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DIARYLPROPANOIDS FROM *IRYANTHERA POLYNEURA**

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Key Word Index—*Iryanthera polyneura*; Myristicaceae; 1,3-diarylpropanes; dihydrochalcone.

Abstract—The trunk wood of *Iryanthera polyneura* Ducke (Myristicaceae) contains pinocembrin, 1-(2′,4′-dihydroxyphenyl)-3-(3″,4″-methylenedioxyphenyl)-propane, 1-(2′,4′-dihydroxy-3′-methylphenyl)-3-(2″-methoxy-4″,5″-methylenedioxyphenyl)-propane and 4,2′,4′-trihydroxy-3-methoxydihydrochalcone.

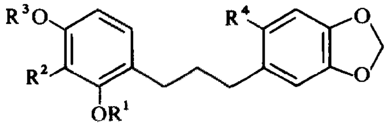
INTRODUCTION

The nomadic and very primitive Maku Indians of the Apaporis basin (Amazonia) employ a plaster made of the crushed leaves of *Iryanthera polyneura* Ducke (Myristicaceae) for treating seriously infected wounds and cuts [3]. This ethnopharmacological observation stimulated interest in the chemistry of the tree, and a study on the composition of its trunk wood was undertaken. The results are reported in the present paper.

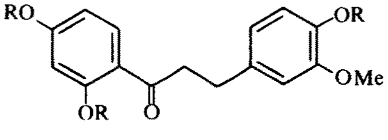
RESULTS

Fractionation of a benzene extract of the trunk wood afforded, besides sitosterol and pinocembrin, the 1,3-diarylpropane **1a**, previously obtained from *I. coriacea* Ducke [4], two novel compounds, the additional diarylpropane **1c** and the dihydrochalcone **2a**, and a small quantity of a mixture containing two chalcones tentatively formulated **3a** and **3b**.

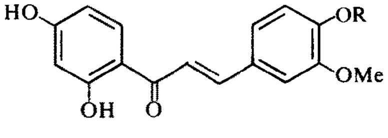
The basic structure of the diarylpropane, $C_{15}H_{10}$-$Me(OH)_2OMe.O_2CH_2$, was indicated by ^1H and ^{13}C NMR spectral evidence which pointed to a $CH_2.CH_2.CH_2$ chain flanked by two aryl groups. One must bear 2-methoxy-4,5-methylenedioxy substitutions. The base peak in the MS shows the correct mass for a methoxymethylenedioxytropylium ion; the ^1H NMR spectrum includes two singlets (δ 3.34 and 3.42). The other aryl group bears 2,4-dihydroxy-3-methyl substitution. The ^1H NMR spectrum includes two doublets (δ 6.36 and 6.72, $J = 8$ Hz); oxidation of the compound does not lead to *ortho* or *para*-quinones; a ^{13}C NMR quartet at high field (δ 8.9) is compatible only with a methyl between two vicinal substituents [5]. The ^{13}C NMR assignments for this 1,3-diarylpropane (**2c**) are compatible with the analogous data for **1a** [4] and virolane (**1b**) (see Experimental), previously obtained from *Virola multinervia* Ducke [6].



1a R¹ = R² = R³ = R⁴ = H
1b R¹ = R² = R⁴ = H, R³ = Me
1c R¹ = R³ = H, R² = Me, R⁴ = OMe
1d R¹ = R³ = OAc, R² = Me, R⁴ = OMe



2a R = H
2b R = Ac



3a R = H
3b R = Me

The basic structure of the dihydrochalcone, $C_{15}H_{10}O$-$(OH)_3OMe$, was indicated by ^1H and ^{13}C NMR spectral evidence which pointed to a $CH_2.CH_2$ group flanked by benzoyl and aryl substituents. The benzoyl group must be 2,4-dihydroxylated: the molecule has chelated and acidic hydroxyls evidenced by IR and UV ($AlCl_3$ and NaOAc shifts) spectra; acetylation produces NMR shifts of the aromatic C signals which are closely comparable with the values observed for 2,4-dihydroxyacetophenone (see Experimental). The aryl group must bear 4-hydroxy-3-methoxy substitution: the two oxy-functions are located at C-3 and C-4 (H-2, H-5 and H-6 give a NMR multiplet at δ 6.7–6.9); acetylation produces paramagnetic shifts

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(+5.1 to +7.6 ppm) of the C-1, C-3 and C-5 signals, and a small diamagnetic shift (−2.1 ppm) of the C-4 signal, leaving the C-2 and C-6 signals practically unaffected. The MS of this dihydrochalcone (**2a**) is accordingly very simple, since both the dihydroxybenzoyl ion and the hydroxymethoxytropylium ion have *m/e* 137.

The constituents of a mixture obtained in minute amount were tentatively characterized as chalcones **3a** and **3b** by ^{1}H NMR spectroscopy. Not only the molecular peaks 286 (55%) and 300 (45%) of the MS, but also the fragment peaks due to dihydroxybenzoyl (*m/e* 137 (100%)), hydroxy-methoxystyryl (*m/e* 150 (80%)) and dimethoxystyryl (*m/e* 164 (50%)) ions, were consistent with this hypothesis.

DISCUSSION

The biosynthesis of cinnamylphenols in Leguminosae was postulated to involve the cinnamylation of triacetate moieties [7]. The fact that both the Leguminosae and the Myristicaceae are isoflavonoid accumulators invites the hypothesis that, as a further common biochemical feature, cinnamylation also occurs in both families, the 1,3-diarylpropanes of Myristicaceae being simply hydrogenation products of intermediate cinnamylphenols. It has, nevertheless, been suggested recently that the co-occurrence of 1,3-diarylpropanes with 1,3-diarylpropan-2-ols and flavans points to their biosynthetic derivation from chalcones [8], a postulate which receives now additional support by the isolation of a flavanone and, most importantly, by the co-occurrence of chalcone-dihydrochalcone-1,3-diarylpropane with identical oxygenation pattern in *Iryanthera polyneura*.

EXPERIMENTAL

Isolation of the constituents. Trunk wood of *Iryanthera polyneura* was collected near Manaus, Amazonas State, and identified by the botanist Dr. William A. Rodrigues. A C_6H_6 extract (4%, 200 g) was chromatographed on a Si gel column. Petrol, C_6H_6–$CHCl_3$ and MeOH eluted, in order, aliphatic (100 g), aromatic (40 mg) and aliphatic (50 g) fractions. The aromatic fraction (25 g) was rechromatographed on a Si gel column. The following solvents eluted, in order, the indicated compounds C_6H_6: **1c** (150 mg) and pinocembrin (120 mg), C_6H_6–$CHCl_3$ 8:2: sitosterol (500 mg). C_6H_6–$CHCl_3$ 1:1: **1a** (1 g), a mixture of **3a** and **3b** (8 mg after purification by aq. Na_2CO_3) and **2a** (160 mg).

1-(*2′,4′-Dihydroxy-3′-methylphenyl*)-3-(*2″-methoxy-4″,5″-methylenedioxyphenyl*)-*propane* (**1c**). Mp 104–106° (C_6H_6–petrol); ν_{max}^{KBr} cm^{-1}: 3500, 3400, 1620, 1190, 1160, 1060, 1030; λ_{max}^{EtOH} nm: 227, 294 inf., 310 (ε 20200, 6000, 8200), no NaOAc, NaOAc + H_3BO_3, $AlCl_3$ shifts, $\lambda_{max}^{EtOH + NaOH}$ nm: 253, 310 (ε 14200, 3100); Gibbs test: positive. ^{1}H NMR (100 MHz, $(CD_3)_2CO$): δ 1.65–1.95 (*m*, 2H-2), 2.13 (*s*, Me), 2.56 and 2.58 (2*t*, *J* = 6 Hz, 2H-1 and 2H-3), 3.74 (*s*, OMe), 5.86 (*s*, O_2CH_2), 6.36 (*d*, *J* = 8 Hz, H-5′), 6.58 (*s*, H-3″), 6.66 (*s*, H-6″), 6.72 (*d*, *J* = 8 Hz, H-6′), 6.96 and 7.81 (2*s*, 2OH). MS (*m/e*): 316 (48%) M^+, 165 (100), 151 (13), 137 (28). ^{13}C NMR **1a**/**1b**/**1c** (25.2 MHz, $(CD_3)_2CO$): δ —/—/8.9 (*q*, Me), 29.6/28.6/31.5 (*t*, C-2), 32.7/31.7/30.5 (*t*, C-1), 35.7/35.2/30.4 (*t*, C-3), −/56.2/56.5 (*q*, OMe), 101.1/101.6/101.4 (*t*, O_2CH_2), 103.1/100.6/120.4 (*d/d/s*, C-3′), 106.9/105.7/107.1 (*d*, C-5′), 108.3/108.0/109.9 (*d*, C-6″), 109.1/108.3/95.3 (*d*, C-3″), 120.0/120.3/123.7 (*s*, C-1′), 121.5/121.0/152.9 (*d*, C-2″), 130.8/130.4/127.1 (*d*, C-6′), 137.0/136.0/123.7 (*s*, C-1″), 147.9/147.3/141.4 (*s*, C-5″), 148.0/145.3/146.6 (*s*, C-4″), 156.1/154.1/154.1 (*s*, C-2′), 156.7/158.3/154.6 (*s*, C-4′) (for the sake of comparison, the C of **1a** and **1b** substituted by R^4 = H, see formula, was also numbered C-2″). *Diacetate* (**1d**). ^{1}H NMR (100 MHz, $CDCl_3$): δ 1.6–2.0 (*m*, 2H-2), 1.96 (*s*, Me), 2.26 and 2.30 (2*s*, 2OAc), 2.45–2.65 (*m*, 2H-1 and 2H-3), 3.74 (*s*, OMe), 5.87 (*s*, O_2CH_2), 6.50 (*s*, H-3″), 6.63 (*s*, H-6″), 6.87 (*d*, *J* = 8 Hz, H-5′), 7.08 (*d*, *J* = 8 Hz, H-6′).

4,2′,4′-Trihydroxy-3-methoxydihydrochalcone (**2a**). Mp 153–155° (C_6H_6–petrol); ν_{max}^{Nujol} cm^{-1}: 3460, 3350, 1625; λ_{max}^{EtOH} nm: 218, 232 inf., 280, 318 (ε 18400, 12900, 15200, 7200), slight NaOAc and $AlCl_3$ shifts, no NaOAc + H_3BO_3 shift, $\lambda_{max}^{EtOH + NaOH}$ nm: 227, 249, 342 (ε 7200, 12800, 28800), Gibbs test: positive. ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.9–3.2 (*m*, $2CH_2$), 3.90 (*s*, OMe), 6.40 (*dd*, *J* = 8,2 Hz, H-5′), 6.42 (H-3′), 6.7–6.9 (*m*, H-2, 5, 6), 7.80 (*d*, *J* = 8 Hz, H-6′), 12.7 (OH-2′). MS (*m/e*): 288 (58%) M^+, 151 (12), 150 (21), 137 (100). *Triacetate* (**2b**), oil. ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.3 (*s*, 3OAc), 3.0–3.3 (*m*, $2CH_2$), 3.80 (*s*, OMe), 6.85 (H-2), 7.0 (H-3′), 6.85–7.05 (H-5,6), 7.05 (*dd*, *J* = 8, 2 Hz, H-5′), 7.80 (*d*, *J* = 8 Hz, H-6′). ^{13}C NMR **2a**/**2b** (20 MHz, $CDCl_3$): δ −/20.6 (*s*, OAc), −/21.0 (*s*, 2OAc), 30.8/29.9 (*t*, CH_2-β), 40.0/43.0 (*t*, CH_2-α), 56.1/55.9 (*q*, OMe), 103.5/119.1 (*d*, C-3′), 108.4/117.4 (*d*, C-5′), 112.1/112.9 (*d*, C-2), 113.5/128.0 (*s*, C-1′), 115.1/122.7 (*d*, C-5), 121.1/120.4 (*d*, C-6), 132.5/130.7 (*d*, C-6′), 133.0/138.2 (*s*, C-1), 142.1/140.0 (*s*, C-4), 144.8/149.9 (*s*, C-3), 164.8/154.0 (*s*, C-4′), 165.7/151.1 (*s*, C-2′), —/168.3 (*s*, CO), —/169.0 (*s*, 2CO), 206.8/197.9 (*s*, CO). ^{13}C NMR shifts **2a** → **2b**/2,4-dihydroxyacetophenone [9] → 2,4-diacetoxyacetophenone (ppm): +14.5/+13.8 (C-1′), −14.6/−14.9 (C-2′), +15.5/+15.5 (C-3′), −10.8/−11.4 (C-4′), +9.0/+7.7 (C-5′), −1.8/−3.8 (C-6′).

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