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2,5-DIHYDROXY-1,6-DIMETHOXYXANTHONE AND BIFLAVONOIDS OF *GARCINIA THWAITESII*

A A Leslie Gunatilaka, H T Badra Sriyani, Subramaniam Sotheeswaran† and Eric S Waight*

Department of Chemistry, University of Peradeniya, Peradeniya, Sri Lanka, *Department of Chemistry, Imperial College of Science and Technology, London, SW7 2AY, U K

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Key Word Index—*Garcinia thwaitesii*, Guttiferae, β-amyrin, tirucallol, 2,5-dihydroxy-1,6-dimethoxyxanthone, biflavonoids, chemotaxonomy

Abstract—The petrol and methanol extracts of the bark and timber of *Garcinia thwaitesii* have been investigated In addition to β-amyrin and tirucallol, four biflavonoids and a new xanthone, 2,5-dihydroxy-1,6-dimethoxyxanthone have been isolated and characterized

INTRODUCTION

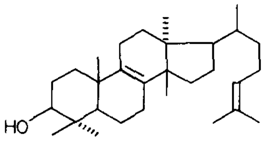
Ten *Garcinia* species have been recorded in Sri Lanka, of which five are endemic to the island Though xanthones [1] and biflavonoids [2] have been isolated from *Garcinia* species, no chemical work has hitherto been reported on *G thwaitesii* This paper reports the chemical investigation of the bark and timber of this endemic species

RESULTS AND DISCUSSION

The petrol and methanol extracts of the bark and timber of *G thwaitesii* were found to be identical on TLC examination The compounds isolated along with their percentage yields are given in Table 1 The petrol extract on CC and purification by prep TLC gave three compounds Two responded to the Liebermann–Burchard test for triterpenoids whilst the third gave a positive reaction for steroids The latter was identified as sitosterol Of the two triterpenoids, one was identified as β-amyrin by comparison with an authentic sample whilst the other was characterized as tirucallol (**1**) from the following data A molecular formula of $C_{30}H_{50}O$ (M^+ 426 3858) was assigned to the compound on the basis of high resolution mass spectral data It was found to be a dammarane type triterpene alcohol from its ^1H NMR spectrum and that of its acetate The proton on the carbon atom bearing the acetate group appeared as a triplet at δ 4 50 The mp (134°) and specific rotation (+5°) data in conjunction with the above spectral data suggested that the triterpene alcohol is tirucallol (**1**), although a direct comparison was not possible with an authentic sample

Table 1 Compounds isolated from *Garcinia thwaitesii* together with their yields

Compound	% yield Timber	% yield Bark
Tirucallol	0 002	0 001
β-Amyrin	0 003	0 002
Sitosterol	0 0005	0 0009
2,5-Dihydroxy-1,6-dimethoxyxanthone	0 0005	0 0005
Biflavanoids	See Table 2	



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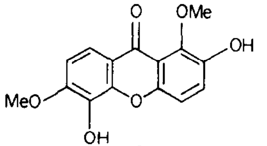

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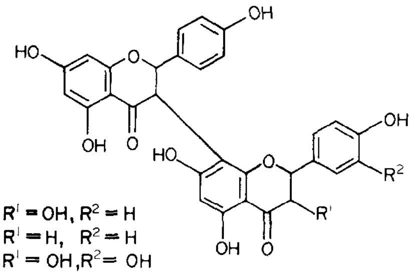

3 R¹ = OH, R² = H
4 R¹ = H, R² = H
5 R¹ = OH, R² = OH
6 R¹ = H, R² = OH

The chloroform-soluble fraction of the methanol extract of the bark yielded a yellow pigment, mp 207–208°, $C_{15}H_{12}O_6$ (M^+ 288 0629) The UV, IR and ^1H NMR data indicated it to be a xanthone The ^1H NMR spectrum in acetone-d_6 showed two doublets at δ 7 90 and 7 00 (J = 9 Hz) for two *ortho*-coupled protons The presence of only one low field aromatic proton (δ 7 90), therefore, indicates that either C-1 or C-8 of the xanthone moiety is free This is confirmed by the absence of a chelated hydroxyl group in the xanthone as shown by its ^1H NMR spectrum The ^1H NMR spectrum of the xanthone also had a 2H-singlet at δ 7 40 which became a double-doublet centred at δ 7 40 (J = 9 Hz) when the ^1H NMR spectrum of its diacetate was recorded in deuterochloroform The

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†To whom correspondence should be addressed

Table 2 Biflavanoids from *Garcinia* species

Species	Plant part	% yields				Ref
		3	**4**	**5**	**6**	
G buchananii	Heart wood	+	+	+	+	[2, 3]
G eugeniifolia	Heart wood	+	+	+	+	[2, 3]
G kola	Nuts	+	+	+	+	[5]
G linii	Bark	+	−	+	+	[6]
G multiflora	Bark	+	+	−	+	[7]
G spicata	Bark	+	−	−	+	[6, 8]
G terpnophylla	Bark, timber	+	+	+	−	[9]
G thwaitesii	Bark, Timber	0 015 0 066	0 025 0 051	0 063 0 066	0 062 0 065	This work
G volkensii	Heart wood	+	−	−	+	[10]
G xanthochymus	Leaves	+	−	+	+	[6, 8]

latter spectrum also showed the presence of a six-proton singlet at δ 2 40 (2 × OAc) and two methoxyl signals at δ 4 0 and 4 10 suggesting the xanthone to be tetraoxygenated The presence of two pairs of *ortho*-coupled protons in two different aromatic rings is evident from the above ^{1}H NMR data The AB doublets at δ 7 50 (1H, *d*, *J* = 9 Hz) and 7 30 (1H, *d*, *J* = 9 Hz) in the ^{1}H NMR spectrum of the diacetate have been assigned to the C-3 and C-4 protons by comparing the chemical shifts with those for the C-3 and C-4 protons of 2,8-diacetoxy-1-methoxyxanthone [3, 4] The xanthone gave a positive Gibbs test All these data confirmed the structure of the pigment as 2,5-dihydroxy-1,6-dimethoxyxanthone (**2**) Although a number of natural tetraoxygenated xanthones are known, this constitutes the first report of the occurrence of a xanthone with a 1,2,5,6-oxygenation pattern

The above chloroform extract on CC separation and purification by prep TLC afforded four biflavanoids which have been identified from their spectroscopic data and comparison with authentic samples as II-3,I-4′,II-4′,I-5,II-5,I-7,II-7-heptahydroxy(I-3,II-8)biflavanone (**3**), I-4′,II-4′,I-5,II-5,I-7,II-7-hexahydroxy(I-3,II-8) biflavanone (**4**), II-3,II-3′,I-4′,II-4′,I-5,II-5,I-7,II-7-octahydroxy(I-3,II-8)biflavanone (**5**) and I-4′,II-3′,II-4′,I-5,II-5,I-7,II-7-heptahydroxy(I-3,II-8)biflavanone (**6**)

All these biflavanoids have been previously isolated from *Garcinia* species The distribution of these biflavanoids are given in Table 2 This is the first report of the occurrence of all four biflavanoids in both the timber and bark of a *Garcinia* species

EXPERIMENTAL

The stem bark and the timber of *G thwaitesii* Pierre were collected from Morapitiya in the south-west of Sri Lanka They were separately chipped, dried and milled The powdered materials were extracted successively with hot petrol and MeOH The petrol extractives when chromatographed over Si gel gave tirucallol (**1**) (mp 134–135°, $[\alpha]_D + 4 50°$, lit [11], mp 135–136°, $[\alpha]_D + 5 0°$, β-amyrin (mp 198–199°, $[\alpha]_D + 88 5°$, lit [11], mp 199°, $[\alpha]_D + 88°$) and sitosterol (mp 136–137°, $[\alpha]_D - 36 0°$, lit [11], mp 139°, $[\alpha]_D - 36 0°$)

2,5-Dihydroxy-1,6-*dimethoxyxanthone* The MeOH extract of both the timber and bark when extracted with hot $CHCl_3$ on evaporation of the solvent gave a yellow pigment which when recrystallized from $CHCl_3$–petrol gave 2,5-dihydroxy-1,6-dimethoxyxanthone (**2**), mp 207–208° MS M^+ 288 0629, calc for $C_{15}H_{12}O_6$, 288 0633, *m/z* 288 (87 %), 270 (100), 259 (14), 258 (23), 245 (23), 240 (14), 230 (23), 227 (20), 215 (14), 199 (14), ^{1}H NMR (CD_3COCD_3, 60 MHz) δ 7 9 (1H, *d*, *J* = 9 Hz), 7 4 (2H, *s*), 7 0 (1H, *d*, *J* = 9 Hz), 4 05 (3H, *s*, OMe), 3 9 (3H, *s*, OMe) UV λ_{max}^{EtOH} nm (log ε) 355 (2 903), 315 (2 95), 250 (3 2), $\lambda_{max}^{EtOH-NaOAc-H_3BO_3}$ no shift, $\lambda_{max}^{EtOH-AlCl_3}$ no shift, IR ν_{max}^{KBr} cm^{-1} 3390, 2900, 1650, 1600, 1460, 1420, 1350, 1300, 1260, 1200, 1170, 1050, 1030, 940, 830, 810, 790

2,5-Diacetoxy-1,6-*dimethoxyxanthone* Compound **2** (5 mg) was acetylated with Ac_2O (0 1 ml) and pyridine (1 ml) at 100° overnight The usual work-up and crystallization from $CHCl_3$–petrol gave yellow crystals (4 mg) of 2,5-diacetoxy-1,6-dimethoxyxanthone, mp 178–179°, ^{1}H NMR ($CDCl_3$, 60 MHz) δ 8 05 (1H, *d*, *J* = 9 Hz), 7 5 (1H, *d*, *J* = 9 Hz), 7 3 (1H, *d*, *J* = 9 Hz), 7 05 (1H, *d*, *J* = 9 Hz), 4 1(3H, *s*, OMe), 4 0 (3H, *s*, OMe) and 2 4 (6H, *s*, –OCOMe)

I-4′,II-4′,I-5,II-5,I-7,II-7-*Hexahydroxy*(I-3,II-8)*biflavanone* (**4**) The hot $CHCl_3$ extract of the MeOH extract on cooling deposited a solid which when chromatographed over Si gel and eluted with EtOAc–CH_2Cl_2 (1 1) gave first a two-component mixture which was further purified by prep TLC The less polar component of the mixture was **4** which was obtained as an amorphous solid, mp 220°, $[\alpha]_D - 9 0°$ (lit [2] mp 200°) MS M^+ 542 1213, calc for $C_{30}H_{22}O_{10}$, 542 1203, *m/z* 542 (10 %), 416 (80), 296 (64), 126 (100), 127 (60) ^{1}H NMR (CD_3COCD_3, 60 MHz) δ12 3 (1H, chelated OH), 12 1 (1H, chelated OH), 7 2–7 5 (4H, aromatic), 6 7–7 1 (4H, aromatic), 6 0 (3H, aromatic), 5 68 (1H, *br d*), 5 45 (1H, *d*, *J* = 12 Hz), 4 8 (1H, *d*, *J* = 12 Hz), 2 78 (2H, *m*) UV λ_{max}^{EtOH} nm (log ε) 293 (4 4), 330 (3 5), IR ν_{max} cm^{-1} 3300, 1655 It was identical with an authentic sample (mmp, co-TLC)

II-3, I-4′, II-4′, I-5, II-5, I-7, II-7-*Heptahydroxy*-(I-3, II-8)-*biflavanone* (**3**) The more polar component of the above mixture was **3** which was obtained as an amorphous solid after prep TLC separation, mp 205–257° (lit [2] 200° dec) MS M^+ 558 1151, calc for $C_{30}H_{22}O_{11}$, 558 1162, *m/z* 558 (25 %), 540 (15), 444 (70), 432 (80), 416 (80), 296 (75), 270 (45), 126 (100), 107 (65) ^{1}H NMR (CD_3COCD_3 60 MHz) δ12 3 (1H, chelated OH), 12 1 (1H, chelated OH), 7 2–7 4 (4H, aromatic), 6 7–6 9 (4H, aromatic), 6 05 (3H, aromatic), 5 76 (1H, *d*, *J* = 12 Hz), 5 5 (1H, *d*, *J* = 12 Hz), 4 8 (1H, *d*, *J* = 12 Hz), 3 6 (1H) UV λ_{max}^{EtOH} nm (log ε) 293 (4 5), 329 (3 6), IR ν_{max} cm^{-1} 3350, 1650

II-3, II-3′, I-4′, II-4′, I-5, II-5, I-7, II-7-*Octahydroxy*-(I-3, II-8)-*biflavanone* (**5**) Further elution of the column with EtOAc–CH_2Cl_2 (1 1) gave a light yellow solid which was a mixture of two biflavanoids The major component was separated by prep TLC to give pure **5**, mp 225–227°, (lit [2] 220° dec) ^{1}H NMR (CD_3COCD_3, 60 MHz) δ12 3 (1H, *s*, OH), 13 1(1H, *s*, OH), 7 1–7 4 (2H, aromatic), 6 2–7 0 (5H, aromatic), 6 08 (3H, aromatic), 5 90 (1H, *d*, *J* = 12 Hz), 5 0 (1H, *d*, *J* = 12 Hz)

I-4′,II-3′,II-4′,I-5, II-5,I-7,II-7-*Heptahydroxy*(I-3,II-8)-*biflavanone* (**6**) The minor component of the above mixture was purified to give **6**, mp 216–218° (lit [2] 210° dec), $[\alpha]_D + 28$ 2° in Me_2CO ^{1}H NMR (CD_3COCD_3, 60 MHz) δ 12 3 (1H, *s*, OH), 13 0 (1H, *br s*, OH), 7 15–7 45 (2H, aromatic), 6 2–7 0 (5H, aromatic), 6 1 (3H, aromatic), 5 90 (1H, *d*, *J* = 12 Hz), 5 0 (1H, *d*, *J* = 12 Hz)

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