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NEOLIGNANS FROM AN *ANIBA* SPECIES*

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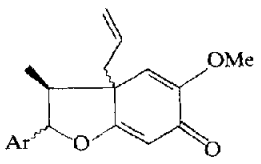
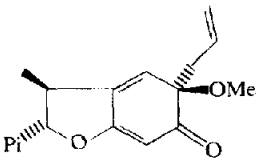
Key Word Index—*Aniba* sp.: Lauraceae; bicyclo[3.2.1]octanoid neolignans; hydrobenzofuranoid neolignans.

INTRODUCTION

The trunk wood of an *Aniba* (Lauraceae) species collected 130 km north of Manaus (Amazonas) contained, besides elemicin (3,4,5-trimethoxyallylbenzene), three burchellin-type neolignans (**1a**, **1b**, **2**) previously isolated from *A. terminalis* [2, 3] and five novel neolignans, four of the canellin type (**3a**, **3b**, **3f**, **4b**) and one of the guianin type (**4a**). For reasons stated in the previous paper in this series [1], nomenclature and numbering of neolignans follow the rules which were outlined in a recent review [4].



1a Ar = α-Pi, β-allyl
1b Ar = β-Pi, α-allyl
1c Ar = β-Mp, α-allyl



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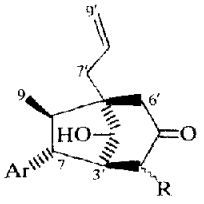
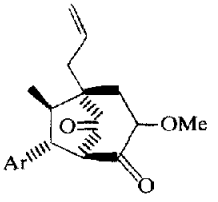


3a Ar = Pi, R = β-OH
3b Ar = Pi, R = β-OMe
3c Ar = Pi, R = α-OMe
3d Ar = Pi, R = β-OAc
3e Ar = Mp, R = β-OH
3f Ar = Mp, R = α-OMe

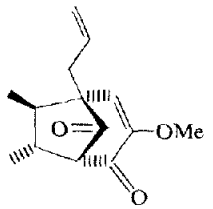


4a Ar = Gu, $\Delta^{5',6'}$
4b Ar = Gu
4c Ar = Mp, $\Delta^{5',6'}$

RESULTS AND DISCUSSION

^{1}H NMR analysis showed **3a**, $C_{18}H_{18}O(OH)_2O_2CH_2$, **3b**, $C_{18}H_{18}O{\cdot}OH{\cdot}OMe{\cdot}O_2CH_2$, and **3c**, $C_{18}H_{18}O{\cdot}OH{\cdot}OMe{\cdot}O_2CH_2$, to belong to the canellin-type of neolignans, represented by **3e**, $C_{18}H_{17}O(OH)_2OMe{\cdot}O_2CH_2$, and **3f**, $C_{18}H_{17}O{\cdot}OH(OMe)_2O_2CH_2$, from *A. simulans* [5]. Constitutional differences concern the nature of the aryl groups with piperonyl (Pi) in **3a**, **3b** and **3c** but 3-methoxy-4,5-methylenedioxyphenyl (Mp) in **3e** and **3f**. Configurational differences concern orientation of H-4′ further from the plane of the carbonyl in **3a**, **3b** and **3e** (δ 4.15 ± 0.03, J = 3 Hz) than in **3c** and **3f** (δ 4.45 ± 0.11, J = 5 Hz). This difference in orientation, which was left undefined in the original report on **3e** and **3f** [5] was confirmed by antipodal Cotton effects at the carbonyl absorptions (*ca* 330 nm) for **3a**, **3b** and **3e** compared with **3c**, **3f**. The Cotton effects for the benzenoid absorptions (*ca* 255 nm), however, are identical for all five compounds, and absolute stereochemical details known for **3e** and **3f** [5] can thus be extended to **3a**, **3b** and **3c**.

Deduction of these details had involved conversion of **3e**, as well as **1c** of known absolute sterochemistry, into the guianin-type neolignan **4c** [5]. ^{1}H NMR analysis indicated the relationship of the novel **4a**, $C_{18}H_{15}O_2{\cdot}OH(OMe)_2$, and of **4c**, $C_{18}H_{14}O_2(OMe)_2O_2CH_2$. Except for the aryl groups, Pi in **4a** and Mp in **4c**, the compounds are identical in all respects, including stereochemistry, as shown by superimposable ORD curves. In contrast, the neolignan **5** from *A. affinis* [6], an isomer of **4a**, shows an antipodal Cotton effect at the absorption wavelength (*ca* 270 nm) of the enone chromophore.



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Like **4a** (ν_{max} 1764, 1680 cm^{-1}), **4b** is also a diketone. One of the carbonyls is again on a cyclopentane ring (ν_{max} 1760 cm^{-1}) but the other is not α, β-unsaturated (ν_{max} 1695 cm^{-1}). Indeed, the compound, $C_{18}H_{17}O_2{\cdot}OH(OMe)_2$, has two additional hydrogens in its formula and is thus tentatively written **4b**. The 60 MHz ^{1}H NMR spectrum, although consistent, is not sufficiently resolved between δ 2.0–3.0 and 4.3–4.7 to confirm this proposal.

*Part 55 in the series "The Chemistry of Brazilian Lauraceae". For Part 54 see ref. [1].

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EXPERIMENTAL

Isolation of the constituents. Trunk wood of an *Aniba* species (voucher Herbarium INPA, Manaus, 43254), collected near km 133 of the Manaus–Itacoatiara highway (Amazonas) was reduced to powder (4.5 kg) and percolated with EtOH. The solvent was evapd and the residue (65 g) extracted with C_6H_6. The extract (5 g) was chromatographed on a dry Si gel (280 g) column. Development with C_6H_6–EtOAc (8:2) gave 6 fractions. Fraction 1 (0.9 g) was a fatty oil. Fraction 2 (0.7 g) gave elemicin, Fraction 3 (0.9 g) was separated with MeOH into an insoluble steroid and a soluble mixture. This was separated by TLC (Si gel; petrol–Me_2CO, 8:2) into **1a** and **3c**. Fractions 4 (0.3 g) and 5 (0.3 g) were separated by the same TLC procedure respectively into **4a**+**4b**, **3a**, **2** and **1b**, **3b**. All products were purified by TLC (Si gel; C_6H_6–Et_2O, 7:3) giving **1a** (8 mg), **1b** (159 mg), **2** (20 mg), **3a** (49 mg), **3b** (13 mg), **3c** (12 mg, **4a** (8 mg), **4b** (5 mg).Identifications of the known compounds elemicin, **1a**, **1b** and **2** involved direct comparison with authentic samples [2, 3].

(7*R*, 8*R*, 1′*R*, 2′*R*, 3′*S*, 4′*S*)-$\Delta^{8'}$-2′, 4′-*Dihydroxy*-3,4-*methylenedioxy*-1′, 2′, 3′, 4′, 5′, 6′-*hexahydro*-5′-*oxo*-7.3′, 8.1′-*neolignan* (**3a**). Mp 137–138° (MeOH) (Found: M^+ 330.1506. $C_{19}H_{22}O_5$ requires: M^+ 330.1467). λ_{max}^{MeOH} nm: 234, 286 (ε 5250, 4550). ν_{max}^{KBr} cm^{-1}: 3300, 1709, 1640, 1610, 1490, 1455, 1250, 1047, 925, 816. MS *m/e*: 331 (20%) M^++1, 330 (66) M^+, 241 (30), 240 (100), 225 (10), 215 (12), 199 (34), 177 (10), 162 (16), 135 (22). *Acetate* (**3a**, Ac_2O, C_5H_5N, room. temp. gave **3d**), viscous oil. λ_{max}^{MeOH} nm: 235, 287 (ε 4550, 4050). ν_{max}^{film} cm^{-1}: 3030, 1739, 1639, 1613, 1493, 1443, 1374, 1235, 1042, 935, 820. ^{1}H NMR (60 MHz, $CDCl_3$) : δ 0.95 (*d*, *J* = 7 Hz, 3H, 3H-9), 1.80–2.20 (*m*, 2H-7′), 2.16 (*s*, 2 OAc), 2.20–2.80 (*m*, H-7, H-8), 2.42 (*s*, H-6′), 2.47 (*d*, *J* = 4 Hz, H-3′), 4.8–5.3 (*m*, 2H-9′), 5.27 (*s*, H-2′), 5.40 (*d*, *J* = 4 Hz, H-4′), 5.5–6.2 (*m*, H-8′), 5.90 (*s*, O_2CH_2), 6.67 (*br s*, H-5, H-6), 6.77 (*s*, H-2). MS *m/e*: 415 (9%) M^++1, 414 (29) M^+, 354 (39), 294 (27), 266 (37), 252 (47), 240 (32), 212 (16), 199 (19), 162 (25), 135 (23), 55 (12), 43 (100). ORD (3.05 mg/10 ml MeOH, 400–240 nm): $[\phi]_{317}^{tr}$ −4200, $[\phi]_{280}^{pk}$ −1350, $[\phi]_{250}^{tr}$ −4750.

(7*R*, 8*R*, 1′*R*, 2′*R*, 3′*S*, 4′*S*)-$\Delta^{8'}$-2′-*Hydroxy*-4′-*methoxy*-3,4-*methylenedioxy*-1′, 2′, 3′, 4′, 5′, 6′-*hexahydro*-5′-*oxoneolignan* (**3b**). Viscous oil (Found: M^+ 344.1635. $C_{20}H_{24}O_5$ requires: M^+ 344.1623). λ_{max}^{MeOH} nm: 233, 286 (ε 5300, 4350). ν_{max}^{film} cm^{-1}: 3300, 1704, 1640, 1610, 1485, 1445, 816. MS *m/e*: 345 (21%) M^++1, 344 (100) M^+, 285 (10), 180 (13), 179 (14), 177 (27), 165 (40), 164 (29), 162 (90), 149 (72), 135 (35), 124 (31).

(7*R*, 8*R*, 1′*R*, 2′*R*, 3′*S*, 4′*R*)-$\Delta^{8'}$-2′-*Hydroxy*-4′-*methoxy*-3,4-*methylenedioxy*-1′, 2′, 3′, 4′, 5′, 6′-*hexahydro*-5′-*oxo*-7.3′, 8.1′-*neolignan* (**3c**). Viscous oil (Found:M^+ 344.1627. $C_{20}H_{24}O_5$ requires: M^+ 344.1623). λ_{max}^{MeOH} nm: 232, 286 (ε 6700, 5150). ν_{max}^{Film} cm^{-1}: 3300, 1704, 1640, 1610, 1490, 1445, 813. MS *m/e*: 345 (25%) M^++1, 344 (100) M^+, 308 (20), 294 (32), 285 (26), 179 (20), 177 (38), 165 (22), 162 (58), 149 (60), 135 (48), 124 (40).

^{1}H NMR *comparison of* **3a**/**3b** (100 MHz, $CDCl_3$)/**3e** [5] (60 MHz, $CDCl_3$) : δ0.88/0.86/0.88 (*d*, *J* = 7 Hz, 3H-9), 1.8–2.4 (*m*, 2H-7′), 2.1–2.5 (*m*, H-7, H-8), 2.40/2.32/2.38 (*s*, 2H-6′), 2.54/2.38/2.54 (*d*, *J* = 3Hz, H-3′),—/3.58/—(*s*, OMe-4′), —/—/3.86 (*s*, OMe-3), 4.18/4.12/4.18 (*d*, *J* = 3 Hz, H-4′), 4.24/4.54/4.24 (*s*, H-2′), 4.9-5.4 (*m*, 2H-9′), 5.6–6.2 (*m*, H-8′), 6.90/6.90/5.88 (*s*, O_2CH_2), —/—/6.57 and 6.72 (2*d*, *J* = 2 Hz, H-2, H6), 6.65–6.85/6.65–6.85/— (*m*, H-5, H-6), 7.03/7.07/—(*d*, *J* = 1.5 Hz, H-2).

^{1}H NMR *comparison of* **3c** (100 MHz, $CDCl_3$)/**3f** (60 MHz, CCl_4[5]): δ 0.90/0.82 (*s*, *J* = 7 Hz, 3H-9), 1.8–2.6/2.0–2.8 (*m*, H-8, H-3′, 2H-6′, 2H-7′), 2.90 (*d*, *J* = 8 Hz, H-7), 3.60/3.52 (*s*, OMe-4′), 4.57/4.34 (*d*, *J* = 5 Hz, H-4′), 4.44/4.3 (*s*, H-2′), 4.8–5.3 (*m*, 2H-9′), 5.5–6.2 (*m*, H-8′), 5.90/5.80 (*s*, O_2CH_2), —/6.53 and 6.60 (2*d*, *J* = 2 Hz, H-2 and H-6), 6.6–6.9/— (*m*, H-5, H-6), 7.07/—(*d*, *J* = 2 Hz, H-2).

ORD comparison of **3a** (3.65 mg/10 ml MeOH, 400–240 nm)/**3e** (4.84 mg/10 ml MeOH, 400–220 nm [5]): $[\phi]_{317\pm0}^{tr}$ −3000/−2750, $[\phi]_{292\pm2}$ 0/0, $[\phi]_{282\pm4}^{pk}$ +700/+150, $[\phi]_{269\pm7}$ 0/0, $[\phi]_{253\pm2}^{tr}$ −750/−2900.

ORD comparison of **3c** (4 mg/10 ml MeOH, 400–250 nm)/**3f** (5 mg/10 ml MeOH, 400–255 nm [5]): $[\phi]_{344.5\pm0.5}^{tr}$ −2050/−1800, $[\phi]_{301.5\pm1.5}$ 0/0, $[\phi]_{289\pm1}^{pk}$ +600/+350, $[\phi]_{280\pm2}$ 0/0, $[\phi]_{255}^{tr}$—/−2600.

(7*R*, 8*R*, 1′*S*, 3′*S*)-$\Delta^{8'}$-4-*Hydroxy*-3,5′-*dimethoxy*-1′, 2′, 3′, 4′-*tetrahydro*-4′-*oxo*-7.3′, 8.1′-*neolignan* (**4a**). Viscous oil (Found: M^+ 342.1493. $C_{20}H_{22}O_5$ requires: M^+ 342.1467). λ_{max}^{MeOH} nm: 227 sh, 273 (ε10 050, 6500). $\lambda_{max}^{MeOH+NaOH}$ nm: 244 sh, 284 (ε 13 700, 9350). ν_{max}^{Film} cm^{-1}: 3330, 1764, 1680, 1600, 1508, 1450, 1370, 1250, 920, 820. MS *m/e*: 343 (21%) M^++1, 342 (100) M^+, 327 (11), 301 (21), 273 (19), 180 (18), 179 (13), 178 (15), 177 (18), 166 (17), 164 (22), 163 (60), 149 (18).

^{1}H *NMR comparison of* **4a**/**4c** [5] (60 MHz, $CDCl_3$): δ 1.05/1.07 (*d*, *J* = 7 Hz, 3H-9), 1.9–2.4 (*m*, H-8), 2.4–2.7 (*m*, 2H-7′), 2.55/2.57 (*d*, *J* = 8 Hz, H-7), 3.54/3.55 (*s*, H-3′), 3.73/3.74 (*s*, OMe-5′), 3.85/3.88 (*s*, OMe-3), 4.8–5.4 (*m*, 2H-9′), 5.4–6.2/5.3–5.6 (*m*, H-8′), —/5.96 (*s*, O_2CH_2), 5.78/5.85 (*s*, H-6′), 6.4–6.85/— (*m*, H-2, H-5, H-6), —/6.27 (*s*, H-2, H-6).

ORD comparison of **4a** (0.75 mg/10 ml MeOH, 400–230 nm)/**4c** (2.82 mg/25 ml MeOH, 400–220 nm [5]): $[\phi]_{356\pm1}^{tr}$ −8210/−11 300, $[\phi]_{335.5\pm0.5}$ 0/0, $[\phi]_{313.5\pm0.5}^{pk}$ +14 150/+20 000, $[\phi]_{295.5\pm0.5}$ 0/0, $[\phi]_{281.5\pm1.5}^{tr}$ −7300/−9500, $[\phi]_{267\pm1}$ 0/0, $[\phi]_{256\pm2}^{pk}$ +5950/+8600.

(7*R*, 8*R*, 1′*R*, 3′*S*)-$\Delta^{8'}$-4-*Hydroxy*-3,5′-*dimethoxy*-1′, 2′, 3′, 4′, 5′, 6′, -*hexahydro*-4′-*oxo*-7.3′, 8.1′-*neolignan* (**4b**). Viscous oil (Found: M^+ 344.1598. $C_{20}H_{24}O_5$ requires: M^+ 344.1623). λ_{max}^{MeOH} nm: 228 sh, 281 (ε 7550, 3050). $\lambda_{max}^{MeOH+NaOH}$ nm: 236 sh, 291 (ε 8050, 5800). ν_{max}^{Film} cm^{-1}: 3330, 1760, 1695, 1600, 1506, 1450, 1370, 1266, 926, 870, 820. ^{1}H NMR (60 MHz, CCl_4): δ 1.18 (*d*, *J* = 7 Hz, 3H-9), 2.0–3.0 (*m*, 2H-6′, H-3′, H-7, H-8, 2H-7′), 3.58 (*s*, OMe-5′), 3.88 (*s*, OMe-3), 4.3–4.7 (*m*, H-5′), 4.8–5.4 (*m*, 2H-9′), 5.4–6.1 (*m*, H-8′), 6.3–6.8 (*m*, H-2, H-5, H-6). MS *m/e*: 344 (13) M^+, 342 (87), 301 (22), 273 (22), 179 (48), 177 (82), 164 (52), 163 (100), 151 (62), 149 (90), 137 (45). ORD (0.65 mg/10 ml MeOH, 400–230 nm): $[\phi]_{315}^{pk}$ +14 300, $[\phi]_{298}$ 0, $[\phi]_{285}^{tr}$ −12 150, $[\phi]_{267}^{pk}$ −9000, $[\phi]_{259}^{tr}$ −9500, $[\phi]_{237}$ 0.

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DIHYDROCHALCONES FROM *BALANOPHORA TOBIRACOLA*

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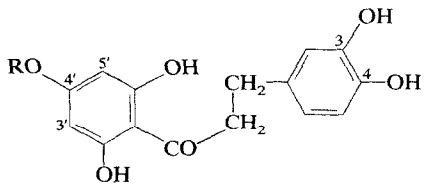
Key Word Index—*Balanophora tobiracola*; Balanophoraceae; dihydrochalcone; 3-hydroxyphloretin 4′-β-D-glucoside; phenylpropanoid; ^{13}C NMR sprectrum.

INTRODUCTION

Balanophora tobiracola Makino (Japanese name *Kiiretsuchitorimochi*), one of seven Balanophoraceous plants in Japan, parasitizes the terminal roots of host plant such as *Pittosporum tobira* Ait. and is distributed from southern Japan to Taiwan [1]. Several triterpenes and phenylpropanoids have been reported previously from *B. japonica* Makino [2], *B. polyandra* Griff. [3] and *B. indica* Wall. [4] and several flavones from *Lophophytum leamdri* Eirchl. [5] and *Juelia subterranea* [6]. This paper describes the phytochemistry of *B. tobiracola* Makino.

RESULTS AND DISCUSSION

Six known phenylpropanoids: *p*-methoxycinnamic acid, *trans*-cinnamic acid, caffeic acid methyl ester, *p*-coumaric acid, *m*-coumaric acid, caffeic acid and two triterpenes: β-amyrin acetate and lupeol were isolated from the ether-soluble fraction of the methanol extract of the whole plant of *B. tobiracola* Makino. Dihydrochalcone **1** was also isolated from the same fraction, while from the ethyl acetate-soluble fraction of the methanol extract, both **1** and the related glucoside **2** were obtained.



1 R = H
2 R = Glc

From measurements of IR, MS, ^1H and ^{13}C NMR spectra of **1** and the corresponding tri-, tetra- and pentamethyl ethers prepared by methylation with diazomethane or dimethyl sulphate, the structure of **1** was assumed to be 3-hydroxyphloretin. This was confirmed by the direct comparisons (IR, MS and ^1H NMR) with an authentic sample. On acid hydrolysis, **2** yielded 3-hydroxyphloretin, and β-D-glucose. Futhermore, the presence of a β-glucopyranose moiety in **2** was shown by the analysis of the coupling constants of the anomeric carbon atoms (C-1″) in the ^{13}C NMR sprectra (Table 1) [7] of **2** and its hepta- and octaacetates. Consequently, **2** is 3-hydroxyphloretin 4′-β-D-glucoside, and this was confirmed by comparison with an authentic sample. Although 3-hydroxyphoretin and its glucoside have already been isolated from the leaves of *Malus sieboldii* Rehd. var. *arborescens* (Rosaceae) [8], this is the first report of a dihydrochalcone and its glucoside in Balanophoraceous plants.

Comparative studies of the constituents of the flowers and the rhizomes of *B. tobiracola* Makino, showed clear differences: i.e. *trans*-cinnamic acid and caffeic acid methyl ester were present in both parts of the plant, the main components ot the flowers were glycosides (80%), while the rhizomes contained 60% of hydrocarbons and triterpenes such as β-amyrin acetate and lupeol, along with 30% of phenylpropanoids.

EXPERIMENTAL

Mps are uncorr. ^1H NMR (100 MHz) and ^{13}C NMR (25 MHz) spectra were recorded in $CDCl_3$ except for noted. Chemical shifts were shown in ppm (δ) with TMS as internal standard.

Isolations. MeOH extract 100 g of fresh whole plant (8 kg) of *Balanophora tobiracola* collected at Ibusuki, Kagoshima, Japan, was divided into the Et_2O- (13.4 g) and the EtOAc-soluble fractions (58.7 g). The Et_2O-soluble fraction (13.4 g) was chromatographed on Si gel (Merck, Kieselgel 60, 300 g).

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