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Article

Synthesis and Structural Confirmation of Natural 1,3-Diarylpropanes

Paulo A. de Almeida*[a], *Silas V. Fraiz Jr.*[a], *and Raimundo Braz-Filho*[b]

[a]*Departamento de Química, Instituto de Ciências Exatas, Universidade Federal Rural do Rio de Janeiro, 23851-970 Seropédica - Rio de Janeiro, Brazil;*

[b]*Setor de Química de Produtos Naturais, LCQUI - CCT, Universidade Estadual do Norte Fluminense, 28051-620 Campos - RJ, Brazil*

1-(4’-Hidroxi-5’-metil-2’-metoxifenil)-3-(2"-hidroxi-4",5"-metileno-dioxifenil)propano (**7**), 1,3-diarilpropano isolado de *Iryanthera laevis* (Myristicaceae), 1-(4’-hidroxi-2’-metoxifenil)-3-(4"-hidroxifenil)propano (**2**, broussonina B) e 1-(2’-hidroxi-4’-metoxifenil)-3-(4"-hidroxifenil) propano (**1**, broussonina A), isolados de *Broussonetia papyrifera* Vent. (Moraceae), e 1-(2’,4’-dimetoxifenil)-3-(4"-hidroxifenil)propano (**4**), um produto sintético oriundo da hidrogenação catalítica da 4-O-benzil-2’,4’-dimetoxichalcona, foram sintetizados. A rota sintética utilizada envolveu hidrogenação catalítica (Pd-C 10%) de chalconas obtidas por condensação aldólica de acetofenonas e benzaldeídos adequadamente substituídos.

1-(4’-Hydroxy-5’-methyl-2’-methoxyphenyl)-3-(2"-hydroxy-4",5"-methylenedioxyphenyl) propane (**7**), 1,3-diarylpropane isolated from *Iryanthera laevis*, 1-(4’-hydroxy-2’-methoxyphenyl)-3-(4"-hydroxyphenyl)propane (**2**, broussonin B) and 1-(2’-hydroxy-4’-methoxyphenyl)-3-(4"-hydroxyphenyl)propane (**1**, broussonin A), isolated from *Broussonetia papyrifera* Vent. (Moraceae), and 1-(2’,4’-dimethoxyphenyl)-3-(4"-hydroxyphenyl)propane, a synthetic product prepared by catalytic hydrogenation of 4-O-benzyl-2’,4’-dimethoxychalcone, were synthesized. The synthetic pathway employed in this work involved the catalytic hydrogenation of chalcones obtained by base condensation of acetophenones and benzaldehydes.

Keywords: Iryanthera laevis, *1,3-Diarylpropanes, reduction of chalcones*

Introduction

1,3-Diarylpropanes have been isolated mainly from *Virola* and *Iryanthera* species (Myristicaceae)[1-4]. However, in 1980 Takasugi and co-workers reported the structures of the new 1,3-diarylpropanes broussonins A (**1**), B (**2**) and C (**3**) isolated from *Broussonetia papyrifera* Vent. (Moraceae), which revealed antifungal activities in tissues of this plant inoculated with *Fusarium solani* f. sp. *mori*[5]. These diarylpropanoids, classified as phytoalexins, were not detected in the uninoculated tissues of this same plant and showed activity against *Bipolaris leersiae* at 10^{-4} -10^{-5} M[6].

1,3-Diarylpropanes have been synthesized to confirm structures of natural products[7-9]. In a previous study[7], the synthesis of 1-(2’-hydroxy-5’-methyl-4’-methoxyphenyl)-3-(2"-hydroxy-4",5"-methylenedioxyphenyl)propane (**6**) was described, in order to confirm the structure proposed for the natural product previously isolated from *Iryanthera laevis*[2]. Comparison of the spectral data of the synthetic and natural products revealed different compounds and, consequently, a new isomeric structure 1-(4’-hydroxy-5’-methyl-2’-methoxyphenyl)-3-(2"-hydroxy-4”,5”-methylenedioxyphenyl)propane (**7**) was proposed[7].

In this paper, we report the synthesis of four 1,3-diarylpropanes: 1-(4’-hydroxy-2’-methoxyphenyl)-3-(4’’-hydroxyphenyl)propane (**2**, broussonin B) to confirm the structure proposal for the natural product isolated from *Broussonetia papyrifera* Vent.[5], 1-(4’-hydroxy-5’-methyl-2’-methoxyphenyl)-3-(2"-hydroxy-4", 5"-methylenedioxyphenyl)propane (**7**) to confirm the structure proposal[7] for the natural product isolated from *Iryanthera laevis*[2], 1-(2’-hydroxy-4’-methoxyphenyl)-3-(4’’-hydroxyphenyl) propane (**1**, broussonin A), a product previously synthesized by another synthetic pathway[9], and 1-(2’,4’-di-

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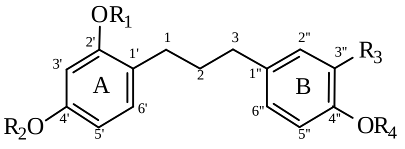
* e-mail: pafonso@ufrrj.br

methoxyphenyl)-3-(4''-hydroxyphenyl)propane (**4**), which was prepared for comparative ^{13}C-NMR analysis.

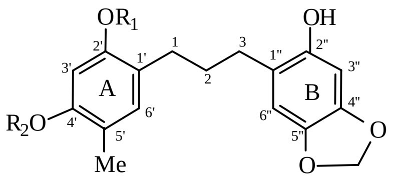
The structures of the synthetic compounds were characterized by analysis of spectral data, mainly mass, one-(1D) and two-dimensional (2D) ^{1}H and ^{13}C-NMR.

Results and Discussion

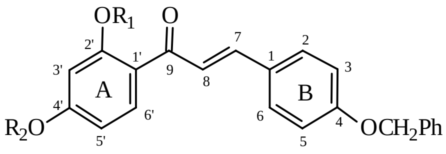
The synthetic pathway employed in order to obtain the desired 1,3-diarylpropanes (**1**, **2**, **4** and **7**) involved the base-catalysed condensation of the appropriate acetophenones (**16**, **18**, **19** and **20**, Scheme 1) with benzaldehydes (**23** and **25**, Scheme 2) to produce the corresponding chalcones (**8**, **9**, **10** and **11**) which were submitted to catalytic hydrogenation. Acetophenones **15** and **17** were prepared from resorcinol (**12**, Scheme 1) and protected by hydroxyl group benzylation, before or after appropriate methylation to furnish **16**, **18** and **19** or dimethylated **20**. Benzaldehyde **22** obtained from piperonal (**21**, Scheme 2) and **24** were



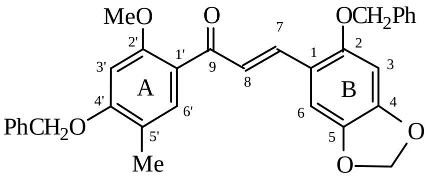
1 R_1=R_3=R_4=H, R_2=Me (Broussonin A)
2 R_1=Me, R_2=R_3=R_4=H (Broussonin B)
3 R_1=R_2=R_4=H, R_3=Prenyl (Broussonin C)
4 R_1=R_2=Me, R_3=R_4=H
5 R_1=R_4=Me, R_2=H, R_3=OH



6 R_1=H, R_2=Me
7 R_1=Me, R_2=H



8 R_1=Me, R_2=CH_2Ph
9 R_1=CH_2Ph, R_2=Me
10 R_1=R_2=Me



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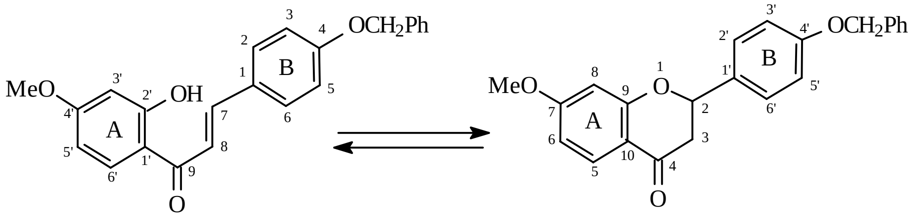
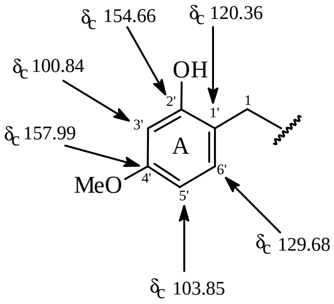
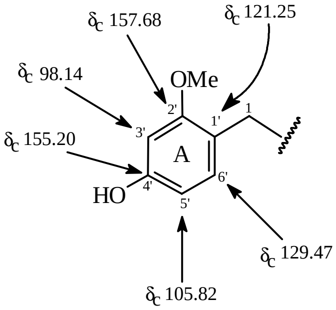


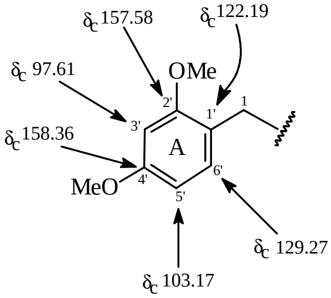
9a **9b**



1a



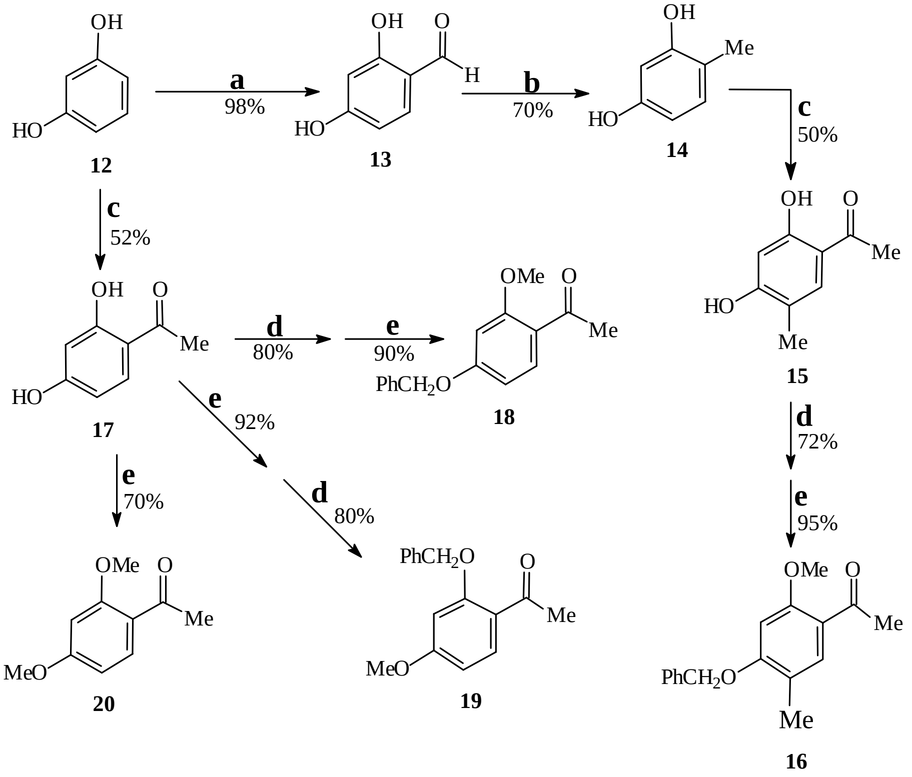
2a



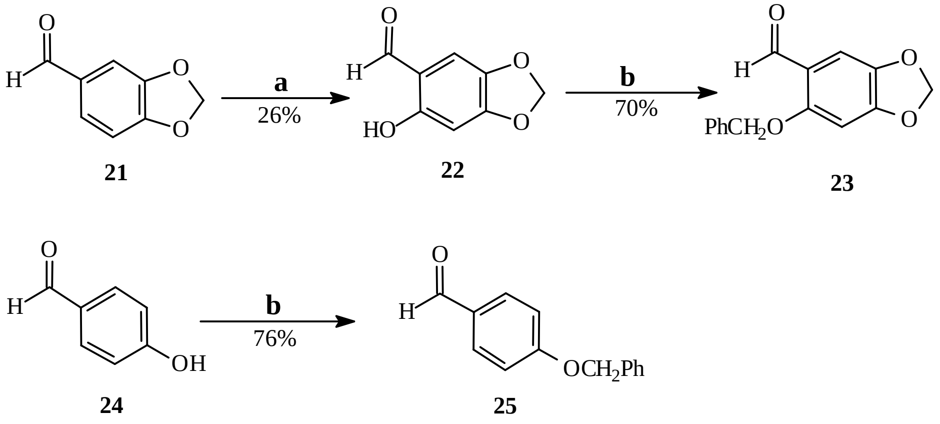
4a

protected by hydroxyl group benzylation, in order to stabilize the substrates towards the basic conditions of the condensation reaction: **18** + **25** → **8**; **19** + **25** → **9**; **20** + **25** → **10**; **16** + **23** → **11**. Thus, 1,3-diarylpropanes **1**, **2**, **4** and **7** were prepared by catalytic hydrogenation of the chalcones **8**, **9**, **10**, and **11**, respectively. Chalcone **9a** which has an unprotected 2'-hydroxyl group can undergo chalcone(**9a**)-flavanone(**9b**) equilibrium under the catalytic hydrogenation conditions which were used. Thus, a mixture of 1,3-diarylpropane and the corresponding dihydrochalcone was obtained. Using the same conditions, this partial reduction was not observed after the isomeric equilibrium was blocked by a 2'-hydroxyl group benzylation (**9**) or methylation (**10**).

The structure of 1-(4'-hydroxy-2'-methoxyphenyl)-3-(4''-hydroxyphe-nyl)propane (**2**) proposed for the natural product isolated from *Broussonetia papyrifera* Vent.[5] and 1-(4'-hydroxy-5'-methyl-2'-methoxyphenyl)-3-(2"-hydroxy-4",5"-methylenedioxyphenyl)propane (**7**) proposed for the natural product isolated from *Iryanthera laevis*[2] were confirmed by comparison with the synthetic products.



Scheme 1. a) 1. $Zn(CN)_2$, HCl, ether; 2. H_2O, Δ (Gatterman-Adams)[12]. b) Zn/Hg, HCl (d = 1.19), H_2O, toluene, Δ (Clemmensen reduction)[13]. c) 1. AcOH, $ZnCl_2$, Δ; 2. HCl (1:1) (Houben/Hoesch reaction)[14]. d) $PhCH_2Cl$, K_2CO_3, KI, acetone, Δ[15]. e) Me_2SO_4, K_2CO_3, acetone, Δ[16].



Scheme 2. a) 1. HNO_3 (d = 1.38); 2. $FeSO_4$, NH_4OH, EtOH; 3. $NaNO_2$, $CuSO_4$, H_2SO_4[8]. b) $PhCH_2Cl$, K_2CO_3, KI, acetone, Δ[15].

Comparative analysis of the ^{13}C-NMR spectral data of **1**, **2** and **4** revealed chemical shift values for the characterization of the aromatic ring A 2'-methoxy-4'-hydroxy-, 2'-hydroxy-4'-methoxy- and 2',4'-dimethoxy-, as shown in the partial structures **1a**, **2a** and **4a** corresponding to 1,3-diarylpropanoids **1**, **2** and **4**, respectively. This analysis also allowed observation of chemical shift modifications of the signals of the methine carbons CH-3' and CH-5' as a consequence from a γ-effect of the methyl group of the 2'-methoxy or 4'-methoxy: i) CH-3' [δ_C =97.61(**4a**) - 100.84(**1a**) = - 3.23 ppm and δ_C = 97.61(**4a**) - 98.14(**2a**) = - 0.53 ppm]; ii) CH-5' [δ_C =103.17(**4a**) - 105.82(**2a**) = - 2.65 ppm]. The modifications, a consequence of methylation of a hydroxyl group, may be deduced by comparison of the chemical shifts of the quaternary carbons C-2' and C-4' revealing a deshielding β-effect.

The homonuclear ^{1}Hx^{1}H-COSY and heteronuclear (^{13}C detected, conventional method) ^{13}Cx^{1}H-COSY-$^1J_{CH}$ (direct spin-spin interaction of carbon-13 and hydrogen via one bond) and ^{13}Cx^{1}H-COSY-$^nJ_{CH}$ [n = 2 and 3, COLOC, long-range coupling of carbon-13 and hydrogen via two ($^2J_{CH}$) and three ($^3J_{CH}$) bonds] 2D shift-correlated NMR spectra of the synthetic products were also used to assign unambiguously the chemical shifts of the carbon and hydrogen atoms and to reexamine values described in the literature[10,11]. The results obtained by careful analysis of these spectra of **1**, **2**, **4** and **7** are summarized in Tables 1-4.

The ^{1}H-NMR, ^{1}Hx^{1}H-COSY, ^{13}C-NMR, ^{13}Cx^{1}H-COSY-$^1J_{CH}$ and ^{13}Cx^{1}H-COSY-$^nJ_{CH}$ (n = 2 and 3) spectra of the 1,3-diarylpropane **1** [2'-hydroxy-4'-methoxy- (**1a**)] and **2** [4'-hydroxy-2'-methoxy- (**2a**)] were used to unambiguously assign the ^{1}H and ^{13}C chemical shifts of the aromatic ring A (Tables 1 and 2) and on the basis of these data to confirm the presence of a 4'-hydroxy-2'-methoxyphenyl (ring A) moiety in the structure of the natural 1-(4'-hydroxy-2'-methoxyphenyl)-3-(3"-hydroxy-4''-methoxyphenyl)propane (**5**) isolated from *Knema austrosiamensis* (Myristicaceae) and reported by Gonzaléz *et al.*[10], as well as revealing the interchanged chemical shifts attributed to C-2' and C-4' and CH$_2$-1(shielded by γ-effect of the OR located at C-2') and CH$_2$-2. The structure **5**, 1-(4'-hydroxy-2'-methoxyphenyl)-3-(3"-hydroxy-4''-methoxyphenyl)propane, had been previously proposed for a natural product isolated from *Virola multinervia*[4]. However, this structure was later revised to 1-(2'-hydroxy-4'-methoxyphenyl)-3-(3"-hydroxy-4''- methoxyphenyl) propane[7]. Therefore, the 1,3-diarylpropane **5** isolated from *Knema austrosiamensis* can be regarded as a novel natural product structure.

Comparative analysis of the ^{1}H-NMR spectra of the synthetic 1,3-diarylpropanes **6** (previously sinthesized)[7] and **7** (this paper) with the natural product isolated from *I. Laevis*[2] showed, as anticipated, small but significant differences in the chemical shifts of H-3' and H-3", which were clearly revealed only after recording these spectra: i) natural product isolated from *I. laevis* [^{1}H-NMR (60 MHz, CDCl$_3$): δ_H 6.40 (*sl*, H-3' and H-3"), $\Delta\delta_H$ = 0 ppm]; ii) synthetic **6** [^{1}H-NMR (100 MHz, CDCl$_3$): δ_H 6.37 (*s*, H-3'), 6.32 (*s*, H-3"), $\Delta\delta_H$ = 0.05 ppm]]; iii) synthetic **7** [^{1}H-NMR (200 MHz, CDCl$_3$): δ_H 6.38 (*s*, H-3'), 6.36 (*s*, H-3"), $\Delta\delta_H$ = 0.02 ppm]. On the basis of this comparative analysis, the

Table 1. ^{1}H (200 MHz, CDCl$_3$), ^{13}C (50.3 MHz CDC1$_3$ + MeOH-d$_4$), ^{13}Cx^{1}H-COSY-$^1J_{CH}$ and ^{13}Cx^{1}H-COSY-$^nJ_{CH}$ (n = 2 and 3) NMR of 1-(2'-hydroxy-4'-methoxyphenyl)-3-(4"-hydroxyphenyl)propane (**1**)*.

	^{13}Cx^{1}H-COSY -$^1J_{CH}$		^{13}Cx^{1}H-COSY -$^nJ_{CH}$ (n = 2 and 3)	
	δ_C	δ_H	$^2J_{CH}$	$^3J_{CH}$
C				
1'	120.36	-	2H-1	2H-2; H-3'; H-5'
2'	154.66	-	H-3'	2H-1; H-6'
4'	157.99	-	H-3'; H-5'	H-6; MeO-4'
1"	132.94	-	2H-3	2H-2; H-3", 5"
4"	153.83	-	H-3", 5"	2H-2", 6"
CH				
3'	100.84	6.37 (*d*, J = 2.5)	-	H-5'
5'	103.85	6.43 (*dd*, J = 8.3 and 2.5)	-	H-3'
6'	129.68	7.00 (*d*, J = 8.3)	-	2H-1
2"	6"	128.50	7.05 (*d*, J = 8.5)	-
3"	5"	114.36	6.75 (*d*, J = 8.5)	-
CH$_2$				
1	28.34	2.59 (*t*, J = 8.1)	2H-2	H-6'
2	31.88	1.87 (*m*)	2H-3; 2H-1	-
3	33.96	2.56 (*t*, J = 7.5)	2H-2	2H-2", 6"
CH$_3$				
4'-OMe	54.03	3.76 (*s*)	-	-
OH	-	5.23 (*s*)	-	-

* Multiplicity of signals of carbon atoms deduced by comparative analysis of PND- and DEPT-^{13}C-NMR. Homonuclear ^{1}Hx^{1}H-COSY spectrum was also used for these assignments. Chemical shifts and coupling constants (J) of the hydrogen atoms were obtained from the ^{1}H-NMR (1D).

Table 2. ^{1}H (200 MHz, $CDCl_3$), ^{13}C (50.3 MHz $CDC1_3$ + MeOH-d_4), ^{13}Cx^{1}H-COSY-$^1J_{CH}$ and ^{13}Cx^{1}H-COSY-$^nJ_{CH}$ (n = 2 and 3) NMR of 1-(4'-hydroxy-2'-methoxyphenyl)-3-(4"-hydroxyphenyl)propane (**2**)*.

	^{13}Cx^{1}H-COSY -$^1J_{CH}$		^{13}Cx^{1}H-COSY -$^nJ_{CH}$ (n = 2 and 3)	
	δ_C	δ_H	$^2J_{CH}$	$^3J_{CH}$
C				
1'	121.25	-	2H-1	2H-2; H-3'; H-5'
2'	157.68	-	H-3'	MeO-2'; 2H-1; H-6'
4'	155.20	-	H-5'	H-6'
1'	133.28	-	2H-3	2H-2; 2H-3", 5"
4"	153.74	-	2H-3", 5"	2H-2", 6"
CH				
3'	98.14	6.40 (*d*, J = 2.4)	H-5'	-
5'	105.82	6.33 (*dd*, J = 7.9 and 2.4)	-	H-3'
6'	129.47	6.95 (*d*, J = 7.9)	-	2H-1
2"	6"	128.80	7.06 (*d*, J = 8.5)	-
3"	5"	114.26	6.75 (*d*, J = 8.5)	2H-2", 6"
CH$_2$				
1	28.42	2.57 (*t*, J = 8.0)	2H-2	H-6'
2	31.43	1.83 (*m*)	2H-3; 2H-1	-
3	33.98	2.56 (*t*, J-7.3)	2H-2	2H-2", 6"
CH$_3$				
2'-OMe	53.99	3.78 (*s*)	-	-
OH	-	4.70 (*s*)	-	-

* Multiplicity of signals of carbon atoms deduced by comparative analysis of PND- and DEPT-^{13}C-NMR. Homonuclear ^{1}Hx^{1}H-COSY spectrum was also used for these assignments. Chemical shifts and coupling constants (J) of the hydrogen atoms were obtained from the ^{1}H-NMR (1D).

Table 3. ^{1}H (200 MHz, $CDCl_3$), ^{13}C (50.3 MHz, $CDC1_3$ + MeOH-d_4), ^{13}Cx^{1}H-COSY-$^1J_{CH}$ and ^{13}Cx^{1}H-COSY-$^nJ_{CH}$ (n = 2 and 3) NMR of 1-(2',4'-dimethoxyphenyl)-3-(4"-hydroxyphenyl)propane (**4**).*

	^{13}Cx^{1}H-COSY -$^1J_{CH}$		^{13}Cx^{1}H-COSY -$^nJ_{CH}$ (n = 2 and 3)	
	δ_C	δ_H	$^2J_{CH}$	$^3J_{CH}$
C				
1'	122.19	-	2H-1	2H-2; H-3'; H-5'
2'	157.58	-	H-3'	MeO-2'; 2H-1; H-6'
4'	158.36	-	H-3'; H-5'	MeO-4'; H-6'
1''	132.99	-	2H-3	2H-2; 2H-3", 5"
4"	153.96	-	-	2H-2", 6"
CH				
3'	97.61	6.45 (*s*)	-	-
5'	103.17	6.43 (*d*, J = 8.1)	-	-
6'	129.27	7.02 (*d*, J = 8.1)	-	-
2"	6"	128.67	7.06 (*d*, J = 8.4)	-
3"	5"	114.45	6.75 (*d*, J = 8.4)	-
CH$_2$				
1	28.49	2.58 (*t*, J = 7.5)	2H-2	H-6'
2	31.28	1.85 (*m*)	2H-3; 2H-1	-
3	34.04	2.58 (*t*, J = 7.5)	2H-2	2H-2", 6"
CH$_3$				
4'-ÓMe	54.27	3.79 (*s*)	-	-
2'-OMe	54.27	3.81 (*s*)	-	-
OH	-	5.10 (*s*)	-	-

* Multiplicity of signals of carbon atoms deduced by comparative analysis of PND- and DEPT-^{13}C-NMR. Homonuclear ^{1}Hx^{1}H-COSY spectrum was also used for these assignments. Chemical shifts and coupling constants (J) of the hydrogen atoms were obtained from the ^{1}H-NMR (1D).

synthetic product **7** confirms the structure proposed[7] for the natural diarylpropanoid isolated from *I. laevis*[2].

Comparison of the ^{13}C-NMR spectral data of the synthetic 1,3-diarylpropane **7** with values reported by Conserva *et al*[11], for the same natural product isolated later from *I. ulei*, confirmed the identity of these two compounds. However, the possibility of interchange of the chemical shifts of C-1' (δ_C 119.4) and C-1" (δ_C 119.6) was reported[11]. Homonuclear ^{1}H x ^{1}H-COSY and heteronuclear ^{13}C x ^{1}H-COSY - $^nJ_{CH}$ (n = 1; n = 2 and 3, COLOC) 2D shift-correlated spectra of the synthetic product **7** were used for unambiguous assignment of chemical shifts of hydrogen and carbon atoms (Table 4). In fact, the chemical shifts of the quaternary carbon atoms C-1' (δ_C 119.4) and C-1''

Table 4. ^{1}H (200 MHz, $CDCl_3$), ^{13}C (50.3 MHz, acetone-d_6), ^{13}Cx^{1}H-COSY-$^{1}J_{CH}$ and ^{13}Cx^{1}H-COSY-$^{n}J_{CH}$ (n = 2 and 3) NMR of 1-(4’-hydroxy-5’-methyl-2’-methoxyphenyl)-3-(2"-hydroxy-4"-5"-methylenedi oxyphenyl)propane (**7**)*.

	^{13}Cx^{1}H-COSY -$^{1}J_{CH}$		^{13}Cx^{1}H-COSY -$^{n}J_{CH}$ (n = 2 and 3)	
	δ_C^{a}	δ_H	$^{2}J_{CH}$	$^{3}J_{CH}$
C				
1’	121.95 (119.4)	2H-1	H-3’	
2’	156.93 (154.9)	-	-	MeO-2’; H-6’
4’	154.45 (152.7)	-	-	Me-5’; H-6’
5’	115.63 (113.7)	-	Me-5’	H-3’
1"	121.35 (119.6)	-	2H-3	H-3"
2"	149.88 (148.2)	-	-	H-6", OCH_2O; 2H-3
4"	146.40 (144.3)	-	-	H-6", OCH_2O
5"	141.08 (138.8)	-	-	H-3"
CH				
3’	99.45 (97.5)	6.38 (*s*)	-	-
6’	132.27 (130.2)	6.83 (*s*)	-	Me-5’
3"	98.30 (96.2)	6.36 (*s*)	-	-
6"	109.90 (107.9)	6.59 (*s*)	-	2H-3
CH_2				
1	29.81 (28.2)	2.49 (*t*, J = 8.1)		H-6’
2	31.42 (29.5)	1.80 (*m*)	2H-3 and/or 2H-1	-
3	30.34 (27.3)	2.54 (*t*, J = 7.2)		H-6"
OCH_2O	101.23 (99.2)	5.85 (*s*)	-	-
CH_3				
2’-OMe	55.42 (53.61)	3.74 (*s*)	-	-
5’-Me	15.27 (13.31)	2.14 (*s*)	-	H-6’
OH	-	5.23 (*s*)	-	-

* Multiplicity of signals of carbon atoms deduced by comparative analysis of PND- and DEPT-^{13}C-NMR. Homonuclear ^{1}Hx^{1}H-COSY spectrum was also used for these assignments. Chemical shifts and coupling constants (J) of the hydrogen atoms were obtained from the ^{1}H-NMR (1D). ^{a} Chemical shifts of carbon atoms (50.3 MHz, acetone-d_6) of natural product 7 (in parenthesis) described in the literature[11].

(δ_C 119.6) had been interchanged [δ_C 121.95 (C-1’) and 121.35 (C-1’’)], the same occurring with C-1 (δ_C 29.81)and C-3 (δ_C 30.34), as shown in Table 4. Other heteronuclear spin-spin interactions ($^{n}J_{CH}$, n = 1; n = 2 and 3) of hydrogen and carbon-13 are summarized in Table 4.

Homonuclear ^{1}H x ^{1}H-COSY and heteronuclear ^{13}C x ^{1}H-COSY - $^{n}J_{CH}$ (n = 1; n = 2 and 3, COLOC) 2D shift-correlated spectra were also used for unambiguous assignment of chemical shifts of hydrogen and carbon atoms of the compounds **1** (Table 1), **2** (Table 2) and **4** (Table 3).

Experimental

General experimental procedures

Melting point determinations were made in open capillaries and are uncorrected. Identification of compounds was established by TLC, IR, MS, ^{1}H-NMR, ^{13}C-NMR (PND and DEPT) and two-dimensional (2D) carbon-hydrogen shift correlation [carbon-hydrogen spin-spin interaction via one bond ($^{1}J_{CH}$) and two ($^{2}J_{CH}$) and three ($^{3}J_{CH}$) bonds, long-range coupling of carbon-hydrogen]. TLC was carried out on Merck kieselgel 60 GF 254. TMS was used as int. standard in NMR spectra. EIMS spectra were recorded at 70 eV on a low resolution spectrometer.

Preparation of the chalcones

In accordance with the literature[12], appropriately substituted acetophenones and benzaldehydes gave, by aldol condensation, **8** (yield, 85 %), **9** (88 %), **10** (72 %) and **11** (74 %).

4,4’-Di-O-benzyl-2’-methoxychalcone (**8**)

Mp 88-90° (MeOH). IR (neat) 1648, 1620, 1602, 1575 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$) δ_H 7.71 (*dd*, J = 8.5, 2,0 Hz, H-6), 7.63 (*d*, 16.0 Hz, H-7), 7.53 (*d*, J = 8.3 Hz, 2H-2’,6’), 7.36 (*d*, J = 16.0 Hz, H-8), 7.35 (*m*, phenyl), 6.96 (*d*, J = 8.3 Hz, 2H-3’,5’), 6.61 (*d*, J = 8.5 Hz, H-5), 6.57 (*d*, J = 2.0 Hz, H-3), 5.10 (*s*, O$CH_2C_6H_5$), 5.08 (*s*, O$CH_2C_6H_5$), 3.86 (*s*, OMe).

2’,4-Di-O-benzyl-4’-methoxychalcone (**9**)

Mp 101-103° (MeOH). IR (neat) 1652, 1624, 1604, 1575, 1512 cm^{-1}. ^{1}H-NMR (200 MHz,$CDCl_3$) δ_H 7.89 (*d*, J = 8.4 Hz, H-6), 7.66(*d*, J = 15.8 Hz,H-7), 7.52 (*d*, J = 15.8 Hz, H-8), 7.44 -7.26 (*m*, phenyl and 2H-2’,6’), 6.86 (*d*, J = 8.9 Hz, 2H-3’,5), 6.60 (*dd*, J = 8.4 and 2.4 Hz, H-5), 6.58 (*d*, J = 2.4 Hz, H-3), 5.14 (*s*, 2’-O$CH_2C_6H_5$), 5.10 (*s*, 4-O$CH_2C_6H_5$), 3.88 (*s*, OMe).

4-O-Benzyl-2’,4’-dimethoxychalcone (**10**)

Mp 74-76° (MeOH). IR (neat) 1644, 1619, 1575, 1512 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$) δ_H 7.74 (*d*, J = 8.5 Hz, H-6), 7.65 (*d*, J = 15.8 Hz, H-7), 7.55 (*d*, J = 8.8 Hz, 2H-2’,6’), 7.39 (*d*, J = 15.8 Hz, H-8), 7.35 (*s*, phenyl), 6.99 (*d*, J = 8.5 Hz, 2H-3’,5’), 6.56 (*dd*, J = 8.7 and 2.1 Hz, H-5), 6.50 (*d*, J = 2.1 Hz, H-3), 5.11 (*s*, O*CH*$_2$C$_6$H$_5$), 3.90 (*s*, OMe), 3.87 (*s*, OMe).

*4',2-Di-O-benzyl-5'-methyl-4,5-methylenedioxy-2'-methoxychalcone (**11**)*

Yellow oil. IR (neat) 1648, 1624,1610, 1580, 1500 cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$) δ_H 8.06 (*d*, J = 16.0 Hz, H-7), 7.50 (*d*, J = 16.0 Hz, H-8), 7.53 (*s*, H-6), 7.46-7.26 (*m*, phenyl), 7.08 (*s*, H-2'), 6.53 (*s*, H-3), 6.44 (*s*, H-6'), 5.93 (*s*, O-CH$_2$-O), 5.13 (*s*, O*CH$_2$*C$_6$H$_5$), 3.75 (*s*, OMe), 2.20 (*s*, MeAr).

Hydrogenation of the chalcones

A soln. of chalcone (1 g) in CHCl$_3$ (5 ml) and EtOH (50 ml), in Parr apparatus was flushed with N$_2$. Catalyst (0.5 g, 10 % Pd-C) and AcOH (10 mL) was added, vacuum applied and H$_2$ was admitted under pressure (50 psi, 4.5 hr). The usual work-up, followed by crystallization or silica gel chromatography of the crude reaction mixture, gave from **8** → **2** (yield 98 %), **9** → **1** (85 %), **10** → **4** (80 %) and **11** → **7** (90 %).

*1-(2'-Hydroxy-4'-methoxyphenyl)-3-(4"-hydroxyphenyl) propane (**1**)*

Mp 81-82° (C$_6$H$_6$). IR (neat) 3388, 1617, 1590, 1512 cm^{-1}. EIMS *m/z* (rel. int.): 258 ([M]$^{\cdot+}$, 20), 151 (9), 137 (100), 121 (10), 120 (14), 107 (38), 91 (6). ^{1}H and ^{13}C-NMR: Table 1.

*1-(4'-Hydroxy-2'-methoxyphenyl)-3-(4"-hydroxyphenyl) propane (**2**)*

Mp 80-82° (C$_6$H$_6$). IR (neat) 3230, 1617, 1605, 1513 cm^{-1}. EIMS *m/z* (rel. int.): 258 ([M]$^{\cdot+}$, 14), 152 (23), 151 (13), 138 (10), 137 (100), 121 (6),107 (55), 78 (30), 77 (19). ^{1}H and ^{13}C-NMR: Table 2.

*1-(2',4'-Dimethoxyphenyl)-3-(4"-hydroxyphenyl) propane (**4**)*

Oil. IR (neat) 3408, 1617, 1584, 1512 cm-^{1}. EIMS *m/z* (rel. int.) : 272 ([M]$^{\cdot+}$, 28), 165 (10), 151 (100), 138 (6), 120 (5). ^{1}H and ^{13}C-NMR: Table 3.

*1-(4'-Hydroxy-5'-methyl-2'-methoxyphenyl)-3-(2"-hydroxy-4",5"-methylenedi-oxyphenyl)propane (**7**)*

Mp 137-139° (C$_6$H$_6$). IR (neat) 3322, 1623, 1602, 1520, 1499 cm^{-1}. EIMS *m/z* (rel. int.): 316 ([M]$^{\cdot+}$, 4), 178 (11), 165 (7), 166(25), 152 (26), 151 (100), 149 (10), 121 (16). ^{1}H and ^{13}C-NMR: Table 4.

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