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UNUSUAL BENZOFURANOID NEOLIGNANS FROM *LICARIA CHRYSOPHYLLA*[*]

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Key Word Index—*Licaria chrysophylla*; Lauraceae; 3-aryl-2-methylbenzofuranoids; neolignans; chrysophyllins; chrysophyllons.

Abstract—Trunk wood, bark and fruit calyx of *Licaria chrysophylla* contain eight neolignans which differ from the normal benzofuranoid types by showing 7.1′,8.*O*.2′ (rather than 8.1′,7.*O*.2′) linkages between the propenylphenol and allylphenol derived moieties. The fundamental chrysophyllon I types, with the allyl at C-1′, can rearrange to chrysophyllon II and III types, with the allyl respectively at C-5′ and O-4′.

INTRODUCTION

The trunk wood of *Licaria chrysophylla* contains the hexahydrobenzofuranoids **1a** and **1b** (chrysophyllins A and B) [2]. These neolignans are unusual in possessing the 3-aryl-2-methyl instead of the common 2-aryl-3-methyl benzofuranoid substitution. The present paper reports the analysis of bark, wood and fruit calyx of the same species. Besides **1a** four tetrahydrobenzofuranoids **2a** and **2b** (chrysophyllons I-A and I-B), **3a** and **3b** (chrysophyllons II-A and II-B), as well as two dihydrobenzofuranoids **4a** and **4b** (chrysophyllons III-A and III-B) were isolated. All these novel neolignans also possess the unusual 3-aryl-2-methyl benzofuranoid skeleton. In the bark the neolignans are accompanied by 2,3,4,5-tetramethoxyallylbenzene (**5**) [3], 2,3,4,5,-tetramethoxycinnamyl alcohol (**6**) and 2,3,4,5-tetramethoxycinnamaldehyde (**7**). Except when considering derivatives of benzofuran (as above) nomenclature and numbering of neolignans follow the rules outlined in a review [4]. This practice facilitates spectral comparisons of biogenetically analogous positions.

RESULTS

Hydrogen and carbon counts by NMR combined with molecular weight determinations by low resolution mass spectrometry led to the elementary formulas $C_{22}H_{24}O_7$ (**2a**, **3a**, **4a**) and $C_{23}H_{28}O_7$ (**2b**, **3b**, **4b**) for the six new neolignans. ^{1}H and ^{13}C NMR spectra showed furthermore that, as in the case of **1a** and **1b**, the difference between the **a** and **b** series is due to the presence of a 3-methoxy-4,5-methylenedioxyphenyl in the former *vs* a 3,4,5-trimethoxyphenyl in the latter. The similarity with the chrysophyllins goes beyond the structures of the aryl substituents. As for **1a** and **1b** the *C*-Me group is represented by ^{1}H and ^{13}C NMR signals respectively at δ1.5 (d, $J = 6$ Hz) and 19 *vs* 1 (d, $J = 7$ Hz) and 8.5 for *trans* aryl/methyl burchellins (**8a**) or 0.5 (d, $J = 7$ Hz) and 12 for *cis* aryl/methyl burchellins (**8b**) [5]. Thus, as for **1a** and **1b**, the six new compounds should again be 'unusual' hydrobenzofuranoid neolignans with the aryl/methyl substituents at interchanged positions on the furan ring. In all their spectra the *C*-methyls are represented by doublets at relatively low field, due certainly to the paramagnetic influence of the vicinal oxymethine, and possibly to a *trans* relationship with the aryl. The confirmation of this latter feature requires comparison with epimeric neolignans which are not yet available.

The H-7 NMR signals for **1a**, **1b**, **2a** and **2b** (δ3, d, $J = 10$ Hz) are closely comparable and appear at higher field than the analogous signals for **3a**, **3b**, **4a** and **4b** (δ *ca* 3.7). The vicinal position, C-1′, should thus be occupied by a sp^3-carbon in the former case and a sp^2-carbon in the latter. It is this sp^3-carbon in **2a** and **2b** which must be substituted by the allyl with non-equivalent methylene protons (δ2.00 and 2.65, two dd, $J = 14$ and 6 Hz). One of these H-7′ is relatively shielded, providing evidence for a *cis* relationship between allyl and aryl. The remaining information concerns an α,β-unsaturated carbonyl (ν_{max} 1660 cm^{-1}, ^{13}C NMR δ178), two methoxyls (^{13}C NMR δ55, 56) and one olefinic proton (^{1}H NMR δ5.3) and can best be accommodated as shown in **2a** and **2b**.

As indicated by signals at relatively high field (δ *ca* 2.4, d, $J = 6$ Hz) for their methylene protons, the allyl of **3a** and **3b** must also be located on a fully substituted sp^3-carbon. The same is true for one of the methoxyls (δ3.1, s). Since there can be but one such carbon in the cyclohexane moiety, the allyl and methoxyl groups must be localized on the same carbon. The remaining information concerns an $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl ($\nu_{max}$ 1660 cm^{-1}; ^{13}C NMR δ195), an additional methoxyl (δ3.8) and one olefinic proton (^{1}H NMR δ5.8, d, $J = 2$ Hz). The small coupling constant of this proton signal is due to long

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[*] Part 81 in the series "The chemistry of Brazilian Lauraceae". For Part 80 see ref. [1]. Based in part on the M.Sc. thesis presented by M.N.L. to Universidade de São Paulo (1985).

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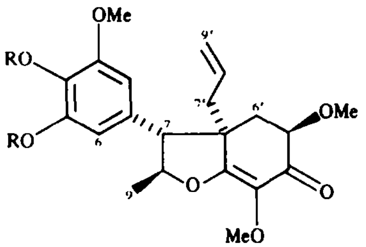
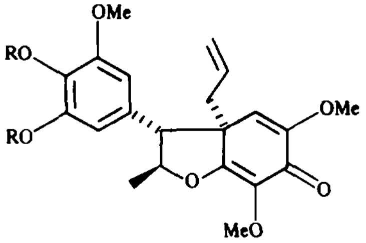


1a R-R = CH_2
1b R = Me



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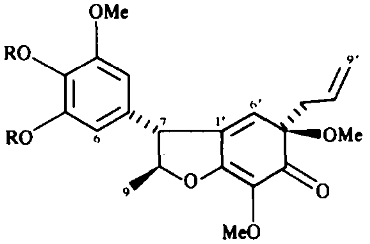
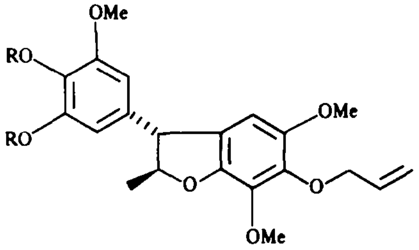
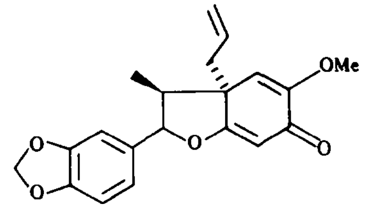


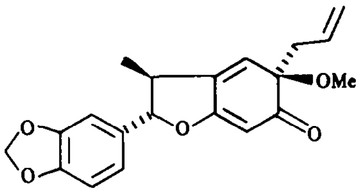
3a R-R = CH_2
3b R = Me



4a R-R = CH_2
4b R = Me



8a α - Ar
8b β - Ar



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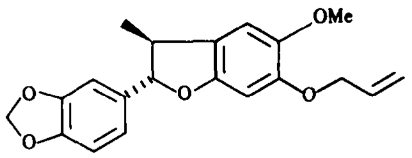

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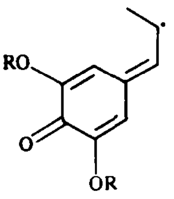

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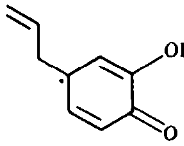

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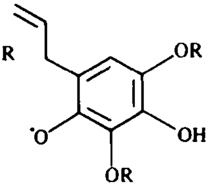

13

range coupling of H-6′ and H-7. This information can best be accommodated as shown in **3a** and **3b** with an α-allyl. The rearrangement of the allyl from C-1′ to C-5′ was demonstrated to take place in the common tetrahydrobenzofuranoid neolignans (e.g. **8a** → **9**) [6]. The co-occurrence of **2a** and **2b** with **3a** and **3b** indicates that an analogous reaction also takes place in the 'unusual' series. Thus if the 1′-allyl is α-oriented in the compounds of type **2** it should possess the same orientation in the compounds of type **3**.

In the common series the continuation of rearrangements, now by a retro-Claisen mechanism, transposes the allyl from C-5′ to the oxygen at C-4′ (e.g. **9** → **10**) [6]. The analogous reaction also occurs in the 'unusual' series as demonstrated by the occurrence of **4a** and **4b**. The IR spectra of these compounds lack maxima which could be assigned to carbonyl absorption. ^{13}C NMR confirms the absence of C=O and together with ^{1}H NMR provides evidence for the localization of the allylic methylene on an oxy-group (^{1}H δ4.47, *d*, $J = 6$ Hz; ^{13}C δ74) and of the lone H-6′ on an aromatic ring (^{1}H δ6.2, *s*; ^{13}C 103).

DISCUSSION

Biosynthesis of the common benzofuranoid neolignans is thought to involve coupling of the propenylphenol and allylphenol derived radicals **11** and **12**. Di- and trioxygenation of allylphenols is common, a reason for the wide distribution of neolignans belonging to the common series. The biosynthesis of 'unusual' benzofuranoid neolignans is thought to involve coupling of the radicals **11** and **13**. Tetraoxygenation of allylphenols is a rare feature, and hence the restricted occurrence of benzofuranoid neolignans belonging to the 'unusual' series. It is certainly significant that in *Licaria chrysophylla* such neolignans are accompanied by 2,3,4,5-tetramethoxyallylbenzene (**5**) and other simple $C_6 \cdot C_3$-derivatives of the same oxygenation pattern (**6**, **7**). Thus 2,4-dihydroxy-3,5-dimethoxyallylbenzene could be the general precursor of **5**, void of free hydroxyls and thus less prone to oxidation, and of **13**, an intermediate in the oxidative process of neolignan formation.

EXPERIMENTAL

Isolation of the constituents. Plant material was collected near Humaitá, Amazonas State by Dr. Hipolito P. Ferreira Fo., UNESP, Araraquara, and classified as stemming from *Licaria chrysophylla* (Meissn.) Kośterm. by Prof. Klaus Kubitzki, Universität, Hamburg. Bark (50 g) was extracted with light petroleum. The solvent was evapd and the residue (4.4 g) was partitioned between light petroleum and MeOH. The MeOH solution was evapd and the residue (2.8 g) was submitted to column chromatography (silica gel, 30 g). Elution was performed with light petrol–EtOAc 4:1 (fr. 1), C_6H_6–EtOAc 4:1 (fr. 6–11), C_6H_6–EtOAc 4:1 (fr. 12–15), C_6H_6–EtOAc 7:3 (fr. 38–40), C_6H_6–EtOAc 7:3 (fr. 41), EtOAc (fr. 43–45). The solvent of each fraction was evapd and the residues submitted to preparative TLC. Fr. 1 (920 mg) gave **5**. Fr. 6–11 (210 mg) gave **4a** (25 mg), **4b** (26 mg) and **7** (30 mg). Fr. 12–15 (160 mg) gave **4b** (60 mg). Fr. 38–40 (74 mg) gave **3a** (10 mg). Fr. 41 (145 mg) gave **3a** (40 mg) and **6** (12 mg). Fr. 43–45 (157 mg) gave **3b** (100 mg).

Wood (1 kg), by the same process, gave **5** (1.5 g), **4b** (66 mg), 7 (29 mg), **3a** (20 mg), **3b** (20 mg), **2a** (10 mg), **2b** (9 mg).

Fruit calyxes (514 g), by the same process, gave **2b** (200 mg), 3a (140 mg), **3b** (1.3 g), **4b** (97 mg).

Identification. The known compounds **1a** [2] and **5** [3] were identified, respectively, by comparison with an authentic sample and by spectral data.

rel-(7R,8S,1'S)-$\Delta^{8'}$-3,3',5'-*Trimethoxy-4,5-methylenedioxy*-1',4'-*dihydro-4'-oxo-7.1',8.O.2'-neolignan* (*chrysophyllon I-A*, **2a**). Oil. UV $\lambda_{\max}^{\text{MeOH}}$ nm: 269 (ε 8700). IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 1660, 1640, 1610, 1500, 1440, 1350, 1280, 1240, 1200, 1110, 1040, 920, 825. ^{1}H NMR (Table 1); ^{13}C NMR (Table 2). MS m/z (rel. int.): 400 $[M]^{+\cdot}$ (22), 370 (20), 359 (50), 208 (27), 193 (27), 192 (67), 191 (17), 189 (19), 180 (12), 179 (45), 178 (11), 177 (22), 171 (10), 165 (36), 163 (13), 161 (24), 152 (16), 151 (16), 149 (22), 148 (13), 147 (30), 141 (15), 135 (63).

rel-(7R,8S, 1'S)-Δ^8-3, 4,5 ,3' ,5'-*Pentamethoxy*-1', 4'-*dihydro-4'-oxo-7.1',8.O.2'-neolignan* (*chrysophyllon I-B*, **2b**). Oil. UV $\lambda_{\max}^{\text{MeOH}}$ nm: 269 (ε 8700). IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 1640, 1610, 1590, 1500, 1450, 1425, 1350, 1280, 1240, 1190, 1120, 1060, 1010, 910, 820. ^{1}H NMR (Table 1); ^{13}C NMR (Table 2). MS m/z (rel. int.): 416 $[M]^{+\cdot}$ (26), 386 (22), 375 (52), 208 (60), 195 (33), 193 (35), 181 (18), 179 (13), 177 (12), 168 (12), 167 (12), 165 (19), 163 (12), 153 (14), 151 (10), 149 (22), 148 (10), 147 (18), 137 (15), 135 (15). CD (*c* 0.01; MeOH): $[\theta]_{330}^{\max}$ + 14 550, $[\theta]_{282}^{\max}$ − 15 180.

rel-(7R,8S,5'R)-$\Delta^{8'}$-3,3',5'-*Trimethoxy-4,5-methylenedioxy*-1',4'-*dihydro-4'-oxo-7.1',8.O.2'-neolignan* (*chrysophyllon II-A*, **3a**). Oil. UV $\lambda_{\max}^{\text{MeOH}}$ nm: 334 (ε 7200). IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 1660, 1630, 1610, 1500, 1450, 1430, 1350, 1310, 1225, 1200, 1130, 1110, 1070, 1040, 910, 830. ^{1}H NMR (Table 1); ^{13}C NMR (Table 2). MS m/z (rel. int.): 400 $[M]^{+\cdot}$ (10), 359 (37), 208 (12), 193 (14), 192 (21), 179 (21), 165 (23), 152 (16), 147 (11), 133 (13). CD (*c* 0.01; MeOH): $[\theta]_{365}^{\max}$ + 14 400, $[\theta]_{315}^{\max}$ − 21 200, $[\theta]_{236}^{\max}$ + 20 400.

rel-(7R,8S,5'R)-$\Delta^{8'}$-3,4,5,3',5'-*Pentamethoxy*-1,4' -*dihydro-4'-oxo-7.1',8.O.2'-neolignan* (*chrysophyllon II-B*, **3b**). Mp 138–140° (C_6H_6). UV $\lambda_{\max}^{\text{MeOH}}$ 334 (ε 7200). IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 1660, 1610, 1590, 1510, 1460, 1430, 1360, 1320, 1300, 1250, 1200, 1130, 1100, 1070, 1050, 1000, 960, 920, 840. ^{1}H NMR (Table 1); ^{13}C NMR (Table 2). MS m/z (rel. int.): 416 $[M]^+$ (10), 375 (45), 208 (50), 195 (24), 193 (22), 181 (17), 179 (14), 177 (14), 168 (12), 165 (20), 153 (17), 147 (23), 137 (12), 135 (15), 133 (15). CD (*c* 0.01; MeOH): $[\theta]_{365}^{\max}$ + 15 800, $[\theta]_{315}^{\max}$ − 23 700, $[\theta]_{236}^{\max}$ + 16 220.

rel-(7R,8S)-$\Delta^{8'}$-3,3',5'-*Trimethoxy-4,5-methylenedioxy*-7.1', 8.O.2',4'.O.7'-*neolignan* (*chrysophyllon III-A*, **4a**). Oil. IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 1635, 1610, 1500, 1450, 1380, 1350, 1200, 1130, 1050, 930, 820. ^{1}H NMR (Table 1); ^{13}C NMR (Table 2).

rel-(7R,8S)-$\Delta^{8'}$-3,4,5,3',5'-*Pentamethoxy*-7.1', 8.O.2', 4.O.7'-*neolignan* (*chrysophyllon III-B*, **4b**). Oil. UV $\lambda_{\max}^{\text{MeOH}}$ nm: 294 (ε 10 000). IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 1590, 1500, 1460, 1420, 1350, 1240, 1120, 1040, 1000, 920, 820. ^{1}H NMR (Table 1); ^{13}C NMR (Table 2). MS m/z (rel. int.): 416 $[M]^{+\cdot}$ (5), 375 (15), 207 (12), 147 (10). CD (*c* 0.01; MeOH): $[\theta]_{390}^{\max}$ − 6450, $[\theta]_{234}^{\max}$ + 27 660.

2,3,4,5-*Tetramethoxyallylbenzene* (*3-methoxy-γ-asarone*, **5**). Oil. IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 1640, 1590, 1500, 1460, 1410, 1340, 1230, 1200,

Table 1. ^{1}H NMR data (chemical shift, multiplicity, coupling constant in Hz) for the chrysophyllons ($CDCl_3$, 60 MHz)

H	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**
2,6	6.53 *s*	6.60 *s*	6.40 *s*	6.42 *s*	6.33 *s*	6.42 *s*
7	3.07 *d* 10	3.13 *d* 10	3.67 *dd* 9,2	3.67 *dd* 9,2	*ca* 3.83 *m*	*ca* 3.80 *m*
8	4.7–5.2 *m*	4.7–5.2 *m*	4.2–4.7 *m*	4.3–4.8 *m*	4.3–4.8 *m*	4.3–4.8 *m*
9	1.48 *d* 6	1.52 *d* 6	1.53 *d* 6	1.57 *d* 6	1.50 *d* 6	1.50 *d* 6
6'	5.30 *s*	5.37 *s*	5.80 *d* 2	5.82 *d* 2	6.17 *s*	6.23 *s*
7'	2.03 *dd* 14,6	1.96 *dd* 14,6	2.43 *d* 6	2.43 *d* 6	4.47 *d* 6	4.48 *d* 6
7'	2.57 *dd* 14,6	2.70 *dd* 14,6				
8'	5.1–5.5 *m*	5.1–5.5 *m*	5.2–5.7 *m*	5.2–5.7 *m*	5.7–6.1 *m*	5.8–6.2 *m*
9'	4.9–5.2 *m*	4.9–5.2 *m*	4.7–5.1 *m*	4.8–5.2 *m*	5.0–5.5 *m*	5.1–5.6 *m*
CH_2O_2	6.10 s	—	6.00 *s*	—	5.93 *s*	—
OMe	3.67 *s*	3.70 *s*	3.07 *s*	3.07 *s*	3.67 *s*	3.67 *s*
OMe	3.87 *s*	3.87 *s*	3.83 *s*	3.80 *s*	3.87 *s*	3.75 *s*
OMe	4.00 *s*	3.97 *s*	3.88 *s*	3.87 *s*	3.93 *s*	3.80 *s*
OMe	—	3.97 *s*	—	3.87 *s*	—	3.97 *s*

Table 2. ^{13}C NMR chemical shifts for the chrysophyllons ($CDCl_3$, 20 MHz)

C	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**
1	133.2	132.5	131.8	131.1	136.1	136.8
2	103.0	105.8	101.9	104.8	102.0	104.9
3	149.3	151.8	149.3	152.9	149.1	153.1
4	135.1	137.3	134.7	138.8	136.1	136.7
5	143.5	151.8	143.5	152.9	143.5	153.1
6	110.0	105.8	108.4	104.8	107.8	104.9
7	60.2	59.0	59.8	59.9	60.4	60.3
8	83.0	82.4	89.8	89.9	88.7	88.4
9	19.2	18.7	19.1	18.7	19.8	19.7
1′	50.5	50.1	139.1	137.1	125.0	125.0
2′	166.0	165.5	158.8	158.4	145.5	145.3
3′	126.0	127.3	131.6	130.9	140.6	140.6
4′	178.4	177.8	195.7	195.1	138.2	138.2
5′	152.6	152.7	82.6	81.9	148.1	147.9
6′	107.1	106.8	131.6	132.6	103.5	103.3
7′	37.5	36.8	45.1	44.5	74.3	74.0
8′	131.0	130.3	130.6	130.3	134.4	134.2
9′	120.0	118.9	119.0	118.2	117.2	116.9
CH_2O_2	101.4	—	101.3	—	101.3	—
OMe	55.2	54.5	53.4	53.0	56.6	56.5
OMe	56.9	55.6	53.8	53.6	56.8	55.7
OMe	59.5	59.4	56.6	55.5	57.1	57.1
OMe	—	59.9	—	59.2	—	60.1

1120, 1080, 1040, 1010, 910, 870, 830. ^{1}H NMR ($CDCl_3$, 60 MHz): δ6.38 (*s*, H-6), 5.5–6.3 (*m*, H-β), 4.8–5.2 (*m*, 2H-γ), 3.28 (*d*, *J* = 6 Hz, 2H-α), 3.80, 3.87 (2*s*, 4 OMe). ^{13}C NMR ($CDCl_3$, 20 MHz): δ127.1 (C-1), 144.7 (C-2), 146.4 (C-3), 140.9 (C-4), 148.7 (C-5), 107.2 (C-6), 33.4 (C-α), 136.6 (C-β), 114.7 (C-γ), 60.1 (OMe-2,4), 55.3 (OMe-3,5). MS *m/z* (rel. int.): 237 $[M-1]^+$ (57), 227 (15), 222 (13), 221 (15), 211 (11), 209 (15), 208 (25), 207 (26), 206 (79), 197 (11), 196 (12), 194 (16), 193 (32), 192 (13), 191 (40), 181 (12), 179 (27), 178 (21), 177 (16), 175 (13), 168 (14), 167 (15), 166 (17), 165 (18), 164 (19), 163 (36), 151 (28), 147 (22), 135 (32).

2,3,4,5-*Tetramethoxycinnamyl alcohol* (**6**). Needles, mp 72–74° ($MeOH–C_6H_{14}$). IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 3480, 1720, 1670, 1590, 1490, 1460, 1410, 1340, 1220, 1190, 1080, 1040, 925, 880, 840. ^{1}H NMR ($CDCl_3$, 60 MHz): δ6.6 (*s*, H-6), 6.3 (*m*, 2H-α), 5.9 (*m*, H-β), 4.22 (*d*, *J* = 6 Hz, 2H-γ), 3.7 (*s*, OMe-2), 3.8 (*s*, 2 OMe-3,5), 3.83 (*s*, OMe-4). ^{13}C NMR ($CDCl_3$, 20 MHz): δ130.3 (C-1), 142.2 (C-2), 145.1 (C-3), 137.3 (C-4), 149.3 (C-5), 103.5 (C-6), 128.8 (C-α), 124.8 (C-β), 63.5 (C-γ), 60.9 (OMe-2), 55.9 (OMe-3,5), 61.1 (OMe-4). MS *m/z* (rel. int.): 254 $[M]^{+\cdot}$ (24), 227 (26), 226 (17), 225 (18), 222 (15), 221 (100), 212 (10), 211 (29), 209 (14), 208 (11), 206 (12), 198 (12), 197 (15), 196 (13), 195 (11), 194 (17), 193 (19), 191 (12), 184 (12), 181 (15), 179 (21), 178 (27), 177 (14), 168 (14), 167 (21), 166 (12), 165 (13), 163 (20), 153 (16), 152 (12), 151 (23), 150 (11), 149 (19), 139 (13), 137 (14), 136 (12), 135 (17), 133 (10).

2,3,4,5-*Tetramethoxycinnamaldehyde* (7). Oil. IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 1670, 1620, 1590, 1490, 1460, 1410, 1350, 1230, 1200, 1120, 1080, 1040, 1000, 930, 870, 830. ^{1}H NMR ($CDCl_3$, 60 MHz): δ9.67 (*d*, *J* = 7 Hz, CHO), 6.80 (*s*, H-6), 7.63 (*d*, *J* = 16 Hz, H-α), 6.50 (*dd*, J = 7, 16 Hz, H-β), 3.87 (*s*, 4 OMe). ^{13}C NMR ($CDCl_3$, 60 MHz): δ104.5 (C-6), 147.0 (C-α), 128.4 (C-β), 193.9 (CHO), 61.3 (OMe-2), 56.3 (OMe-3,5), 61.9 (OMe-4). MS *m/z* (rel. int.): 252 $[M]^{+\cdot}$ (5), 222 (14), 221 (100), 193 (10), 179 (18), 178 (33), 177 (17), 166 (14), 163 (83), 151 (32), 150 (11), 136 (16), 135 (24), 133 (12).

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REFERENCES

1. Dias, D. A., Yoshida, M. and Gottlieb, O. R. (1986) *Phytochemistry* **25**, 2613.
2. Ferreira, Z. S., Roque, N. C., Gottlieb, O. R. and Gottlieb, H. E. (1982) *Phytochemistry* **21**, 2756.
3. Thoms, H. (1908) *Ber.* **41**, 2753.
4. Gottlieb, O. R. (1978) *Prog. Chem. Org. Nat. Prod.* **35**, 1.
5. Wenkert, E., Gottlieb, H. E., Gottlieb, O. R., Pereira, M. O. da S. and Formiga, M. D. (1976) *Phytochemistry* **15**, 1547.
6. Aiba, C. J., Fernandes, J. B., Gottlieb, O. R. and Maia, J. G. S. (1975) *Phytochemistry* **14**, 1597.