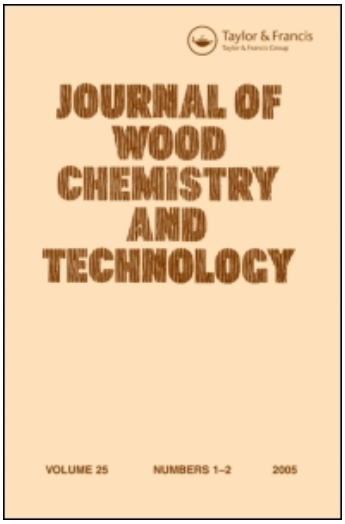

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Reilly, Mary J. , Wallis, Adrian F. A. , Lundquist, Knut and Stomberg, Rolf(1992) 'Stereochemistry of Neolignans - A Revised Structure for a Neolignan Isolated from the Roots of *Piper capense*', Journal of Wood Chemistry and Technology, 12: 4, 471 — 483
To link to this Article: DOI: 10.1080/02773819208545792
URL: http://dx.doi.org/10.1080/02773819208545792

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 12(4), 471-483 (1992)

STEREOCHEMISTRY OF NEOLIGNANS - A REVISED STRUCTURE FOR A NEOLIGNAN ISOLATED FROM THE ROOTS OF *PIPER CAPENSE*

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Dedicated to the memory of Professor Kyösti V. Sarkanen

ABSTRACT

The *erythro* 8-O-4' neolignan IIIb was synthesized and was found to have identical ^{1}H and ^{13}C NMR characteristics to a neolignan reported as a component of the roots of *Nardostachys jatamansi*. The NMR spectral characteristics of compound IIIb were also identical with those of a neolignan previously obtained from the roots of *Piper capense*, for which the unlikely 8-O-3' structure IVa had been proposed. Two further *erythro* 8-O-4' compounds IIIc and IIId were prepared, and their assigned ^{13}C NMR signals were consistent with those of IIIb. At this time, there appears to be no evidence for the existence of 8-O-3' neolignans as plant extracts.

INTRODUCTION

Lignans and neolignans are an important group of optically active natural products containing two phenylpropane moieties linked through carbon-carbon or carbon-oxygen bonds.[1] In one class of neolignans, the dimers are ether-linked through the 8-O-4' atoms as in formula I, and an increasing number of examples of the class are being reported.

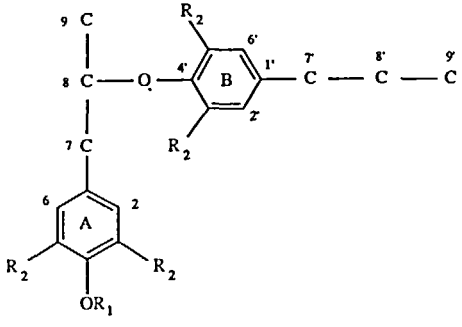
The *threo* and *erythro* neolignans IIa and IIIa were first described as products of oxidative dimerisation of *(E)*-isoeugenol, and their configurations followed from ^{1}H NMR spectra and from the stereochemistry of borohydride reduction of their derived C-7 carbonyl compound.[2] The configurations have been confirmed for *threo* and *erythro* guaiacyl[3] and syringyl[4] ethers of type II and III by x-ray crystal-structure studies.

Both neolignans IIa and IIIa were subsequently found as extracts of the bark of *Machilus thunbergii*[5] and the aril of *Myristica fragrans*.[6] The veratryl neolignans IIb and IIIb have also been isolated from plant extracts; the *threo* isomer virolin (IIb) from the leaves of *Virola surinamensin*[7] and both virolin and the *erythro* isomer IIIb from the roots of *Nardostachys jatamansi*.[8]

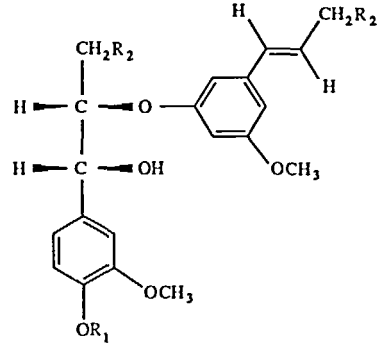
Green *et al.*[9,10] recently isolated a neolignan from the roots of *Piper capense* which was assigned the unusual 8-O-3' structure IVa. In support of this structure, the authors cited the analogous 8-O-3' neolignan glucoside IVb found as a component of citrus peelings.[11] However, structure IVb was later revised to that of an 8-O-4' neolignan.[12] We present evidence to show that the compound described by Green *et al.* is the recently-described 8-O-4' neolignan IIIb rather than IVa.

RESULTS AND DISCUSSION

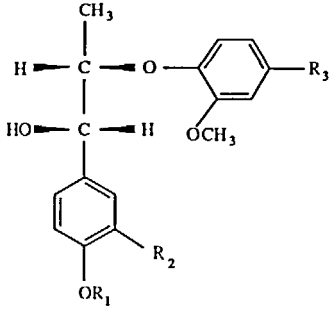
The three *erythro* 8-O-4' compounds IIIb-d were prepared by the three-step reaction sequence of Adler *et al.*;[13] IIIb and IIId from propioveratrone and IIIc from 4'-methoxypropiophenone. In the final step, the *erythro* isomers (III)



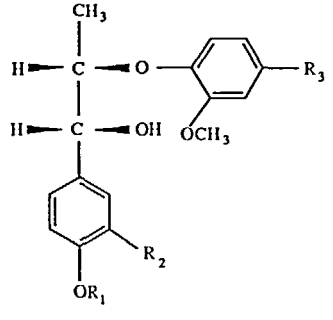
I R_1 = H or CH_3
R_2 = H or OCH_3



IV		R_1	R_2
	a	CH_3	H
	b	Glc	OH



II



III

	R_1	R_2	R_3
a	H	OCH_3	*(E)*-CH=CH-CH_3
b	CH_3	OCH_3	*(E)*-CH=CH-CH_3
c	CH_3	H	*(E)*-CH=CH-CH_3
d	CH_3	OCH_3	CH_3

TABLE 1

^{13}C NMR Signals of *erythro* Compounds III in $CDCl_3$

Carbon no.	IIIb		IIIc	IIId
	This work	Ref. 8		
1	132.66	132.6	132.10	132.67
2	109.66	109.6	113.61	109.55
3	148.27	148.2	127.41	148.17
4	148.93	148.9	158.88	148.87
5	110.95	110.0	127.41	110.87
6	119.67	119.8	113.61	121.63
7	73.68	73.7	73.57	73.44
8	82.30	82.4	82.38	82.62
9	13.45	13.6	13.33	13.50
1'	133.63	133.7	133.66	133.38
2'	109.44	109.4	109.47	113.11
3'	151.46	151.5	151.51	151.31
4'	145.74	145.7	145.77	144.37
5'	118.54	118.5	119.03	118.46
6'	119.03	119.0	110.83	120.08
7'	130.53	130.6	130.56	21.24
8'	124.94	125.0	124.91	--
9'	18.36	18.5	18.37	--
OMe	55.91	56.1	55.86	55.88
OMe'	55.91	56.1	55.24	55.88

were obtained by a stereoselective reduction of the 7-keto function with sodium borohydride. Although both IIIc and IIId have been synthesized previously, this is the first reported synthesis of compound IIIb.

Both the ^{1}H and ^{13}C NMR spectra of IIIb correspond to those reported for the neolignan IIIb by Bagchi *et al.*[8] with the exception of the ^{13}C signal assigned to C-5 (Table 1), which occurred 0.95 ppm upfield (δ 110.0) in Bagchi's spectrum. However, this chemical shift was reported incorrectly, and should be amended to δ 110.8,[14] consistent with the signal in the spectrum of synthetic IIIb. Thus the proposed structure of IIIb is confirmed. The ^{13}C NMR data for the *erythro* compounds IIIc and IIId, with modified substitution in ring

A and ring B respectively, serve to reinforce the spectral assignments for IIIb. Compound IIIc, the methyl ether of an 8-O-4' neolignan, has been synthesized previously by Achenbach *et al.*,[15] while IIId has been prepared for use as a lignin model compound.[16,17]

The NMR data reported for the neolignan from *Piper capense* by Green *et al.*[9] were obtained in deuteriobenzene, and are thus not directly comparable to those of IIIb measured in deuteriochloroform by Bagchi *et al.*[8] Comparison of the ^{13}C NMR spectrum of the synthetic *erythro* IIIb in C_6D_6 with that of Green's neolignan shows that the compounds have signals which correspond within experimental error (Table 2). The ^{13}C NMR spectral data of the IIIb analogues, IIIc and IIId, are also given, and are consistent with the assignments made to the spectral signals of IIIb.

The ^{1}H NMR spectrum of the synthetic IIIb in C_6D_6 also has corresponding signals to those reported for the neolignan isolated by Green *et al.*[9] (Table 3), although the chemical shifts of the signals assigned to H-8, H-9 and H-7' differ by up to 0.1 ppm. These authors recognised the signals centred at δ 6.63, 6.92 and 7.11 as an AMX pattern, consistent with the 1,3,4-trisubstituted ring A, and they carried out several correlation NMR experiments, establishing the connectivity of the ^{1}H and ^{13}C signals. As expected, the same AMX pattern of signals was found in the ^{1}H NMR spectrum of compound IIId in deuteriobenzene, but not in the spectrum of the 4-methoxyphenyl neolignan IIIc. Green *et al.* reported that the signals of the three protons on ring B occurred as two singlets at δ 6.75 (1H) and 6.86 (2H), and the two protons *ortho* to the propenyl side-chain had differing chemical shifts.[9] The absence of significant coupling between these protons prompted these authors to propose the 1,3,5 substitution pattern for ring B and thus the unusual 8-O-3' structure IVa for the neolignan. An alternative explanation consistent with the data is to consider structure IIIb for the neolignan, with the coincident signals assigned to H-5' and H-6', and the higher field signal to H-2'. The assignments of the ^{1}H and ^{13}C NMR signals for deuteriobenzene solutions of IIIb were confirmed by a C-H 2-D correlation and an extended DEPT experiment.[18]

The correspondence of the spectral data for Green's neolignan with those of the synthetic neolignan IIIb indicates that both compounds are identical.

TABLE 2

^{13}C NMR Signals of *erythro* Compounds III in C_6D_6

Carbon no.	IIIb		IIIc	IIId
	This work	Ref. 9		
1	133.69	133.39	133.06	133.91
2	111.15	110.99	113.91	111.11
3	149.45	149.40	*	149.31
4	150.20	150.10	159.38	150.10
5	112.26	112.18	*	112.20
6	119.67	120.17	113.91	119.74
7	74.27	74.02	74.03	74.26
8	82.45	82.78	82.38	82.44
9	13.68	13.74	13.45	13.69
1'	133.69	133.84	133.64	132.71
2'	110.27	110.12	110.26	113.75
3'	152.01	152.10	151.97	151.73
4'	146.77	146.60	146.74	145.44
5'	118.98	118.82	119.47	118.97
6'	119.50	119.43	119.66	121.91
7'	131.38	131.31	131.38	21.15
8'	124.36	124.37	124.30	--
9'	18.42	18.43	18.41	--
OMe	55.70	55.59	54.77	55.66
OMe'	55.50	55.37	55.50	55.66

*signals obscured by solvent signals

There appears to be no evidence for the existence of 8-O-3' neolignans, a B-ring substitution pattern not found in Nature. Braga *et al.*[19] earlier discussed the NMR spectra and conformational analysis of selected 8-O-4' neolignans. They suggested a connection between the occurrence of the *threo* isomer virolin (IIb) and the preponderence of the *threo* isomer IIa over the *erythro* isomer IIIa among the oxidative dimerisation products of isoeugenol.[2] However, both *erythro* neolignans IIIa and IIIb have subsequently been isolated, and an alternative biogenetic route to these compounds is probable. In support of this, Umezawa *et al.*[20] have recently demonstrated that lignans in *Forsythia* species

TABLE 3

^{1}H NMR Signals of the *erythro* Neolignan IIIb in C_6D_6

Proton no.	This work	Ref. 9
H-9 (3H)	1.32 (d)	1.22 (d)
	(J = 6.4 Hz)	(J = 6.4 Hz)
H-9' (3H)	1.72 (dd)	1.70 (dd)
	(J = 6.1, 1.0 Hz)	(J = 6.6, 2.0 Hz)
OMe (3H)	3.34 (s)	3.30 (s)
OMe (3H)	3.43 (s)	3.40 (s)
OMe (3H)	3.48 (s)	3.48 (s)
H-8 (1H)	4.45 (dq)	4.35 (dq)
	(J = 6.3, 3.1 Hz)	(J = 6.4, 3.2 Hz)
H-7 (1H)	5.05 (br s)	5.05 (br s)
H-8' (1H)	6.00 (dq)	5.99 (dq)
	(J = 15.6, 6.4 Hz)	(J = 15.7, 6.6 Hz)
H-7' (1H)	6.33 (dd)	6.40 (dd)
	(J = 15.6, 1.2 Hz)	(J = 15.7, 2.0 Hz)
H-5 (1H)	6.63 (d)	6.63 (d)
	(J = 8.2 Hz)	(J = 8.3 Hz)
H-2' (1H)	6.77 (s)	6.75 (s)
H-5',6' (2H)	6.86 (s)	6.86 (s)
H-6 (1H)	6.94 (dd)	6.92 (dd)
	(J = 8.4, 2.0 Hz)	(J = 8.3, 2.0 Hz)
H-2 (1H)	7.14 (d)	7.11 (d)
	(J = 2.2 Hz)	(J = 2.0 Hz)

are formed *via* a direct stereochemically-controlled coupling of monomers rather than a typical peroxidase-catalysed reaction in the presence of hydrogen peroxide.

EXPERIMENTAL

NMR spectra were measured at 200 or 100 MHz for protons, and 50 or 25 MHz for carbon, on Bruker AM-100 and AC-200 instruments, and chemical shifts are reported in ppm downfield from TMS.

(E)-Isoeugenol acetate was obtained from A. Boake, Roberts & Co. Ltd., and 4'-methoxypropiophenone and creosol were from the Aldrich Chemical Company. Propioveratrone, m.p. 62-3°C, was prepared by methylation of propioguaiacone, which in turn was prepared by treatment of guaiacol with propionic acid/BF_3.[21]

(E)-Isoeugenol

This was prepared by the mild deacetylation procedure of Marcuccio.[22] A solution of *(E)*-isoeugenol acetate (10.0 g) and zinc acetate dihydrate (1.05 g, 0.1 equiv.) in ethanol (250 mL) was heated under reflux for 8 h. The solvent was removed, and the residue was dissolved in dichloromethane (250 mL), washed successively with water and saturated salt solution (50 mL), and dried with sodium sulfate. After evaporation of the solvent, a colourless liquid remained (7.8 g), identified as *(E)*-isoeugenol by gc-ms.

2-Bromo-4'-methoxypropiophenone

The bromoketone was obtained by direct crystallisation of the bromination reaction mixture in ethanol.[23] To a solution of 4'-methoxypropiophenone (5.0 g) in ethanol (10 mL) a solution of bromine (5.37 g, 1.1 equiv.) in ethanol (20 mL) was added and the mixture was kept at

20°C for 3 h. The resulting hydrogen bromide was removed from the solution by bubbling with nitrogen. On cooling to 0°C, white crystals appeared, which were washed with ethanol to give the 2-bromo-4'-methoxypropiophenone as needles (3.9 g), m.p. 65-7°C. (Lit.[14] m.p. 66-7°C). After concentration of the mother liquor, a further amount of product (1.5 g) was obtained.

2-Bromopropioveratrone

Bromination of propioveratrone (1.5 g) in ethanol (8 mL) as above gave 2-bromopropioveratrone (1.05 g) as needles, m.p. 82-3°C. (Lit.[24] m.p. 82-82.6°C). A second crop of crystals gave further material (440 mg).

1-(4-Methoxyphenyl)-2-[2-methoxy-4-*(E)*-propenylphenoxy]-propan-1-one

To a solution of 2-bromo-4'-methoxypropiophenone (1.0 g) and *(E)*-isoeugenol (1.0 g, 1.48 equiv.) in dry acetone (20 mL) anhydrous potassium carbonate (1.0 g) was added and the mixture was heated under reflux for 4 h. The potassium carbonate was separated by filtration, washed with acetone, and the acetone was removed by distillation. The residue was dissolved in dichloromethane and washed twice with 1M sodium hydroxide, water, saturated salt solution and dried. Evaporation of the solvent gave a gum (1.32 g). (Lit.[14] oily product). ^{1}H NMR ($CDCl_3$) δ 1.70 (3H, d, J = 6.9 Hz, H-9), 1.83 (3H, d, J = 5.1 Hz, H-9'), 3.84 (6H, s, 2 x OCH_3), 5.44 (1H, q, J = 6.9 Hz, H-8), 5.88-6.20 (1H, m, H-8'), 6.30 (1H, d, J = 16.0 Hz, H-7'), 6.7-7.0 (3H, m, H-2',5',6'), 6.91 (2H, d, J = 9.0 Hz, H-2,6) and 8.11 (2H, d, J = 9.0 Hz, H-3,5).

1-(3,4-Dimethoxyphenyl)-2-[2-methoxy-4-*(E)*-propenylphenoxy]-propan-1-one

A solution of 2-bromopropioveratrone (1.0 g) and *(E)*-isoeugenol (900 mg, 1.5 equiv.) in acetone containing anhydrous potassium carbonate (1.0 g) was heated under reflux for 4 h. The reaction mixture was

worked up as above to give the product as an gum (1.25 g), which exhibited one spot on tlc. (Lit.[7] m.p. 123-5°C). ^{1}H NMR ($CDCl_3$) δ 1.71 (3H, d, J = 6.9 Hz, H-9), 1.83 (3H, d, J = 5.0 Hz, H-9'), 3.84 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 5.41 (1H, q, J = 6.9 Hz, H-8), 5.88-6.20 (1H, m, H-8'), 6.31 (1H, d, J = 16.0 Hz, H-7'), 6.7-6.9 (3H, m, H-2',5',6'), 6.87 (1H, d, J = 8.5 Hz, H-5), 7.67 (1H, d, J = 2.0 Hz, H-2) and 7.81 (1H, J = 9.0, 2.0 Hz, H-6). The ^{1}H NMR characteristics are identical with those reported.[7]

erythro-1-(4-Methoxyphenyl)-2-[2-methoxy-4-*(E)*-propenylphenoxy]-propan-1-ol (IIIc)

A solution of 1-(4-methoxyphenyl)-2-[2-methoxy-4-*(E)*-propenylphenoxy]-propan-1-one (500 mg) and sodium borohydride (106 mg, 2 equiv.) in ethanol (20 mL) was kept at 20°C for 3 h. The excess sodium borohydride was destroyed by dropwise addition of acetic acid, and the solvent was removed *in vacuo*. Water (20 mL) was added, and the product IIIc was isolated *via* dichloromethane extraction to give an oil (490 mg). (Lit.[14] oil). ^{1}H NMR ($CDCl_3$) δ 1.17 (3H, d, J = 6.9 Hz, H-9), 1.87 (3H, d, J = 5.2 Hz, H-9'), 3.78 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 4.33 (1H, dq, J = 6.4, 3.0 Hz, H-8), 4.85 (1H, d, J = 2.9 Hz, H-7), 6.0-6.3 (1H, m, H-8'), 6.38 (1H, d, J = 16.0, H-7'), 6.7-7.0 (3H, m, H-2',5',6'), 6.86 (2H, d, J = 8.9 Hz, H-3,5) and 7.27 (2H, d, J = 8.5 Hz, H-2,6). ^{1}H NMR (C_6D_6) δ 1.27 (3H, d, J = 6.3 Hz, H-9), 1.74 (3H, d, J = 5.8 Hz, H-9'), 3.32 (6H, s, 2 x OCH_3), 4.38 (1H, dq, J = 6.4, 3.1 Hz, H-8), 5.04 (1H, br s, H-7), 5.8-6.2 (1H, m, H-8'), 6.33 (1H, d, J = 16.0, H-7'), 6.7-7.0 (3H, m, H-2',5',6'), 6.81 (2H, d, J = 7.8 Hz, H-3,5) and 7.36 (2H, d, J = 8.8 Hz, H-2,6). ^{13}C NMR, see Tables 1 and 2.

erythro-1-(3,4-Dimethoxyphenyl)-2-[2-methoxy-4-*(E)*-propenylphenoxy]-propan-1-ol (IIIb)

1-(3,4-Dimethoxyphenyl)-2-[2-methoxy-4-*(E)*-propenylphenoxy]-propan-1-one (500 mg) reduced with sodium borohydride as above gave IIIb as an oil

(486 mg). (Lit.[8] oil). ^{1}H NMR ($CDCl_3$) δ 1.18 (3H, d, J = 6.3 Hz, H-9), 1.87 (3H, d, J = 5.3 Hz, H-9'), 3.86 (3H, s, OCH_3), 3.88 (6H, s, 2 x OCH_3), 4.34 (1H, dq, J = 7.0, 2.8 Hz, H-8), 4.85 (1H, br s, H-7), 6.0-6.3 (1H, m, H-8'), 6.38 (1H, d, J = 16.0, H-7') and 6.75-7.05 (6H, m, ArH). For further NMR data, see Tables 1-3.

erythro-1-(3,4-Dimethoxyphenyl)-2-[2-methoxy-4-methylphenoxy]-propan-1-ol (IIId)

Compound IIId was prepared from 2-bromopropioveratrone and creosol by the methods above, and was crystallised from hexane-ether, m.p. 42-5°C (Lit.[17] crystalline substance). ^{1}H NMR ($CDCl_3$) δ 1.21 (3H, d, J = 6.4 Hz, H-9), 2.37 (3H, s, H-7') 3.90 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 4.31 (1H, dq, J = 6.4, 3.0 Hz, H-8), 4.84 (1H, d, J = 3.0 Hz, H-7), 6.7-7.0 (6H, m, ArH). ^{1}H NMR (C_6D_6) δ 1.33 (3H, d, J = 6.2 Hz, H-9), 2.15 (3H, s, H-7') 3.37 (3H, s, OCH_3), 3.45 (3H, s, OCH_3), 3.49 (3H, s, OCH_3), 4.45 (1H, dq, J = 6.3, 3.1 Hz, H-8), 5.10 (1H, br s, H-7), 6.5-7.0 (3H, m, H-2',5',6'), 6.64 (1H, d, J = 8.2 Hz, H-5), 7.04 (1H, dd, J = 8.1, 1.8 Hz, H-6) and 7.15 (1H, d, J = 1.8 Hz, H-2). ^{13}C NMR, see Tables 1 and 2.

ACKNOWLEDGEMENTS

The authors thank Mr R. I. Willing, CSIRO, for suggesting and assisting with the extended DEPT experiment, and Mr L. R. Biltris, CSIRO, for his valuable technical assistance.

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