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MINOR XANTHONES FROM *RHEEDIA GARDNERIANA*[*]

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Key Word Index—*Rheedia gardneriana*; Guttiferae; prenylated xanthones.

Abstract—8-Deoxygartanin and two new xanthones, 1,5-dihydroxy-6′,6′-dimethyl-2H-pyrano(2′,3′:3,2)-6″,6″-dimethyl-2H-pyrano(2″,3″:6,7)xanthone and 1,5,6-trihydroxy-6′,6′-dimethyl-2H-pyrano(2′,3′:3,2)-7-(3-methylprop-2-enyl)xanthone, have been isolated from the roots of *Rheedia gardneriana*. The latter of the two new xanthones has been assigned the trivial name 7-prenyljacareubin while the former has the structure erroneously assigned to pyranojacareubin reported from *Garcinia densivenia*. The correct identity of the *G. densivenia* xanthone has been shown to be rheediaxanthone-A.

INTRODUCTION

The genus *Rheedia* (tribe Clusioideae, family Guttiferae), as well as the closely related genus *Garcinia*, has been shown to be quite rich in xanthones. Prenylated xanthones have been isolated from the roots of *Rheedia benthamiana* [1] and *R. gardneriana* [2]. We now report the isolation from the latter species of three further prenylated xanthones which are present in the extract in small amounts.

One xanthone was identified as 8-deoxygartanin (**1**) while the other two were novel and were assigned structures **2** and **4** and the trivial names pyranojacareubin and 7-prenyljacareubin, respectively. Pyranojacareubin has been reported as a constituent of *Garcinia densivenia* [3] but in the course of this study the identity of the *G. densivenia* xanthone was revised to rheediaxanthone-A (**3**) with the isolation of authentic pyranojacareubin.

RESULTS AND DISCUSSION

In the first product, **1**, $C_{23}H_{24}O_5$ (MW 380) two γ,γ-dimethylallyl chains (^{1}H NMR evidence) and a 1,3,5-trioxygenated xanthone chromophore (UV maxima) [4] were present. In the ^{1}H NMR spectrum the aromatic protons appeared as an AXY system, where the lowest field signal (H-8 proton) was an *ortho* and *meta*-split quartet; the prenyl methylene signals experienced different shifts (+0.43 vs +0.33 ppm) in C_5D_5N and were consistent with the placement of the two chains at C-2 and C-4 [5]. The presence of a bulky substituent at C-2 was also indicated by the delay in the appearance of the bathochromic shift with $AlCl_3$ of the UV maximum [6].

The compound is therefore 1,3,5-trihydroxy-2,4-bis(3-methyl-but-2-enyl)xanthone, **1**; it has been already isolated from *G. mangostana* [7] and named 8-deoxygartanin. Physical and spectral data were in agreement with those reported in the literature.

Spectral data indicated the second minor compound, $C_{23}H_{20}O_6$, **2**, (MW 392) was a 1,3,5,6-tetraoxygenated xanthone, with two 2,2-dimethyl-2H-pyran rings, thus isomeric with rheediaxanthone-A, **3** [1]. The H-8 proton was still present in the ^{1}H NMR spectrum (δ 7.43 vs 7.45 in $CDCl_3$), but the second isolated aromatic proton had a different chemical shift (δ 6.40 vs 6.20) and was not shifted downfield in C_5D_5N (−0.02 vs +0.23 ppm). Moreover, the bathochromic shift with $AlCl_3$ in the UV spectrum was not immediate, as in **3**, but was complete only after 30 min; this behaviour is typical of chelated 1-OH compounds with a substituent in position 2 [6].

From a comparison of the H-α chemical shifts of the two isomers with those of suitable reference compounds [8–11] (Table 1), it was concluded that the substitution of ring B is the same for **2** and **3**, but the ring A chromene has in **2** a linear fusion. Accordingly, band II was at a longer wavelength than in **3** [11].

Recently two of us [3] isolated from *G. densivenia* a dichromenoxanthone which was assigned structure **2** and the trivial name pyranojacareubin. However, direct comparison of this material with the compound isolated here

Table 1. H-α resonances (δ) of pyranoxanthones

		H-α at		
		C-2	C-4	C-7
Jacareubin	[8]	6.73*		
Macluraxanthone	[8]	6.75*		
Calabaxanthone	[9]	6.75*		
6-Deoxyisojacareubin	[10]		6.94†	
Lorostemin	[11]		6.83†	
Rheediachromenoxanthone	[2]			6.55†
Rheediaxanthone-A	[1]		6.85* 6.90†	6.40* 6.50†
Isorheediaxanthone-A, 2		6.70*		6.38*

*In $CDCl_3$.
†In CD_3COCD_3.

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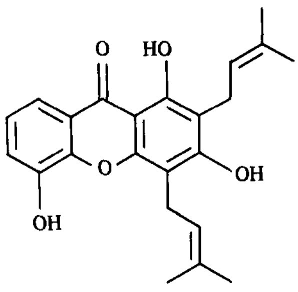
[*] Part III in the series "Chemical Investigation of the Genus *Rheedia*". For Part II see ref. [2].



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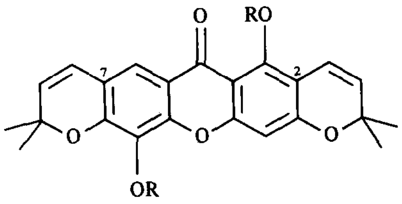
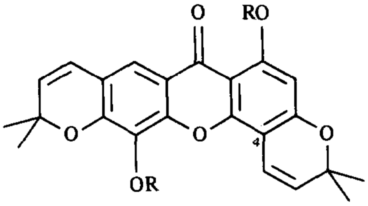
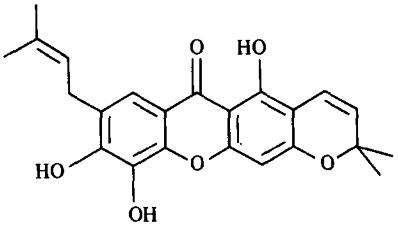


	R
2	H
2a	Ac



	R
3	H
3a	Ac



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and with authentic rheediaxanthone-A (**3**) (co-chromatography and spectral data recorded on the same instrument) showed it to be identical to **3**. This error arose from misinterpretation of the shift of the H-4′ proton in the diacetate (**3a**) which shows a rather large value of +0.19 ppm, less than that anticipated for H-4′ *peri* to an acetyl [8] but at the time considered to be too large for placement at C-4. However, by comparison, the diamagnetic shift of the H-4′ proton in the diacetate (**2a**) was larger (+0.26 vs 0.19 ppm) and in better agreement with the postulated value of +0.30 ppm. Therefore we attribute structure **2** to the minor component of *R. gardneriana* and we retain the trivial name pyranojacareubin for this compound, with the structure of the xanthone previously isolated from *G. densivenia* revised to that of rheediaxanthone-A (**3**).

The third compound, $C_{23}H_{22}O_6$, **4** (MW 394), was also a 1,3,5,6-tetraoxygenated xanthone. The typical UV spectrum underwent modifications with additives which indicated free hydroxyl groups in positions 1,5 and 6. The ^1H NMR spectrum (CD_3COCD_3) indicated the presence of a γ,γ-dimethylallyl chain, a 2,2-dimethyl-2H-pyran ring and two isolated aromatic protons. The former (δ7.47) was postulated as H-8 and the latter (δ6.24 with an upfield shift in C_5D_5N [5]) as H-4. The identity of ring A in **4** and **2** was corroborated by the chemical shift of H-α (δ6.65 with a downfield shift in C_5D_5N [5]), while position 7 for the prenyl chain was substantiated by the paramagnetic effect of C_5D_5N [5] on the CH_2 resonance, by the long-range coupling between the methylene and H-8 signals, and by the loss of 56 amu [12] from the base peak $[M - Me]^+$ in the mass spectrum. The shortage of the product has so far prevented any chemical transformation, e.g. conversion of **4** into **2** by DDQ. Finally, we want to emphasize the interesting behaviour of these diprenylated xanthones in the mass spectral fragmentation: the formation of doubly-charged ions of quite strong intensity due to the typical losses of two substituents, i.e. $[M - Me - Me]^{2+}$ for **2** and $[M - Me - C_4H_7]^{2+}$ for **4**.

EXPERIMENTAL

Isolation. The pure xanthones were obtained by extended CC and prep. TLC of the C_6H_6 extract of the roots of *R. gardneriana* Pl. and Tr. [2].

General. Mps are uncorr. Elemental analyses were in agreement with molecular formulae. ^{1}H NMR was at 60 MHz. MS were recorded by direct inlet at 70 eV.

1,3,5-*Trihydroxy*-2,4-*bis*(3-*methylbut*-2-*enyl*)*xanthone* (8-*deoxygartanin*, **1**). $C_{23}H_{24}O_5$ (MW 380), mp 162–164° (Et_2O–hexane); ^{1}H NMR (CD_3COCD_3): δ13.30 (1H, *s*, exchang. D_2O, 1-OH), 8.00 + 7.77 (1H + 1H, *s* + *s*, exchang. D_2O, 3-OH + 5-OH), 7.68 (1H, *dd*, $J = 2$ and 8.5 Hz, H-8), 7.50–7.10 (2H, *m*, H-6 + H-7), 5.55–5.00 (2H, *m*, 2 × CH=), 3.75 (2H, *d*, $J = 7$ Hz, 2-CH_2), 3.50 (2H, *d*, $J = 7$ Hz, 4-CH_2), 1.84 + 1.78 + 1.66 (3H + 3H + 6H, 3 × *s*, 4 × Me); $\Delta\delta = \delta$ (C_5D_5N) $- \delta$ (CD_3COCD_3) = 2-CH_2 (+0.43), 4-CH_2 (+0.33); IR, UV and MS data were coincident with those of 8-deoxygartanin [7].

1,5-*Dihydroxy*-6′,6′-*dimethyl*-2*H*-*pyrano*(2′,3′:3,2)-6″,6″-*dimethyl*-2H-*pyrano*(2″,3″:6,7)*xanthone* (*pyranojacareubin*, **2**). $C_{23}H_{20}O_6$, mp 259.5–260.5° (yellow needles from Et_2O); UV λ_{max}^{MeOH} nm (log ε): 288 (4.71), 296 (4.72), 346 (4.10), 395 sh (3.72); $\lambda_{max}^{AlCl_3}$ nm (after 30 min): 255, 264, 302, 375, 430 sh; λ_{max}^{NaOMe} nm: 300; ^{1}H NMR ($CDCl_3$): δ13.28 (1H, *s*, exchang. D_2O, 1-OH), 7.43 (1H, *s*, H-8), 6.66 (1H, *d*, $J = 10$ Hz, H-4′), 6.40 (1H, *s*, H-4), 6.38 (1H, *d*, $J = 10$ Hz, H-4″), 5.65 (1H, *d*, $J = 10$ Hz, H-5″), 5.53 (1H, *d*, $J = 10$ Hz, H-5′), 1.51 + 1.45 (6H + 6H, *s* + *s*, 4 × Me); $\Delta\delta$:δ (C_5D_5N) $- \delta$ ($CDCl_3$) = H-8 (+0.11), H-4 (−0.02), H-4′ (+0.13), H-4″ (0), H-5′ (−0.05), H-5″ (−0.08); IR ν_{max}^{KBr} cm^{-1}: 1640. MS *m*/*z* (rel. int.): 392 $[M]^+$ (26), 377 $[M - Me]^+$ (100), 361 (4), 359 (4), 295 (3), 188.5 $[M - Me]^{2+}$ (2), 181 $[M - Me - Me]^{2+}$ (29).

Diacetyl derivative. Acetylation of **2** with pyridine–Ac_2O overnight at 0° gave a mixture of mono- and diacetyl derivatives (^{1}H NMR evidence). Reacetylation of the mixture at room temp. gave mainly the diacetyl derivative (prep. TLC, $CHCl_3$) **2a**: $C_{25}H_{24}O_8$, vitreous solid; ^{1}H NMR: δ7.70 (1H, *s*, H-8), 6.68 (1H, *s*, H-4), 6.40 (1H, *d*, $J = 10$ Hz, H-4′), 6.34 (1H, *d*, $J = 10$ Hz, H-4″), 5.70 (1H, *d*, $J = 10$ Hz, H-5″), 5.68 (1H, *d*, $J = 10$ Hz, H-5), 2.47 (3H, *s*, 1-OCOMe), 2.40 (3H, *s*, 5-OCOMe), 1.44 (12H, *s*, 4 × Me).

1,5,6-*Trihydroxy*-6′,6′-*dimethyl*-2*H*-*pyrano*(2′,3′:3,2)-7-(3,3-*dimethylprop*-2-*enyl*)*xanthone* (7-*prenyljacareubin*, **4**). $C_{23}H_{22}O_6$, mp 218–220° (yellow plates from CH_2Cl_2); UV λ_{max}^{MeOH} nm (log ε): 280 (4.61), 334 (4.30); λ_{max}^{NaOAc} nm: 283, 365; $\lambda_{max}^{H_3BO_3}$ nm: 283, 352; $\lambda_{max}^{AlCl_3}$ nm (after 20 min: 295, 400; λ_{max}^{HCl} nm: 294, 365; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3540, 1645; ^{1}H NMR (CD_3COCD_3): δ12.78 (in CCl_4) (1H, *s*, exchang. D_2O, 1-OH), 7.47 (1H, *s*, H-8), 6.65 (1H, *d*, $J = 10$ Hz, H-4′), 6.24 (1H, *s*, H-4), 5.66 (1H, *d*, $J = 10$ Hz, H-5′), 5.25 (1H, *m*, CH =), 3.40 (2H, *d*, $J = 7$ Hz, CH_2), 1.76 (6H, *s*, 2 × butenyl Me), 1.52 (6H, *s*, 2 × chromene Me); $\Delta\delta = \delta$ (C_5D_5N) $- \delta$ (CD_3COCD_3) = H-8 (+0.48), H-4′ (+0.17), H-5′ (−0.15), H-4 (−0.12), CH_2 (+0.30); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3540, 1640; MS *m*/*z* (rel. int.): 394 $[M]^+$ (33), 379 $[M - Me]^+$ (100), 339 $[M - C_4H_7]^+$ (4), 323 $[M - Me - 56]^+$ (35), 197 $[M]^{2+}$ (3), 182 $[M - Me - Me]^{2+}$ (9), 162 $[M - Me - C_4H_7]^+$ (12); m* 275.2 (379 → 323).

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