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1,11-DIARYLUNDECAN-1-ONE AND 4-ARYLTETRALONE NEOLIGNANS FROM *VIROLA SEBIFERA**

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Key Word Index— *Virola sebifera*; Myristicaceae; seeds; 1-(2′,6′-dihydroxyphenyl)-11-phenylundecan-1-one; 4-aryl-2,3-dimethyl-1-tetralones.

Abstract—The seed of *Virola sebifera* contains besides the polyketide 1-(2′,6′-dihydroxyphenyl)-11-phenylundecan-1-one, four neolignans: (2*S*, 3*S*, 4*R*)-4-hydroxy-2,3-dimethyl-5,6-methylenedioxy-4-piperonyl-1-tetralone and its 2-epimer, as well as (2*R*, 3*R*, 4*S*)-4-hydroxy-6,7-dimethoxy-2,3-dimethyl-4-piperonyl-1-tetralone and its (2*R*, 3*S*, 4*R*)-dehydroxy analogue.

INTRODUCTION

Virola sebifera is widely distributed over South America. The species has been reported (under the synonym *V. venezuelensis* Warb.) to yield a fat that is valued for treatment of rheumatism in Venezuela [2]. Although in Brazil this "ucuhuba" fat is expressed for industrial purposes, and the bark of the tree serves in the preparation of hallucinogenic snuffs by Amazonian Indians [2], such uses are seemingly restricted to northern regions and *V. sebifera* remains without conspicuous use in São Paulo State.

The compositions of the triacylglycerols [3, 4] and of the psychotomimetic drug [2, 5] are fairly well known. Since the biological activity of the crude fat can hardly be due to the lipids the chemical analysis of the seed seemed in order. Indeed, the present work shows this to be a rich source of novel compounds, the polyketide **1a**, the oxo-otobains **2a**, **2b**, **3a**, **3b**, as well as further metabolites to be described in a subsequent report.

RESULTS AND DISCUSSION

Compound **1a**, $C_{23}H_{30}O_3$, was recognized as a diarylundecanone by the ^1H NMR signals for two symmetrical aromatic rings, a phenyl group and a 2,6-dihydroxybenzoyl group, as well as for ten methylene units, two of which placed α to carbonyl or aryl moieties. Acetylation of **1a** led to the monoacetate **1b** which, as the parent compound, showed an $AlCl_3$ UV shift and a 1620 cm^{-1} IR band, both indicative of an *ortho*-hydroxycarbonyl substituted aromatic ring. In contradistinction, no $AlCl_3$ UV shift was observed for the diacetate (**1c**) and, as expected, the IR carbonyl band appeared at 1700 cm^{-1}. The mass spectra were compatible with the structures, showing the base peaks at *m/z* 137 (dihydroxybenzoyl ions) and peaks of moderate relative intensity at *m/z* 91 (tropylium ions). In the spectra of **1b** and **1c** peaks at *m/z* 179 (acetoxyhydroxybenzoyl ion) and 221 (diacetoxybenzoyl ion) were also present.

The structure of the diarylundecanoid **1a** from *V. sebifera* belongs to a type previously detected in the fruits of *Myristica malabarica* Lam. [6]. The most significant difference between **1a** and the malabaricones (**1d**, **1e**, **1f**, **1g**) refers to the biosynthesis which seemingly involves the condensation of cinnamic acid with myristic acid in the former case and with lauric acid in the latter case.

Compounds **2a**, **2b**, **3a** and **3b** were recognized as 4-aryltetralin neolignans by joint consideration of the formulae, respectively $C_{18}H_{13}OH\ (O_2CH_2)_2O$, $C_{18}H_{13}OH(O_2CH_2)_2O$, $C_{18}H_{13}OH(OMe)_2\ O_2CH_2O$ and $C_{18}H_{14}(OMe)_2\ O_2CH_2O$, the ^1H NMR spectra of which all contained a pair of methyl doublets ($J = 7$ Hz), and the mass spectra, which all contained prominent $[M - MeCH{=}CHMe]^{+\cdot}$ peaks. The uncharacterized oxygen atom of the formulae must belong to a carbonyl which in all four compounds is part of a benzoyl unit (ν_{max}^{KBr} 1674 ± 9 cm^{-1}), and thus can occupy only position 1 of the tetralins. The vicinal aromatic position 8 must be unsubstituted, as indicated by ^1H NMR signals at relatively low field: δ 7.65 ± 0.05 (*d*, $J = 8$ Hz) for **2a** and **2b**; δ 7.51 ± 0.05 (*s*) for **3a** and **3b** (Table 1). While these data define the constitution of the bis-methylenedioxytetralins of series **2**, doubts remain concerning the relative position of the vicinal methoxyls and the methylenedioxy units in the compound of series **3**.

Conclusive proof of the carbon skeleton was obtained for **3a**. Acid dehydration of this compound leads to the 4-aryl-1-naphthol, similar in respect to UV, IR and ^1H NMR characteristics to tetradehydroisogalactin (**4b**). Conspicuous spectral differences

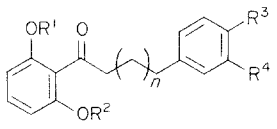
*Part XVI in the series "The Chemistry of Brazilian Myristicaceae". For Part XV see ref. [1]. Taken from part of the M.S. thesis presented by L.M.X.L. to the Universidade de São Paulo (1980).

Table 1. ^{1}H NMR data of 4-aryltetralone neolignans (**2a**, **2b** in CCl_4; **3a**, **3b** in $CDCl_3$; 60 MHz, δ J in Hz)

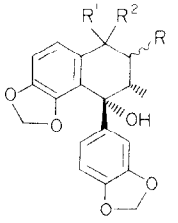
	2a	**2b**	**3a**	**3b**
H-8	7.60 (*d*, *J* = 8)	7.69 (*d*, *J* = 8)	7.46 (*s*)	7.56 (*s*)
H-7	7.0–6.7 (*m*)	6.87 (*d*, *J* = 8)	—	—
H-6′		6.46 (*dd*, *J* = 8, 2)	7.1–6.5 (*m*)	7.0–6.5 (*m*)
H-5′		6.6 (*d*, *J* = 8)		
H-2′		6.86 (*d*, *J* = 2)		
H-5	—	—	6.29 (*s*)	6.26 (*s*)
3′,4′-CH_2O_2	5.96 (*s*)	5.96 (*s*)	5.98 (*s*)	6.07 (*s*)
5,6-CH_2O_2	5.78 (*d*, *J* = 2)	6.03 (*d*, *J* = 2)	—	—
	5.66 (*d*, *J* = 2)	6.00 (*d*, *J* = 2)		
OMe	—	—	3.87 (*s*)	3.95 (*s*)
OMe	—	—	3.61 (*s*)	3.68 (*s*)
H-4	—	—	—	3.91 (*d*, *J* = 8)
H-2	2.79 (*dq*, *J* = 6.5, 12)	2.75–2.17 (*m*)	2.95 (*dq*, *J* = 7, 12)	3.6–2.0 (*m*)
H-3	2.05 (*dq*, *J* = 6.5, 12)		2.33 (*dq*, *J* = 6.5, 12)	
Me-2	1.16 (*d*, *J* = 6.5)	1.06 (*d*, *J* = 8)	1.21 (*d*, *J* = 7)	1.31 (*d*, *J* = 6)
Me-3	0.88 (*d*, *J* = 6.5)	1.02 (*d*, *J* = 8)	0.88 (*d*, *J* = 6.5)	0.97 (*d*, *J* = 6)
4-OH	2.43 (*s*)	3.30 (*s*)	2.60 (*s*)	

concern the hydroxyl IR band at 3448 cm^{-1} and the aromatic ^{1}H NMR singlet at δ 7.48 respectively only present in the spectra of **4a** and **4b**.

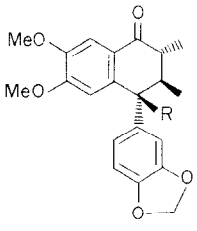
The difference between compounds **2a** and **2b** is of a stereochemical nature as shown by ^{1}H NMR measurements. Indeed, the coupling constant of the H-2, H-3 interaction is much larger for **2a** (12 Hz) than for **2b** (3 Hz) and a *trans* diaxial relation characterizes this system in the former compound. Both methyl substituents of **2a** must hence be equatorial, a conformation which can be equally assigned to the piperonyl group in view of its differential shielding effect on the methylene protons (δ 5.66 and 5.78, doublets, J = 2 Hz) of the CH_2O_2 substituent on positions 5 and 6. Acid or alkaline treatment of **2a**, a reaction which would be expected to epimerize C-2, generates **2b**. In this compound, the steric strain resulting from the 1,3-*cis* interaction of the methyl at C-2 and the hydroxyl at C-4 should cause a change of conformation whereby the carbonyl and the piperonyl



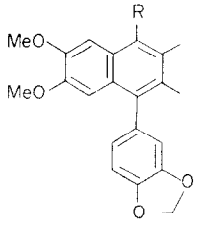
1a $R^1 = R^2 = R^3 = R^4 = H$, $n = 8$
1b $R^1 = R^3 = R^4 = H$, $R^2 = Ac$, $n = 8$
1c $R^1 = R^2 = Ac$, $R^3 = R^4 = H$, $n = 8$
1d $R^1 = R^2 = R^3 = R^4 = H$, $n = 6$
1e $R^1 = R^2 = R^3 = H$, $R^4 = OH$, $n = 6$
1f $R^1 = R^2 = H$, $R^3 = R^4 = OH$, $n = 6$
1g $R^1 = R^2 = H$, R^3-R^4 = CH_2O_2, $n = 6$



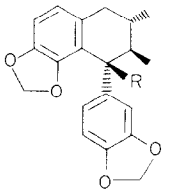
2a R = βMe, R^1-R^2 = O
2b R = αMe, R^1-R^2 = O
2c R = βMe, R^1 = H, R^2 = OH
2d R = βMe, R^1 = H, R^2 = OAc
2e R = βMe, R^1 = H, R^2 = H



3a R = OH
3b R = H



4a R = OH
4b R = H



5a R = OH
5b R = H

groups move somewhat from their location in the equatorial plane. Indeed, the carbonyl of **2b** (ν_{max} 1683 cm^{-1}) shows less conjugation with the aromatic ring than the carbonyl of **2a** (ν_{max} 1670 cm^{-1}); and although the differential action on the methylene protons of the CH_2O_2 group at positions 5 and 6 remains, no shielding effect is perceptible (δ 6.03 and 6.00, doublets, $J = 2$ Hz).

The *trans, trans*-configuration of the two methyl and the aryl substituents, which prevails in **2a**, is also observed for **3a** and **3b**. Again $J_{H\text{-}2,H\text{-}3}$ (12 Hz for **3a** and **3b**) is rather large, as is $J_{H\text{-}3,H\text{-}4}$ (8 Hz) in **3b**; and again the equatorial piperonyl group causes shielding effects, on H-5 and on Me-3 (δ 6.29, 0.88 respectively for **3a** and 6.26, 0.97 respectively for **3b**).

While 4-aryltetralone neolignans have not been reported previously, 4-aryltetralin neolignans are well known [7]. According to Crabbé and Klyne [8] the sign of the Cotton effect of the benzenoid chromophore between 275 and 290 nm is indicative of the configuration of the 4-aryl substituent, a positive effect pointing to an α-aryl group and vice versa. Based on this rule, Klyne *et al.* [9] assigned the (2*S*, 3*R*, 4*S*) and (2*S*, 3*R*, 4*R*) stereochemistries to hydroxyotobain (**5a**) and otobain (**5b**), constituents of *Dialyanthera otoba* (Myristicaceae).

Defunctionalization of **2a** at C-1, by sequential $LiAlH_4$ reduction to **2c** and hydrogenolysis, gave hydroxyotobain (**2e**) identical, with respect to the ORD curve, to the compound from *D. otoba*. The CD curve, however, shows that the Cotton effect in the 280–290 nm region is negative (Table 2) and that hence, according to Crabbé and Klyne's rule [8], the β-aryl (4*R*) configuration must be assigned to hydroxyotobain **2e**, not **5a**). The wrong stereochemical assignments for hydroxyotobain and for otabain in the published report [9] is due to the fact that the authors deduced the sign of the Cotton effect considering the spectral region above instead of below 280 nm.

Transformation of **2a** into **2e** excluding alterations in chirality implies that **2a** must possess the (2*S*, 3*S*, 4*R*)-configuration. Its positive Cotton effect at the absorption of the carbonyl chromophore (333 nm) contrasts with the negative effects at the same wavelength of **2b**, **3a** and **3b** which thus must possess respectively the (2*R*, 3*S*, 4*R*), (2*R*, 3*R*, 4*S*) and (2*R*, 3*S*, 4*R*) configurations.

EXPERIMENTAL

Isolation of constituents. Ripening fruits of *V. sebifera* Aubl. were collected by Hipolito F. Paulino Filho, UNESP, Araraquara, from a specimen, identified by Dr. William A. Rodrigues, INPA, Manaus, near São Sebastião do Paraiso, Minas Gerais State. The seeds had their epicarp removed, were air dried (72 hr) and ground to a mass (225 g) which was exhaustively extracted with C_6H_6 at room temp. The solvent was evapd and the residue (60 g) partitioned between petrol and MeOH–H_2O (9:1). The former soln was evapd yielding fats. The latter soln was evapd and the residue dissolved in EtOAc. The soln was washed with H_2O, 10% aq. $NaHCO_3$ and 2% aq. HCl. The EtOAc soln was evapd and the residue (22 g) submitted to dry CC (400 g Si gel, $CHCl_3$–EtOAc, 97:3). The column was cut into 33 portions. Portions 1–9 were crystallized from MeOH to yield fats (3.5 g). The mother liquor was evapd and the residue separated by prep. TLC (Al_2O_3, $CHCl_3$) into **1a** (400 mg) and **3b** (38 mg). Portions 10–14, 15–23 and 24–28 gave products which were purified by repeated prep. TLC (Si gel) into **2b** (114 mg), **2a** (2.1 g), **3a** (164 mg) respectively. Portions 29–33 were reserved for work to be reported in a later paper.

1-(2′,6′-*Dihydroxyphenyl*)-11-*phenyl-undecan*-1-*one* (**1a**). Mp 69–71° (MeOH) (M^+ found: 354.2185; $C_{23}H_{30}O_3$ requires: 354.2195). λ_{max}^{MeOH} nm: 267, 340 (ϵ 9550, 2500), $\lambda_{max}^{MeOH+NaOH}$ nm: 234, 283, 378 (ϵ 13150, 9400, 5000), $\lambda_{max}^{MeOH+AlCl_3}$ nm: 235, 293, 400 (ϵ 8500, 15300, 4800), no shift in presence of H_3BO_3 + NaOAc. ν_{max}^{film} cm^{-1}: 3280, 1620, 1590, 1500, 1450, 1370, 1340, 1250, 1200, 785, 742, 718, 697. ^1H NMR (60 MHz, CCl_4) δ 9.7 (*s*, 2 OH), 7.23 (*t*, $J = 8$ Hz, H-4′), 7.0–7.3 (*m*, C_6H_5), 6.33 (*d*, $J = 8$ Hz, H-3′, H-5′), 3.10 (*t*, $J = 7$ Hz, $ArCOCH_2$), 2.58 (*t*, $J = 7$ Hz, $ArCH_2$), 1.30 (*br s*, 8 CH_2). MS *m/z* (rel. int.): 354 (M^+, 11), 336 (14), 326 (14), 189 (13), 175 (4), 165 (31), 152 (31), 147 (4), 138 (11), 137 (100), 123 (13), 91 (17).

Acetylation of **1a** (180 mg, Ac_2O 1 ml, C_5H_5N 1 ml, room temp., 14 hr) gave a mixture of **1a** (150 mg), **1b** (10 mg) and **1c** (19 mg) which were separated by TLC (Si gel, C_6H_6).

Monoacetate (**1b**). Mp 58–59° (MeOH). λ_{max}^{MeOH} nm: 250, 302, 330, 350 (ϵ 5550, 2700, 2000, 1200). $\lambda_{max}^{MeOH+AlCl_3}$ nm: 274, 370 (ϵ 16300, 8300). ν_{max}^{film} cm^{-1}: 3150–3000, 1775, 1620, 1450, 1370, 1185, 806, 746, 720, 697. ^1H NMR (60 MHz, $CDCl_3$) δ 12.66 (*s*, OH), 7.46 (*t*, $J = 8$ Hz, H-4′), 7.30 (*s*, C_6H_5), 6.92 (*dd*, $J = 3$, 8 Hz, H-3′), 6.63 (*dd*, $J = 3$, 8 Hz, H-5′), 2.96 (*t*, $J = 7$ Hz, $ArCOCH_2$), 2.64 (*t*, $J = 7$ Hz, $ArCH_2$), 2.37 (*s*, AcO), 1.31 (*br s*, 8 CH_2). MS *m/z* (rel. int.): 396 (M^+, 10), 354 (10), 336 (22), 189 (37), 179 (10), 175 (10), 165 (37), 152 (56), 138 (15), 137 (100), 123 (10), 97 (10), 91 (17).

Diacetate (**1c**). Viscous oil. λ_{max}^{MeOH} nm: 270, 305 (ϵ 3000, 1850). ν_{max}^{film} cm^{-1}: 1775, 1700, 1605, 1455, 1368, 1190, 746, 700. ^1H NMR (60 MHz, $CDCl_3$) δ 7.6–6.95 (*m*, H-3′, H-4′, H-5′), 7.58 (*s*, C_6H_5), 2.73 (*t*, $J = 7$ Hz, $ArCOCH_2$), 2.63 (*t*, $J = 7$ Hz, $ArCH_2$), 2.20 (*s*, 2AcO), 1.33 (*br s*, 8 CH_2). MS *m/z* (rel. int.): 438 (M^+, 1), 396 (5), 354 (8), 336 (6), 221 (13), 194 (19), 189 (53), 179 (60), 175 (22), 165 (89), 152 (90), 151 (16), 147 (14), 138 (29), 137 (100), 136 (25), 123 (31), 105 (16), 91 (87).

(2S, 3S, 4R) - 4 - *Hydroxy* - 2,3 - *dimethyl* - 5,6 - *methylenedioxy* - 4 - *piperonyl* - 1 - *tetralone* (**2a**). Mp 115–117° (MeOH) (M^+ found: 354.1095; $C_{20}H_{18}O_6$ requires: 354.1103). λ_{max}^{MeOH} nm: 234, 282, 300 inf., 315 sh. (ϵ 21150, 9900, 6900, 6300). ν_{max}^{film} cm^{-1}: 3840, 1670, 1615, 1590, 1470, 1360, 1250, 1040, 885, 815. MS *m/z* (rel. int.): 354 (M^+, 37), 336 (18), 298 (100), 269 (6), 240 (10), 149 (13), 119 (7), 117 (7), 91 (9), 83 (15).

Epimerization into **2b**. Treatment of **2a** with TsOH or with $(CO_2H)_2$ according to the aromatization procedure (see **3a** below) gave a mixture of **2a** and **2b**. Alternatively **2a** (120 mg) in MeOH (60 ml) was treated with $NaBH_4$ (40 mg) with stirring at room temp. (30 min). Aq. satd NH_4Cl (10 ml) was then added and the mixture extracted with Et_2O and $CHCl_3$. The organic solns were combined, dried ($MgSO_4$), filtered and evapd. The residue (115 mg) was separated by TLC (Si gel, C_6H_6–EtOAc, 4:1) into **2a** (40 mg) and **2b** (33 mg).

(2R, 3S, 4R) - 4 - *Hydroxy* - 2,3 - *dimethyl* - 5,6 - *methylenedioxy* - 4 - *piperonyl* - 1 - *tetralone* (**2b**). Mp 111–113° (MeOH) (M^+ found: 354.1090; $C_{20}H_{18}O_6$ requires: 354.1103). λ_{max}^{MeOH} nm: 233, 283, 300 inf., 315 sh (ϵ 24800, 10200, 7450, 6000). ν_{max}^{film} cm^{-1}: 3640, 1683, 1600, 1480, 1440, 1370, 1242, 1117, 845, 816. MS *m/z* (rel. int.): 354 (M^+, 17), 336 (5), 298 (32), 271 (15), 269 (2), 149 (23), 85 (98), 84 (20), 83 (100), 65 (9).

Transformation into hydroxyotobain (**2e**). A soln of **2a**

Table 2. ORD and CD curves of 4-aryltetraline neolignans (25°, MeOH)

2a	nm	248	255	278	292	303	312	322	341	346
ORD	[Φ]	-9950^{tr}	-7750^{sh}	0	$+9450^{pk}$	$+4500^{sh}$	0	-4000^{tr}	0	$+650^{pk}$
2a	nm	243	260	278	288	310	327	333		
CD	[θ]	-2400^{max}	0	$+3000^{max}$	0	-2850^{max}	0	$+650^{max}$		
2b	nm	248	263	284	297	312	322	343		
ORD	[Φ]	-9500^{in}	-11150^{tr}	0	$+14900^{pk}$	$+9650^{sh}$	0	-10400^{tr}		
2b	nm	250	257	262	284	296	323	333		
CD	[θ]	0	-900^{max}	0	$+3150^{max}$	0	-6700^{max}	-5500^{sh}		
2e	nm	250	276	288						
ORD	[Φ]	-12000^{tr}	-600^{in}	-5400^{tr}						
2e	nm	234		284						
CD	[θ]	-9450^{max}		-3100^{max}						
3a	nm	264	280	296	297	318	338	347		
ORD	[Φ]	-850^{in}	-26700^{tr}	0	$+3800^{sh}$	$+18250^{pk}$	0	-3400^{tr}		
3a	nm	242	257	275	283	295	305	312	319	333
CD	[θ]	-7700^{max}	−1700	-6800^{max}	0	$+8900^{max}$	+5950	+3800	0	-4400^{max}
3b	nm	235	246	265	282	299	317	335	346	
ORD	[Φ]	0	-25600^{tr}	-11050^{in}	-42350^{tr}	0	$+22450^{pk}$	0	-8700^{tr}	
3b	nm	256	275	280	293	305	310	317	333	
CD	[θ]	−400	-6700^{max}	0	$+14450^{max}$	+7900	+6700	0	-7350^{max}	

(113 mg) in dry THF (5 ml) was added drop-wise to a suspension of $LiAlH_4$ (70 mg) in THF (16 ml). The mixture was then stirred (3 hr), treated with THF satd with H_2O until H_2 ceased to evolve, and then with aq. satd NH_4Cl soln. The soln was extracted with Et_2O (4 × 10 ml), the Et_2O soln dried ($MgSO_4$) and then evapd. The residue (105 mg) was characterized as a mixture of epimeric alcohols (**2c**) by the acetylation product (**2d**). ν_{max}^{film} cm^{-1}: 3570, 1736, 1500, 1450. ^1H NMR (60 MHz, $CDCl_3$) δ 2.38 (*s*, AcO), 2.13 (*s*, AcO). MS *m/z* (rel. int.): 398 (M^+, 6), 339 (11), 338 (39), 43 (100). Part of the residue **2c** (54 mg) in MeOH (10 ml) was hydrogenated in the presence of Pd/C (10%, 29 mg) (room temp. and pres.). The product was purified by TLC (Si gel, C_6H_6–EtOAc, 9:1) to **2e** (12 mg), mp 116–117°.

(2R, 3R, 4S) - 4 - *Hydroxy* - 2,3 - *dimethyl* - 6,7 - *dimethoxy* - 4 - *piperonyl* - 1 - *tetralone* (**3a**). Mp 177–180° (MeOH) (M^+ found: 370.1422; $C_{21}H_{22}O_6$ requires: 370.1416). λ_{max}^{MeOH} nm: 233, 277, 300 inf., 313 sh. (ϵ 24400, 12600, 7200, 6650). ν_{max}^{film} cm^{-1}: 3520, 1665, 1600, 1500, 1493, 1450, 1360, 1270, 1235, 1155, 1040, 885, 815, 800. MS *m/z* (rel. int.): 370 (M^+, 25), 354 (16), 353 (77), 352 (100), 351 (16), 314 (84), 313 (12), 307 (12), 279 (12), 255 (12), 165 (15), 149 (16).

Aromatization into **4a**. A soln of **3a** (30 mg) and of TsOH (3 mg) in C_6H_6 (50 ml) was heated under reflux (4 hr), cooled to room temp., washed with aq. satd $NaHCO_3$ soln, dried ($MgSO_4$), filtered and evapd. The residue was purified by TLC (Si gel, C_6H_6–EtOAc, 4:1) to **4a** (8 mg).

6,7 - *Dimethoxy* - 2,3 - *dimethyl* - 4 - *piperonyl* - 1 - *naphthol* (**4a**). Viscous oil. λ_{max}^{MeOH} nm: 236, 255 sh. 275 inf. 285 sh 310, 335 sh (ϵ 17900, 11600, 9700, 8800, 5100, 3000). ν_{max}^{film} cm^{-1}: 3450, 1600, 1504, 1460, 1370, 1280, 1235, 1040, 833, 813. ^1H NMR (60 MHz, $CDCl_3$) δ 7–6.5 (*m*, 5ArH), 6.03 (*s*, CH_2O_2), 4.51 (*s*, OH), 3.87, 3.66 (2*s*, 2MeO), 2.29 (*s*, Me-2), 2.08 (Me-3). MS *m/z* (rel. int.): 352 (M^+, 31), 351 (62), 336 (15), 325 (23), 246 (77), 218 (15), 203 (15), 149 (54), 121 (31), 119 (88), 117 (100), 91 (13).

(2R, 3S, 4R) - 6,7 - *Dimethoxy* - 2,3 - *dimethyl* - 4 - *piperonyl* - 1 - *tetralone* (**3b**). Mp 118–120° (MeOH) (M^+ found: 354.1460, $C_{21}H_{22}O_5$ requires: 354.1467). λ_{max}^{MeOH} nm: 232, 275, 300 inf., 313 sh (ϵ 21950, 12750, 7450, 6800). ν_{max}^{film} cm^{-1}: 1667, 1600, 1480, 1450, 1360, 1250, 1150, 1040, 880, MS *m/z* (rel. int.): 354 (M^+, 90), 339 (18), 338 (3), 326 (8), 299 (20), 298 (100), 267 (18), 255 (24), 194 (29), 165 (14), 149 (59).

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