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BICYCLO(3.2.1)OCTANE NEOLIGNANS FROM AN *OCOTEA* SPECIES*

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Key Word Index—*Ocotea* species, Lauraceae, bicyclo(3 2 1)octanoid neolignans

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Abstract—The trunk wood of an *Ocotea* species from the Atlantic coast of southern Brazil contains five new neolignans *rel*-(1*R*,4*S*,5*S*,6*S*,7*R*,8*R*)-4-acetoxy-1-allyl-8-hydroxy-3,5-dimethoxy-7-methyl-6-(3′,4′-methylenedioxyphenyl and 3′-methoxy-4′,5′-methylenedioxyphenyl)-bicyclo(3 2 1)oct-2-enes, *rel*-(1*R*,4*S*,5*R*,6*S*,7*R*)-4-acetoxy-1-allyl-3,5-dimethoxy-7-methyl-6-(3′,4′,5′-trimethoxyphenyl)-8-oxobicyclo(3 2 1)oct-2-ene and *rel*-(1*S*,4*R*,5*S*,6*S*,7*R*,8*R*)-4-acetoxy-1-allyl-8-hydroxy-5-methoxy-7-methyl-6-(3′4′-methylenedioxyphenyl and 3′-methoxy-4′,5′-methylenedioxyphenyl)-3-oxobicyclo(3 2 1)octanes The latter two compounds are considered to be acid-catalysed demethylation products of the former pair of compounds

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INTRODUCTION

The genus *Ocotea* (Lauraceae) encompasses many species which are difficult to identify One of these species, from the mountainous Atlantic forest region of São Paulo State, where it is known as ‘canela parda’, is under investigation by Professor Klaus Kubitzki, Hamburg Its trunk wood yielded five new neolignans based on the novel constitutional types **1a** and **1b**, and the known type [2] **1e**

Like **2a** and **3a**, **1a** represents a fundamental bicyclo(3 2 1)octane neolignan [2] type from which all others can be formally derived by oxidation at C-2 (**1b**, **2b**, **3b**), C-4 (**1c**, **3c**) or at both positions (**1d**, **2d**) Constitution and natural occurrence of the known derivatives of each type are indicated in Table 1. Such compounds have so far been isolated only from Lauraceae Derivatives of the fundamental constitutional type (**3a**) of the bicyclo(3 2 1)octanoid series **3** have not been reported

For reasons stated in a previous paper of this series [16], nomenclature and numbering of neolignans follow the rules which were outlined in a recent review [2]

RESULTS AND DISCUSSION

The spectral properties of many bicyclo-octanoid neolignans having been reported, the constitutional elucidation of additional representatives is now a trivial matter In the present case the formulae, established by high resolution mass spectrometry and expanded by inspection of UV, IR and 60 MHz ^{1}H NMR spectra (Table 2), showed that the two C_6 C_3 units in all five neolignans are linked only by C–C bonds and suggest the compounds to be bicyclo-octanoids Mass spectra were, as usual, very helpful in defining one of the C_6 C_3 units by the registry of intense peaks corresponding to $[ArCH{=}CHMe]^+$ fragments The constitution of the second C_6 C_3 unit was defined by IR, ^{1}H and ^{13}C NMR studies (Tables 3 and 4) A carbonyl, registered by an IR absorption, is part either of the five-membered ring (**5**, IRν_{max} 1760 cm^{-1}), the six-membered ring (**6a**, **6b**, IRν_{max} (1730 cm^{-1}) or the acetate group (all compounds, IRν_{max} 1750 cm^{-1}). The mode of linkage of the central two carbons of the first unit with the C_6 part of the second unit is easy to determine only if the benzylic methine is vicinal to another methine at the bridgehead of the bicyclo(3 2.1)octane system In this case vicinality of methines, revealed by $J_{\text{H-7 H-4}'}$, indicates C-7 and C-4′ and hence also C-8 and C-1′ to be connected If, however, both bridgeheads are tetrasubstituted, as in the present cases, elucidation of the atomic sequence is a difficult task

For the five *Ocotea* compounds (**4a**, **4b**, **5**, **6a**, **6b**) this problem was solved by careful analysis of expanded 270 MHz ^{1}H NMR spectra Indeed, in addition to all required features, small couplings were observed between H-7 and H-4′ (J = 1 5–2 Hz), H-4′ and H-6′ (J = 1 Hz), as well as H-8 and H-2′ (J = 1 Hz) (Table 3) and confirmed by double resonance experiments These data not only confirm the proposed constitutions, but also indicate the orientation of the OH-2′ towards the pentacycle and the relative configurations of all chiral centres, since each of the three pairs of protons mentioned must occupy the extremes of a planar *W*-arrangement

Some of these stereochemical assignments are

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*Part LXVI in the series “The Chemistry of Brazilian Lauraceae” For Part LXV see ref [1] Taken from part of the M Sc thesis presented by M C C P G, on leave of absence from Universidade Federal do Rio Grande do Norte, Natal, to Universidade de São Paulo (1981)

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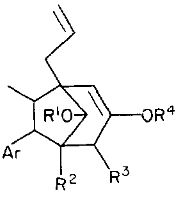

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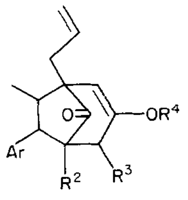

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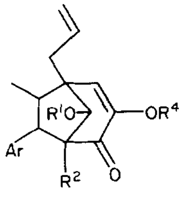

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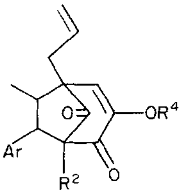

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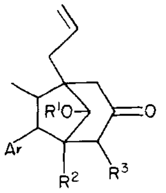

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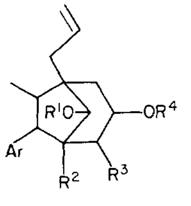

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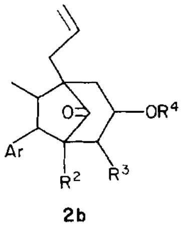

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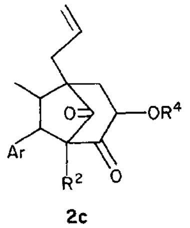

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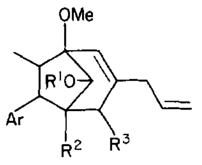
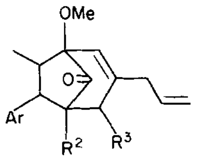


3a



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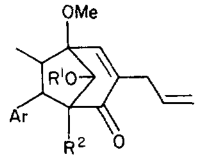

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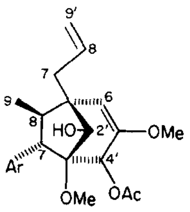
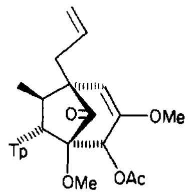


4a Ar = Pi
4b Ar = Mp



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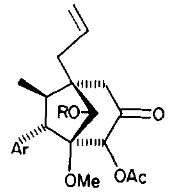
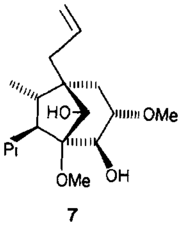


6a Ar = Pi, R = H
6b Ar = Mp, R = H
6c Ar = Pi, R = Ac
6d Ar = Mp, R = Ac



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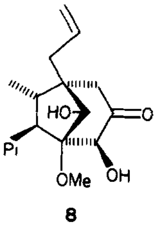

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corroborated by ^{13}C NMR spectral comparisons with the model compounds canellin A (**7**) and canellin C (**8**) In these bicyclo-octanoids the C-methyls occupy endo-configurations and are hence protected by γ-effects (δ 11 7 ± 0 1) which do not act on the exo-methyls of the *Ocotea* compounds (δ 18 4 ± 0 4) Accordingly, only the methyl of **8** reciprocates a γ-effect on C-6′ (δ 43 1) In the *Ocotea* compounds **6a** and **6b**, C-6′ resonates at δ 50 85 ± 0 05 Similarly, in **7** C-7 is protected by the γ-effect exerted by C-5′ (δ 51 9), which is absent in the case of **4a**, **4b** and **5** (δ 59 3 ± 0 8) where there is no endo-H to transmit the γ

Table 1 Constitution and occurrence of bicyclo (3 2 1) octanoid neolignans in Lauraceae

Type	Substituents					Species
	Ar	R^1	R^2	R^3	R^4	
1a	Pi	H	OMe	OAc	Me	*Ocotea* sp (**4a**)
1a	Mp	H	OMe	OAc	Me	*O* sp (**4b**)
1b	Tp	—	OMe	OAc	Me	*O* sp (**5**)
1c	Pi	H	H	—	Me	*Aniba affinis* [3], *A burchellii* [4] *A guianensis* [5]
1c	Pi	H	OMe	—	Me	*A affinis* [3]
1c	Pi	Ac	OMe	—	H	*A affinis* [3]
1c	Pi	Ac	OMe	—	Me	*A affinis* [3], *Licania armeniaca* [6]
1c	Mp	H	H	—	H	*A simulans* [7], *A ferrea* [8]
1d	Gu	—	H	—	Me	*A* sp [9]
1d	Pi	—	H	—	Me	*A affinis* [3]
1e	Pi	H	H	OH	—	*A* sp [9]
1e	Pi	H	H	α-OMe	—	*A* sp [9]
1e	Pi	H	H	β-OMe	—	*A* sp [9]
1e	Pi	H	OMe	OH	—	*L canella* [10], *L rigida* [11]
1e	Pi	H	OMe	OAc	—	*O* sp (**6a**)
1e	Mp	H	OMe	OAc	—	*O* sp (**6b**)
1e	Mp	H	H	OMe	—	*A simulans* [7]
1e	Mp	H	OMe	OMe	—	*A simulans* [7]
1e	Mp	H	H	OH	—	*A simulans* [7, 12]
1e	Mp	H	OMe	α-OH	—	*A* sp [13]
1e	Mp	H	OMe	β-OH	—	*A simulans* [7, 12]
2a	Pi	H	OMe	OH	Me	*L canella* [10], *L rigida* [11]
2a	Mp	H	OMe	OH	Me	*A ferrea* [8], *A* sp [13]
2b	Mp	—	OMe	OH	Me	*A* sp [13]
2b	Tp	—	OMe	OH	Me	*A* sp [13]
2d	Gu	—	H	—	Me	*A* sp [9]
3b	Tp	—	H	OH	—	*Nectandra* sp [14]
3c	Mp	H	OMe	—	—	*L macrophylla* [15]

Gu, Guiacyl (4-hydroxy-3-methoxyphenyl), Pi, piperonyl (3,4-methylenedioxyphenyl), Mp, methoxypiperonyl(3-methoxy-4,5-methylenedioxyphenyl), Tp, tri-*O*-methylpyrogallyl (3,4,5-trimethoxyphenyl)

Table 2 Formulae of neolignans

4a	$C_{23}H_{28}O_7 = C_8H_5(C_6H_3O_2CH_2)Me\ CH_2CH{=}CH_2\ OH(OMe)_2OAc$
4b	$C_{24}H_{30}O_8 = C_8H_5(C_6H_2\ OMe\ O_2CH_2)Me\ CH_2CH{=}CH_2\ OH(OMe)_2OAc$
5	$C_{25}H_{32}O_8 = C_8H_5(C_6H_2(OMe)_3)Me\ CH_2CH{=}CH_2({=}O)\ (OMe)_2OAc$
6a	$C_{22}H_{26}O_7 = C_8H_6(C_6H_3O_2CH_2)Me\ CH_2CH{=}CH_2\ OH({=}O)OMe\ OAc$
6b	$C_{23}H_{28}O_8 = C_8H_6(C_6H_2\ OMe\ O_2CH_2)Me\ CH_2CH{=}CH_2\ OH({=}O)OMe\ OAc$

effect to C-7 The endo-configuration of both the aryl and acetate moieties puts these two groups in close proximity, a fact emphasized by the extremely high field absorption (δ 1 48–1 54) of the COMe protons in **4a**, **4b** and **5** In compound **6**, this resonance is at slightly lower field, presumably, the substitution of the double bond by a carbonyl next to a CH_2 group allows some relaxation of the molecule

While compound **5** is quite stable, both **4a** and **4b** in chloroform solutions are slowly transformed into **6a** and **6b**, respectively Since a trace of acid was sufficient to effect this decomposition it is probable that the latter compounds are artifacts of the isolation procedure Indeed, only **4a**, **4b** and **5** were detected by TLC (Si gel, C_6H_6–EtOAc in different proportions) of a crude hexane extract of the wood Should this observation be correct, the reported derivatives of type **1e** may all be artifacts The constitution of their natural precursors is obtained by transference of the compounds defined under **1e** to **1a** (Table 1) with the provision that Me is specified in the column headed by R^4

EXPERIMENTAL

Isolation of constituents Trunk wood was collected by Professor Klaus Kubitzki, Hamburg University, from a tree of 'canela parda' in the Atlantic forest, municipality of Cunha, State of São Paulo Dried powdered wood (1 2 kg) was percolated with C_6H_{14} The extract (15 g) was chromatographed on a dry column (300 g Si gel deactivated by 10% H_2O, C_6H_6–EtOAc, 4 1) The column was extruded and cut into 10 equal segments numbered 1–10 from bottom to top

Table 3 ^{1}H NMR data of neolignans*

	4a		**4b**	**5**	**6a**		**6b**
H-2	6 84 *d* (1 5)		6 53 *s*	6 57 *s*	6 77 *d* (1 5)		6 40 *d* (1 5)
H-5	6 70 *d* (8)		—	—	6 71 *d* (8)		—
H-6	6 77*dd* (8,1 5)		6 53*s*	6 57*s*	6 65*dd* (8, 1 5)		6 44*d* (1 5)
H-7	3 24	*dd* (7,2)	3 23	2 93*dd* (6,1 5)	3 26	*dd* (9,2)	3 23
H-8	2 48	*dq* (7,1)	2 45	2 74*q* (6 5)	2 15	*br q* (7 5)	2 11
3H-9	1 12	*d* (7)	1 14	1 04 *d* (7)	1 08	*d* (7)	1 09
H-2′	3 88	*d* (1)	3 89	—	4 16	*d* (1)	4 16
H-4′	6 03	*dd* (2,1)	6 04	6 07 *dd* (1 5,1)	5 55	*dd* (2,1)	5 48
H-6′ eq	4 88	*d* (1)	4 87	4 96 *d* (1)	2 52	*dd* (16,1)	2 54
H-6′ ax	—		—	—	2 37	*d* (16)	2 38
H-7′	2 59	*ddt* (14,8,1)	2 59	2 44 *ddt* (14 5,7,1)	2 76	*ddt* (13 5,6 5,1)	2 74
H-7′	2 26	*ddt* (14,6 5,1 5)	2 25	2 28 *ddt* (14 5,7,1)	2 06	*dd* (13 5,8)	2 06
H-8′	5 87	*m*	5 87	5 89*m*	5 89	*m*	5 87
H-9′	5 21	*br d* (17)	5 21	5 21 *br d* (16 5)	5 20	*br d* (14 5)	5 20
H-9′	5 13	*br d* (10)	5 13	5 20 *br d* (10 5)	5 19	*br d* (11 5)	5 19
CH_2O_2	5 89	*s*	5 91	—	5 90	*s*	5 92
MeO-3	—		3 87*s*	3 85 *s*	—		3 89 *s*
MeO-4	—		—	3 83 *s*	—		—
MeO-5	—		—	3 85*s*	—		—
MeO-3′	3 34	*s*	3 35	3 56 *s*	3 31	*s*	3 31
MeO-5′	3 51	*s*	3 51	3 61 *s*	—		—
AcO-4′	1 49	*s*	1 54	1 48 *s*	1 76	*s*	1 79

*Chemical shifts in δ values from internal TMS for $CDCl_3$ solutions at 270 MHz, coupling constants (Hz) in parentheses

The segments were eluted with Me_2CO Eluate 6 (4 6 g) was crystallized from MeOH to sitosterol (1 g) The mother liquor was evaporated and the residue chromatographed on a Si gel (150g) column Mixtures of C_6H_{14}–EtOAc of gradually increasing polarities eluted 40 fractions (250 ml) Fractions 9–12 (0 4 g), 13–18 (0 3 g) 19 (0 1 g), 20–23 (0 3 g), 24–29 (0 2 g) were purified by prep TLC (Si gel, resp $CHCl_3$–Et_2O 4 1, C_6H_{14}–Me_2CO, 7 3, Et_2O–Me_2CO, 7 3, $CHCl_3$–Et_2O, 4 1, $CHCl_3$–Et_2O, 4 1) resp into **6a** (180 mg), **4a** (15 mg), **4b** (13 mg), **6b** (18 mg), and **5** (18 mg) **4b** (11 mg)

rel - (7S,8R,1′R,2′R,3′S,4′S) - Δ^8 - 4′ - *Acetoxy* - 2′ - *hydroxy* - 3′,5′ - *dimethoxy* - 3,4 - *methylenedioxy* - 1′,2′,3′,4′ - *tetrahydro* - 7 3′,8 1′-*neolignan* (**4a**) Oil (Found 416 1855, $C_{23}H_{28}O_7$ requires 416 1835) IR $\nu_{max}^{CCl_4}$ cm^{-1} 1750

rel - (7S,8R,1′R,2′R,3′S,4′S) - Δ^8 - 4′ - *Acetoxy* - 2′ - *hydroxy* - 3,3′,5′ - *trimethoxy* - 4,5 - *methylenedioxy* - 1′,2′,3′,4′ - *tetrahydro* - 7 3′,8 1′ - *neolignan* (**4b**) Oil (Found 466 1905 $C_{24}H_{30}O_8$ requires 466 1941) UV λ_{max}^{MeOH} nm 239, 276 (ϵ 5300, 1500) IR $\nu_{max}^{CCl_4}$ cm^{-1} 1750 MS *m/z* (rel int) 446 (55), 253 (5), 211 (10), 192 (49), 179 (53), 165 (57)

rel - (7S,8R, 1′R,3′R,4′S) - Δ^8 - 4′ - *Acetoxy* - 3,4,5,3′,5′ - *pentamethoxy* - 1′,2′,3′,4′ - *tetrahydro* - 5′ - *oxo* - 7 3′, 8 1′ - *neolignan* (**5**) Oil (Found 460 2143 $C_{25}H_{32}O_8$ requires 460 2097) UV λ_{max}^{MeOH} nm 280 (ϵ 1400) IR $\nu_{max}^{CCl_4}$ cm^{-1} 1760, 1750 MS *m/z* (rel int) 460 (37), 251 (23), 210 (90), 209 (36), 208 (93), 181 (16), 179 (8)

rel - (7S,8R,1′S,2′R,3′S,4′R) - Δ^8 - 4 - *Acetoxy* - 2′ - *hydroxy* - 3′ - *methoxy* - 3,4 - *methylenedioxy* - 1′,2′,3′,4′,5′,6 - *tetrahydro* - 5′-*oxo*-7 3′, 8 1′-*neolignan* (**6a**) Mp 104–106° (MeOH–hexane) (Found 402 1622 $C_{22}H_{26}O_7$ requires 402 1679) UV λ_{max}^{MeOH} nm 234, 286 (ϵ 3600, 4400) IR $\nu_{max}^{CCl_4}$ cm^{-1} 1750, 1735 MS *m/z* (rel int) 402 (80), 197 (6), 181 (19), 162 (53), 151 (100), 135 (26) *Acetate* (**6a**, Ac_2O, pyridine, 18 hr, room temp), mp 102–107° (MeOH–hexane) IR ν_{max}^{KBr} cm^{-1} 1750, 1730 ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6 9–6 7 (*m*, H-2, H-5, H-6), 5 93 (*s*, CH_2O_2), 5 9–5 55 (*m*, H-8′), 5 57 (*br s*, H-4′), 5 50 (*br s*, H-2′), 5 3–4 9 (*m*, 2H-9′), 3 4–3 1 (*m*, H-7), 3 23 (*s*, MeO-3′), 2 30 (*s*, AcO-2′), 1 76 (*s*, AcO-4′), 1 1 (*d*, $J = 7$ Hz 3H-9) MS *m/z* (rel int) 444 (100), 352 (38), 329 (18), 311 (23), 310 (90), 301 (15), 292 (20), 287 (18), 283 (15), 282 (30), 281 (12), 270 (17), 269 (66), 268 (29), 251 (15), 242

Table 4 ^{13}C NMR data of neolignans*

	4b	**5**	**6a**	**6b**	**7**[11]	**8**†
C-1	135 5	135 8	131 1	131 8	135 6	134 3
C-2	104 2	107 4	107 3	104 1	107 5	107 6
C-3	148 0	152 5	147 0	148 0	147 4	147 5
C-4	133 5	137 0	146 3	133 9	145 8	146 2
C-5	142 7	152 5	110 4	142 8	110 5	110 3
C-6	109 7	107 4	122 1	108 4	123 3	123 2
C-7	60 2	53 4	58 5	59 0	51 9	55 0
C-8	48 8	44 9	41 7	42 1	47 4	47 9
C-9	18 4	18 8	18 0	18 1	11 8	11 6
CH_2O_2	101 0	—	100 7	101 4	100 7	100 8
MeO-3	56 6	56 2	—	56 4	—	—
MeO-4	—	60 9	—	—	—	—
MeO-5	—	56 2	—	—	—	—
C-1′	46 1	48 5	44 4	44 3	47 4	47 9
C-2′	78 3	208 2	78 1	78 0	78 3	78 0
C-3′	87 7	87 2	86 4	86 4	85 3	86 4
C-4′	69 0	71 3	75 2	75 2	71 4	77 7
C-5′	150 3	151 9	201 5	201 9	77 2	208 0
C-6′	106 3	102 5	50 9	50 8	30 4	43 1
C-7′	34 8	32 7	34 9	34 9	38 9	37 4
C-8′	135 0	133 6	133 9	133 9	135 6	133 7
C-9′	117 7	118 9	119 1	119 2	117 4	118 6
MeO-3′	52 2	52 7	52 0	52 0	52 2	52 2
MeO-5′	55 1	55 3	—	—	57 4	—
AcO-4′	20 2	20 1	20 1	20 2	—	—
	170 3	169 4	169 8	169 9	—	—

*Chemical shifts in δ values from internal TMS for $CDCl_3$ solutions at 22 6 MHz

†[Haraguchi, M , personal communication]

(18), 241 (35), 249 (12), 223 (45), 213 (29), 181 (23), 163 (20), 162 (63), 161 (23), 151 (32), 149 (25), 135 (52), 131 (13), 109 (13), 91 (17), 77 (16)

rel - (7S,8R,1′S,2′R,3′S,4′R) - Δ^8 - 4 - *Acetoxy* - 2′ - *hydroxy* - 3,3′ - *dimethoxy* - 4,5 - *methylenedioxy* - 1′,2′,3′,4′,5′,6′ - *hexahydro* - 5′ - *oxo* - 7 3′,8 1′ - *neolignan* (**6b**) Mp 133–135° (MeOH–hexane) (Found 432 1751 $C_{23}H_{28}O_8$ requires 432 1784) UV λ_{max}^{MeOH} nm 237, 275 (ϵ 6300, 2000) IR $\nu_{max}^{CCl_4}$ cm^{-1} 1750, 1735 MS *m/z* (rel int) 432 (100), 197 (4), 192 (34), 181 (40), 165 (31), 151 (40) *Acetate* (**6b** Ac_2O, pyridine, 18 hr, room temp), mp 68–71° (MeOH–hexane) IR ν_{max}^{KBr} cm^{-1} 1750, 1735 ^1H NMR ($CDCl_3$, 60 MHz) δ 6 46 (*s*, H-2, H-6), 5 93 (*s*, CH_2O_2), 5 9–5 5 (*m*, H-8′), 5 57 (*br s*, H-4′), 5 50 (*br s*, H-2′), 5 3–4 9 (*m*, 2H-9′), 3 4–3 1 (*m*, H-7), 3 90 (*s*, MeO-3), 3 23 (*s*, MeO-3′), 2 3 (*s*, AcO-2′), 1 76 (*s*, AcO-4′), 1 1 (*d*, *J* = 7 Hz, 3H-9)

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REFERENCES

1 Cavalcante, S de H , Rocha, A I da, Yoshida, M and Gottlieb, O R *Acta Amazonica* **11** (in press)

2 Gottlieb, O R (1978) *Prog Chem Org Nat Prod* **35**, 1

3 Fernandes, J B , Gottlieb, O R and Maia, J G S (1976) *Phytochemistry* **15**, 1033

4 Alvarenga, M A da, Brocksom, U , Castro, C O , Gottlieb, O R and Magalhães, M T (1977) *Phytochemistry* **16**, 1797

5 Bulow, M V von, Franca, N C , Gottlieb, O R and Puentes, S A M (1973) *Phytochemistry* **12**, 1805

6 Alegrio, L V , Braz Fo R , Gottlieb, O R and Maia, J G S (1981) *Phytochemistry* **20**, 1963

7 Alvarenga, M A de, Castro C O , Giesbrecht, A M and Gottlieb, O R (1977) *Phytochemistry* **16**, 1801

8 Andrade, C H S , Braz Fo R and Gottlieb, O R (1980) *Phytochemistry* **19**, 1191

9 Martinez, V J C , Maia, J G S , Yoshida, M and Gottlieb, O R (1980) *Phytochemistry* **19**, 474

10 Giesbrecht, A M , Franca, N C , Gottlieb, O R and Rocha, A I da (1974) *Phytochemistry* **13**, 2285

11 Braz Fo R , Carvalho, M G de, Gottlieb, O R , Maia, J G S and Silva, M L (1981) *Phytochemistry* **20**, 2049

12 Aiba, C J , Fernandes, J B , Gottlieb, O R and Maia, J G S (1975) *Phytochemistry* **14**, 1597

13 Dias, S M C , Fernandes, J B , Maia, J G S , Gottlieb, O R and Gottlieb, H E (1982) *Phytochemistry* **20**, 1737

14 Braz Fo R , Figliuolo, R and Gottlieb, O R (1980) *Phytochemistry* **19**, 659

15 Franca, N C , Gottlieb, O R and Maia, J G S (1974) *Phytochemistry* **13**, 2839

16 Diaz, D P P , Yoshida, M and Gottlieb, O R (1980) *Phytochemistry* **19**, 285