OH), 5.95 (1H, *s*, 4′″″-OH), 5.97 (1H, *s*, 4‴″-OH), 6.26 (1H, *d*, $J=15.9$ Hz,

H-α), 6.31 (1H, *d*, *J* = 15.9 Hz, H-α′), 6.46 (2H, *s*, H-3″,5″), 6.77 (1H. *dd*, *J* = 1,2 and 8.1 Hz, H-6′), 6.87 (1H, *d*, *J* = 8.1 Hz, H-5′), 6.90* (1H, *d*, *J* = 8.1 Hz, H-5‴″), 6.92* (1H, *d*, *J* = 8.1 Hz, H-5‴), 7.01–7.05 (4H, m, H-2′,2‴,2‴″,6‴″), 7.08 (1H, *dd*, *J* = 1.5 and 8.1 Hz, H-6‴), 7.52 (1H, *d*, *J* = 15.9 Hz, H-β), 7.62 (1H, *d*, *J* = 15.9 Hz, H-β′). *They can be interchanged. ^{13}C NMR: δ 30.3 (C-2‴), 32.7 (C-1‴), 55.9 (2″,6″,3‴,3‴″-OCH_3), 56.1 (3′-OCH_3), 62.5 (C-3), 63.6 (C-3‴), 71.5 (C-1), 83.1 (C-2), 105.3 (C-3″,5″), 108.4 (C-2′), 109.2 (C-2‴″), 109.3 (C-2‴), 114.0 (C-5′), 114.6* (C-5‴″), 114.7* (C-5‴), 115.2 (C-α′), 115.5 (C-α), 118.8 (C-6′), 123.0 (C-6‴,6‴″), 126.8 (C-1‴,1‴″), 130.7 (C-1′), 132.6 (C-1″), 137.9 (C-4″), 144.7 (C-β,4′), 145.0 (C-β′), 146.6 (C-3‴″), 146.7 (C-3′,3‴), 147.9 (C-4‴″), 148.0 (C-4‴), 151.3 (C-2″,6″), 167.1 (CO_2R on C-3), 167.3 (CO_2R on C-3‴). *They can be interchanged. FABMS *m*/*z* (rel. int.): 783 $[M+Na]^+$ (14).

3.4. Transesterification of boehmenan **5**

Compound **5** (~ 50 mg) was added to a 1% solution of NaOMe in MeOH (7.5 ml) and the resulting mixture was refluxed for 3 h. After this period, the mixture was acidified (pH 6) with 2 M H_2SO_4, extracted with Et_2O and separated by prep. silica gel TLC, eluting with $CHCl_3$–EtOAc (9:1). The three most abundant spots were collected and identified as methyl ferulate **21**, 3-hydroxymethyl-5-(3-hydroxypropyl)-2-(4-hydroxy-3-methoxyphenyl)-7-methoxybenzodihydrofuran **22** and 2,4′-dihydroxy-3,3′-dimethoxy-5-(3-hydroxypropyl) stilbene **23**.

3.4.1. 3-Hydroxymethyl-5-(3-hydroxypropyl)-2-(4-hydroxy-3-methoxyphenyl)-7-methoxybenzodihydrofuran **22**

Colourless oil, ^{1}H NMR: δ 1.88–1.92 (2H, *m*, H-2‴), 2.68 (2H, *t*, *J* = 7.7 Hz, H-1‴), 3.58–3.64 (1H, *m*, H-3), 3.70 (2H, *t*, *J* = 6.3 Hz, H-3‴), 3.87 and 3.89 (2×3H, 2*s*, 2×OCH_3), 3.87–3.92 (2H, *m*, H-1″), 5.55 (1H, *d*, *J* = 7.5 Hz, H-2), 5.63 (1H, *s*, 4′-OH), 6.68 (2H, *s*, H-4,6), 6.95 (3H, *m*, H-2′,5′,6′). ^{13}C NMR: δ 32.0 (C-1‴), 34.6 (C-2‴), 53.8 (C-3), 56.0 (7,3′-OCH_3), 62.3 (C-3‴), 63.9 (C-1″), 87.9 (C-2), 108.8 (C-2′), 112.7 (C-6), 114.2 (C-5′), 115.9 (C-4), 119.4 (C-6′), 127.7 (C-9), 133.1 (C-5), 135.4 (C-1′), 144.2 (C-8), 145.6 (C-4′), 146.5 (C-3′), 146.6 (C-7). EIMS 70 eV, *m*/*z* (rel. int.): 360 $[M]^+$ (85), 342 (100), 330 (66), 167 (30), 137 (36), 77 (13).

3.4.2. 2,4′-Dihydroxy-3,3′-dimethoxy-5-(3-hydroxy propyl)stilbene **23**

Colourless oil, ^{1}H NMR: δ 1.89–1.92 (2H, *m*, H-2″), 2.67 (2H, *t*, *J* = 7.7 Hz, H-1″), 3.71 (2H, *t*, *J* = 6.5 Hz, H-3″), 3.90 and 3.96 (2×3H, 2*s*, 2×OCH_3), 5.67 (1H, *s*, 4′-OH), 5.82 (1H, *s*, 2-OH), 6.61 (1H, *d*, *J* = 1.8 Hz, H-4), 6.90 (1H, *d*, *J* = 8.3 Hz, H-5′), 7.00 (1H, *d*, *J* = 1.8 Hz, H-6), 7.04 (1H, *dd*, *J* = 1.9 and 8.3 Hz, H-6′), 7.09 (1H, *d*, *J* = 1.9 Hz, H-2′), 7.10 (1H, *d*, *J* = 16.4 Hz, H-β), 7.27 (1H, *d*, *J* = 16.4 Hz, H-α). ^{13}C NMR: δ 32.0 (C-1″), 34.5 (C-2″), 55.9 and 56.1 (2×OCH_3), 62.3 (C-3″), 108.2 (C-2′), 109.5 (C-4), 114.4 (C-5′), 118.0 (C-6), 120.6 (C-6′), 120.7 (C-α), 123.5 (C-1), 129.2 (C-β), 130.5 (C-1′), 133.0 (C-5), 141.3 (C-2), 145.4 (C-4′), 146.6 (C-3, 3′). EIMS 70 eV, *m*/*z* (rel. int.): 330 $[M]^+$ (100), 286 (13), 253 (10), 137 (13), 77 (4).

3.5. Identification of formaldehyde by GC–MS

The boehmenan **5** transesterification mixture, obtained as described above, was directly injected in the GC–MS chromatograph. The identification of the formaldehyde peak was done by comparison its mass spectrum with the equipment's mass spectral library.

Acknowledgements

The authors thank the University of Aveiro and FCT-Lisbon for funding the Research Unit 62/94. One of us (A.M.L.S.) is grateful to PRAXIS XXI for a grant (BD/3412/94).

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