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Lignans from *Ochroma lagopus* Swartz

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Abstract: An investigation of the chemical constituents of the ethanolic extract of the heartwood of ***Ochroma lagopus*** Swartz led to the isolation of nine new lignans named boehmenan B-D and carolignan A-F. Their chemical structures have been deduced on the basis of ^{1}H, ^{13}C, ^{1}H-homonuclear COSY, HETCOR, NOEDIFF and DEPT nmr spectral studies.

INTRODUCTION

Ochroma lagopus Swartz, from the Bombacaceae family, is a tree widely distributed from southern Mexico through the West Indies to Bolivia[1], including the Amazon region in Brazil. Due to the low density of its wood (0.12 g.cm^{-3}) it is widely used in the Guianas and the Amazon state in Brazil in the manufacture of raft floats and coffins[2]. An infusion from its bark is also given to cows postpartum[3].

Previous studies on this plant have lead to the isolation and identification of the fatty acids palmitic, stearic, oleic, linoleic and linolenic; the steroids β-sitosterol and stigmasterol; the coumarins scopoletin and cleomiscosin A and the lignans boehmenan and secoisolariciresinoyl diferulate[4]. A continuation of our phytochemical investigation of ***Ochroma lagopus*** wood ethanolic extract has led to the isolation and structural elucidation of nine new lignans designated as boehmenan B-D and carolignan A-F.

The structures of these new compounds have been elucidated by detailed NMR spectroscopic studies.

RESULTS AND DISCUSSION

The ethanolic extract of the heartwood of ***Ochroma lagopus*** was submitted to repeated column chromatography on silica gel, and finally to preparative-scale recycling HPLC. This led to the separation of fractions A-J. All these fractions were very viscous oils, some of which solidified on standing, after some time.

Fractions A, B, E and J consisted of the pure compounds **1**, **2**, **5** and **7** respectively. Fractions C, D and I consisted of an isomeric mixture of compounds (**3a** + **3b** + **2**), (**4a** + **4b** + **5**) and (**6a** + **6b**) respectively. Fractions F, G and H showed IR and ^{1}H-NMR spectra very similar to all the other fractions, but they were all very complex mixtures and therefore it was not possible to identify any compounds from them.

FRACTION E (Compound **5**): The ^{1}H-NMR spectrum revealed that this fraction consisted of a pure compound 5. This compound, boehmenan, has previously been isolated from ***Boehmeria tricuspis***[5] and from ***Ochroma lagopus***[4]. A detailed discussion of its structural elucidation is given by Paula[4]. In the present paper, its ^{1}H-NMR and ^{13}C-NMR data are reproduced in tables 1 and 3 for purposes of comparison.

The infrared spectrum of all fractions were very similar to that of boehmenan **5** with absorptions at 3400 cm^{-1} (OH), 1700 cm^{-1} (α,β-unsaturated ester carbonyl) and 1630, 1600, 1518 cm^{-1} (υ C=C).

FRACTION D (Compounds **4a**, **4b** and **5**): The EIMS of this fraction was identical to that of compound **5**, and showed a M$^+$ ion peak at m/z 712, corresponding to the molecular formula $C_{40}H_{40}O_{12}$. The ^{1}H-NMR spectrum was very complex and clearly showed the presence of boehmenan (ca. 20 %) together with two other compounds. The resonances from these two compounds were only slightly different from those of boehmenan (Table 1), suggesting that all three compounds were very close analogues.

Table 1. ^{1}H-NMR Data (400 MHz) for Compounds **4a**, **4b**, **5** and **7**

H	**5** δ(m,J)	**4a** δ(m,J)	and	**4b** δ(m,J)	**7** δ(m,J)
2	6.96(d.2.1)	7.77(d,2.0)	and	7.72(d,2.0)	6.96(d,2.0)
3 (**OMe**)*	3.82(s)	3.82(s)	and	3.82(s)	3.92(s) or 3.91(s)
4 (**OH**)	5.92(s,br)	5.89(s)	and	5.85(s)	5.84(s) or 5.83(s)
5	6.92(d.8.3)	6.91(d.8.0)	and	6.90(d,8.0)	6.90(d,8.0)
6	7.05(dd.8.3;2.1)	7.08(dd,8.0;2.0)	and	7.11(dd,8.0;2.0)	7.02(dd,8.0;2.0)
7	7.48(d.16.0)	6.80(d.12.8)	and	6.79(d,12.8)	7.47(d,16.0)
8	6.22(d.16.0)	5.81(d.12.8)	and	5.75(d,12.8)	6.22(d,16.0)
2'	6.93(m)	6.92(m)	and	6.89(m)	6.65(s)
3' (**OMe**)	3.88(s)	3.82(s)	and	3.82(s)	3.83(s)
4' (**OH**)	5.65(s,br)	5.59(s)	and	5.58(s)	5.48(s)
5'	6.89(m)	6.90(m)	and	6.90(m)	3.83 (s, **OMe**)
6'	6.87(m)	6.92(m)	and	6.86(m)	6.65(s)
7'	5.48(d.7.7)	5.50(d.7.4)	and	5.42(d,7.4)	5.44(d,7.8)
8'	3.85(m)	3.85(m)	and	3.78(m)	3.86(m)
9'	4.41(dd.11.1;7.8)	4.40(dd,11.1;7.8)	and	4.36(dd,11.0;7.0)	4.43(dd,11.2;8.0)
	4.57(dd.11.1;5.1)	4.58(dd,11.0;5.7)	and	4.47(dd,11.0;5.7)	4.60(dd,11.2;5.0)
2"	6.68(s,br)	6.66(s,br)	and	6.64(s,br)	6.65(s,br)
3" (**OMe**)	3.91(s)	3.92(s)	and	3.92(s)	3.89(s)
6"	6.70(s,br)	6.66(s,br)	and	6.65(s,br)	6.70(s,br)
7"	2.69(t,7.5)	2.68(t,7.8)	and	2.62(t,7.8)	2.70(t,7.5)
8"	2.02(tt,7.5;6.5)	2.00(tt,7.8;6.5)	and	1.95(tt,7.8;6.5)	2.02(tt,7.5;6.5)
9"	4.22(t,6.5)	4.21(t,6.5)	and	4.14(t,6.5)	4.22(t,6.5)
2'''	7.00(d,2.1)	7.04(d,2.0)	and	6.98(d,2.0)	7.02(d,2.0)
3''' (**OMe**)	3.91(s)	3.92(s)	and	3.92(s)	3.92(s) or 3.91(s)
4''' (**OH**)	5.92(s,br)	5.84(s,br)	and	5.84(s,br)	5.83(s) or 5.84(s)
5'''	6.91(d,8.3)	6.88(d,8.0)	and	6.86(d,8.0)	6.91(d,8.0)
6'''	7.05(dd,8.3;2.1)	7.09(dd,8.0;2.0)	and	7.04(dd,8.0;2.0)	7.06(dd,8.0;2.0)
7'''	7.58(d,16.0)	7.60(d,16.0)	and	7.48(d,16.0)	7.58(d,16.0)
8'''	6.28(d,16.0)	6.29(d,16.0)	and	6.21(d,16.0)	6.29(d,16.0)

* Some of the -OMe assignments for compounds **4a** and **4b** could be reversed.

The region of δ=3.82-3.92 contained singlets corresponding to 8 methoxyl groups (not including the 4xOMe from boehmenan itself).

The major difference between the spectrum of boehmenan and the two new compounds was the presence of two pairs of doublets at 6.80/5.81 (12.8 Hz) and 6.79/5.75 (12.8 Hz) due to a *cis*-α,β-unsaturated ester, confirmed by the large (11 %) NOE effect between the *cis* hydrogens H7-H8. The other sets of doublets at 7.60/6.29 (16.0 Hz) and 7.48/6.21 (16.0 Hz) are due to α,β-unsaturated ester units having a *trans* arrangement, and thus closely resembling boehmenan in this part of each molecule. As both double bonds are *trans* in boehmenan, the only possible structures to fit these data are compounds **4a** and **4b**, having the *trans-cis* and *cis-trans* arrangements respectively.

As all four sets of signals have about the same intensity, it is not possible to say which *cis* double bond is related with which *trans* double bond, nor with which other sets of signals. Despite this, from a COSY experiment it was possible to make many assigments in more detail, as can be seen in Table 1.

The doublets at 7.77 (2.0 Hz) and 7.72 (2.0 Hz) are assigned to H2 (**4a and 4b**). These protons are each strongly deshielded by the *cis* double bonds compared with H2 and H2‴ in boehmenan.

FRACTION J (Compound **7**): The infrared spectrum of this fraction was also very similar to that of boehmenan, and showed absorptions due to OH, α,β-unsaturated ester and C=C stretching.

The presence of two α,β-unsaturated ester units having a *trans* double bond, as in boehmenan itself, was clearly indicated by the two pairs of doublets at 7.58 (16.0 Hz, H7‴)/6.29 (16.0 Hz, H8‴) and 7.47 (16.0 Hz, H7)/6.22 (16.0 Hz, H8).

The presence of two guaiacol units attached to the double bonds was evident from the following sets of resonances: 7.06 (dd, 8.0 and 2.0 Hz; H6‴); 6.91 (d, 8.0 Hz; H5‴); 7.02 (d, 2.0 Hz; H2‴); 7.02 (dd, 8.0 and 2.0 Hz; H6); 6.90 (d, 8.0 Hz; H5) and 6.96 (d, 2.0 Hz; H2). The two OCH_3 groups appeared at δ=3.92 and 3.91.

The major difference between this compound and boehmenan was the presence of one extra methoxyl group (δ=3.83, singlet, 6H) at the aromatic nucleus attached to the dihydrofuran ring. The introduction of this methoxyl greatly simplified the spectrum, compared with boehmenan. The three multiplets around 6.87-6.93 due to protons H2', H5' and H6' in boehmenan, became a singlet at δ=6.65, due to the two chemically equivalent protons H2' and H6' in compound **7**. All the other resonances for compound **7** were very similar to those of boehmenan. The relative stereochemistry at carbons C-7' and C-8' is probably *trans*, as in boehmenan, for in both cases $J_{7',8'}$=7.8 Hz.

FRACTION A (Compound **1**): The infrared spectrum of this compound also showed a striking resemblance to that from boehmenan. The ^{1}H-NMR spectrum of **1** showed basically the same (J and δ) resonances as boehmenan (see Table 2), but with a few differences. The absence of the dihydrofuran ring was suggested by the following data: a doublet at δ=6.76 (J=2.0 Hz) attributed to H2"; a double doublet at δ=6.76 (J=7.9 Hz; J=2.0 Hz) attributed to H6" and a doublet at δ=7.01 (J=7.9 Hz) due to H5". This attribution was confirmed by a ^{13}C-NMR (DEPT) spectrum showing a protonated carbon resonance at δ=120.63 due to C5", in place of the signal at δ=127.30 in the spectrum of boehmenan from the quaternary carbon C5". Also, the H7' resonance in boehmenan (doublet, J=7.7 Hz, δ=5.48) became a doublet (J=3.0 Hz) at δ=4.91.

The hydrogen H8' in compound **1**, is on a carbon attached to an oxygen, but also further removed from the nearest aromatic ring compared with boehmenan. The net result is a deshielding by 0.6 ppm, i.e. a resonance at δ=4.45 (multiplet). Carbon C8' was also deshielded by 34 ppm in relation to boehmenan and appeared at δ=84.40 (CH from DEPT).

The positioning of the ether bridge at C8' and C4'' was further confirmed by the 9 % NOE effect between H8' and H5'', the 4 % between H7' and H6'. It was also clear from the four ^{1}H-NMR resonances at δ=5.89 (2 OH), 5.60 and 4.20 from the four hydroxyl, which were identified *via* mutual tranfer of saturation, in the course of the NOEDIFF experiments.

FRACTION B (Compound **2**): The ^{1}H-NMR and ^{13}C-NMR spectra for this fraction showed it to be a single compound and as can be seen from tables 2 and 3, all the resonances were very similar to those of compound **1**. The difference between their two spectra were attributed to a difference in relative stereochemistry at carbons C7' and C8'. The resonance of H7' appeared in both compounds **1** and **2** as a doublet at δ=4.91 and 4.92 respectively. However, in compound **2** the coupling constant $J_{7',8'}$=8.0 Hz is much higher than $J_{7',8'}$=3.0 Hz for compound **1**. Although it was not possible to attribute the absolute stereochemistries of **1** and **2** from the NMR data, computer model of these compounds using a PCModel (P/3.2) program (Serena Software) gives calculated couplings in agreement with the proposed structures.

FRACTION C (Compounds **3a**, **3b** and **2**): Despite extensive preparative HPLC separation on this fraction, its ^{1}H-NMR spectrum showed the presence of 36 % of compound **2** and two other compounds accounting for 36 % and 28 %.

Some resonances of these two compounds (Table 2) were superimposed upon those corresponding to **2** but the assignment of the hydrogen absorptions of each was possible with the help of a 2D-homonuclear (COSY) spectrum.

The ^{1}H-NMR spectrum included eight singlets between δ=3.81-3.94 due to 8 methoxyls (the singlets of the 4 methoxyls due to compound **2** were also present in the same region).

A pair of doublets at δ=7.61/6.30 (J=16.0 Hz) was assigned to H7'''/H8''', and the other pair of doublets at δ=6.82/5.80 (J=12.8 Hz) was due to H7/H8 of the major isomer **3a** (36 %) which has a *cis* double bond at C7/C8.

The minor isomer **3b** (28 %), having a *cis* double bond at the other side of the molecule, showed a pair of doublets at δ=7.53/6.20 (J=16.0 Hz, *trans* double bond) due to H7''' and H8''' respectively, and another pair of doublets at δ=6.81/5.82 (J=12.8 Hz, *cis* double bond) attributed to H7 and H8.

The resonances of H2 for **3a** and **3b** were deshielded by 0.7 ppm, in comparison with the same hydrogens in compound **2**, because of the *cis* double bond, and appeared respectively at δ=7.71 (J=2.0 Hz) and δ=7.73 (J=2.0 Hz). This deshielding effect of the *cis* double bond, on the hydrogen ortho to the methoxyl group, was also observed in the case of compounds **4a** and **4b**.

Although there is a possibility of free rotation around the C7'-C8' single bond, the doublets at δ=4.82 and δ=4.92 attributed to H7' of **3a** and **3b** respectively, showed a large coupling constant of J=8.2 Hz. As the value of this constant is very close to the coupling between H7' and H8' ($J_{7',8'}$=8.0 Hz) for **2**, we assume that compounds **3a** and **3b** had the same relative stereochemistry at C7'-C8' as compound **2**.

FRACTION 1 (Compound **6a** and **6b**): This fraction is composed of two diastereoisomers at C7'/C8' in the ratio of 4:1.

The ^{1}H-NMR spectrum showed three singlets at δ=3.92, 3.91, 3.88 (one methoxyl each) and another one at δ=3.84 integrating for 2 methoxyls, for the major isomer. The corresponding methoxyls for the minor isomer appeared at δ=3.94, 3.92, 3.84 (6H) and 3.81.

The presence of two equivalent methoxyls at carbons C3" and C5", making the C-ring symmetrical, was confirmed by the broad singlet at δ=6.44 for **6b** (δ=6.42 for the minor isomer **6a**), assigned to the two equivalent hydrogens H2" and H6".

The resonances from the hydrogens of the *trans* alkene (J=16.0 Hz) for the major isomer appeared at δ=7.61 (H7'''), 7.50 (H7), 6.29 (H8''') and 6.24 (H8). The corresponding signals for the minor isomer appeared at δ=7.62, 7.55, 6.35 and 6.30.

The resonances for the aromatic hydrogens appeared between δ=6.80-7.10, and a full assignment was possible only for the major isomer (Table 2) with the help of decoupling experiments.

For the major isomer, H7' appeared as a triplet at δ=4.89 ($J_{7',8'}$=$J_{7',OH}$=3 Hz), and the 7'-OH as a doublet at δ=4.30. This was confirmed by irradiation at both signals and also at δ=4.54 (H8'). The coupling between H7' and H8' was identical to the coupling for the same hydrogens in compound **1**, and this lead us to suggest that the relative stereochemistry at C7'/C8' is the same for these two compounds.

In the case of the minor isomer, the 7'-OH appeared as a doublet at δ=4.75 (J=1.6 Hz), and H7' as a double doublet at δ=5.09 ($J_{7',8'}$=8.4 Hz and $J_{7',OH}$=1.6 Hz). These assignments were also confirmed by decoupling experiments. The relative stereochemistry at C7'/C8' for this minor isomer and compound **2** is believed to be the same, for in both cases the value of $J_{7',8'}$ is approximately 8.0 Hz.

EXPERIMENTAL

Infrared spectra were recorded on a Shimadzu IR408 spectrophotometer. NMR spectra were measured at 400 MHz for ^{1}H and 100.6 MHz for ^{13}C, on a Bruker AC400 instrument. Samples were dissolved in a suitable solvent, usually $CDCl_3$, and referenced indirectly to TMS as internal standard. Mass spectra were recorded on a V.G. Analytical ZAB-IF mass spectrometer. Flash chromatography was performed using Crosfield Sorbil C60 (40-60μm). Preparative-scale recycling HPLC analysis were performed in a system consisted of a Shimadzu LC-6AD pump, a SPD-6AV detector operated at 290 nm, a Rheodyne 7125 injector fitted with a 500 μL loop, and a Shimadzu C-R4A chromatopac recorder.

Plant Material, Extraction and Isolation: Trunks of ***O. lagopus*** were collected at the Dendrology Sector at the Federal University of Viçosa-MG-Brazil in July 1993. After having their bark removed, they were cut into short lengths, dried at room temperature and powdered. This powder (3850 g) was extracted in a Soxhlet apparatus with hexane to yield 11 g of an oil, and then with ethanol to yield 40 g of a solid material. The ethanolic extract (40 g) was fractioned on a silica gel column (50 x 8 cm), eluting with a mixture of petrol:diethyl ether of increasing polarity and finally with diethyl ether:methanol (9:1 v/v).

A total 383 fractions of 80 mL each were collected, concentrated and monitored by TLC analysis on silica gel. Fractions 255-272 were combined (4 g) and submitted to another fractionation on silica gel column (25 x 3 cm), eluting with a mixture of dichloromethane:ethyl acetate (5:2 v/v). Fractions of 20 mL were collected, and fractions 35 to 46 were combined. This combined fraction (550 mg) was then submitted to a preparative-scale recycling HPLC using a Shim-Pack silica column (25 x 2.0 cm) and dichloromethane:ethyl

Table 2. ^{1}H-NMR Data (400 MHz) for Compounds **1**, **2**, **3a**, **3b**, **6a** and **6b**#

H	**1** δ(m,J)	**2** δ(m,J)	**3a** δ(m,J)	and	**3b** δ(m,J)	**6a** δ(m,J)	and	**6b** δ(m,J)
2	6.99(d,2.1)	7.02(d,2.0)	7.71(d,2.0)	and	7.73(d,2.0)	7.00(m)		*
3 (**OMe**)	3.86(s)	3.93(s)	3.81(s)	and	3.82(s)	3.94(s)	and	3.92(s)
4 (**OH**)	5.89(s,br)	5.92(s,br)	5.85(s,br)	and	5.85(s,br)	5.87(s,br)	and	5.86(s,br)
5	6.91(d,8.3)	6.90(d,8.3)	6.92(m)	and	6.92(m)	6.86(m)		*
6	7.02(dd,8.3,2.1)	7.07(dd,8.3,2.1)	7.10(dd,8.0,2.0)	and	7.06(m)	7.01(m)		*
7	7.49(d,16.0)	7.53(d,16.0)	6.82(d,12.8)	and	6.81(d,12.8)	7.55(d,16.0)	and	7.50(d,16.0)
8	6.22(d,16.0)	6.25(d,16.0)	5.80(d,12.8)	and	5.82(d,12.8)	6.30(d,16.0)	and	6.24(d,16.0)
2'	7.01(d,2.0)	7.02(d,2.0)	7.02	and	7.02	7.01(d,1.8)		*
3' (**OMe**)	3.86(s)	3.92(s)	3.81(s)	and	3.82(s)	3.92 (s)	and	3.91(s)
4' (**OH**)	5.60(s,br)	5.62(s,br)	5.58(s,br)	and	5.58(s,br)	5.57(s,br)	and	5.53(s,br)
5'	6.87(d,8.0)	6.90(d,8.0)	6.92(m)	and	6.86(m)	6.76(dd,8.0,1.8)	and	6.76(dd,8.0,1.8)
6'	6.82(dd,8.0;2.0)	6.87(dd,8.0,2.0)	6.76	and	6.76	6.88(d,8.0)		*
7'	4.91(d,3.0)	4.92(d,8.0)	4.82(d,8.2)	and	4.92(d,8.2)	5.09(dd,8.4,1.6)	and	4.89(t,3.0)
7'-**OH**	4.20(s,br)					4.75(d,1.6)	and	4.30(d,3.0)
8'	4.45(m)	4.20(m)	4.10(m)	and	4.20(m)	4.54(ddd,7.7;4.0,3.0)		*
9'	4.28(dd,16.1,7.0)	4.11(dd,12.0,5.0)	4.04(dd,12.0,5.4)	and	4.11(dd,12.0,5.4)	4.13(dd,12.0;6.0)	and	4.43(dd,11.8,7.7)
	4.47(m)	4.34(dd,12.0;3.4)	4.28(dd,12.0;3.2)	and	4.34(dd,12.0;3.2)	3.99(dd,12.0;3.0)	and	4.31(dd,11.8;4.0)
2"	6.76(d,2.0)	6.76(d,2.0)	6.70	and	6.70	6.42(s,br)	and	6.44(s,br)
3" (**OMe**)	3.92(s)	3.89(s)	3.94(s)	and	3.94(s)	3.89(s)	and	3.88(s)
5"	7.01(d,7.9)	7.13(d,7.9)			---			---
6"	6.76(dd,7.9;2.0)	6.74(dd,7.9;2.0)			---	6.42(s,br)	and	6.44(s,br)
7"	2.69(dd,7.7;2.0)	2.69(dd,7.2;7.0)	2.69(t,7.8)	and	2.62(t,7.8)	2.68(m)	and	2.69(t,7.5)
8"	2.01(m)	2.00(m)	2.01(tt,7.8;6.5)	and	1.94(tt,7.8;6.5)	2.03(m)	and	2.03(tt,7.5;6.5)
9"	4.21(t,6.5)	4.20(t,6.5)	4.13(t,6.5)	and	4.20(t,6.5)	4.22(t,6.5)	and	4.23(t,6.5)
2"'	7.01(d,2.1)	7.02(d,2.0)	7.01(m)	and	7.01(m)	7.01(m)		*
3"' (**OMe**)	3.92(s)	3.84(s)	3.93(s)	and	3.94(s)	3.81(s)	and	3.84(s)
4"' (**OH**)	5.89(s,br)	5.92(s,br)	5.85(s,br)	and	5.85(s,br)	5.87(s,br)	and	5.84(s,br)
5"'	6.94(d,8.3)	6.89(d,8.3)	6.86(d,8.0)	and	6.85(d,8.0)	6.86(m)		*
6"'	7.08(dd,8.3;2.1)	7.08(d,br)	7.11(dd,8.0;2.0)	and	7.08(m)	7.08(dd,8.0;2.0)		*
7"'	7.60(d,16.0)	7.60(d,16.0)	7.61(d,16.0)	and	7.53(d,16.0)	7.62(d,16.0)	and	7.61(d,16.0)
8"'	6.29(d,16.0)	6.29(d,16.0)	6.30(d,16.0)	and	6.20(d,16.0)	6.35(d,16.0)	and	6.29(d,16.0)

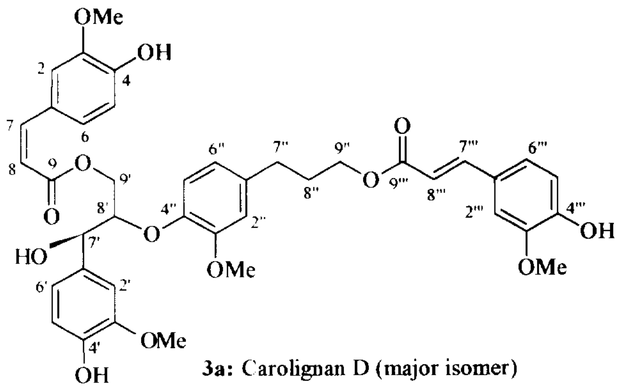
(#) Assignments made via COSY spectra.

(*) The resonances of these hydrogens for the minor isomer were similar to those of the major isomer but were not fully assignable.

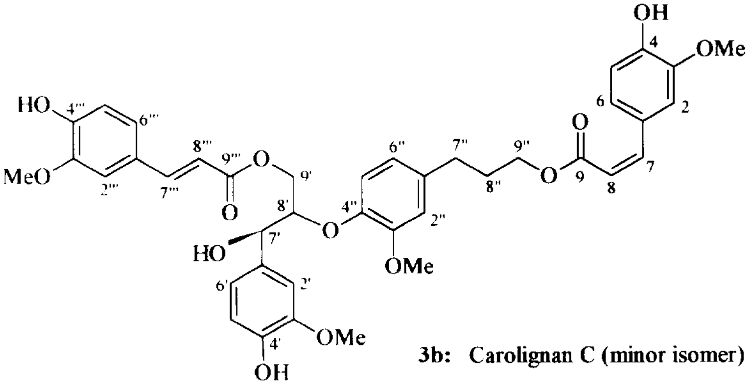
Table 3. ^{13}C-Shifts (100.6 MHz) for Compounds **1**, **2** and **5** $^{(a)}$

C	**5**	**1**	**2**
1	126.58	126.75	126.68
2	109.27 (or 109.34)	109.24	109.26
3	146.68	146.64	147.60
4	145.58	145.00	145.93
5	114.61 (or 114.59)	114.62	114.63
6	122.92 (or 122.87)	122.93	123.10
7	145.37	145.11	145.35
8	114.64	114.86	114.63
9	165.84	166.98	166.68
1'	134.81	137.27	137.31
2'	108.73	108.70	109.19
3'	146.52	147.89	147.66
4'	148.04	151.26	150.66
5'	114.01	114.00	114.25
6'	119.57	119.12	120.30
7'	88.77	71.94	74.28
8'	50.55	84.40	86.19
9'	65.26	62.49	62.91
1"	132.43	130.92	131.10
2"	112.40	112.29	112.24
3"	147.87	147.92	148.03
4"	146.16	146.47	146.55
5"	127.30	120.63	120.55
6"	116.03	120.96	120.90
7"	32.01	31.89	31.89
8"	30.56	30.25	30.28
9"	63.60	63.52	63.51
1"'	126.58	126.75	126.68
2"'	109.34 (or 109.27)	109.20	109.26
3"'	146.68	146.64	147.60
4"'	144.01	144.96	145.55
5"'	114.59 (or 114.61)	114.57	114.63
6"'	122.87 (or 122.92)	122.93	122.95
7"'	144.74	144.83	144.84
8"'	115.24	115.23	115.26
9"'	167.18	167.19	167.19
OMe	55.81	55.83	55.86
OMe	55.81	55.83	55.83
OMe	55.88	55.83	55.69
OMe	55.81	55.75	55.81

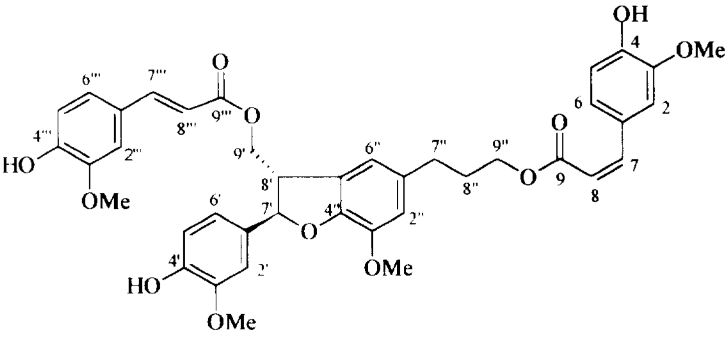
(a) Assignments have been made by HETCOR and DEPT



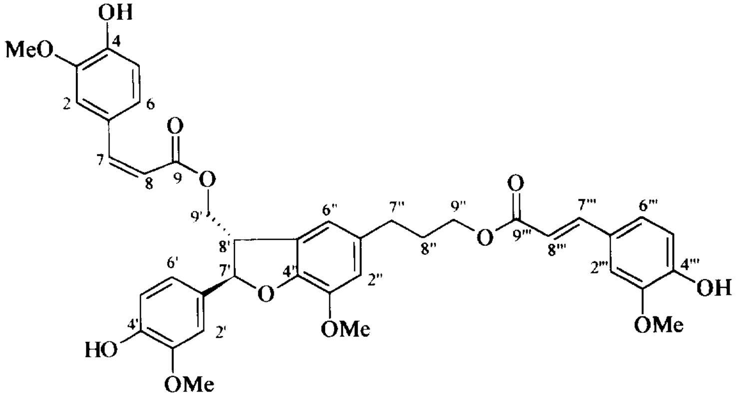
3a: Carolignan D (major isomer)



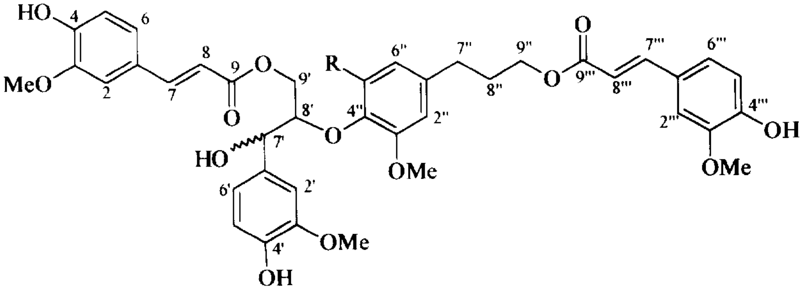
3b: Carolignan C (minor isomer)



4a: Boehmenan B



4b: Boehmenan C

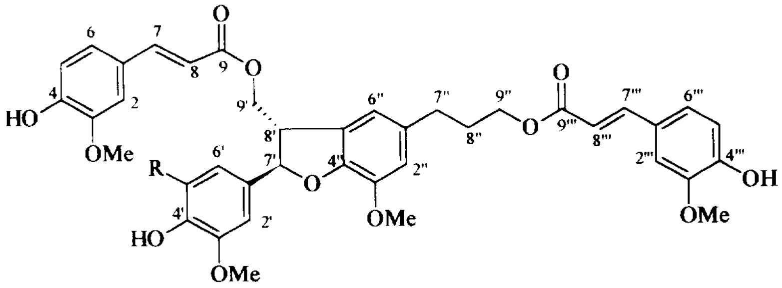


1: 7'α-OH, R = H

2: 7'β-OH, R = H

6a: 7β-OH, R = OCH_3 (minor isomer)

6b: 7'α-OH, R = OCH_3 (major isomer)



5: R = H, Boehmenan

7: R = OMe, Boehmenan D

acetate (3:1 v/v) as solvent at a flow rate of 3 mL/min, and a mean value of 100 mg/500μL per injection. Six cycles of 40 min each were carried out. Ten fractions were colleted: A (12 mg), B (13 mg), C (3.6 mg), D (3.6 mg), E (50 mg), F (0.6 mg), G (3.9 mg), H (29 mg), I (5.1 mg) and J (1.4 mg). All fractions were then analyzed by HPLC, using a Shim-Pack silica column (25 x 0.46 cm) at a flow rate of 1 mL/min using dichloromethane:ethyl acetate (3:1 v/v) as solvent, to shown on those conditions only one peak.

FRACTIONS A, B and C: Very viscous colorless oils and showed the same IR and MS data.

EIMS (70 eV) m/z (%): 730($M^{+\cdot}$, not found), 712(9) (M^+ - H_2O), 536(3) (M^+ - ferulic acid), 518(7) (M^+ - H_2O - ferulic acid), 506(11), 358(24), 194(43), 177(37), 164(100), 150(17), 137(28), 123(7); **IR** (KBr) υ_{max}/cm^{-1}: 3400 (OH), 3070, 3005, 2982, 2930, 2840, 1704, 1630, 1600, 1523, 1460, 1435, 1365, 1272, 1160, 1120, 1042, 850, 774; **^{1}H-NMR** and **^{13}C-NMR** of each of these fractions see Table 2.

FRACTION D: Viscous colorless oil that solidifies on standing after several days.

EIMS (70 eV) m/z (%): 712(7) (M^+), 536(3) (M^+ - ferulic acid), 518(100) (M^+ - H_2O - ferulic acid), 342(16), 324(22) (M^+ - 2 x ferulic acid), 309(7), 194(46), 177(88), 145(17), 51(43); **IR** (KBr) υ_{max}/cm^{-1}: 3400, 3063, 3003, 2930, 2840, 1705, 1631, 1600, 1518, 1270, 1158, 1125, 963; **^{1}H-NMR**: see Table 1.

FRACTION I: Viscous colorless oil.

EIMS (70 eV) m/z (%): 766(M^+; not found), 548(1) (M^+ - H_2O - ferulic acid), 388(26), 194(100), 177(33), 164(20), 137(16), 91(9); **IR** (KBr) υ_{max}/cm^{-1}: 3400 (OH), 3072, 3000, 2980, 2932, 2843, 1702, 1628, 1600, 1520, 1457, 1437, 1360, 1270, 1161, 1119, 1040, 850, 770; **^{1}H-NMR**: see Table 2.

FRACTION J: Viscous colorless oil.

EIMS (70 eV) m/z (%): 742 (M^+ not found), 548(100) (M^+ - ferulic acid), 372(22), 354(15), 315(5), 194(40), 177(85); **IR** (KBr) υ_{max}/cm^{-1}: 3400, 3060, 3000, 2928, 2841, 1702, 1630, 1600, 1520, 1267, 1162, 1128, 960; **^{1}H-NMR**: see Table 1.

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