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BIFLAVANOIDS, NORDITERPENES AND A NORTRITERPENE FROM *PODOCARPUS URBANII*

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Key Word Index—*Podocarpus urbanii*; Podocarpaceae; biflavanoid; urbalactone, a new norditerpene; 2,3-dihydropodolide; podolide; nagilactone C; nortriterpene, $C_{27}H_{44}O_6$.

Abstract—The structures of a biflavanoid, two new norditerpenes, urbalactone and 2,3-dihydropodolide, an ecdysterol, as well as a known biflavanoid, nagilactone C and podolide from *Podocarpus urbanii* were elucidated.

INTRODUCTION

Some species of the genus *Podocarpus* have been the subject of extensive chemical investigations because of their usefulness as building material. Compounds isolated include norditerpene dilactones [1–5], terpene hydrocarbons [6, 7] and biflavanoids [8, 9]. This work describes the isolation and structural elucidation of some new natural products from the Jamaican plant, *Podocarpus urbanii*, which to date had not been investigated.

RESULTS AND DISCUSSION

The compound A, $C_{33}H_{24}O_{10}$, isolated as described in the Experimental, mp 290° (dec), $[\alpha]_D^{25}$ +15° (Py) was identical to sciadopitysin [10]. This identification was confirmed by monomethylation of A to the biflavanoid, (+)-4′,4‴,7,7″-tetra-*O*-methylamentoflavone (W 13) isolated from *Dacrydium cupressinum* [11] and *Araucaria cookii* [12], and by direct comparison of the ^{1}H NMR spectra of the triacetates of compound A and sciadopitysin.

Another biflavanoid, compound E, $C_{31}H_{20}O_{10}$, contained a single methoxy group. On acetylation it gave a pentaacetate, $C_{41}H_{30}O_{15}$, mp 242–245° (dec), and on methylation gave a trimethyl derivative, $C_{34}H_{26}O_{10}$, mp 280–282°, which had ^{1}H NMR spectral data consistent with that of the 7‴-methyl ether of sciadopitysin.

The mass fragment, *m/e* 135 (18%), for the *p*-methoxybenzoyl ion in the high resolution mass spectrum of the pentaacetate characteristically located the methoxy group at the 4‴-position. Structure **1** is therefore proposed for this biflavanoid which is podocarpus flavone A.

Compound D, a norditerpene, $C_{19}H_{22}O_7$, mp 306–308° (dec), $[\alpha]_D^{23}$ +105° (Py), gave a diacetate, mp 279–80°, $C_{23}H_{26}O_9$. The ^{1}H NMR, IR, UV and mass spectra were consistent with the known compound nagilactone C.

Compound F, named urbalactone (**2**), $C_{19}H_{24}O_7$, mp 270–272° (dec), gave a triactate, $C_{25}H_{30}O_{10}$, mp 199–200°. The UV spectrum showed absorption at 297 nm (ε = 5308), with the IR spectrum showing bands at 3350 (OH), 1768 (γ-lactone), 1743, 1685, 1620 cm^{-1} (δ-lactone). The ^{1}H NMR spectrum could be interpreted as follows: δ 1.23, 1.30 (tertiary methyl groups), 1.14 and 1.21 (J = 6.8 Hz), secondary methyl groups, 6.3 (α-H of an α, β-unsaturated carbonyl system). These data were consistent with the subgroup type A norditerpenes [14]. In the ^{1}H NMR spectrum of the triacetate a one-proton doublet (δ 6.29, J = 9 Hz) established the location and orientation of the C-7 acetate group, in keeping with the assignment in the related compound nagilactone C diacetate (δ 6.37, J = 9 Hz). The other two hydroxyl groups, being secondary, were at two of three positions (i.e. C-1, C-2 or C-3). The triacetate of **3**, mp 237–239° (dec) is already known from *Podocarpus nagi* [15], while structure **4** is the compound nagilactone B, mp 258–261° (dec), with its triacetate, mp 254–5°, also isolated from *Podocarpus nagi* [1]. This leaves the C-2, C-3 positions available and this vicinal substitution pattern was supported by Jones oxidation at 0° to give a compound with UV absorptions at values 275 and 300 nm, and which with base shifted to 375 and 312 nm. The 275 nm to 321 nm shift is comparable to the shift noted in the diosphenol chromophore in the enolisation of cyclohexan-1,2-dione [16, 17]. Structure **2** was therefore assigned to this new norditerpene.

Compound B, mp 282–286° (sublimed), $C_{19}H_{24}O_5$, had λ_{max}^{EtOH} 220 nm (ε = 12051); ν_{max} 1780 (γ-lactone) and 1720, 1650 cm^{-1} (α,β-unsaturated δ-lactone). In the subgroup B of norditerpenes [14], the C-6 proton appears at δ 4.96 (J = 4.5 and 2 Hz) and supports the location of the epoxide at C-7, C-8. This moiety was also indicated by the signal at δ 4.94, (J = 4.5 and 2 Hz) in the ^{1}H NMR spectrum of compound B. Except for the obvious differences relating to the 1,2-positions this spectrum compared favourably with that of podolide from *Podocarpus gracilion* [14] and compound B has been assigned structure **5**, that of 2,3-dihydropodolide.

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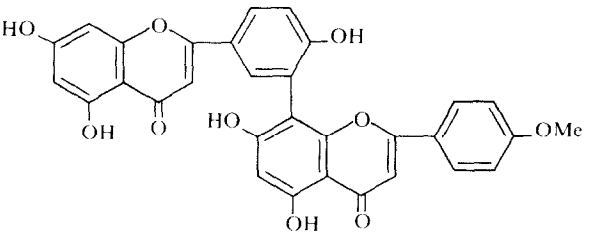

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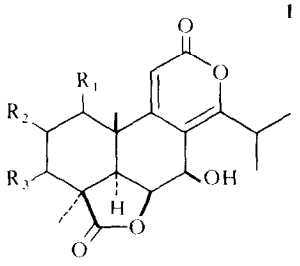
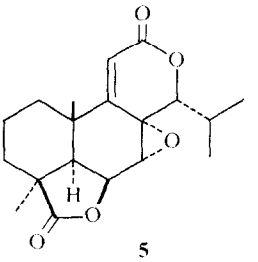


2 $R_2 = R_3 = OH$, $R_1 = H$
3 $R_1 = R_3 = OH$, $R_2 = H$
4 $R_1 = R_2 = OH$, $R_3 = H$



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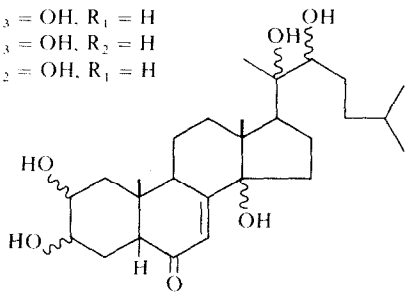

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Compound H, $C_{19}H_{22}O_5$, mp 277–279°, λ_{max}^{EtOH} 220 nm, ν_{max} 1780 (γ-lactone), 1725 and 1650 (α,β-unsaturated δ-lactone), was not available in sufficient quantity to allow unequivocal structural assignment but from high resolution mass spectral comparison appeared to be podolide contaminated by a trace of compound **5**.

Compound G, $C_{27}H_{44}O_6$, mp 265–268° (dec), λ_{max}^{EtOH} 242 nm, ν_{max} 3410 (OH) and 1645 (α,β-unsaturated CO) showed all the features of an ecdysterol. ^{1}H NMR spectral singlets at δ 0.81, 1.10 and 1.26 were assigned to tertiary methyl groups, while doublets at 0.81 and 0.91 (J = 6 Hz each) were due to secondary methyl groups. A signal at 5.2 (1H, *bd*, J = 2 Hz) represented the α-hydrogen (H-7) of the α,β-unsaturated system. This had allylic and long range coupling to H-9 and H-5 respectively. These data coupled with the five exchangeable (D_2O) protons in the ^{1}H NMR spectrum confirmed that compound G was very similar to ponasterone A, B and C isolated from *Podocarpus nakaii* [15, 17–20].

The location of two hydroxyl groups in the side chain was supported by MS data [20, 21]. The molecule lost two tertiary hydroxyl groups as water producing an ion at *m/e* 428 ($C_{27}H_{40}O_4$). Two alternative and more facile cleavages gave the base peak, *m/e* 345 ($C_{21}H_{29}O_4$) and the peak *m/e* 301 ($C_{19}H_{25}O_3$) which with other smaller fragments are characteristic of an ecdysterol with a 20,22-vicinal diol and the usually substituted 5 β-H nucleus. Compound G must therefore have the planar structure **6** common both to ponasterone A and B. Ponasterone B is non-crystalline. The difference in the mp of compound G and ponasterone A suggests there is a stereochemical difference. The small quantity of G available was not sufficient for further investigation.

EXPERIMENTAL

Mps are uncorr. Unless otherwise stated ^{1}H NMR spectra were obtained at 60 MHz in $CDCl_3$ with TMS as internal standard and MS at 70 eV on a low resolution spectrometer. TLC was on Si gel plates and prep. TLC on plates 0.75–1.0 mm thick. The neutral Al_2O_3 used for CC was Brockmiann grade II or III. Si gel for columns was Kieselgel 60 (70–230 mesh ASTM), activity 2–3.

Isolation of compounds. Dried, milled leaves and twigs of *Podocarpus urbanii** (1.2 kg) were extracted exhaustively in a Soxthlet firstly with C_6H_6 and then with EtOH to give 32 g and 120 g of crude extract respectively. The C_6H_6 extract was redissolved in a minimum of C_6H_6 and set aside. A yellow ppt. (300 mg) was filtered and purified by prep. TLC using $CHCl_3$–EtOAc (2:1) to give compound A (150 mg). The filtrate (30 g) was separated on Al_2O_3 (1 kg). Elution of the column with C_6H_6 yielded a fraction (400 mg) which after prep. TLC using petrol–Me_2CO (4:1) gave compound B (40 mg). The EtOH extract was diluted with H_2O (1 l.) and extracted with EtOAc to give a product (18 g) which was purified on Al_2O_3 (540 g). The fraction obtained by eluting with C_6H_6–EtOAc (20:1–10:1) contained two compounds which by prep. TLC in Me_2CO–petrol (1:4) gave compounds B (10 mg) and C (50 mg).

* Specimen of these plants were identified at the Herbarium: Botany Dept., U.W.I., Mona, Kingston 7, Jamaica, W.I.

A second collection of plant material (1.1 kg) was similarly extracted to yield 90 g from the C_6H_6 extraction and 219 g from the EtOH extraction. The C_6H_6 extract was redissolved in a minimum of C_6H_6 and set aside to give a crude yellow mixture (10 g). Purification of this mixture (972 mg) by prep. TLC ($CHCl_3$–EtOAc, 2:1), gave compound A and compound D (280 mg). The filtrate was triturated with petrol to remove fatty components and the residue (17 g) separated on a Si gel column (500 g). Elution with EtOAc–C_6H_6 (1:4) gave a fraction (600 mg) which after prep. TLC (petrol–Me_2CO, 4:1) and repeated recrystallization from EtOH yielded compound H (10 mg). Compound B (20 mg) was obtained from later fractions, while the C_6H_6–EtOAc (3:2–2:1) fractions gave compound **1**. Recrystallization from Me_2CO yielded yellow plates, mp 278–280°, $C_{34}H_{26}O_{10}$ by high resolution MS. The EtOH extract (219 g) was diluted with 2:1 of H_2O and extracted consecutively with $CHCl_3$ and EtOAc. The EtOAc extract (20 g) was separated on Si gel (800 g). The fraction eluted by EtOAc–C_6H_6 (4:1) gave a mixture of 3 compounds which by prep. TLC (petrol–Me_2CO, 1:1) gave a non-crystalline compound E (137 mg). The fractions eluted with EtOAc–EtOH (9:1–8:2) gave a residue (1.7 g) which gave crystals of compound D (148 mg) from EtOH. Prep. TLC of the mother liquor in petrol–Me_2CO (3:2) gave a mixture of two compounds (186 mg). This was rechromatographed in petrol–EtOAc (1:4) to give compound D (14 mg) and compound F (34 mg). Other fractions yielded compound G (12 mg).

Compound A. Recrystallization from Me_2CO gave yellow rods, mp 290° (dec.), $[\alpha]_D^{25}$ +15° (Py); MS 580.1383, $C_{33}H_{24}O_{10}$; IR ν_{max}^{nujol} cm^{-1}: 3200 (chelated OH), 1660 (CO), 1600, 1575 (aromatic); UV λ_{max}^{EtOH} nm: 271, 337 shifting in alkali to 286 and 372. ^1H NMR (DMSO d_6–$CDCl_3$, 1:3): δ3.80, 3.84, 3.86 (3 × 3H, *s*, aromatic OMe), 6.32 (1H, *d*, *J* = 2 Hz), 6.54 (2H), 6.64, 6.70 (1H each, δ), 6.86 (2H, *d*, *J* = 8 Hz), 7.26 (1H, *d*, *J* = 8 Hz), 7.54 (2H, *d*, *J* = 8 Hz), 7.98 (1H, *s*), 8.04 (1H, *d*, *J* = 8 Hz), 12.82, 12.96 (2 × 1H, exchanged with D_2O). Methylation of A (22 mg) in dry dioxan with CH_2N_2 in Et_2O gave a yellow crystalline product which was further purified by prep. TLC ($CHCl_3$:EtOAc) to give the monomethylated product 17 mg, mp 292–294°, $[\alpha]_D^{24}$ +21.25°($CHCl_3$). ^1H NMR, UV and IR spectra were recorded. High resolution MS, 594.1533, $C_{34}H_{26}O_{10}$. Compound A (100 mg) was acetylated ($NaOAc$–Ac_2O) and purified by prep. TLC to give rods, mp 258–260°; MS; 706.1715, $C_{39}H_{30}O_{13}$. UV and IR spectra were determined and the ^1H NMR spectrum (100 MHz) compared with that of sciadopitysin triacetate.

Compound B (**5**). Recrystallization from EtOH gave rods, mp 282–286° (sublimed); IR ν_{max} cm^{-1}: 1780 (γ-lactone), 1720, 1650 (α,β-unsaturated δ-lactone); UV λ_{max}^{EtOH} nm: 220 (ε = 12051); ^1H NMR: δ 1.09 (3H, *d*, *J* = 6 Hz, C-16 Me), 1.11 (3H, *d*, *J* = 6 Hz, C-17 Me), 1.29 (3H, *s*, C-20 Me), 1.56 (3H, *s*, C-18 Me), 1.84 (1H, *d*, *J* = 4.4 Hz, H-5), 3.97 (1H, *d*, *J* = 2 Hz, H-7), 4.43 (1H, *d*, *J* = 3.5 Hz, H-14), 4.94 (1H, *dd*, *J* = 4.5, 2 Hz, H-6), 6.00 (1H, *s*, H-11); MS 332.1615, $C_{19}H_{24}O_5$. (Found: C, 68.52; H, 7.43; O, 24.05. $C_{19}H_{24}O_5$ requires C, 68.65; H, 7.28; O, 24.07%).

Compound C. Recrystallized from MeOH as needles, mp 134–136°. TLC, IR, ^1H NMR spectra found to be identical with sitosterol and mmp with an authentic sample showed no depression.

Compound D. Mp 306–308° (dec), $[\alpha]_D^{23}$ +105° (Py); IR ν_{max}^{nujol} cm^{-1}: 3450, 3200 (OH), 1780 (γ-lactone), 1710, 1640, 1560 ($\alpha,\beta,\gamma,\delta$-unsaturated δ-lactone). UV λ_{max}^{EtOH} nm: 300. ^1H NMR(DMSO d_6–$CDCl_3$, 3:1): δ 1.21 (3H, *d*, *J* = 6.5 Hz, C-16 Me), 1.24 (3H, *d*, *J* = 6.8 Hz, C-17 Me), 1.36 (3H, *s*, C-18 Me), 1.39 (3H, *s*, C-20 Me), 2.08 (1H, *d*, *J* = 6.5 Hz, H-5), 3.20–3.50 (1H, *m*, H-15), 3.30 (1H, *m*, H-2), 3.57 (1H, *d*, *J* = 4 Hz, H-1), 4.35 (1H, *d*, *J* = 6 Hz, H-3), 4.9 (1H, *dd*, H-6), 5.32 (1H, *d*, *J* = 8.5 Hz, H-7), 6.24 (1H, H-11); MS, 362.1334, $C_{19}H_{22}O_7$. Compound D (80 mg) was acetylated (Py–Ac_2O) to give an acetate, mp 279–280°; MS, 446.1597, $C_{23}H_{26}O_9$. ^1H NMR, MS, UV, IR spectra recorded and data consistent with that of the known compound nagilactone C.

Compound E (**1**). Yellow amorphous compound, $[\alpha]_D^{25}$ +10° (Py–EtOH, 1:4); IR ν_{max}^{nujol} cm^{-1}: 3200 (OH), 1660 (CO), 1610, 1580; UV λ_{max}^{EtOH} nm: 210, 270, 335 shifting in base to 212, 277, 388 respectively. ^1H NMR(DMSO d_6–$CDCl_3$, 4:1): δ 3.80 (3H, *s*, ArOMe), 6.2 (1H, *d*, *J* = 2 Hz, H-6, I), 6.40 (1H, *d*, *J* = 2 Hz, H-8, I), 6.44 (1H, *s*, H-6, II), 6.66 (1H, *s*, H-3, I), 6.72 (1H, *s*, H-3, II), 6.90 (2H, *d*, *J* = 9 Hz, H-3′, H-5′, II), 7.20 (1H, *d*, *J* = 9 Hz, H-5′, I), 7.69 (2H, *d*, *J* = 9 Hz, H-2′, H-6′, II), 8.10 (1H, H-2′, I), 8.14 (1H, *d*, *J* = 9 Hz, H-6′, I), 12.90 (1H, *s*, OH), 13.00 (1H, *s*, OH), MS, 552.1056, $C_{31}H_{20}O_{10}$. Acetylation (30 mg) with (Ac_2O–$HClO_4$) gave on work-up a product which was recrystallized from EtOAc, mp 242–245° (dec.); MS, 762.1600, $C_{41}H_{30}O_{15}$; UV λ_{max}^{EtOH} nm: 260 and 325 shifting in base to 272 and 345 respectively. ^1H NMR: δ 2.03, 2.08, 2.32, 2.42, 2.48 (each 3H, *s*, 5 × OAc), 3.75 (3H, *s*, ArOMe), 6.62 (1H, *s*, H-3, I), 6.66 (2H, H-8, I; H-3, II), 6.88 (2H, *d*, *J* = 9 Hz, H-3′, H-5′, II), 7.42 (2H, *d*, *J* = 9 Hz, H-2′, H-6′, II). Methylation of E with CH_2N_2 in dioxan followed by prep. TLC gave a product, mp 280–282°; MS, 594.1516, $C_{34}H_{26}O_{10}$. ^1H NMR: δ 3.76, 3.83, 3.80, 3.86 (each 3H, *s*, 4 × ArOMe), 6.35 (1H, *d*, *J* = 2 Hz, H-6, I), 6.45 (1H, *d*, *J* = 2 Hz, H-8, I), 6.57 (1H, *s*, H-6, II), 6.60 (1H, *s*, H-3, I), 6.63 (1H, *s*, H-3, II), 6.83 (2H, *d*, *J* = 8 Hz, H-3′, H-5′, II), 7.17 (1H, *d*, *J* = 8 Hz, H-5′, I), 7.50 (2H, *d*, *J* = 8 Hz, H-2′, H-6′, II), 7.90 (1H, *d*, *J* = 2 Hz, H-2′, I), 7.97 (1H, *d*, *J* = 8 Hz, H-6′, I), 12.73 (1H, *s*, OH), 13.07 (1H, *s*, OH). UV λ_{max} nm: 270, 330; IR ν_{max} cm^{-1}: 3500 (chelated OH), 1660 (CO), 1610, 1590 (Ar).

Compound F—urbalactone (**2**). Recrystallized from MeOH gave needles, mp 270–272° (dec.), $[\alpha]_D^{25}$ +90° (Py): IR ν_{max}^{nujol} cm^{-1}: 3350 (OH), 1768 (γ-lactone), 1743 (δ-lactone), 1685, 1620 (conj. CO); UV λ_{max}^{EtOH} nm: 297 (ε = 5308); ^1H NMR (DMSO d_6): δ 1.14 (3H, *d*, *J* = 6.8 Hz, C-16 Me), 1.21 (3H, *d*, *J* = 6.8 Hz, C-17 Me), 1.28 (3H, *s*, C-18 Me), 1.30 (3H, *s*, C-20 Me), 5.00 (1H, *dd*, H-6), 5.24 (1H, *d*, *J* = 8 Hz, H-7), 6.30 (1H, *s*, H-11); MS, 364.1543, $C_{19}H_{24}O_7$. Acetylation (Py–Ac_2O) gave a product which on crystallization from EtOH, mp 199–200°; UV λ_{max}^{EtOH} nm: 297; MS, 490.1814, $C_{25}H_{30}O_{10}$ ^1H NMR: δ 1.22 (3H, *d*, *J* = 6.5 Hz, C-16 Me), 1.25 (3H, *d*, *J* = 6.5 Hz, C-17 Me), 1.43 (3H, *s*, C-18 Me), 1.48 (3H, *s*, C-20 Me), 2.00 (3H, OAc), 2.14 (6H, 2OAc), 4.87–5.50 (3H, H-1, H-3, H-6), 5.8 (1H, *s*, H-11), 6.29 (1H, *d*, *J* = 9 Hz, H-7). Jones oxidation on 3 mg in dry Me_2CO gave a product. UV λ_{max}^{EtOH} nm: 300, 275 shifting to 375 and 312 in base.

Compound G (**6**). Crystallization from MeOH yielded needles, mp 265–268° (dec); IR ν_{max}^{nujol} cm^{-1}: 3410 (OH), 1645 (CO); UV λ_{max}^{EtOH} nm: 242; ^1H NMR ($CDCl_3$, DMSO): δ 0.81 (3H, *s*, tert-Me), 0.86 (3H, *d*, *J* = 6 Hz, sec. Me), 0.91 (3H, *d*, *J* = 6 Hz, sec-Me), 1.10 (3H, *s*, tert-Me), 1.26 (3H, *s*, tert-Me), 2.90–3.26 (2H, *m*, H-9 and H-23 or H-24), 3.48 (1H, *s*, tert. OH), 3.54–3.90 (2H, *m*, H-2, H-3), 4.12–4.34 (3H, 3 × sec. –OH), 4.52 (1H, *s*, tert.OH), 5.7 (1H, *d*, *J* = 2.5 Hz, H-7). (Found: C, 66.98; H, 9.37, O, 19.92, $C_{27}H_{44}O_6 \cdot H_2O$ requires C, 67.20; H, 9.13; O, 19.92%).

Compound H. EtOH recrystallized gave needles, mp 277–279° (sub); UV λ_{max}^{EtOH} nm: 220; IR ν_{max}^{nujol} cm^{-1}: 1780 (γ-lactone), 1725, 1650 (α,β-unsaturated δ-lactone). ^1H NMR: δ 1.08 (3H, *d*, *J* = 6.0 Hz, C-16 Me), 1.11 (3H, *d*, *J* = 6.0 Hz, C-17 Me), 1.29 (3H, *s*, C-20 Me), 1.38 (3H, *s*, C-18 Me), 1.84 (1H, *d*, *J* = 4.5 Hz, H-5), 3.97 (1H, *d*, *J* = 2 Hz, H-7), 4.43 (1H, *d*, *J* = 4 Hz, H-14), 4.94 (1H, *dd*, *J* = 4.5, 2 Hz, H-6), 6.0 (1H, H-11); MS *m/e* M^+ 330 (low resolution).

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