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ARYLTETRALONE AND ARYLINDANONE NEOLIGNANS FROM *VIROLA SEBIFERA**

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Key Word Index—*Virola sebifera*; Myristicaceae; fruits; tetralone neolignans; indanone neolignans.

Abstract—The fruits of *Virola sebifera* contain several tetralone neolignans, including 2,4-dihydroxy-6,7-methylenedioxy-2,3-dimethyl-4-veratryltetralin-1-one. The 3-hydroxylated derivative of this compound may undergo a biosynthetic pinacol–pinacolone rearrangement to give 2-acetyl-3-hydroxy-2-methyl-5,6-methylenedioxy-3-veratrylindan-1-one which, together with other indanone neolignans, was also isolated.

INTRODUCTION

The fruits of *Virola sebifera* Aubl. have been found to contain a 1,11-diarylundecan-1-one [2], four dibenzylbutyrolactone lignans [3] and four 4-aryltetralin-1-one neolignans [2]. Three of the latter compounds have a hydroxyl at position 4. The present paper describes the isolation from the same plant material of four further hydroxyaryltetralones of still higher oxidation state (**1a**, **1b**, **2** and **3**), and three 3-arylindan-1-ones (**4**, **5** and **6**).

RESULTS

The molecular formulae $C_{21}H_{22}O_7$ (**1a**, **1b**) and $C_{21}H_{20}O_6$ (**2**, **3**), determined by mass spectra, differ by 18 mass units. Indeed **1a**, upon treatment with acid, looses water and gives **2**. This compound possesses two aromatic rings, one in the form of a 3,4-dioxyphenyl (^{1}H NMR: δ6.5–7.1, 3H) and one in the form of a 3,4-dioxyphenylene (δ6.26, 7.50, 2*s*, 2H) (Table 1). In addition to twelve aromatic carbons, ^{13}C NMR reveals the presence of a carbonyl (δ203.7), two disubstituted olefinic carbons (δ130.2, 154.7, 2*s*), one tertiary carbinolic carbon (δ101.3, *s*) and two methyls (δ14.8, 29.2, 2*q*) (Table 2). As already suggested by these data, and confirmed by the ^{1}H NMR singlets at δ1.86 and 1.58 respectively, the methyls are linked to one of the olefinic carbons and the carbinolic carbon. The evidence is consistent with formula **2** in which the methoxyls, rather than the methylenedioxy group, are located on the tetralone system on account of the considerably larger shielding by the non-coplanar piperonyl of one of the methoxyls ($\Delta\delta_{OMe}$ 0.23 ppm). The analogous $\Delta\delta_{OMe}$ value for **1a** is also 0.23, against 0.10 for its isomer **1b**.

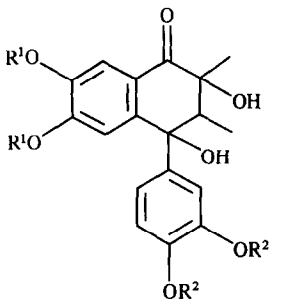
Since **2** is obtained from **1a** by dehydration, this latter compound can be formulated as shown. Indeed, its mass spectrum includes a peak at *m/z* 149, indicative of the substitution of the carbinol by piperonyl. An ion of identical mass is also formed by **3**, but not by **2** which cannot form a piperonylacylium ion. The mass spectra of **1a** and **1b**, in contrast to the mass spectrum of **2**, provide evidence for a facile retro-Diels–Alder cleavage with loss of the 72 mass units pertaining to MeCOHCHMe. The analogous fragmentation of **3** expels the 54 mass units of MeCCMe. This fact and the presence of the intense peak at *m/z* 149 are adduced in justification for the proposed formula.

The molecular formula of **6**, $C_{19}H_{16}O_5$, was determined by mass spectroscopy. The compound possesses two aromatic rings, one in the form of a 3,4-dioxyphenyl (^{1}H NMR: *ca* δ7, *m*, 3H) and one in the form of a 3,4-dioxyphenylene (δ6.69, 7.17, 2*s*, 2H) (Table 3). In addition to twelve aromatic carbons, ^{13}C NMR reveals the presence of a carbonyl (δ208.0), two disubstituted olefinic carbons (δ128.9, 168.6, 2*s*) and one methyl (δ18.0, *s*) (Table 4). The methyl is thus probably linked to one of the olefinic carbons. This is confirmed by the ^{1}H NMR singlet at δ1.89, a signal, which appears, in the hydrogenated derivative, as a doublet (J = 8 Hz) at δ1.33. The evidence is consistent with formula **6**. The alternative formula with the methyl and aryl groups at interchanged positions cannot represent the compound since this, as the flavones, possesses a cinnamoyl chromophore (UV λ_{max} 340 nm). The alternative structure, by analogy with the isoflavones, would be expected to show an intense benzoyl absorption (λ_{max} 240–280 nm). The methylenedioxy group of **6** is located on the indanone system on account of the near equivalence of the methoxyls ($\Delta\delta_{OMe}$ 0.03).

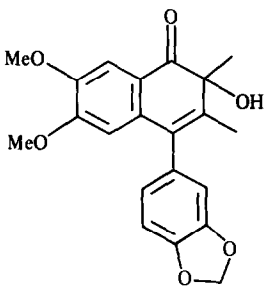
While **4** is quite stable, **5** is easily decomposed by contact with the usual trace of DCl in $CDCl_3$ to **6**. Compound **5** was thus not isolated in pure state and its MS could not be determined. Its ^{1}H and ^{13}C NMR spectra (Tables 3 and 4) were obtained by subtraction of the peaks due to the impurities, i.e. **4** and **6**. These spectra of **5** are closely comparable to the analogous spectra of **4**. Compounds **4** and **5** are thus isomeric and the molecular formula $C_{21}H_{20}O_7$, determined for **4** by mass spectroscopy, must also be valid for **5**.

The formulae of **4** and **5** differ from that of **6** by $C_2H_4O_2$ and the decomposition of **5** should thus involve loss of acetic acid. Effecting mentally the reverse operation, i.e. the addition of acetyl/hydroxyl onto **6** in the

*Part 21 in the series "The Chemistry of Brazilian Myristicaceae". For part 20 see ref. [1] Taken from part of the Doctorate thesis presented by L.M.X.L. to the Universidade de São Paulo (1983).



1a $R^1 = Me, R^2 — R^2 = CH_2$
1b $R^1 — R^1 = CH_2, R^2 = Me$



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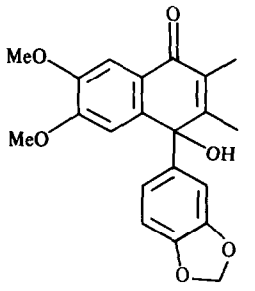

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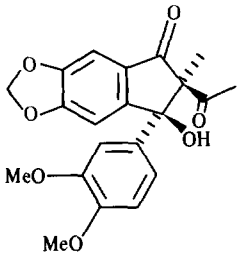

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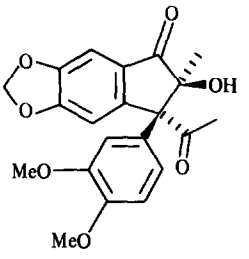

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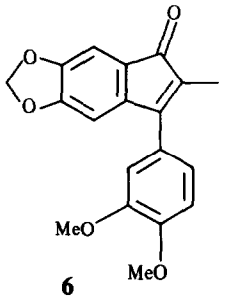

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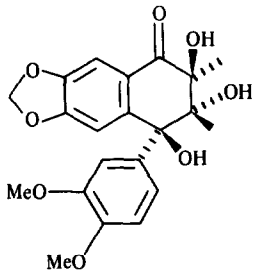

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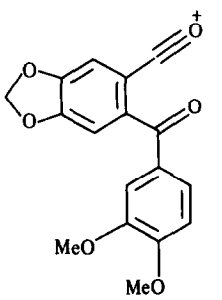

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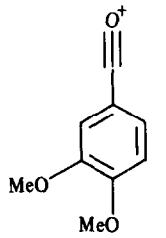

9

Table 1 ^{1}H NMR data of tetralones (60 MHz, $CDCl_3$)

Protons	1a	1b	2	3
5	6.36 *s*	6.22 *s*	6.26 *s*	6.93 *s*
8	7.48 *s*	7.07 *s*	7.50 *s*	7.34 *s*
2′				6.93 *d* (2)*
5′	6.6–7	6.5–6.9	6.5–7.1	6.64 *d* (8)
6′				6.68 *dd* (2, 8)
O_2CH_2	5.96 *s*	5.96 *s*	6.03 *s*	5.89 *s*
OMe	3.92 *s*	3.73 *s*	3.96 *s*	3.89 *s*
OMe	3.69 *s*	3.63 *s*	3.73 *s*	3.78 *s*
OH	4.33 *s*	4.36 *s*	3.10 *s*	3.15 *s*
OH	3.36 *s*	3.46 *s*	—	—
Me-2	1.53 *s*	1.53 *s*	1.58 *s*	2.00 *s*
Me-3	1.07 *d* (7)	1.05 *d* (7)	1.86 *s*	2.00 *s*
3	2.41 *q* (7)	2.43 *q* (7)	—	—

*Coupling constants (J, in Hz) are given in parentheses.

trans-form leads to unstable **5**, while *cis*-addition would lead to the stable isomer **4**. In each case two alternative addition products can be formulated. The ambiguity can be resolved in the *cis*-case by interpretation of the relatively intense mass spectral peaks at *m/z* 313 (**8**) and 165 (**9**) which require the localization of the hydroxyl at the doubly benzylic position as shown in **4**. The ambiguity can be resolved in the *trans*-case by observing the conspicuous differences of the ^{13}C NMR spectra of the isomers. A signal at relatively low field (δ209.0) in the spectrum of **4** suggests the existence of hydrogen bonding [4] and again points to the *cis*-relationship of acetyl/hydroxyl. More importantly, the C-Me signals for **4** (δ17.6) and **5** (δ24.5) are quite different. The 6.9 ppm downfield shift observed upon passing from **4** to **5** can be ascribed mainly to the replacement on the α-carbon (CαMe) of the acetyl (**4**) by the hydroxyl (**5**) [5]. All ^{1}H and ^{13}C NMR data for **4** and **5** are comparable and consistent with these proposals. Again, for **4** and **5** $\Delta\delta_{OMe}$ are very

Table 2. ^{13}C NMR data of tetralones (20 MHz, $CDCl_3$)

Carbons	2	3
1	203.7 *s*	184.5 *s*
2	101.3 *s*	130.5 *s*
3	154.7 *s*	156.8 *s*
4	130.2 *s*	73.7 *s*
4a	142.1 *s*	137.6 *s*
5	109.1 *d*	109.9 *d*
6	148.2 *s*	153.5 *s*
7	147.0 *s*	148.9 *s*
8	105.1 *d*	106.4 *d*
8a	123.1 *s*	122.9 *s*
Me-2	29.2 *q*	11.6 *q*
Me-3	14.8 *q*	15.8 *q*
1′	131.9 *s*	143.7 *s*
2′	108.1 *d*	107.4 *d*
3′	147.7 *s*	147.9 *s*
4′	146.8 *s*	146.7 *s*
5′	108.7 *d*	108.2 *d*
6′	122.0 *d*	118.9 *d*
O_2CH_2	101.2 *t*	101.1 *t*
OMe	55.9 *q*	56.0 *q*
OMe	56.1 *q*	56.0 *q*

Table 4. ^{13}C NMR data of indanones (20 MHz, $CDCl_3$)

Carbons	4	5	6
1	199.4 *s*	203.9 *s*	208.0 *s*
2	73.7 *s*	83.9 *s*	128.9 *s*
3	85.0 *s*	72.6 *s*	168.6 *s*
3a	155.4 *s*	152.5 *s*	156.9 *s*
4	109.0 *d*	108 9 *d*	108.5 *d*
5	151.1 *s*	151.3 *s*	151.7 *s*
6	148.3 *s*	149.6 *s*	149.3 *s*
7	106.3 *d*	106.1 *d*	105.9 *d*
7a	129.2 *s*	128.2 *s*	127.9 *s*
CMe	17.6 *q*	24.5 *q*	18.0 *q*
COMe	27.5 *q*	28.8 *q*	—
COMe	209.0 *s*	195.3 *s*	—
1′	140.3 *s*	137.4 *s*	132.4 *s*
2′	107.6 *d*	107.8 *d*	108.0 *d*
3′	147.7 *s*	147.0 *s*	147.7 *s*
4′	147.9 *s*	147.6 *s*	148.2 *s*
5′	108.7 *d*	111.3 *d*	111.7 *d*
6′	120.3 *d*	122.1 *d*	120.8 *d*
O_2CH_2	101.5 *t*	101.2 *t*	103.5 *t*
OMe	56.6 *q*	56.2 *q*	55.8 *q*
OMe	56.4 *q*	55.9 *q*	55 7 *q*

Table 3. ^1H NMR data of indanones (60 MHz, $CDCl_3$)

Protons	4	5	6	Dihydro-6
7	7.30 *s*	7.16 *s*	7.17 *s*	7 20 *s*
4	7.13 *s*	6.5–7	6.69 *s*	*ca* 6.8
2′, 5′, 6′	6.5–7		7 m	6.4–6.8
C–Me	0.78 *s*	1.12 *s*	1.89 *s*	1.33 *d* (J = 8 Hz)
COMe	2.12 *s*	2.23 *s*	—	—
OH	6.9	*ca* 4	—	—
O_2CH_2	6.00 *s*	5.91 *s*	6.10 *s*	5.92 *s*
OMe	3.9	3.9	3 89 *s*	3.92 *s*
OMe	3.9	3.9	3.86 *s*	3.86 *s*
2	—	—	—	1.5–2
3	—	—	—	*ca* 3.9

small, a fact which suggests the methoxyls rather than the methylenedioxy group to be located on the phenyl substituent.

DISCUSSION

The concomitant isolation of dihydroxytetralones and acetylhydroxyindanones suggests the intermediate existence of trihydroxytetralones. Indeed, **7**, a putative oxidation product of **1b**, would be expected to form **4** and **5** by pinacol–pinacolone type rearrangements.

EXPERIMENTAL

Compound numbers immediately followed by references refer to compounds represented by these numbers in the given references. Compound numbers not followed by references refer to compounds described in the present paper. Asterisked compound numbers refer to compounds to be described in subsequent papers.

Isolation of the constituents of ripening fruits of *V. sebifera* from São Sebastião do Paraíso, Minas Gerais State, collected by Hipolito F. Paulino Filho, UNESP, Araraquara, and identified by Dr. William A. Rodrigues, INPA, Manaus [2]. Air dried seeds (225 g) and pericarp (360 g) were percolated with C_6H_6 (room temp.). The extract of the seeds (60 g) was partitioned between petrol and MeOH–H_2O (9:1). The former soln was evapd yielding fats (27 g). 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) was submitted to dry CC (450 g silica gel, $CHCl_3$–EtOAc, 97:3). The column (A) was cut into 33 equal portions. The eluate of portions 1–9 (4.2 g) was 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** [2] (400 mg) and **3b** [2] (38 mg). The eluate of portions 10–14 (1.7 g) was separated by prep TLC (silica gel, $CHCl_3$) into **2b** [2] (144 mg) and **3*** (28.5 mg). The eluate of portions 16–21 (2.9 g) was submitted to dry CC (30 g silica gel +10% H_2O, $CHCl_3$–EtOAc, 19:1). The column (B) was cut into 13 equal portions. The eluate of portions 2–5 was separated by repeated prep. TLC into **3** (47 mg), **4** (60 mg), **5** (70 mg) and **6** (6 mg). The eluate of portions 6 and 7 was separated by prep. TLC (silica gel, C_6H_6–EtOAc, 4:1) into **7*** (34 mg) and **2a** [3] (32 mg). The eluate of portions 10–13 was separated by prep. TLC (silica gel, C_6H_6–EtOAc, 9:1) into **7*** (182 mg), **6b*** (20 mg) and **6a*** (19 mg). The eluate of portion 23 (2.1 g) of column A was purified by TLC to **2a** [2] (2 g). The eluate of portion 28 (0.8 g) was fractionally crystallized from MeOH into **3a** [2] (164 mg) and **4*** (49 mg). The eluate of portions 29 and 30 (1.1 g) was separated by prep. TLC (silica gel, $CHCl_3$–MeOH, 9:1) into **4*** (33 mg) and **10*** (30 mg).

The extract of the pericarp (31 g) was suspended in MeOH. The insoluble portion, consisting of fats, was separated by filtration. The MeOH soln was evapd and the residue (20 g) was submitted to dry CC (silica gel, $CHCl_3$–EtOAc, 19:1). The column was cut into three equal portions. The eluate of portion 1

(2.8 g) was separated by prep. TLC (silica gel, $CHCl_3$–EtOAc, 19:1) into **8*** (105 mg), **2c** [3] (118 mg) and **1** [3] (130 mg). The eluate of portion 3 (6.8 g) was submitted to CC (silica gel). The following products were obtained upon elution with the indicated solvents: fats ($CHCl_3$), **8*** (120 mg) and **9*** (40 mg) ($CHCl_3$–EtOAc, 49.1), **2a** [2] (8 mg) ($CHCl_3$–EtOAc, 19:1), **1** [3], **2b** [3] and **2c** [3] (300 mg, $CHCl_3$–EtOAc, 9:1), **2b** [3] (255 mg, $CHCl_3$–EtOAc, 4.1)

Isolation of the constituents of mature fruits of *V. sebifera* from a savannah near Humaitá, Amazonas State, collected by Hipolito F. Paulino Filho, UNESP, Araraquara, and identified by Dr. William A. Rodrigues, INPA, Manaus. The fruits (5.8 kg) were separated into hair (15 g), epicarp (3.2 kg) and seeds (2.6 kg). The latter were separated into aril (0.2 kg), tegument (0.7 kg) and kernel (1.7 kg). Each of these parts was extracted separately with $CHCl_3$. The extract of hair (5 g) was suspended in MeOH. The filtered soln was evapd and part (1 g) of the residue (2.5 g) separated by prep. TLC (silica gel, C_6H_6–EtOAc, 9:1) into fat (30 mg), **2a** [2] (20 mg), **3a** [2] (10 mg) and **2b** [3] (50 mg). The extract of pericarp (214 g) was suspended in MeOH. The filtered soln was evapd and part (1 g) of the residue (129 g) was separated by prep TLC (silica gel, C_6H_6–EtOAc, 19:1) into aliphatic material (300 mg), **1a*** (48 mg) and **3a** [2] (132 mg). The extract of aril (24 g) was suspended in MeOH. The filtered soln was evapd and part (0.5 g) of the residue (10.5 g) was separated by prep TLC (Al_2O_3, C_6H_6–EtOAc, 9·1) into **3*** (26 mg), **2a** [2] (13 mg) and **3a** [2] (258 mg) The extract of tegument (32 g) was suspended in Me_2CO The filtered soln was evapd and part (11 g) of the residue (25 g) was submitted to CC (120 g silica gel + 10% H_2O). The following products were obtained in order upon elution with C_6H_6–EtOAc (4.1) fats (7 g), **3a** [2] (95 mg), **1a** (4 mg), **2** (26 mg), **1b*** (23 mg), **1b** (4 mg), **4*** (17 mg), **2*** (22 mg) and **5*** (4 mg). Part (32 g) of the extract of kernel (673 g) was suspended in MeOH. The filtered soln was evapd and part (160 mg) of the residue (6 g) was separated by prep TLC (silica gel, C_6H_6–EtOAc, 4:1) into **3a** [2] (50 mg), **3*** (25 mg) and **2a** [2] (30 mg).

2,4-*Dihydroxy*-6,7-*dimethoxy*-2,3-*dimethyl*-4-*piperonyl*-*tetralin*-1-*one* (**1a**). Mp 81–85° (MeOH). IR ν_{max}^{KBr} cm^{-1}: 3460, 1675, 1595, 1500, 1440, 1280, 1230, 1130, 1120, UV λ_{max}^{MeOH} nm. 235, 275, 315 (ε 24 200, 11 550, 7200); ORD (MeOH): $|\phi|_{224}^{pk} + 31\,050$, $|\phi|_{260}^{sh} + 14\,700$, $|\phi|_{272}$ 0, $|\phi|_{300}^{tr} - 18\,050$, $|\phi|_{330}^{pk} - 5850$ CD (MeOH): $|\theta|_{233}^{max} + 3800$, $|\theta|_{250}^{max} - 3350$, $|\theta|_{260}^{inf} - 2950$, $|\theta|_{267}^{max} - 4600$, $|\theta|_{325}^{max} + 4600$, MS *m/z* (rel. int.): 386 $[M]^+$ (8), 368 (15), 352 (8), 325 (100), 314 (6), 310 (10), 281 (5), 201 (9), 165 (5), 149 (5), 85 (5), 83 (8)

2,4-*Dihydroxy*-6,7-*methylenedioxy*-2,3-*dimethyl*-4-*veratryl*-*tetralin*-1-*one* (**1b**). Amorphous solid IR ν_{max}^{KBr} cm^{-1}· 3460, 1675, 1595, 1495, 1440, 1280, 1230, 1130, 1120, 870, 785, UV λ_{max}^{MeOH} nm: 235, 248, 254, 260, 277, 310 (ε 24 150, 11 600, 11 000, 11 400, 12 750, 5950), MS *m/z* (rel. int.) 386 $[M]^+$ (8), 368 (14), 353 (8), 341 (10), 325 (100), 314 (45), 310 (6), 297 (9), 283 (5), 163 (35), 149 (24).

2-*Hydroxy*-6,7-*dimethoxy*-2,3-*dimethyl*-4-*piperonyltetralin*-3-*en*-1-*one* (**2**). Amorphous solid. IR ν_{max}^{KBr} cm^{-1}: 3460, 1710, 1600, 1500, 1480, 1440, 1290, 1275, 1240, 1225, 1040, UV λ_{max}^{MeOH} nm: 237, 265, 284, 315 (ε 15 700, 6950, 7650, 4700), ORD (MeOH): $|\phi|_{240}^{pk} + 2000$, $|\phi|_{251}$ 0, $|\phi|_{280}^{tr} - 13\,900$, $|\phi|_{320}^{inf} - 4250$, $|\phi|_{340}^{pk} - 1650$. CD (MeOH): $|\theta|_{225}^{max} + 3700$, $|\theta|_{258}^{max} - 1400$, $|\theta|_{317}^{max} + 3100$, $|\theta|_{330}^{max} + 1400$; MS *m/z* (rel. int.): 368 $[M]^+$ (< 1), 162 (9), 149 (5), 87 (17), 85 (78), 83 (100).

4-*Hydroxy*-6,7-*dimethoxy*-2,3-*dimethyl*-4-*piperonyltetralin*-2-*en*-1-*one* (**3**). Yellow, mp 215–217° (MeOH). IR ν_{max}^{KBr} cm^{-1}: 3450, 1650, 1600, 1500, 1250, 1130, 1100, 1040; UV λ_{max}^{MeOH} nm: 289, 245 (ε 11 600, 33 500); $[\alpha]_{577}^{25°} - 7°$ ($CHCl_3$); MS *m/z* (rel. int.): 368 $[M]^+$ (50), 353 (22), 350 (5), 335 (14), 325 (10), 247 (16), 219 (25), 165 (16), 150 (11), 149 (100), 121 (10).

rel-(2R,3S)-2-*Acetyl*-3-*hydroxy*-2-*methyl*-5,6-*methylenedioxy*-3-*veratrylindan*-1-*one* (**4**). Mp 250–255° ($Me_2CO + H_2O$). IR ν_{max}^{KBr} cm^{-1}: 3534, 1724, 1600, 1495–1440, 1357, 1295, 1127, 1110, 1040, 1013, 935, 870, 816, 756, UV λ_{max}^{MeOH} nm: 236, 280, 310 sh (ε 24 200, 11 100, 8000); MS *m/z* (rel. int.): 384 $[M]^+$ (1), 342 (45), 341 (100), 325 (27), 324 (68), 313 (43), 309 (9), 300 (15), 299 (70), 298 (20), 284 (7), 283 (7), 269 (10), 268 (17), 267 (12), 253 (6), 225 (5), 191 (8), 165 (8), 149 (25), 121 (26), 119 (80), 117 (75)

2-*Methyl*-5,6-*methylenedioxy*-3-*veratrylindan*-2-*en*-1-*one* (**6**). red, mp 214–216° (MeOH) [M found 324.0909, $C_{19}H_{16}O_5$ requires 324.0997]. IR ν_{max}^{KBr} cm^{-1}: 1692, 1600, 1484–1440, 1361, 1280–1212, 1093, 1035, 1008, 935, 867, 823, 797, 752, UV λ_{max}^{MeOH} nm. 240 inf., 265, 340 (ε 17 200, 32 400, 7600); MS *m/z* (rel int.). 324 $[M]^+$ (100), 325 (75), 309 (65), 298 (31), 293 (28), 281 (26), 271 (20), 263 (14), 251 (16), 223 (29), 195 (21), 165 (21), 152 (38), 151 (22), 149 (48), 121 (30).

rel-(2S,3S)-2-*Methyl*-5,6-*methylenedioxy*-4-*veratryl*-*indan*-1-*one* (*dihydro*-**6**). Oil. IR ν_{max}^{KBr} cm^{-1}: 1692, 1590, 1485–1420, 1280–1212, 1105, 1047, 1008, 935, 866, 823, 755; MS *m/z* (rel int.): 326 $[M]^+$ (100), 327 (21), 325 (10), 312 (13), 311 (63), 298 (7), 297 (13), 283 (6), 265 (8), 253 (6), 225 (6), 205 (6), 204 (7), 191 (5), 167 (8), 165 (8), 164 (22), 163 (9), 149 (32).

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