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NEOLIGNANS FROM *OCOTEA CATHARINENSIS**

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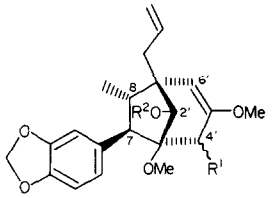
Key Word Index—*Ocotea catharinensis*; Lauraceae; bicyclo(3.2.1)octanoid neolignans; hydrobenzofuranoid neolignans.

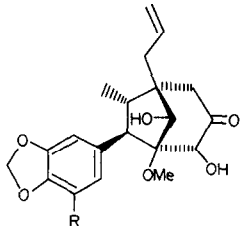
Abstract—The trunk bark of *Ocotea catharinensis* yielded, besides the known bicyclo(3.2.1)octanoid neolignans canellin-C and 5'-methoxycanellin-C, two epimers rel-(1R,4*S* and 4*R*,5*S*,6*R*,7*S*,8*R*)-1-allyl-4,8-dihydroxy-3,5-dimethoxy-7-methyl-6-piperonyl-bicyclo(3.2.1)oct-2-enes and rel-(1*R*,5*S*,6*R*,7*S*,8*R*)-1-allyl-3,8-dihydroxy-5-methoxy-7-methyl-6-piperonyl-4-oxobicyclo(3.2.1)oct-2-ene. The hydrobenzofuranoid neolignans are represented by the equally novel (2*S*,3*S*,5*R*)-5-allyl-5,7-dimethoxy-3-methyl-2-piperonyl-2,3,5,6-tetrahydro-6-oxobenzofuran and (2*R*,3*S*,3a*S*)-3a-allyl-5,7-dimethoxy-3-methyl-2-piperonyl-2,3,3a,6-tetrahydro-6-oxobenzofuran.

INTRODUCTION

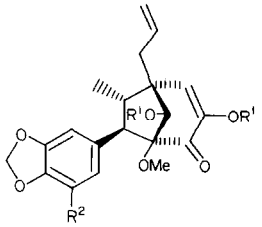
The wood of *Ocotea catharinensis* Mez is a much appreciated article of commerce [2]. The tree, popularly known as 'canela preta', occurs in the Atlantic forest. A specimen was collected in the Cunha region, São Paulo State, and identified by Professor Klaus Kubitzki, University of Hamburg. Fractionation of the light petrol extract of its bark gave the neolignans **1a**, **1b**, **2a**, **2b**, **3a**, **4a** and **5a**. For reasons stated in a previous paper of this series [3], nomenclature and numbering of neolignans follow the rules outlined in a recent review [4].



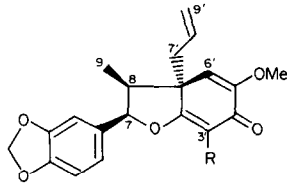
1a R^1 = α-OH, R^2 = H
1b R^1 = β-OH, R^2 = H
1c R^1 = α-OAc, R^2 = H
1d R^1 = α-OAc, R^2 = Ac
1e R^1 = β-OAc, R^2 = Ac



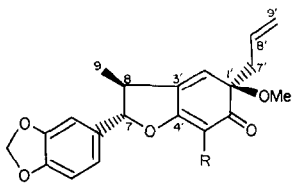
2a R = H
2b R = OMe



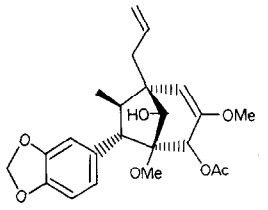
3a R^1 = R^2 = H
3b R^1 = Ac, R^2 = H
3c R^1 = H, R^2 = OMe



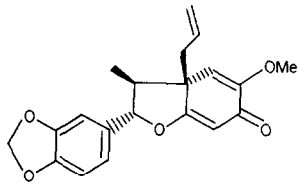
4a R = OMe
4b R = H



5a R = OMe
5b R = H



6



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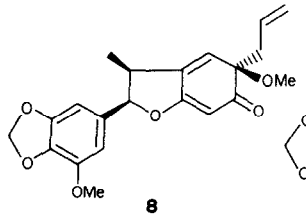

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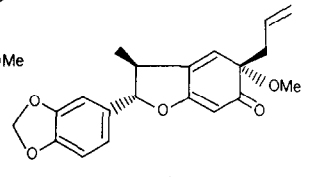

9

RESULTS AND DISCUSSION

Compounds **2a** and **2b** have been isolated respectively from *Licaria canella* (Meissn.) Kosterm. [5] and from *Aniba williamsii* O. C. Schmidt. The analysed samples of the latter species were originally designated *A. simulans* Allen [6], an error which was recently corrected [7]. We have indicated previously that compounds of type **2** should be artifacts of isolation [8]. Indeed, the putative precursors of **2a**, namely **1a** and **1b**, are also present in the extract of *O. catharinensis*. As expected [8], compound **1a** in chloroform is demethylated into **2a** in

*Part LXIX in the series " The Chemistry of Brazilian Lauraceae". For Part LXVIII see ref. [1]. Based on the M.S. thesis presented by M.H. to Universidade de São Paulo (1982).

the presence of a trace of acid at room temperature. Compounds **1a** and **1b** show very similar IR and mass spectra. According to their ^1H and ^{13}C NMR data they differ only with respect to the configuration of the hydroxyl group at C-4′, endo-oriented in **1a** (γ-effects on C-7 and C-6′ for **1a** vs **1b** each $\delta -2.0$) and exo-oriented in **1b** (γ-effect on C-2′ for **1b** vs **1a** $\delta 4.2$).

Acetylation (acetic anhydride, pyridine) at room temperature transformed **1a** into the monoacetate **1c**, and **1b** into the diacetate **1e**. Complete acetylation of **1a** into **1d** required heating. The monoacetate **1c** is constitutionally identical with **6**, a compound isolated from *Ocotea* sp. [8]. Stereochemically the compounds differ in the configurations of the aryl group at C-7 and the methyl group at C-8. The former is endo-situated in **6**, exerting protection on the acetate protons ($\delta 1.54$), and exo-situated in **1c** (acetate, $\delta 2.14$). The latter is exo-situated in **6** (Me-8, $\delta 1.14$) and endo-situated in **1c**, suffering protection by the bicyclo-octane system ($\delta 0.85$).

Spectral comparison of **3a** and of its diacetate **3b**, the latter prepared by acetylation (acetic anhydride, pyridine) of the former at room temperature, with **3c** from *Aniba williamsii* [6, 7] showed that all differences can be accounted for by the absence of methoxyl substitution of the aromatic ring in **3a** and **3b**.

Structure **4a** was established by ^1H and ^{13}C NMR as well as ORD comparison with **4b** from *Aniba terminalis* Ducke [9, 10] and **7** from *A. burchellii* Kosterm. [9, 11, 12]. The sole constitutional difference between the novel **4a** and the model compounds is the presence of an additional methoxyl group at C-3′ of the former. Stereochemically, **4a** is identical with **4b**, both showing the absence of the reciprocal γ-effect of C-9 ($\delta 11.95 \pm 0.05$) and C-7′ ($\delta 43.85 \pm 0.05$) which exists in **7** with *cis*-C-9 ($\delta 8.3$)/C-7′ ($\delta 36.6$) [9]; both showing the protection exerted by the aryls on the *C*-methyl protons ($\delta 0.50$) which is absent from **7** with *trans*-Ar/Me ($\delta 1.16$) [9]; and both showing positive/negative Cotton effects which are negative/positive at the same wavelengths, respectively 260/295 nm, for **7** [13].

Structure **5a** was established by ^1H and ^{13}C NMR comparison with **5b** from *Aniba terminalis* [10, 14], as well as by ORD comparison with **5b** and **8** from *A. williamsii* [15] and **9** from *A. burchellii* [14]. As in the case of **4a**, the sole constitutional difference between the novel **5a** and the model compound **5b** is the presence of an additional methoxyl at C-3′ of the former. Stereochemically, **5a**, **5b** and **9** do not show the methyl protection ($\delta 1.31 \pm 0.06$) which exists in **8** (Me-8, $\delta 0.93$) due to the *cis*-relationship of the aryl and methyl groups. The 7*S*, 1′*R*-configurations are deduced for **5a** in view, respectively, of its negative Cotton effects at 280 nm which it shares with **5b** and **9**, and at 315 nm which is shares with **5b** and **8**. Positive Cotton effects at 280 and 315 nm respectively, are diagnostic for the 7*R*-configuration in **8** and the 1′*S*-configuration in **9** [13].

EXPERIMENTAL

Isolation of the constituents of O. catharinensis. Dry trunk bark was powdered (1.2 kg) and percolated with petrol. The extract (50 g) was chromatographed (CC-1) on Si gel [300 g, petrol–EtOAc (9:1), fractions of 200 ml]. Fractions 35 and 36 (15 g) were rechromatographed (CC-2) on Si gel [200 g, $CHCl_3$–EtOAc (19:1), fractions of 100 ml]. Fractions 13–23 were purified on an alumina column (CC-3) (petrol–EtOAc, 9:1) to a binary mixture which, on a Si gel column (CC-4) (Et_2O), gave **5a** (2 g). Fractions 24–28 (CC-2) were rechromatographed (CC-5) on Si gel (100 g, $CHCl_3$, fractions of 50 ml). TLC of fractions 22–47 (CC-5) on Si gel developed with $CHCl_3$–EtOAc (4:1) and then on Si gel developed with C_6H_6–EtOAc (4:1) gave **3a** (70 mg) and **1a** (100 mg). Fractions 33–35 (CC-2) were rechromatographed (CC-6) on Si gel [150 g CH_2Cl_2–Me_2CO (9:1), fractions of 50 ml]. Fractions 13–15 (CC-6) gave **2a** (500 mg). TLC of fractions 16–25 on Si gel (CH_2Cl_2–Me_2CO, 9:1) gave a mixture, **2a** (200 mg) and **1b** (200 mg). TLC of the mixture on Si gel ($CHCl_3$–Me_2CO) gave **2b** (30 mg). The residue of fractions 42–47 (CC-1) was recrystallized from CCl_4 to give **4a** (1.5 g).

rel-(7R, 8S, 1′R, 2′R, 3′S, 4′S)-$\Delta^{8'}$-2′, 4′-*Dihydroxy*-3′, 5′-*dimethoxy*-3,4-*methylenedioxy*-1′,2′,3′,4′-*tetrahydro*-7.3′,8.1′ *neolignan* (**1a**). Amorphous solid (M found: 374; $C_{21}H_{26}O_6$ requires: 374). IR ν_{max}^{film} cm^{-1}: 3521, 1647, 1484, 1443, 1379, 1235, 1136, 1099, 1042, 939, 917, 809, 760; UV λ_{max}^{MeOH} nm: 231 (ε 6700), 284 (ε 4800); ^1H NMR ($CDCl_3$, 60 MHz): δ6.95 (*s*, H-2), 5.87 (*s*, CH_2O_2), 6.73 (*br s*, H-5, H-6), 3.11 (*d*, $J = 9$ Hz, H-7), 2.1–2.7 (*m*, H-8, 2H-7′), 0.80 (*d*, $J = 7$ Hz, 3H-9), 3.83 (*s*, H-2′), 3.15 (*s*, MeO-3′), 4.70 (*s*, H-4′), 3.57 (*s*, MeO-5′), 4.47 (*s*, H-6′), 5.7–6.1 (*m*, H-8′), 4.9–5.3 (*m*, 2H-9′); ^{13}C NMR ($CDCl_3$, 20 MHz): δ135.6 (*s*, C-1), 107.4 (*d*, C-2), 147.3 (*s*, C-3), 145.8 (*s*, C-4), 111.1 (*d*, C-5), 123.6 (*d*, C-6), 53.2 (*d*, C-7), 50.6 (*d*, C-8), 12.4 (*q*, C-9), 48.3 (*s*, C-1′), 77.6 (*d*, C-2′), 85.4 (*s*, C-3′), 72.7 (*d*, C-4′), 153.6 (*s*, C-5′), 100.1 (*d*, C-6′), 36.6 (*t*, C-7′), 134.7 (*d*, C-8′), 116.8 (*t*, C-9′), 100.9 (*t*, O_2CH_2), 52.7 (*s*, MeO-3′), 55.0 (MeO-5′); MS *m/z* (rel. int.): 374 $[M]^+$ (100), 356 (4), 333 (7), 315 (13), 301 (5), 207 (47), 195 (47), 179 (24), 177 (18), 175 (18), 165 (78), 163 (40), 162 (36), 154 (40), 151 (32), 149 (58), 135 (46), 91 (36), 84 (31), 77 (30).

^1H *NMR spectral differences of the monoacetate* ($\delta 2.14$) **1c** *and the diacetate* ($\delta 2.15$, 2.30) **1d** *with* **1a**. $\Delta\delta$ **1c** **1a**/**1d** **1a**: -0.04/-0.04 (H-2), $+0.08$/$+0.06$ (O_2CH_2), 0.00/-0.03 (H-5, H-6), $+0.05$/$+0.04$ (H-7), 0.0/0.0 (H-8, 2H-7′), $+0.05$/$+0.06$ (3H-9), $+0.03$/$+1.44$ (H-2′), $+0.05$/0.00 (MeO-3′), $+1.33$/$+1.45$ (H-4′), $+0.01$/$+0.04$ (MeO-5′), $+0.11$/$+0.06$ (H-6′), 0.0/0.0 (H-8′), 0.0/0.0 (2H-9′).

Canellin-C (**2a**) *and methoxycanellin-C* (**2b**). See refs. [5, 6], except for ^{13}C NMR of **2a** ($CDCl_3$, 20 MHz): δ134.3 (*s*, C-1), 107.6 (*d*, C-2), 147.5 (*s*, C-3), 146.2 (*s*, C-4), 110.3 (*d*, C-5), 123.2 (*s*, C-6), 55.0 (*d*, C-7), 47.9 (*d*, C-8), 11.6 (*q*, C-9), 47.9 (*s*, C-1′), 78.0 (*d*, C-2′), 86.0 (*s*, C-3′), 77.7 (*d*, C-4′), 208.0 (*s*, C-5′), 43.1 (*d*, C-6′), 37.4 (*t*, C-7′), 133.7 (*d*, C-8′), 118.6 (*t*, C-9′), 100.8 (*t*, CH_2O_2), 52.0 (*q*, MeO-3′).

rel-(7R, 8S, 1′R, 2′R, 3′S, 4′R)-$\Delta^{8'}$-2′, 4′-*Dihydroxy*-3′, 5′-*dimethoxy*-3, 4-*methylenedioxy*-1′,2′,3′,4′-*tetrahydro*-7.3′,8.1′-*neolignan* (**1b**). Amorphous solid (M found: 374; $C_{21}H_{26}O_6$ requires: 374). IR ν_{max}^{film} cm^{-1}: 3500, 1645, 1481, 1439, 1370, 1232, 1136, 1042, 995, 820; UV λ_{max}^{MeOH} nm: 234 (ε 7050), 285 (ε 5250); ^1H NMR ($CDCl_3$, 60 MHz): δ7.03 (*s*, H-2), 5.93 (*s*, CH_2O_2), 6.73 (*br s*, H-5, H-6), 2.0–2.5 (*m*, H-7, H-8, 2H-7′), 0.78 (*d*, $J = 7$ Hz, 3H-9), 4.00 (*s*, H-2′), 2.90 (*s*, MeO-3′), 4.30 (*s*, H-4′), 3.65 (*s*, MeO-5′), 4.58 (*s*, H-6′), 5.6–6.1 (*m*, H-8′), 4.9–5.3 (*m*, 2H-9′); ^{13}C NMR ($CDCl_3$, 20 MHz): δ134.2 (*s*, C-1), 107.6 (*d*, C-2), 147.7 (*s*, C-3), 146.3 (*s*, C-4), 111.1 (*d*, C-5), 123.6 (*d*, C-6), 55.2 (*d*, C-7), 50.8 (*d*, C-8), 12.5 (*q*, C-9), 48.2 (*s*, C-1′), 73.4 (*d*, C-2′), 85.0 (*s*, C-3′), 76.5 (*d*, C-4′), 154.2 (*s*, C-5′), 102.1 (*d*, C-6′), 36.5 (*t*, C-7′), 135.7 (*d*, C-8′), 116.8 (*t*, C-9′), 100.9 (*t*, CH_2O_2), 52.8 (*s*, MeO-3′), 57.7 (*s*, MeO-5′); MS *m/z* (rel. int.): 374 $[M]^+$ (100), 333 (7), 315 (8), 225 (7), 207 (52), 195 (46), 179 (28), 165 (74), 163 (52), 162 (34), 154 (33), 151 (32), 149 (98), 135 (52), 105 (20), 91 (34), 79 (24), 77 (30).

^1H *NMR spectral differences of the diacetate* ($\delta 2.08$, 2.21) **1e** *with* **1b**. $\Delta\delta$ **1d**–**1b**: -0.12 (H-2), -0.05 (CH_2O_2), -0.05 (H-5, H-6), 0.0 (H-7, H-8, 2H-7′), -0.03 (3H-9), $+1.38$ (H-2′), -0.33 (MeO-3′), $+1.36$ (H-4′), -0.10 (MeO-5′), -0.02 (H-6′), 0.0 (H-8′), 0.0 (H-9′).

rel-(7R, 8S, 1'R, 2'R, 3'S)-$\Delta^{8'}$-2', 5'-*Dihydroxy*-3'-*methoxy*-3,4-*methylenedioxy*-1', 2', 3', 4'-*tetrahydro*-4'-*oxo*-7.3', 8.1'-*neolignan* (**3a**). Amorphous solid (M found: 358; $C_{20}H_{22}O_6$ requires: 358). IR ν_{max}^{film} cm^{-1}: 3475, 1670, 1625, 1500, 1450, 1380, 1230, 1210, 1095, 1030, 925, 860, 805; UV λ_{max}^{MeOH} nm: 233 (ε 4750), 272 (ε 4450); ^{1}H NMR ($CDCl_3$, 60 MHz): δ6.67 (*s*, H-2), 5.90 (*s*, CH_2O_2), 6.97 (*br s*, H-5, H-6), 2.4–2.7 (*m*, H-7, H-8, 2H-7'), 0.92 (*d*, J = 7 Hz, 3H-9), 4.00 (*s*, H-2'), 3.30 (*s*, MeO-3'), 6.05 (*s*, H-6'), 5.9–6.1 (*m*, H-8'), 5.0–5.4 (*m*, 2H-9'); MS *m/z* (rel. int.): 358 $[M]^+$ (5), 317 (8), 299 (2), 271 (2), 208 (1), 196 (1), 193 (1), 180 (19), 167 (78), 163 (27), 162 (100), 158 (19), 151 (30), 149 (27), 135 (16), 107 (9), 105 (5), 103 (6).

^{1}H *NMR spectral differences of the diacetate* (δ2.28, 2.28) **3b** *with* **3a**. $\Delta\delta$ **3b–3a** 0.0 (H-2), 0.0 (CH_2O_2), −0.02 (H-5, H-6), +0.08 (3H-9), +1.50 (H-2'), −0.05 (MeO-3'), +0.45 (H-6'), 0.0 (H-8'), 0.0 (H-9').

(7R, 8S, 1'S)-$\Delta^{8'}$-3', 5'-*Dimethoxy*-3, 4-*methylenedioxy*-1', 4'-*dihydro*-4'-*oxo*-7.O.2', 8.1'-*neolignan* (**4a**). Crystals, mp 137–139° (CCl_4) (M found: 370; $C_{21}H_{22}O_6$ requires: 370). IR ν_{max}^{film} cm^{-1}: 3025, 2850, 1640, 1500, 1458, 1380, 1360, 1240, 1100, 1040, 924, 830; UV λ_{max}^{MeOH} nm: 267 (ε 17400), 285 (ε 9200); ^{1}H NMR ($CDCl_3$, 60 MHz): δ6.76 (*br s*, H-2, H-5, H-6), 5.96 (*s*, CH_2O_2), 5.93 (*d*, J = 5 Hz, H-7), 2.3–2.8 (*m*, H-8, 2H-7'), 0.50 (*d*, J = 7 Hz, 3H-9), 3.90 (*s*, MeO-3'), 3.65 (*s*, MeO-5'), 5.46 (*s*, H-6'), 5.9–6.0 (*m*, H-8'), 4.9–5.3 (*m*, 2H-9'); ^{13}C NMR ($CDCl_3$, 20 MHz): δ130.9 (*s*, C-1), 106.3 (*s*, C-2), 148.0 (*s*, C-3), 147.4 (*s*, C-4), 108.3 (*d*, C-5), 119.0 (*d*, C-6), 87.8 (*d*, C-7), 45.0 (*d*, C-8), 11.9 (*q*, C-9), 53.0 (*s*, C-1'), 165.9 (*s*, C-2'), 133.4 (*s*, C-3'), 178.6 (*s*, C-4'), 152.6 (*s*, C-5'), 109.1 (*d*, C-6'), 43.8 (*t*, C-7'), 131.9 (*d*, C-8'), 119.9 (*t*, C-9'), 101.3 (CH_2O_2), 60.4 (*s*, MeO-3'), 55.5 (*s*, MeO-5'); MS *m/z* (rel. int.): 340 M^+ (35), 338 (8), 330 (62), 329 (100), 297 (24), 284 (5), 269 (15), 254 (5), 208 (39), 207 (40), 205 (7), 165 (13), 162 (9), 149 (16), 147 (12), 135 (50); ORD (*c* 5 mg/100 ml MeOH): $[\phi]_{400}$ + 2950, $[\phi]_{346}^{pk}$ + 10350, $[\phi]_{303}$ 0, $[\phi]_{310}^{tr}$ − 41450, $[\phi]_{292}$ 0, $[\phi]_{283}^{pk}$ + 20000, $[\phi]_{263}^{tr}$ + 5200, $[\phi]_{250}$ + 11100.

(7S, 8S, 1'R)-$\Delta^{8'}$-1', 5'-*Dimethoxy*-3, 4-*methylenedioxy*-1', 6'-*dihydro*-6'-*oxo*-7.O.4', 8.3'-*neolignan* (**5a**). Oil (M found: 370, $C_{21}H_{22}O_6$ requires: 370). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1665, 1610, 1490, 1450, 1360, 1330, 1290, 1240, 1190, 1170, 1095, 1040, 940, 910, 840; UV λ_{max}^{MeOH} nm: 238 (ε 16450), 285 (ε 11100), 325 (ε 9200); ^{1}H NMR (CCl_4, 60 MHz): δ6.75 (*br s*, H-2, H-5, H-6), 5.91 (*s*, CH_2O_2), 4.95 (*d*, J = 8 Hz, H-7), 2.9–3.2 (*m*, H-8), 1.33 (*d*, J = 7 Hz, 3H-9), 3.05 (*s*, MeO-1'), 5.83 (*d*, J = 3 Hz, H-2'), 3.78 (*s*, MeO-5'), 2.40 (*d*, J = 7 Hz, 2H-7'), 5.3–5.6 (*m*, H-8'), 4.7–5.2 (*m*, 2H-9'); ^{13}C NMR ($CDCl_3$, 20 MHz): δ131.8 (*s*, C-1), 106.4 (*d*, C-2), 148.4 (*s*, C-3, C-4), 108.3 (*d*, C-5), 120.4 (*s*, C-6), 93.8 (*d*, C-7), 43.8 (*d*, C-8), 15.8 (*q*, C-9), 82.6 (*s*, C-1'), 132.3 (*d*, C-2'), 140.1 (*s*, C-3'), 158.8 (*s*, C-4'), 129.0 (*s*, C-5'), 195.7 (*s*, C-6'), 45.1 (*t*, C-7'), 131.0 (*d*, C-8'), 119.2 (*t*, C-9'), 101.5 (*t*, CH_2O_2), 53.5 (*s*, MeO-1'), 60.0 (*s*, MeO-5'); MS *m/z* (rel. int.): 370 (24), 341 (42), 331 (51), 330 (100), 298 (16), 284 (7), 269 (11), 213 (6), 208 (22), 207 (34), 165 (10), 162 (9), 149 (30), 147 (16), 135 (60); ORD (*c* 5 mg/100 ml MeOH): $[\phi]_{450}$ + 2600, $[\phi]_{381}^{pk}$ + 12600, $[\phi]_{332}^{tr}$ − 34400, $[\phi]_{305}$ 0, $[\phi]_{287}^{pk}$ + 23700, $[\phi]_{275}^{inf}$ + 22950, $[\phi]_{267}^{pk}$ + 25550, $[\phi]_{250}$ + 14450.

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REFERENCES

1. Ferreira, Z. S., Roque, N. F., Gottlieb, O. R. and Gottlieb, H. E. (1982) *Phytochemistry* **21**, 2756.
2. Rizzini, C. T. (1971) *Árvores e Madeiras Úteis do Brasil–Manual de Dendrologia Brasileira* p. 71. Universidade de São Paulo.
3. Diaz, D. P. P., Yoshida, M. and Gottlieb, O. R. (1980) *Phytochemistry* **18**, 285.
4. Gottlieb, O. R. (1978) *Prog. Chem. Org. Nat. Prod.* **35**, 1.
5. Giesbrecht, A. M., Franca, N. C., Gottlieb, O. R. and Rocha, A. I. da (1974) *Phytochemistry* **13**, 2285.
6. Alvarenga, M. A. de, Castro C., O., Giesbrecht, A. M. and Gottlieb, O. R. (1977) *Phytochemistry* **16**, 1801.
7. Gottlieb, O. R. and Kubitzki, K. (1981) *Biochem. Syst. Ecol.* **9**, 5.
8. Gomes, M. C. C. P., Yoshida, M., Gottlieb, O. R., Martinez, J. C. and Gottlieb, H. E. (1983) *Phytochemistry* **22**, 269.
9. Wenkert, E., Gottlieb, H. E., Gottlieb, O. R., Pereira, M. O. da S. and Formiga, M. D. (1976) *Phytochemistry* **15**, 1547.
10. Gottlieb, O. R., Silva, M. L. da and Ferreira, Z. S. (1975) *Phytochemistry*, **14**, 1825.
11. Lima, O. A., Gottlieb, O. R. and Magalhães, M. T. (1972) *Phytochemistry* **11**, 2031.
12. Aiba, C. J., Fernandes, J. B., Gottlieb, O. R. and Maia, J. G. S. (1975) *Phytochemistry* **14**, 1597.
13. Gottlieb, O. R., Mourão, J. C., Yoshida, M., Mascarenhas, Y. P., Rodrigues, M., Rosenstein, R. and Tomita, K. (1977) *Phytochemistry* **16**, 1003.
14. Alvarenga, M. A. de, Brocksom, U., Castro C., O., Gottlieb, O. R. and Magalhães, M. T. (1977) *Phytochemistry* **16**, 1797.
15. Aiba, C. J., Alvarenga, M. A. de, Castro C., O., Giesbrecht, A. M., Gottlieb, O. R. and Pagliosa, F. M. (1977) *Phytochemistry* **16**, 741.