111. Novel Prenylated Xanthones from *Garcinia gerrardii* HARVEY

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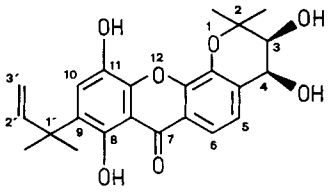
Three novel prenylated xanthones, **1**–**3**, have been isolated from the root bark of *Garcinia gerrardii* HARVEY *ex* T.R. SIM (*G. natalensis* SCHLECHTER; *G. transvaalensis* BURTT DAVY; Guttiferae). Structure elucidation was achieved by a combination of one- and two-dimensional NMR spectroscopic techniques, including long-range HETCOR, mass spectroscopy, and chemical methods. Garcigerrin A (**1**) and B (**2**) are pyrano derivatives of **3**. They all show a rare 1,4,5 oxygenation pattern of the xanthone nucleus. Xanthone **3** is fungicidal against *Cladosporium cucumerinum*.

Introduction. – *Garcinia gerrardii* HARVEY (Guttiferae) is a large shrub or small tree 4 to 5 m in height, but sometimes reaching 10 to 13 m. It occurs in evergreen forest and on mountain outcrops and is endemic to South Africa and Swaziland [1] [2]. The fruit is edible. *G. gerrardii,* which is investigated phytochemically for the first time here, belongs to the largest genus of the tropical family Guttiferae (excluding the Hypericaceae). The genus contains *ca.* 400 species and is a significant source of xanthones [3–5]. Dioxygenated, tetraoxygenated, and various prenylated xanthones have been isolated [4]. Benzophenones, biflavonoids, and condensed tannins are also a major feature of some of the species [6]. In addition, gum and seed oil of some plants yield fatty acids and their esters.

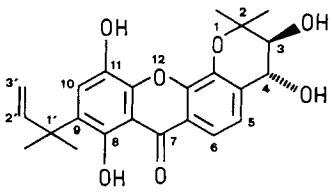
The most studied species of the genus are *G. mangostana* and *G. kola.* Investigations on *G. mangostana* have resulted in the isolation of anthocyanin glycosides, a benzophenone, maclurin, and several xanthones [7]. One of these, mangostin and four of its derivatives have antimicrobial activity [8]. The seeds of *G. kola* contain flavonoids, antihepatotoxic biflavonoids, xanthones [9], and kolanone, a polyisoprenylated benzophenone with antimicrobial properties [10].

During our study of different Guttiferae species, it was found that the root bark extracts of *G. gerrardii* exhibited fungicidal activity. Here we report the isolation of the major xanthonoid constituents.

Results. – The root bark of *G. gerrardii,* collected in South Africa, was extracted successively with CH_2Cl_2 and MeOH. In a TLC bioassay [11], the CH_2Cl_2 extract was fungicidal to *Cladosporium cucumerinum,* a plant pathogenic fungus. Flash chromatography of the orange-brown gummy CH_2Cl_2 extract on silica gel gave 6 fractions. Subsequent *Sephadex-LH-20* and low-pressure liquid chromatography on *RP-8* and *RP-18* adsorbents yielded three yellow compounds, garcigerrin A (**1**), garcigerrin B (**2**), and 12b-hydroxy-des-*D*-garcigerrin A (**3**).



1



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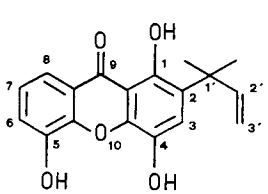

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Garcigerrin A (**1**; $C_{23}H_{24}O_7$) gave a molecular ion at *m/z* 412 by EI-MS. Upon acetylation, a tetraacetate **1a** (= 3,4,8,11-tetra-*O*-acetyl-**1**), was obtained, indicating the presence of 4 OH groups. Although no bathochromic shift was observed in the UV spectrum of **1** upon addition of $AlCl_3$ [12], the presence of a broad *s* at 12.89 ppm in the ^{1}H-NMR spectrum was indicative of a chelated OH.

Table 1. *^{1}H-NMR Spectral Data for Compounds* **1** *and* **2**

	1[a])	**1**[b])	**2**[c])
CH_3–C(2)	1.25 (*s*)	1.41 (*s*)	1.48 (*s*)
CH_3–C(2)	1.23 (*s*)	1.38 (*s*)	1.22 (*s*)
H–C(4)	5.41 (*d*, *J* = 5.1)	5.45 (*d*, *J* = 5.1)	4.45 (*d*, *J* = 7.9)
H–C(3)	4.39 (*d*, *J* = 5.1)	4.57 (*dd*, *J* = 5.1, 0.9)	3.50 (*d*, *J* = 7.9)
H–C(5)	7.40 (*d*, *J* = 8.1)	7.34 (*d*, *J* = 8.1)	7.46 (*d*, *J* = 8.4)
H–C(6)	7.72 (*d*, *J* = 8.1)	7.84 (*dd*, *J* = 8.1, 0.9)	7.67 (*d*, *J* = 8.4)
OH–C(8)	12.89 (*s*)		12.88 (*s*)
2 CH_3–C(1′)	1.47 (*s*)	1.53 (*s*)	1.46 (*s*)
H–C(2′)	6.24 (*dd*, *J* = 17.6, 10.3)	6.27 (*dd*, *J* = 18.0, 10.1)	6.23 (*dd*, *J* = 17.7, 10.4)
CH_2(3′)	4.99 (*m*)	5.02 (*dd*, *J* = 18.0, 1.3)	4.99 (*m*)
		5.04 (*dd*, *J* = 10.1, 1.3)	
H–C(10)	7.36 (*s*)	7.31 (*s*)	7.33 (*s*)

[a]) Measured at 400 MHz, in (D_6)DMSO.
[b]) Measured at 200 MHz, in $CDCl_3/CD_3OD$ 10:1.
[c]) Measured at 200 MHz, in (D_6)DMSO.

The ^{1}H-NMR spectrum of **1** *(Table 1)* showed the signals for 4 CH_3 groups, an *AB* system of a 1,2,3,4-tetra-substituted aromatic ring and a *s* at 7.36 ppm of an isolated aromatic proton. An *ABX* system at 6.24 and 4.99 ppm was indicative of a side chain with a terminal olefinic methylidene group, whereas the resonances at 4.39 and 5.41 ppm suggested the presence of two vicinal secondary OH groups. A spectrum measured in $CDCl_3/CD_3OD$ 10:1 and a delayed COSY experiment revealed some informative long-range couplings. An allylic coupling and a five-bond coupling were observed between H–C(4) and H–C(5) and H–C(4) and H–C(6), respectively. An additional correlation over five bonds between H–C(10) and H–C(2′) located the side chain *ortho* to the proton of the pentasubstituted aromatic ring. NOE difference measurements were in support of the position of the side chain. Upon irradiation of the CH_3–C(1′) signal, enhancement of the signals at 7.36 (H–C(10)) and 12.89 ppm (chelated OH) was observed. The 1,1-dimethylallyl side chain had, therefore, also to be *ortho* to the chelated OH group.

The ^{13}C-NMR spectrum of **1** *(Table 2)* was indicative of the presence of a carbonyl and two heterocyclic O-atoms. The 1,1-dimethylallyl side chain was identified by comparison with published data [13]. A quaternary C-atom at 69.6 ppm in conjunction with two vicinal secondary OH groups and two CH_3 groups suggested a 3,4-dihydroxy-2,2-dimethylchroman moiety. At that stage, it became obvious that compound **1** had to be a xanthone, despite its atypical UV spectrum. While the nature of the substituents of the xanthone was elucidated, their positions of attachment remained to be shown by 2D heteronuclear shift correlation. Protonated C-atoms were assigned by one-bond correlation, and long-range connectivities were established with the aid of a HETCOR

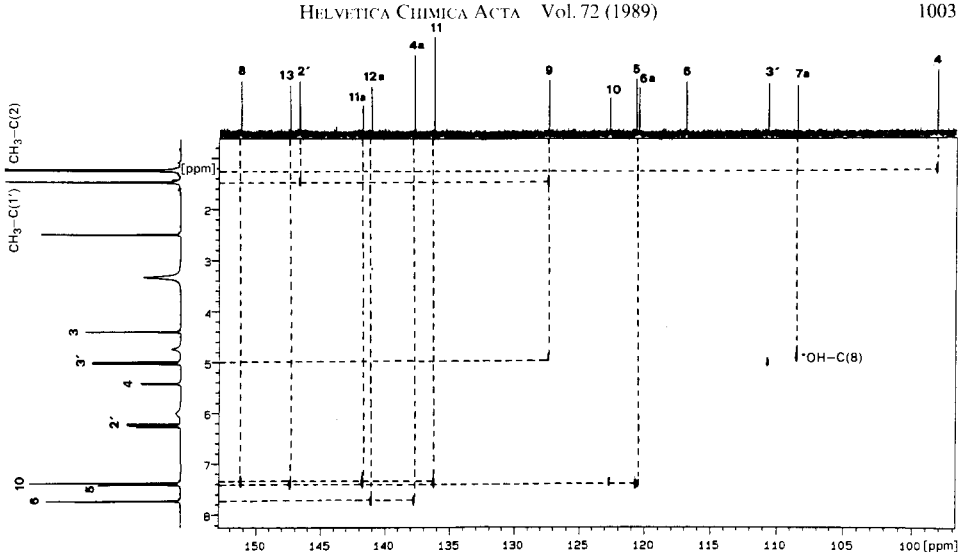

Figure. *Aromatic region of long-range HETCOR spectrum of garcigerrin A* (**1**). Delays optimized for $J(C,H) = 7$ Hz. Cross peaks originating from residual direct couplings have not been traced out. * Cross peak resulting from foldover of OH–C(8).

Table 2. *^{13}C-NMR Spectral Data for Compounds* **1**–**3**[a])

C-Atom	**1**[b])[c])	**2**[d])	C-Atom	**3**[d])
C(2)	69.6	80.3	C(1)	151.0
CH_3–C(2)	25.6	26.3	C(2)	127.5
CH_3–C(2)	25.4	19.6	CH(3)	121.9
CH(3)	98.2	73.7	C(4)	136.2
CH(4)	71.8	67.7	C(4a)	141.2
C(4a)	137.7	132.1	C(10a)	144.7
CH(5)	120.7	122.4	C(5)	146.5
CH(6)	116.9	114.9	CH(6)	120.7
C(6a)	120.5	119.5	CH(7)	124.2
C(7)	182.4	182.5	CH(8)	114.6
C(7a)	108.5	108.6	C(8a)	120.5
C(8)	151.2	150.9	C(9)	182.8
C(9)	127.4	127.2	C(9a)	108.1
CH(10)	122.7	123.4	C(1')	40.0
C(11)	136.2	136.4	2 CH_3–C(1')	26.4
C(11a)	141.8	142.1	CH(2')	146.6
C(12a)	141.1	140.5	CH_2(3')	110.7
C(12b)	147.4	145.1		
C(1')	39.8	39.0		
CH_3–C(1')	26.3	26.3		
CH(2')	146.6	146.7		
CH_2(3')	110.6	110.7		

[a]) Chemical shifts in ppm; solvent: (D_6)DMSO.

[b]) Measured at 100.5 MHz.

[c]) In addition to the C,H connectivities given in the text and the *Figure*, the following long-range couplings were observed by HETCOR: CH_3–C(2)/C(2), H–C(3)/C(2), H–C(4)/C(3), H–C(5)/C(6a), H–C(5)/C(12b), OH–C(8)/C(9), CH_3–C(1')/C(9), and H–C(2')/2 CH_3–C(1').

[d]) Measured at 50.7 MHz.

experiment [14] (delays optimized for $J = 7$ Hz; *Figure* and *Table 2*). The cross peaks observed for H–C(6) with C(4a), C(7), and C(12a), in conjunction with the homonuclear long-range couplings of H–C(4) established the position of the chromane ring as depicted. Its substitution pattern could be confirmed by additional long-range couplings. Noteworthy is the three-bond correlation of the chelated OH–C(8) with C(7a). Long-range connectivities between H–C(10) and C(8), C(11), and C(11a) proved the position of the 1,1-dimethylallyl moiety at C(9).

The above data establish structure **1** for garcigerrin A, the *cis* configuration of the 3,4-dihydroxy moiety being based on the coupling constant $J(3,4)$ (5.1 Hz) in the ^{1}H-NMR spectrum, comparison with the isomeric xanthone **2** ($J(3,4) = 7.9$ Hz), and comparison with data reported for 3,4-*cis*- and 3,4-*trans*-dihydroxy-2,2-dimethylchromans [15] [16]. In the case of chromans from *Helianthella quinquenervis*, the configuration at C(3) and C(4) of *cis*-2,2-dimethyl-3,4,7-trihydroxy-6-acetylchroman was confirmed by partial synthesis from the corresponding chromene *via* oxidation with OsO_4; the coupling constant $J(3,4)$ was 4 Hz [15]. Similarly, for establishing the configurations of 1,2-dihydroxyacronycine derivatives from *Sarcomelicope glauca* leaves, the *cis*-1,2-dihydroxy-1,2-dihydro isomer ($J(1,2) = 4.5$ Hz) was prepared from acronycine by OsO_4 oxidation, while the *trans* isomer ($J(1,2) = 8.0$ Hz) was obtained by Cr_2O_3 oxidation [17].

Garcigerrin B (**2**) ($C_{23}H_{24}O_7$) showed UV, IR, and EI-MS data similar to those of garcigerrin A (**1**). Noticeable differences in the ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*) were observed only for the signals attributable to the chroman ring. A coupling constant of 7.9 Hz for H–C(3) and H–C(4) indicated that **2** was the *trans* isomer of **1** [15] [16].

Compound **3** ($C_{17}H_{16}O_5$) gave a molecular ion at m/z 312 by EI-MS. Its UV spectrum closely resembled those of **1** and **2**, suggesting a xanthone with a similar substitution pattern. Its structure was deduced from NMR data and NOE's of its dimethyl ether **3a** (= 4,5-di-*O*-methyl-**3**; *Table 3*).

Table 3. *^{1}H-NMR Spectral Data for Compounds* **3** *and* **3a**

	3[a])	**3a**[b])
OH–C(1)	12.77 (*s*)	12.86 (*s*)
H–C(3)	7.29 (*s*)	7.35 (*s*)
H–C(6)	7.36 (*dd*, $J = 7.9, 2.1$)	7.25 (*dd*, $J = 7.9, 2.1$)
H–C(7)	7.29 (*dd*, $J = 7.9, 7.5$)	7.31 (*dd*, $J = 7.9, 7.5$)
H–C(8)	7.60 (*dd*, $J = 7.5, 2.1$)	7.85 (*dd*, $J = 7.5, 2.1$)
CH_3O–C(4)		4.01 (*s*)
CH_3O–C(5)		4.04 (*s*)
2 CH_3–C(1′)	1.49 (*s*)	1.57 (*s*)
H–C(2′)	6.25 (*dd*, $J = 17.8, 10.4$)	6.30 (*dd*, $J = 18.0, 10.1$)
CH_2(3′)	5.01 (*dd*, $J = 10.5, 1.3$)	5.07 (*dd*, $J = 10.1, 1.3$)
	5.01 (*dd*, $J = 17.8, 1.3$)	5.06 (*dd*, $J = 18.0, 1.3$)

[a]) Measured at 200 MHz, in (D_6)DMSO.
[b]) Measured at 200 MHz, in $CDCl_3$.

The ^{1}H-NMR spectrum of **3** displayed signals of an *ABM* system attributable to a 1,2,3-trisubstituted benzene ring and a *s* of an isolated aromatic proton. An olefinic *ABX* system and two allylic CH_3 groups were typical of a 1,1-dimethylallyl moiety, whereas a *s* at 12.77 ppm indicated the presence of a chelated OH. In the ^{13}C-NMR spectrum of **3**, the signals attributable to the pentasubstituted benzene ring were almost identical with the corresponding signals of xanthone **1**. The substituents were, therefore, tentatively placed as depicted. The proposed substitution pattern was corroborated by NOE difference measurements on the dimethyl ether **3a**. Irradiation of the CH_3O signal at 4.01 ppm resulted in an enhancement of the *s* attributable to H–C(3). Upon presaturation of

the CH_3–C(1') signal, NOE's to H–C(3) and OH–C(1) were observed. In addition, an enhancement of H–C(6) was obtained upon irradiation of the CH_3O signal at 4.04 ppm. The observed NOE's were of the order 5–10%. Thus, the substitution pattern of xanthone **3** was confirmed.

Discussion. – Three xanthones have been isolated from the root bark of *Garcinia gerrardii*. They are new natural products and have the rare 1,4,5-oxygenation pattern. Furthermore, the UV spectra of garcigerrin A (**1**) and B (**2**) give a fourth maximum at *ca.* 410 nm, a value higher than that normally recorded for xanthones [18]. Both **1** and **2** contain a dimethylpyran ring with a 3,4-dihydroxy substitution pattern. The presence of this moiety has been reported in two furoquinoline alkaloids from *Sarcomelicope glauca* leaves (Rutaceae) [17], in chromans from *Helianthella quinquenervis* (Asteraceae) [15], and in chromans from the basidiomycete *Panus rudis* [16]. Pyranoxanthones are very rare [4] [19], and this is probably the first time a dihydropyranoxanthone has been found. Both the *cis*- and *trans*-diols exist together in the plant.

Since they were optically inactive, both **1** and **2** were obtained as racemic mixtures. The same results ($[\alpha]_D^{20} = 0$) were obtained for the *cis*- and *trans*-chromans from *Helianthella quinquenervis* [15] and for the *cis*-chroman from the fungus *Panus rudis* [16]. Although the corresponding chromene derivative of **1** and **2** was not found in the *G. gerrardii* extract, it is reasonable to expect that biosynthesis of the garcigerrins involves the chromene as a precursor.

Biogenetically, xanthones **1** and **2** are isoprenylated derivatives of **3**, in which cyclisation of the isoprenylated substituent has occurred.

Compounds **1–3** were tested for their activity against the plant pathogenic fungus *Cladosporium cucumerinum* using a TLC biossay [11]. Garcigerrin A (**1**) and B (**2**) were inactive at 50 μg, whereas xanthone **3** prevented growth of the fungus at 0.2 μg. Another xanthone, mangostin, is also reported to be fungicidal to five fungi, including *Alternaria solani* and *Cunninghamella echinulata* [8]. In addition, **3** exhibited moderate *in vitro* growth-inhibitory activity against the Co-115 human colon carcinoma cell line (ED_{50} = 3 μg/ml) [20].

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Experimental Part

General. TLC: silica-gel precoated Al sheets *(Merck)*, $CHCl_3$/MeOH 20:1 (system *1*) or petroleum ether/AcOEt 1:1 (system *2*); *RP-8* and *RP-18* precoated glass plates (HPTLC, *Merck*), MeOH/H_2O mixtures; detection 254 and 366 nm. Low-pressure liquid chromatography (LPLC): *Lobar RP-8* and *RP-18* columns (40–63 μm; i.d. 2.5 × 27 cm; *Merck*, Darmstadt), equipped with *Duramat-80* pump (*Chemie und Filter*, Regensdorf). Purity of compounds was checked on an HPLC system consisting of a *Spectra-Physics* (San Jose, CA, USA) *8700* pump, *Rheodyne* injector, photodiode-array detector *HP 1040 A (Hewlett Packard)*, an *HP-85* computer, and an *HP 7470* plotter; a *NovaPak C 18* column (4 μm; i.d. 3.9 mm × 15 cm) was used. M.p.: *Mettler FP 80/82* hot stage apparatus; uncorrected. $[\alpha]_D$: *Perkin-Elmer-241* polarimeter. UV spectra: *Perkin Elmer Lambda 3* spectrophotometer; λ_{max} (log ε) in nm; MeOH solns. and after addition of shift reagents according to [12]. IR spectra: *Perkin-Elmer 781* IR spectrometer. ^{1}H- and ^{13}C-NMR spectra: *Varian VXR 200* and *400* instruments; multiplicities of ^{13}C signals by DEPT experiments. 2D NMR experiments: quadrature detection in *F1* and *F2*. COSY spectra: 256 × 1 K data sets; after zero filling to 1 K × 1 K complex data points, pseudo-echo weighting in both dimensions was used and the data displayed in the absolute value mode; an additional delay of 100 ms was employed for

measuring the delayed COSY. 2D HETCOR spectrum: at 35° as a 128 × 8 K data set; the spectral widths were 3192 Hz in *F*1 and 17160 Hz in *F*2; after zero-filling to 512 × 8 K, sine-bell weighting was applied in both dimensions prior to *Fourier* transformation; the long-range HETCOR experiment was performed with delays optimized for $J(C,H) = 7$ Hz. NOE difference spectra: at 20° with a presaturation delay of 5 s and varying power levels in order to ascertain selectivity of irradiation; typically 300–500 transients were recorded; a 1–2 Hz line broadening function was applied to the difference FID prior to *Fourier* transformation. EI-MS: *Nermag R 3010* quadrupole instrument.

Plant Material. Root bark of *Garcinia gerrardii* was collected in Kaarkloof Nature Reserve Durban, South Africa, in February 1988. A voucher specimen is deposited at the Roddy Ward Herbarium, University of Durban-Westville.

Extraction and Isolation. The powdered root bark of *G. gerrardii* (340 g) was extracted at r.t. with CH_2Cl_2. A portion (2 × 10 g) of the extract (28 g) was fractionated by flash chromatography on a silica-gel column (63–200 μm; i.d. 7 × 90 cm) using a step-gradient $CHCl_3$/MeOH 50:1→10:1. *Fr. I–VI* were collected. Repetitive LPLC of *Fr. V* (1600 mg) in 4 batches of 400 mg each on *RP-8* with MeOH/H_2O 75:25 yielded a fraction (360 mg) containing **1** and **2**. Pure **1** (92 mg) and **2** (24 mg) were obtained by separation of the mixture on a *Sephadex-LH-20* column (i.d. 4.5 × 70 cm) using MeOH. The fungicidal *Fr. III* (3600 mg) was chromatographed on *Sephadex LH-20* (MeOH), followed by LPLC on *RP-18* (MeOH/H_2O 95:5 → 100:0): antifungal **3** (102 mg).

Garcigerrin A (= *(3RS,4RS)-9-(1′,1′-Dimethylprop-2′-enyl)-3,4-dihydro-3,4,8,11-tetrahydroxy-2,2-dimethylpyrano[3,2-c]xanthen-7(2H)-one*; **1**). Yellow needles from CH_2Cl_2. M.p. 228–229°. TLC (SiO_2, system *1*): R_f 0.10. HPTLC (*RP-8*, MeOH/H_2O 85:15): R_f 0.55. $[\alpha]_D = 0$ ($c = 0.15$, MeOH). UV (MeOH): 253 (4.46), 271 (4.33, sh), 322 (3.99), 410 (3.50). UV (MeOH + NaOAc): no shift. UV (MeOH + NaOMe): 254, 282 (sh), 337, 455. UV (MeOH + $AlCl_3$): no shift. IR (KBr): 3400 (OH), 2960 (CH), 1580 (C=O). ^{1}H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. EI-MS: 412 (74), 397 (86), 371 (32), 369 (12), 357 (20), 338 (5), 336 (20), 321 (41), 295 (26), 281 (26), 59 (35), 43 (100).

Garcigerrin A Tetraacetate (**1a**). Xanthone **1** (5 mg) was refluxed with Ac_2O/pyridine 1:1 (1 ml) for 12 h. The mixture was poured into ice/H_2O: white amorphous precipitate. Chromatography on a silica gel column (15–40 μm) with AcOEt/petroleum ether 1:3 gave **1a** as a white amorphous solid. M.p. 69–71°. TLC (SiO_2, system *1*): R_f 0.73. UV (MeOH): 252 (4.51), 304 (3.82), 352 (3.54). UV (MeOH + NaOAc): no shift. UV (MeOH + NaOMe): 253 (4.46), 271 (4.33). ^{1}H-NMR ($CDCl_3$): 7.75 (*d*, $J = 7.4$, H–C(6)); 7.56 (*s*, H–C(10)); 7.30 (*d*, $J = 7.4$, H–C(5)); 6.55 (H–C(3)); 6.00 (*dd*, $J = 18.0, 11.5$, H–C(2′)); 5.1 (*d*, $J = 18.0$, 1 H, CH_2(3′)); 5.03 (*d*, $J = 11.5$, 1 H, CH_2(3′)); 5.00 (*s*, H–C(3)); 2.44 (*s*, 1 AcO); 2.38 (*s*, 1 AcO); 2.10 (*s*, 1 AcO); 1.91 (*s*, 1 AcO); 1.64 (*s*, 1 CH_3–C); 1.58 (*s*, 1 CH_3–C); 1.50 (*s*, 1 CH_3–C); 1.44 (*s*, 1 CH_3–C). EI-MS: 580 (1, M^+), 538 (9, $M^+ - CH_2CO$), 496 (35), 436 (17).

Garcigerrin B (= *(3RS,4SR)-9-(1′,1′-Dimethylprop-2′-enyl)-3,4-dihydro-3,4,8,11-tetrahydroxy-2,2-dimethylpyrano[3,2-c]xanthen-7(2H)-one*; **2**). Yellow amorphous solid. M.p. 130–133°. TLC (SiO_2, system *1*): R_f 0.12. HPTLC (*RP-8*, MeOH/H_2O 85:15): R_f 0.44 $[\alpha]_D = 0$ ($c = 0.15$, MeOH). UV (MeOH): 253 (4.48), 271 (4.43, sh), 320 (3.99), 410 (3.61). UV (MeOH + NaOAc): no shift. UV (MeOH + NaOMe): 254, 280 (sh), 335, 455. UV (MeOH + $AlCl_3$): no shift. IR (KBr): 3380 (OH), 2960 (CH), 1590 (C=O). ^{1}H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. EI-MS: 412 (100), 397 (69), 371 (24), 325 (51), 307 (15), 297 (20), 285 (37).

2-(1′,1′-Dimethylprop-2′-enyl)-1,4,5-trihydroxy-9H-xanthen-9-one (**3**). Yellow amorphous solid. M.p. 203–205°. TLC (SiO_2, system *1*): R_f 0.27. HPTLC (*RP-8*, MeOH/H_2O 85:15): R_f 0.30. UV (MeOH): 250 (4.55), 265 (4.57), 320 (4.06), 408 (3.74). UV (MeOH + NaOAc): 265, 322, 355, 424. UV (MeOH + NaOMe): 268, 330, 420. UV (MeOH + $AlCl_3$): no shift. IR (KBr): 3300 (OH), 2960 (CH), 1580 (C=O). ^{1}H-NMR: *Table 3*. ^{13}C-NMR: *Table 2*. EI-MS: 312 (40), 297 (100), 279 (34), 271 (26), 257 (34).

2-(1′,1′-Dimethylprop-2′-enyl)-4,5-dimethoxy-1-hydroxy-9H-xanthen-9-one (**3a**). Methylation was carried out by stirring **3** (5 mg) with ethereal CH_2N_2 (2 ml) in MeOH (2 ml) for 48 h at r.t. Purification on a silica gel column using hexane/EtOAc 9:1 and crystallization from MeOH gave **3a** as yellow needles. M.p. 118–119°. TLC (SiO_2, system *1*): R_f 0.72. UV (MeOH): 239 (4.44), 248 (4.43), 260 (4.38), 315 (3.85), 392 (3.57). UV (MeOH + NaOAc): no shift. UV (MeOH + NaOMe): no shift. UV (MeOH + $AlCl_3$): no shift. IR (KBr): 3450 (OH), 2940 (CH), 1575 (C=O). ^{1}H-NMR: *Table 3*. EI-MS: 340 (100), 325 (100), 307 (24), 294 (76), 179 (31).

REFERENCES

[1] K. Coates Palgrave, 'Trees of Southern Africa', C. Struik Publishers, Cape Town, 1984, p. 613.
[2] J. M. Watt, M. G. Breyer-Brandwijk, 'The Medicinal and Poisonous Plants of Southern and Eastern Africa', E. and S. Livingstone Ltd., Edinburgh–London, 1962, p. 495.
[3] M. U. S. Sultanbawa, *Tetrahedron* **1980,** *36,* 1465.
[4] G. J. Bennett, H.-H. Lee, *Phytochemistry* **1989,** *28,* 967.
[5] P. Kumar, R. K. Baslas, *Herba Hung.* **1980,** *19,* 31.
[6] P. G. Waterman, R. A. Hussain, *Biochem. Syst. Ecol.* **1983,** *11,* 21.
[7] W. Mahabusarakam, P. Wiriyachitra, W. C. Taylor, *J. Nat. Prod.* **1987,** *50,* 474.
[8] B. M. Sundaram, C. Gopalakrishnan, S. Subramanian, D. Shankaranarayanan, L. Kameswaran, *Planta Med.* **1983,** *48,* 59.
[9] A. Sofowora, 'The State of Medicinal Plants Research in Nigeria', Workshop Proceedings, Faculty of Pharmacy, University of Ife, Ile-Ife, Nigeria, 1986, p. 39, p. 56, p. 364.
[10] R. A. Hussain, A. G. Owegby, P. Parimoo, P. G. Waterman, *Planta Med.* **1982,** *44,* 78.
[11] A. L. Homans, A. Fuchs, *J. Chromatogr.* **1970,** *51,* 327.
[12] K. R. Markham, 'Techniques of Flavonoid Identification', Academic Press, New York, 1982.
[13] T. Fujimoto, Y. Hano, T. Nomura, *Planta Med.* **1984,** *50,* 218.
[14] G. E. Martin, A. S. Zektzer, *Magn. Reson. Chem.* **1988,** *26,* 631.
[15] W. Herz, P. P. Kulanthaivel, *Phytochemistry* **1984,** *23,* 435.
[16] Z. Kis, A. Closse, H. P. Sigg, L. Hruban, G. Snatzke, *Helv. Chim. Acta* **1970,** *53,* 1577.
[17] S. Mitaku, A. L. Skaltsounis, F. Tillequin, M. Koch, J. Pusset, G. Chauvière, *J. Nat. Prod.* **1986,** *49,* 1091.
[18] K. R. Markham, *Tetrahedron* **1964,** *20,* 991.
[19] K. Balasubramanian, K. Rajagopalan, *Phytochemistry* **1988,** *27,* 1552.
[20] A. Marston, J.-C. Chapuis, B. Sordat, J. D. Msonthi, K. Hostettmann, *Planta Med.* **1986,** *52,* 207.