CH_2), 2.76 (2H, envelope, CH), 3.78–3.85 (18H, 6 × OMe), 4.00 (2H, *m*, OCH_2), 6.10 and 6.23 (2H each, *s*, ArH). MS *m/z* 446 (45.3), 211 (27), 210 (29.4), 207 (14.1), 197 (25.9), 195 (18.3), 181 (100), 169 (16.9), 167 (18.9), 151 (28.0), 148 (10.8), 137 (24.7) and 136 (10.8).

Compound **4**. Crystallized from EtOH as colourless crystals, mp 58–60°, analysed for $C_{23}H_{30}O_8$ (requires C, 63.58; H, 6.95 observed C, 63.93; H, 7.12%). $[\alpha]_D^{36} - 28°$; ν_{max} 3450 (OH) 1594, 1500, 1460, 1230, 1110, 1020 and 918 cm^{-1}. ^1H NMR: δ 5.90 (2H, *s*, OCH_2O), 2.00 (2H, envelope, CH), 2.6 (4H envelope, ϕ-CH_2), 3.60 (4H, *m*, OCH_2), 3.90 (12H, 4 × OMe), 6.20 (3H, *br s*, ArH) and 6.6 (1H, *d*, J = 2 Hz, ArH). Acetylation with Ac_2O–pyridine gave a diacetate, semisolid, $[M]^+$ *m/z* 518 analysed for $C_{27}H_{34}O_{10}$ (requires C, 62.53; H, 6.60 observed C, 63.00; H, 6.62%). IR showed two bands at 1732 and 1252 cm^{-1} (OCOMe). ^1H NMR δ 1.98 (6H, *s*, OAc), 2.13 (2H, envelope, CH), 2.6 (4H, *m*, ϕ-CH_2), 3.83 (12H, *s*, 4 × OMe), 4.0 (4H, *m*, 2 × $C\underline{H}_2OAc$), 5.87 (2H, *s*, OCH_2O), 6.2 (3H, *br s*, ArH) and 6.8 (1H, *d*, J = 2 Hz, ArH). MS *m/z* 518 (74.7), 488 (44.3), 233 (11.2), 187 (18.3), 181 (100), 166 (38 4), 165 (50.1), 162 (10.1), 151 (14.0) and 135 (61.0).

Compound **5**. Crystallized from EtOH, mp 68–70°, analysed for $C_{22}H_{28}O_7$ (requires C, 65.33; H, 6.97 observed C, 65.86; H, 7.14%). $[\alpha]_D^{28} - 48°$; ν_{max} 3350, 1590, 1500, 1480, 1440, 1330, 1240, 1130, 1120, 1030 and 920 cm^{-1}. ^1H NMR δ 5.90 (2H, *s*, OCH_2O), 1.85 (2H, envelope, CH), 2.30–2.80 (4H, envelope, ϕ-CH_2), 3.60 (4H, envelope, 2 × OCH_2) 3.80 (9H, *s*, 3 × OMe), 6.30 (2H, *s*, ArH) and 6.60 (3H, *m*, ArH). MS $[M]^+$ *m/z* 404 (3.5), 387 (23.2), 386 (10.1), 238 (22.1), 225 (10), 219 (27.4), 202 (10.5), 183 (31.8), 182 (70.6), 181 (71), 167 (63.4), 151 (100) and 105 (33.1). Acetylation with Ac_2O–pyridine gave a diacetate, semi-solid, ($[M]^+$ *m/z* 488) analysed for $C_{26}H_{32}O_9$ (requires C, 63.92; H, 6.60 observed C, 64.10; H, 6.63%). IR showed the disappearance of the band at 3350, and appearance of two bands at 1720 and 1240 cm^{-1} (OCOMe). ^1H NMR: δ 2.03 (6H, *s*, OAc), 2.16 (2H, *m*, CH), 2.56 (4H, *m*, ϕ-CH_2), 3.73–3.83 (9H, *s*, 3 × OMe), 4.10 (4H, *m*, $C\underline{H}_2OAc$), 5.86 (2H, *s*, OCH_2O), 6.30 (2H, *s*, ArH) and 6 60 (3H, *m*, ArH).

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NEOLIGNANS FROM *OCOTEA ACIPHYLLA**

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Key Word Index—*Ocotea aciphylla*; Lauraceae; hydrobenzofuranoid neolignans; bicyclo[3.2.1]octanoid neolignans.

Abstract—The trunk wood of the central Brazilian *Ocotea aciphylla* contains two hydrobenzofuranoid and three bicyclo[3.2.1]octanoid neolignans. The former comprise a novel representative of the rare ferrearin (3a-allyl-2-aryl-7a-hydroxy-3-methyl-2,3,3a,4,7,7a-hexahydro-7-oxobenzofuran) type.

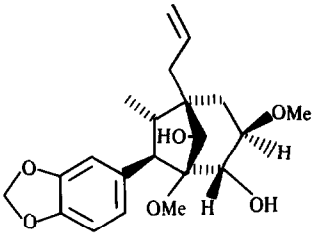
INTRODUCTION

Ocotea aciphylla, a lauraceous tree popularly known as canela-amarela, ranges in central Brazil from Minas Gerais and Espirito Santo to Santa Catarina. Its heartwood resists termites and is used for flooring [2]. Trunk wood, collected in the vicinity of Brasilia, D.F., yielded five neolignans. The three bicyclo[3.2.1]octanoids **1** (canellin-A), **2a** and **2b** (5-methoxyguianin) have been isolated from *Licaria canella* [3], *Ocotea catharinensis* [4] and *Aniba affinis* [5], respectively, and were identified by direct comparison with authentic samples. The neolignan **3a** was identified with ferrearin-B previously isolated from *Aniba ferrea* [6]. Compound **3b** proved to be novel and was designated ferrearin-C.

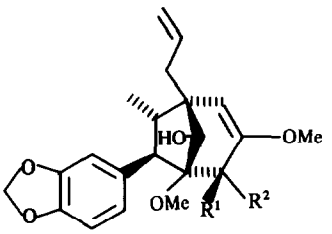
*Part LXXVI in the series "The Chemistry of Brazilian Lauraceae". For Part LXXV see ref. [1]. Based in part on the M.Sc. thesis submitted by P.R. to Universidade de São Paulo (1982).

RESULTS AND DISCUSSION

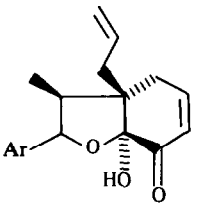
The HR mass spectra of **3a** and **3b** were superimposable

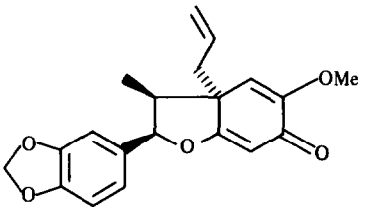


1



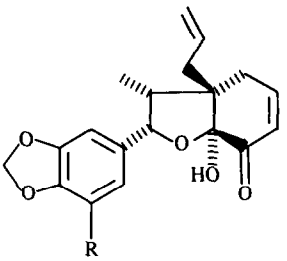
2a $R^1 = H, R^2 = OH$
2b $R^1 = R^2 = O$



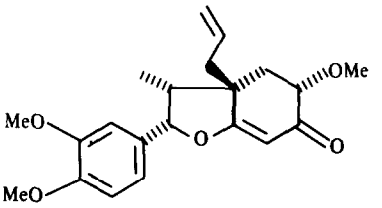


3a Ar = β – piperonyl
3b Ar = α – piperonyl
3c Ar = β – 3 – methoxy – 4, 5 – methylenedioxy

4



R
5a OMe
5b H

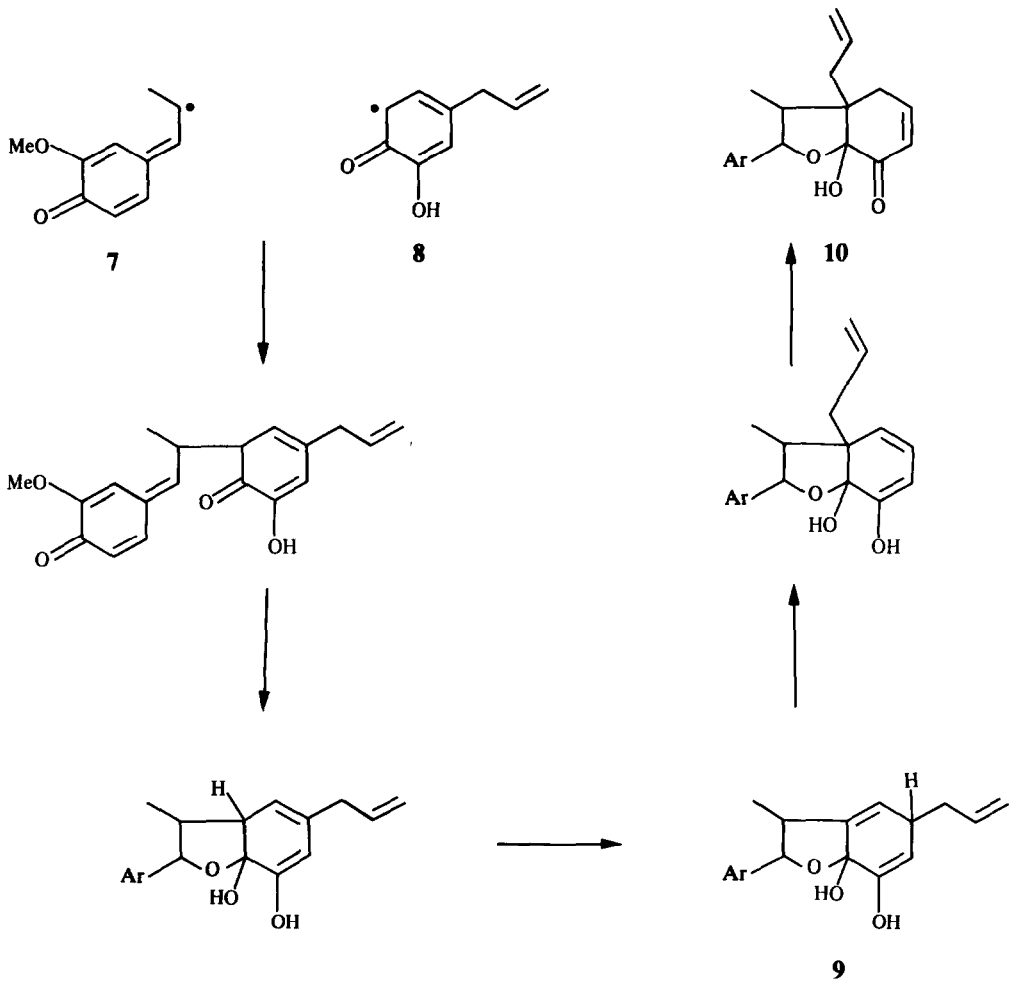


6

and the compounds should thus be stereoisomers. The close correspondence of the ^1H and ^{13}C NMR signals assigned to the cyclohexenone part of the structures indicates that the difference resides in the configuration of C-2 or C-3. Indeed, the compounds differ only in the 2,3-*cis* (**3a**) and 2,3-*trans* (**3b**) arrangement of the aryl/methyl substituents, as shown by the ^1H NMR Me-doublets (J = 8 Hz) at δ0.77 versus 0.96, respectively. The sole other conspicuous difference in these spectra refers to the H-2 doublets (J = 10 Hz) at δ5.40 versus 4.67, respectively. This indicates the association of H-2 with the oxygen atom of HO-7a only in **3a** which thus must sustain both substituents in the *syn*-configuration; in contradistinction to **3b** where H-2 and HO-7a occupy opposite sides of the molecule. As is consequently to be expected, the ^{13}C NMR spectrum reveals hydroxyl-7a to contribute γ-effects on C-2 (δ81.7) and C-3 (δ44.3) of **3a**, but not on C-2 (δ88.7) of **3b**. However, the configurations of C-3 in both compounds are identical and it is less easy to rationalize the fact that as C-2, C-3 (δ50.3) of **3b** also does not feel the γ-effect due to hydroxyl-7a. The H-2, H-3 coupling constants for both compounds are rather large (*ca* 10 Hz) and the H-2–H-3 dihedral angle thus must be close to 0° in **3a** and close to 180° in **3b**. Models of the compounds, constructed considering also this conformational information, indicate the possible existence of a hydrogen bridge between the oxygen at C-7a and the aryl at C-2. This preferential orientation of the hydroxyl towards the aryl in **3b** impedes the transmission of the γ-effect from its oxygen to C-3.

The allylic methylene carbons of **3a** and **3b** are shielded (δ40.1, 39.6, respectively) in comparison with the analogous group of the model compound **4** (δ43.9) [7] and thus occur most probably in a *syn*-relationship with the methyls at C-3. Indeed these substituents appear to be shielded reciprocally if **3a** and **3b** (δ10.6, 9.4, respectively) are again compared with the model compound **4** (δ12.0) [7].

The relative stereochemistries which thus result for ferrearin-B (**3a**) and C (**3b**) differ from those originally proposed for ferrearin-A (**5a**) and B (**5b**) [6]. The structures of the two latter compounds thus must be revised respectively to **3c** and **3a**. The model compound (**6**) on which the previous assignments were based lacks



Scheme 1. Possible biosynthesis of ferrearin type neolignans from propenyl- and allylphenol derived radicals.

the hemiketalic hydroxyl at C-7a shown in the present paper to be of essential importance in the interpretation of NMR data.

The ferrearins are devoid of oxygenation at one of the two ring-carbons *para* related to a C-3 substituent. As for other neolignan types which share this biosynthetically interesting feature [6] their genesis from propenyl- and allylphenol derived radicals (**7** and **8**, respectively) might thus involve an allylic rearrangement (**9** → **10**; Scheme 1).

EXPERIMENTAL

Isolation of the constituents. Trunk wood of *O. aciphylla* (Nees) Mez, identified by Prof José Elias de Paula, Universidade de Brasília, was dried, powdered (3.9 kg) and extracted with petrol. The solvent was evapd and the residue (44 g) crystallized from MeOH to pure **1** (2.4 g) and other less pure fractions. The mother liquor was evapd and the residue (30 g) was submitted to dry CC (300 g silica gel + 10% H_2O, C_6H_6–EtOAc 4:1). The column was divided into 10 equal portions which were eluted separately with Me_2CO. The eluates of portions 2 + 3 (6.8 g) were crystallized from MeOH to **3b** (180 mg). The eluate of portion 4 (3.4 g) was purified by CC and repeated TLC (silica gel) to **2b** (10 mg). The eluates of portions 5 + 6 + 7 (12.6 g) were separated by an analogous procedure into **3a** (30 mg) and **2a** (10 mg).

rel-(2R,3S,3*a*S,7*a*S)-3*a-Allyl-7a-hydroxy-3-methyl-2-piperonyl-2,3,3a,4,7,7a-hexahydro-7-oxobenzofuran* (**3a**, *ferrearin-B*). λ_{max}^{MeOH} nm: 235, 287 (ε3650, 2050). ^{13}C NMR (20 MHz, $CDCl_3$): δ81.7 (C-2, *d*), 44.3 (C-3, *d*), 10.6 (Me-3, *q*), 52.3 (C-3a, *s*), 30.7 (C-4, *t*), 150.8 (C-5, *d*), 125.4 (C-6, *d*), 192.7 (C-7, *s*), 99.6 (C-7a, *s*), 133.2 (C-1′, *s*), 106.3 (C-2′, *d*), 147.3 (C-3′, *s*), 146.3 (C-4′, *s*), 107.6 (C-5′, *d*), 119.0 (C-6′, *d*), 40.1 (C-α, *t*), 133.9 (C-β, *d*), 117.3 (C-γ, *t*), 100.6 (O_2CH_2, *t*). For further data see ref. [6].

rel-(2S,3S,3*a*S,7*a*S)-3*a-Allyl-7a-hydroxy-3-methyl-2-piperonyl-2,3,3a,4,7,7a-hexahydro-7-oxobenzofuran* (**3b**, *ferrearin-C*). Mp 135–136° (MeOH) ($[M]^+$ found 328.060; $C_{19}H_{20}O_5$ requires 328.110). ν_{max}^{KBr} cm^{-1}: 3500, 1680, 1660, 1500, 1450, 1350, 1250, 1110, 985, 915, 890, 830. λ_{max}^{MeOH} nm: 235, 287 (ε8300, 4150). ^{1}H NMR (60 MHz, $CDCl_3$): δ4.67 (H-2, *d*, *J* = 10 Hz), 2.9–2.3 (H-3, *m*), 0.96 (*d*, *J* = 8 Hz), 2.9–1.9 (2H-4, *m*), 7.15–6.6 (H-5, *m*), 6.16 (H-6, *br d*), 7.2–6.6 (3ArH, *m*), 5.97 (O_2CH_2, *s*), 2.9–1.9 (2H-α, *m*), 5.9–5.4 (H-β, *m*), 5–4.9 (2H-γ, *m*). ^{13}C NMR (20 MHz, $CDCl_3$): δ88.7 (C-2, *d*), 50.3 (C-3, *d*), 9.4 (Me-3, *q*), 53.5 (C-3a, *s*), 29.6 (C-4, *t*), 151.3 (C-5, *d*), 125.3 (C-6, *d*), 192.7 (C-7, *s*), 100.1 (C-7a, *s*), 135.2 (C-1′, *s*), 107.7 (C-2′, *d*), 148.0 (C-3′, *s*), 147.4 (C-4′, *s*),

107.7 (C-5′, *d*), 120.8 (C-6′, *d*), 39.0 (C-α, *t*), 134.2 (C-β, *d*), 117 6 (C-γ, *t*), 101.0 (O_2CH_2, *t*). MS *m/z* (rel. int.): 328 (7), 174 (15), 173 (100), 163 (25), 162 (59), 161 (28), 151 (12), 149 (29), 135 (68), 131 (21), 122 (12), 121 (18), 115 (21), 105 (14), 104 (20), 103 (28).

Dihydro-**3b**. To **3a** (70 mg) in THF (40 ml), $LiAlH_4$ (15 mg) was added. The mixture was stirred (4 hr, room temp) Excess reagent was destroyed with NH_4Cl. The mixture was extracted with $CHCl_3$ The $CHCl_3$ soln was washed, dried and evapd. The residue (64 mg) was purified by TLC (silica gel, C_6H_6–EtOAc, 4 . 1) to dihydro-**3b** (40 mg). ^{1}H NMR (60 MHz, $CDCl_3$): δ4 40 (H-2, *d*, *J* = 10 Hz), 2.9–1.9 (H-3, 2H-4, 2H-α, *m*), 6.2–5.3 (H-5, H-6, H-7, H-β, *m*), 7.2–6.7 (3ArH, *m*), 5.97 (O_2CH_2, *s*), 5.37–4 87 (2H-γ, *m*). ^{13}C NMR (20 MHz, $CDCl_3$): δ85 9 (C-2, *d*), 49 7 (C-3, *d*), 9.5 (Me-3, *q*) 49 5 (C-3a, *s*), 28.5 (C-4, *t*), 127 1 (C-5, *d*), 127.3 (C-6, *d*), 72 5 (C-7, *d*), 100.4 (C-7a, *s*), 135.4 (C-1′, *s*), 107.8 (C-2′, *d*), 147.8 (C-3′, *s*), 147 2 (C-4′, *s*), 107.6 (C-5′, *d*), 121.0 (C-6′, *d*), 39 4 (C-α, *t*), 134.5 (C-β, *d*), 117.5 (C-γ, *t*), 101.0 (O_2CH_2, *t*).

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TWO ANTHRAQUINONES FROM *VENTILAGO CALYCULATA*

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Key Word Index—*Ventilago calyculata*; Rhamnaceae; anthraquinones.

Abstract—Two new anthraquinones have been isolated from the root bark of *Ventilago calyculata* and their structures shown to be 2,4,8-trihydroxy-1-methoxy-3-methylanthraquinone and 2,4,8-trihydroxy-1,6-dimethoxy-3-methylanthraquinone.

INTRODUCTION

The genus *Ventilago* is a rich source of anthraquinones [1–4]. Further investigation of the root bark of *Ventilago calyculata* afforded two more new anthraquinones, **2** and **4**, in addition to the eleven anthraquinones reported previously [2].

RESULTS AND DISCUSSION

Pigment **2**, $C_{16}H_{12}O_6$, gives a positive reduction test with $Na_2S_2O_4$, indicating its anthraquinone nature, and forms a trimethyl ether. It is soluble in aqueous sodium carbonate suggesting the presence of a β-hydroxyl group, and as there is only one IR carbonyl band, at 1630 cm^{-1}, the remaining two hydroxyl groups are in α-positions, and from the visible spectrum (λ_{max} 443 nm) it must be a 1,5 or 1,8-dihydroxyanthraquinone. The ^{1}H NMR spectrum confirms the presence of a β-hydroxyl and two *peri*-hydroxyl groups, and shows signals for a methoxyl and a β-methyl group. In addition an ABC pattern for three aromatic protons at δ7.26 (*d*, *J* = 8 Hz), 7.63 (*t*, *J* = 8 Hz) and 7.79 (*d*, *J* = 8 Hz) indicated that one ring carries only a *peri*-substituent. Hydrolysis of the methoxyl group with 80% H_2SO_4 indicates that it is located at a *peri* position, and as the product was 2-hydroxyislandicin **1** the new pigment must be either **2** or **3**. The latter was excluded on the basis of a negative zirconium nitrate test, and the absence of a shift in the visible spectrum on addition of $NaOAc$–H_3BO_3 (for alizarin the shift is 22 nm) thus demonstrating the absence of a vicinal dihydroxy system. Hence the pigment has structure **2**. The trimethyl ether of **2** was identical with the tetramethyl ether of 2-hydroxyislandicin (**1**).

The second new pigment **4**, $C_{17}H_{14}O_7$, shows all the features of **2** except that the ^{1}H NMR spectrum reveals the presence of a second methoxyl group and the ABC system is replaced by two *meta* protons. Demethylation of