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PHENOLIC DITERPENOIDS OF SOME PODOCARPS*

RICHARD C CAMBIE, ROBERT E. COX†, KEVIN D. CROFT† and DAVID SIDWELL

Department of Chemistry, University of Auckland, Private Bag, Auckland, New Zealand; † School of Natural Resources, University of the South Pacific, P.O Box 1168, Suva, Fiji

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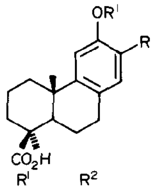
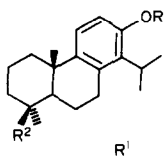
Key Word Index—*Dacrycarpus imbricatus*, *Dacrydium* spp., *Decussorcarpus vitiensis*; *Podocarpus* spp; Podocarpaceae, phenolic diterpenoids, chemotaxonomy.

Abstract—The woods of 10 species of the Podocarpaceae have variously yielded 12 phenolic diterpenoids. These include the Fijian members *Dacrydium nidulum, Decussocarpus vitiensis, Podocarpus neriifolius* and *Dacrycarpus imbricatus*, as well as *Podocarpus gracilior*, *P polystachus*, *P. sylvestris*, *P. gnidioides*, *Dacrydium comosum* and *D. falciforme*.

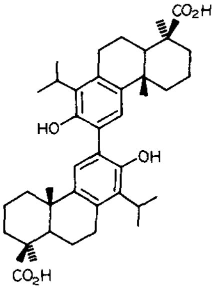
Four members of the Podocarpaceae, viz. *Dacrydium nidulum, Decussocarpus vitiensis, Podocarpus neriifolius* and *Dacrycarpus imbricatus*, constitute a valuable but diminishing timber resource in Fiji. Woods from these species have different uses which partially reflect their differing durabilities. The presence of podocarpic acid [12-hydroxypodocarpa-8,11,13-trien-19-oic acid (**1a**)] in high concentration in the heartshakes of the wood of *Dacrydium nidulum* has been invoked to explain the high resistance of the timber to fungal attack [1, 2]. In order to assess the importance of the presence of phenolic diterpenoids on the durability of such timbers we have examined extracts of the woods for such compounds.



	R^1	R^2
1a	H	H
1b	H	$CHMe_2$
1c	H	$CH(CH_2OH)_2$
1d	Ac	$CH(CH_2OH)_2$
1e	Ac	$CH(CH_2OAc)_2$



	R^1	R^2
2a	H	Me
2b	Ac	Me
2c	H	CH_2OH
2d	H	CH=O
2e	H	CO_2H



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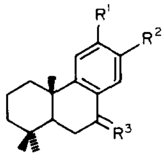

	R^1	R^2	R^3
4a	OH	$CHMe_2$	O
4b	$CHMe_2$	OH	H_2
4c	$CHMe_2$	OAc	H_2

In addition to the Fijian species, extracts of the woods of *Podocarpus gracilior* (natural habitat: Central and East Africa), *P. polystachus* (Malaysia, Phillippines), *P. sylvestris* (New Caledonia), *P. gnidioides* (New Caledonia), *Dacrydium comosum* (Malaysia) and *D falciforme* (Borneo, Phillippines) have also been examined for the presence of phenolic diterpenoids. Apart from the isolation of podocarpic acid from the heartshakes of *Dacrydium nidulum* [1, 2] previous work on these species has been confined to the leaves [3, 4] and bark [5, 6] of *Podocarpus neriifolius*, the leaves [7] and wood [8] of *P. gracilior*, and the leaves [9] and bark [10] of *P. polystachus*. Results from the current work are presented in Table 1. In general, compounds were isolated by CC and/or prep. TLC and, where possible, were identified by comparison (UV, IR, mmp, TLC) with authentic samples, or by conversion to a known acetate. Of the compounds listed, podocarpic acid (**1a**), totarol (**2a**) and its derivatives **2**(c–e) are widely distributed in members of the Podocarpaceae [11]. Lambertic acid (**1b**) has previously been isolated from *Podocarpus lambertii* [12] while sempervirol (**4b**) has hitherto only been obtained from members of the Cupressaceae [13]. Pododacric acid (**1c**) has been found in *Podocarpus dacrydioides* [14] and *P. totara* [15] but totaryl acetate, **2b**, and the monoacetate, **1d**, of pododacric acid have not previously been obtained as natural products. Identification of the latter compound followed from the similarity of its ^1H NMR [16] and ^{13}C NMR spectra with those of pododacric acid and was confirmed by conversion to the triacetate, **1e**. ^{13}C NMR assignments for acetate **1d** and some other compounds were greatly facilitated by application of the 90-t-*iso*-t multiplicity recognition sequence developed by Le Cocq and Lallemand [17] Although implementation of sequences of this type normally requires the use of a programmable pulser unit, we have achieved the required timings on a Jeol FX60 instrument, equipped with a non-programmable PG-10 pulser unit, by using the standard inversion recovery sequence 90-t-180, and introducing the

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*Part LXV in the series "Chemistry of the Podocarpaceae" For Part LXIV see Cambie, R C, Hayward, R. C., Palmer, B D, Robertson, J. D, Rutledge, P S. and Woodgate, P D (1982) *Aust J. Chem* **35**, 1699

Table 1. Wood extractives of podocarps

Compound	*Dacrydium nidulum*	*Decussocarpus vitiensis*	*Podocarpus neriifolius*	*Dacrycarpus imbricatus*	*Podocarpus gracilior*	*Podocarpus polystachus*	*Podocarpus sylvestris*	*Podocarpus gnidiodes*	*Dacrydium comosum*	*Dacrydium falciforme*
Podocarpic acid (**1a**)	+	+	—	—	—	—	—	—	—	+
Lambertic acid (**1b**)	—	—	—	+	—	—	—	—	—	—
Totarol (**2a**)	—	+	+	+	+	+	+	+	+	—
Totaryl acetate (**2b**)	—	—	—	—	—	—	+	+	—	—
19-Hydroxytotarol (**2c**)	—	+	—	—	—	—	+	+	—	—
19-Oxototarol (**2d**)	—	—	—	—	—	+	+	+	—	—
4*β*-Carboxy-19-nortotarol (**2e**)	—	+	+	—	+	+	—	—	—	—
Macrophyllic acid (**3**)	—	—	+	—	—	+	—	—	—	—
Pododacric acid (**1c**)	+	—	+	—	—	—	—	—	+	—
Pododacric acid monoacetate (**1d**)	—	—	—	—	—	—	—	—	+	—
Sugiol (**4a**)	—	—	—	—	+	—	—	—	—	+
Sempervirol (**4b**)	—	—	+	—	—	—	—	—	—	—

additional delay between the final 180° pulse and FID acquisition by extending the delay (or deadtime) period in the acquisition routine.

Of the four Fijian woods, *Dacrydium nidulum* is uniquely rich in the fungistatic podocarpic acid and, in this respect, shows a resemblance to *D cupressinum* [18]. At least some degree of fungistatic effect would be expected from related diterpenoids; Table 2 summarizes the approximate content of phenolic diterpenoids in the Fijian woods sampled and lists their durability to fungal attack when used as timbers. Undoubtedly, factors other than the occurrence of phenolic diterpenoids are involved in such a complex phenomenon as fungal attack on timber. Nevertheless, the data in Table 2 suggest a wider applicability among members of the Podocarpaceae that a high phenolic diterpenoid content implies durability against fungal attack.

EXPERIMENTAL

Mps are uncorr UV EtOH soln IR: $CHCl_3$ or CCl_4 ^1H NMR and ^{13}C NMR $CDCl_3$ with TMS as int reference (phenolic peaks exchanged with D_2O) MS were determined at 70 or 12 eV

Extraction and work-up procedures Wood samples were dried, finely ground, and extracted (Soxhlet) for 24 hr with EtOAc (Fijian species) or with hexane and then Et_2O Except in the cases of a significant hexane extract, the hexane and Et_2O extracts were combined. Preliminary fractionations were made by dry CC on Si gel or by flash chromatography on Al_2O_3 Prep TLC separations were carried out on Si gel G The phenolic compounds were identified as dark blue bands on a yellow background by spraying plates with 0 1 % dichlorofluorescein in MeOH and viewing under UV light Concentrates from the extracts were normally dissolved in Et_2O and fractionated with 10 % NaOH soln to yield a 'neutral' fraction containing non-carboxylic acids and an 'acidic' fraction containing carboxylic acids

Dacrydium nidulum *de Laub var* nidulum (*Fijian name yaka*) The wood (620 g) afforded an acidic fraction (40 g) and a neutral fraction (3 5 g) which contained only traces of phenolic diterpenoids A portion (1 5 g) of the acidic fraction was fractionated on a Si gel column using Et_2O–C_6H_6 (4.1) as eluant A fraction, R_f 0 5–0 9, gave podocarpic acid (**1a**) (0 60 g), mp and mmp 193–194° (UV and IR identical with those of an authentic sample), methyl ester, mp and mmp 211° A fraction, R_f 0 3–0 5, gave impure pododacric acid (**1c**) as a gum Acetylation and prep TLC of the product gave a purer sample of pododacric acid triacetate (**1e**) as a gum (20 mg) (correct UV, IR, and ^1H NMR [15]) ^{13}C NMR δ 19 7 (*t*, C-2, C-6), 20 9 [*q*, $(OCO\underline{Me})_3$], 23 1 (*q*, C-20), 28 6 (*q*, C-18), 31 4 (*t*, C-7), 36 5 (*d*, C-15), 37 2 (*t*, C-3), 38 6 (*s*, C-10), 39 0 (*t*, C-1), 43 8 (*s*, C-4), 52 3 (*d*, C-5), 64 4 (*t*, C-16. C-17), 119 7 (*d*, C-11), 127 1 (*s*, C-12), 128 3 (*d*, C-14), 133 3 (*s*, C-8), 147 0 (*s*, C-9), 148 4 (*s*, C-12), 169 7 (*s*, $ArO\underline{C}OMe$), 170 8 [*s*, $(O\underline{C}OMe)_2$], 183 6 (*s*, C-19)

Decussocarpus vitiensis (*Seem*) *de Laub* (Podocarpus vitiensis *Seem*) (*Fijian name dakua salusalu*) The wood (800 g) afforded a neutral fraction (6 g) and an acidic fraction (2 8 g) A portion (1 8 g) of the neutral fraction was fractionated on a Si gel column using C_6H_6 as eluant A fraction, R_f 0.6–0 9, was purified by prep TLC to give totarol (**2a**) (60 mg), mp and mmp 127–128° (UV, IR and ^1H NMR identical with those of an authentic sample) A fraction, R_f 0–0 2, gave 19-hydroxytotarol (**2c**) (10 mg), mp and mmp 210–214° (UV, IR and ^1H NMR identical with those of an authentic sample) A portion (2.0 g) of the acidic fraction was chromatographed on Si gel using Et_2O–C_6H_6 (4 1) as eluant Prep TLC of a fraction, R_f 0.5–0 9 gave podocarpic acid (80 mg), mp and mmp 189–192° (correct UV and IR) and 4β-carboxy-19-nortotarol (**2e**) (50 mg) as a gum (UV, IR and ^1H NMR identical with those of an authentic sample); acetate, mp and mmp 235–237°. Methylation of **2e** and reduction of the product with $LiAlH_4$ gave 19-hydroxytotarol (correct IR and TLC)

Podocarpus neriifolius *D Don ex Lamb var* neriifolius *or var* degeneri *N E Grey* (*Fijian name kuasi*) The wood (520 g) gave a neutral fraction (1 6 g) and an acidic fraction (3 4 g) A portion (1 0 g) of the neutral fraction was separated by prep TLC (C_6H_6) into totarol (**2a**) (5 mg) (correct UV, IR and R_f) and a gum which was acetylated and purified further by prep TLC to afford semperviryl acetate (**2c**) (10 mg), mp 90–92°, $[\alpha]_D^{22}$ + 50° (EtOH) (lit [13] 92–93°, $[\alpha]_D$ + 51°) (correct UV, IR and ^1H NMR [19]), ^{13}C NMR δ 18 9 (*t*, C-6), 19 3 (*t*, C-2), 21 0 (*q*, $CO\underline{Me}$), 21 6 (*q*, C-19), 23 0, 23 1 (2 × *q*, C-16, C-17), 25 0 (*q*, C-20), 27 6 (*d*, C-15), 29 9 (*t*, C-7), 33 3 (*q*, C-18), 33 4 (*s*, C-4), 37 8 (*s*, C-10), 38 9 (*t*, C-1), 41 6 (*t*, C-3), 50 2 (*d*, C-5), 121 7 (*d*, C-14), 122 5 (*d*, C-11), 133 9 (*s*, C-12), 136 7 (*s*, C-9), 145 4 (*s*, C-8), 147 9 (*s*, C-13), 169.8 (*s*, $\underline{C}OMe$) MS *m/z* (rel int) 328 $[M]^+$ (25), 313 $[M-Me]^+$ (6), 286 $[M-C_2H_2O]^+$ (65), 271 (100), 243 (1), 215 (2), 201 (7), 189 (5), 175 (8)

A portion (0.60 g) of the acidic fraction was separated by prep. TLC (Et_2O–C_6H_6, 4 1) into (i) impure 4β-carboxy-19-nortotarol (**2e**), which was purified as the acetate (40 mg) (correct UV, IR and ^1H NMR), (ii) macrophyllic acid (**3**) (10 mg), mp and mmp 237–239° (decomp) (UV and IR identical with those of an authentic sample), and (iii) pododacric acid (**1c**), purified as the triacetate, **1e** (10 mg) (correct UV, IR and ^1H NMR)

Dacrycarpus imbricatus (*Bl de Laub var* patulus *de Laub*) (*Fijian name amunu*) The wood (650 g) gave a neutral fraction (2 4 g) and an acidic fraction (1 1 g) A portion (1 5 g) of the neutral fraction was refractionated on a Si gel column using C_6H_6 as eluant A fraction, R_f 0 6–0 9, was purified further by prep. TLC to yield totarol (**2a**) (2 mg) as a gum (correct UV, IR and R_f) A portion (1 0 g) of the acidic fraction was fractionated further on a Si gel column using Et_2O–C_6H_6 (4:1) as eluant A

Table 2 Durability of Fijian podocarps

Species	Phenolic diterpenes (% of dry wt of wood)	Durability to fungal attack†
Dacrydium nidulum	3	durable
*Podocarpus neriifolius**	0 07	durable
Decussocarpus vitiensis	0.05	moderately durable
Dacrycarpus imbricatus	0 001	not durable

*Slightly anomalous data could be attributed to the fact that the extraction was carried out on a young tree which may not have developed a full content of phenolic diterpenoids

†A Alston, Department of Forestry, Suva, personal communication

fraction, R_f 0 5–0 9, yielded lambertic acid (**1b**) (5 mg), mp 220–225 (unrecrystallized) (lit [20] 246–248 , [12] 252–254°), (correct IR and ^{1}H NMR [20]) ^{13}C NMR δ 19 6 (*t*, C-2), 21 0 (*t*, C-6), 22 4, 22 5 (2 × *q*, C-16, C-17), 23 0 (*s*, C-20), 26 1 (*d*, C-15), 28 3 (*q*,C-18), 30 7 (*t* C-7), 37 1 (*s*,C-10), 37 6 (*t*, C-1, C-3), 42 9 (*s*,C-4), 51 9 (*d*, C-5), 111 1 (*d*, C-11), 124 8 (*s*, C-8), 125 8 (*d*, C-14), 131 5 (*s*, C-13), 145 6 (*s*, C-9), 152 0 (*s*, C-12), 178 3 (*s* C-19) MS *m/z* (rel int) 316 $[M]^+$ (100), 301 $[M - Me]^+$ (98), 298 (9), 255 (94), 241 (18), 199 (18), 157 (29), 147 (30)

Podocarpus gracilior *Pilger* The wood (165 g) gave an Et_2O extract (3 3 g) which was separated into a neutral fraction (1 4 g) and an acidic fraction (1 1 g) Prep TLC of a portion (0 64 g) of the neutral fraction gave totarol (**2a**) (40 mg), mp and mmp 126–128° (correct UV and IR), and sugiol (**4a**) as a gum (2 mg) which was purified as the acetate, mp and mmp 155–158 (UV and IR identical with those of an authentic sample) Prep TLC of a portion (0 5 g) of the acidic fraction gave 4β-carboxy-19-nortotarol (**2e**) as a gum (70 mg) which was purified as the acetate, mp and mmp 239–245° (correct UV and IR)

Podocarpus polystachus *R Br* The wood (253 g) gave an Et_2O extract (4 1 g) which was separated into a neutral fraction (1 0 g) and an acidic fraction (2 6 g) Prep TLC of a portion (0 6 g) of the neutral fraction gave totarol (**2a**) as a gum (5 mg) (correct UV and IR) and 19-oxototarol (**2d**) (10 mg), mp and mmp 176 179° (UV and IR identical with those of an authentic sample) Prep TLC of a portion (9 65 g) of the acidic fraction gave macrophyllic acid (**3**) (2 mg), mp and mmp 230–240 (correct UV and IR), and 4β-carboxy-19-nortotarol (**2e**) as a gum (10 mg), which was purified as the acetate, mp and mmp 230 235 (correct UV and IR)

Podocarpus sylvestris *Buchholz* The wood (450 g) gave an Et_2O extract (0 28 g) which was chromatographed on alumina Elution with C_6H_6 Et_2O mixtures gave, successively, totaryl acetate (**2b**), totarol (**2a**) and 19-oxototarol (**2d**), each (*ca* 5 mg) identified by UV, IR and TLC comparison with authentic samples Elution with Et_2O gave 19-hydroxytotarol (**2c**), needles (from MeOH) (30 mg), mp and mmp 229 230 (correct UV, IR and ^{1}H NMR) ^{13}C NMR δ 15 3 (C-6), 19 1 (C-2), 20 3 (C-16, C-17), 25 2 (C-20), 27 2 (C-15), 28 1 (C-18), 29 0 (C-7), 37 5 (C-3), 38 8 (C-1) 49 0 (C-5), 78 8 (C-19), 114 4 (C-12), 122 9 (C-12), 131 0 (C-9), 133 7 (C-8), 142 2 (C-14) 152 1 (C-13)

Podocarpus gnidioides *Carr* The wood (64 g) gave an Et_2O extract (0 13 g) which was chromatographed on alumina Elution with C_6H_6–Et_2O mixtures gave, successively, totaryl acetate (**2b**), totarol (**3a**), 19-hydroxytotarol (**2c**) and 19-oxototarol (**2d**), each (*ca* 5 mg) identified by UV, IR and TLC comparison with authentic samples

Dacrydium comosum *Corner* The wood (783 g) gave a hexane extract (0 5 g) and an Et_2O extract (1 0 g) Prep TLC of a portion (0 36 g) of the hexane extract gave totarol (**2a**) as a gum (5 mg) (correct UV, IR and ^{1}H NMR) Prep TLC of a portion (0 50 g) of the Et_2O extract gave (i) pododacric acid (**1c**) as a gum (20 mg) which was purified as the triacetate, **1c** (correct UV IR and ^{1}H NMR), and (ii) the C-12 monoacetate, **1d**, of pododacric acid as a gum (30 mg), UV λ_{max}^{EtOH} nm 228, 284, IR ν_{max} cm^{-1} 3690, 3380 *br* (OH), 1720 (aryl OAc), 1690 (CO_2H), 1180 (OAc), 1120 (OH), ^{13}C NMR [$(CD_3)_2CO$] δ 20 8 (C-2), 22 1 (C-6), 23 6 (C-20), 29 0 (C-15, C-18), 31 9 (C-7), 38 4 (C-10), 39 0 (C-1), 40 2 (C-3), 44 2 (C-4), 46 4 (COMe), 53 5 (C-5), 64 1 (C-16 C-17), 113 5 (C-11), 126 0 (C-13), 126 7 (C-8), 130 4 (C-14), 148 2 (C-9), 154 3 (C-12), 178 9 (O$\underline{C}$OMe), 206 1 (C-19), MS *m/z* (rel int) 390 $[M]^+$ (< 1), 348 $[M - C_2H_2O]^+$ (38), 330 (55), 315 (22) 299 (100), 285 (16), 271 (31), 269 (29) 253 (13), 239 (20), 225 (21), 189 (24) 149 (98), 131 (67) Acetylation gave pododacric acid triacetate mp and mmp 158 161 (correct IR and ^{1}H NMR) MS *m/z* (rel int) 474 $[M]^+$ (6), 432 $[M - C_2H_2O]^+$ (43) 414 (2), 386 (1), 372 (66), 330 (32), 313 (68) 312 (100) 297 (60), 279 (9), 251 (58), 171 (19), 145 (28), 131 (45)

Dacrydium falciforme *Pilger* The wood (766 g) gave an Et_2O extract (1 1 g) which was chromatographed on Al_2O_3 Elution with hexane Et_2O (1 1) gave sugiol (**4a**), while elution with Et_2O–MeOH (19 1) gave podocarpic acid (**1a**), each (*ca* 5 mg) identified by UV, IR and TLC comparison with authentic samples

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