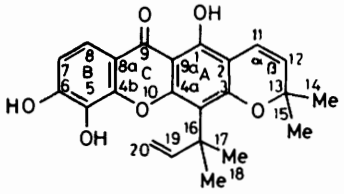
Three New Xanthones and Macluraxanthone from *Rheedia benthamiana* Pl. Triana (Guttiferae)

By **Franco Delle Monache** * and **Bruno Botta**, Centro Chimica dei Recettori, C.N.R., presso Istituto di Chimica U.C.S.C., Via Pineta Sacchetti 644, 00168 Roma, Italy
Marcello Nicoletti, Cattedra di Chimica Generale ed Inorganica, Università di Roma, Piazzale delle Scienze 5, 00185 Roma, Italy
José Sidney de Barros Coêlho and **Francisco Decio de Andrade Lyra**, Universidade Federal de Pernambuco, Departmento de Antiobioticos, 50.000 Recife, Brazil

From the root-bark extract of *Rheedia benthamiana* Pl. Triana (guttiferae) macluraxanthone (1) and three new xanthones, rheediaxanthone A (10), B (2), and C (9) have been isolated and their structures established. The presence of the optically active dihydrofurano-xanthone (2) was established in the crude extract. ^{13}C N.m.r. spectral data of the isolated xanthones and their derivatives are reported.

XANTHONES are characteristic secondary metabolites of the Guttiferae, Gentianaceae, and Moraceae families, to which their occurrence in higher plants is practically restricted: [1-4] particularly in Guttiferae, they are distributed in all seven sub-families [3] and the number of compounds isolated has increased considerably in recent years.

In this paper we report the results of the investigation on xanthone components of *Rheedia benthamiana* Pl. Triana (guttiferae, sub-family clusioideae, tribe garcinieae) collected in north-eastern Brazil. The only species of this genus so far examined, *R. gardneriana* Pl. Triana, contains simple xanthones, *i.e.* 1,5-dihydroxy-, 1,7-dihydroxy-, and 1,6-dihydroxy-5-methoxyxanthones.[5] From the ethanolic extract of the root bark, the known macluraxanthone [6] (1), and three new



(1)

xanthones, named by us rheediaxanthone A, B, and C in decreasing order of polarity, have been isolated and their structures determined by spectroscopical and chemical evidence.

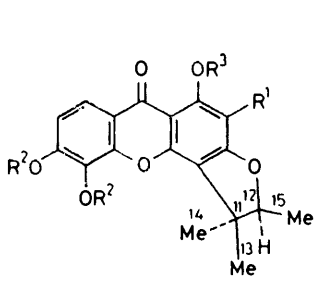
RESULTS AND DISCUSSION

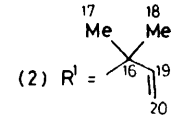
The identification of macluraxanthone (1), was based (see Experimental section) on the spectroscopic and physical data, including its existence in two dimorphous crystalline forms, as found by Wolfrom *et al.*[7] This is the first report on isolation of macluraxanthone in guttiferae, previously found only in *Maclura pomifera* Raf. (moraceae),[6,7] whereas its 5-*O*-methyl derivative occurs [8] in *Kayea stilosa* Thw. (guttiferae, subfamily clusioideae). The main component isolated, rheediaxanthone B, $C_{23}H_{24}O_6$, $M^+ = 396$, showed negative rotatory power and a u.v.–visible spectrum (see Experimental section) in good agreement with those of 1,3,5,6-tetrahydroxyxanthone and of similarly oxygenated xanthones without extended conjugation.[9-13] In the ^1H n.m.r. spectrum of rheediaxanthone B the signals of a hydrogen-bonded hydroxy (δ 14.30) and of only two *ortho*-coupled (J 8 Hz) aromatic protons were evident: the presence of two other phenolic hydroxy-groups, not visible owing to rapid exchange with the solvent ([$^2H_6$]-acetone or [$^2H_5$]pyridine), was established by acetylation, which under mild conditions gave a diacetyl derivative, still displaying the sharp low-field singlet in the ^1H n.m.r. spectrum; finally under severe conditions (Ac_2O–AcONa) a triacetyl derivative was obtained in low yield.

The above data, coupled with the bathochromic shift of the u.v. maxima (see Experimental section) on addition of NaOAc (hydroxy-group in the 6- or 3-position) and with the change in the presence of NaOH (indicative of an *ortho*-dihydroxy-grouping [14]), established a B-ring substitution pattern identical to that of macluraxanthone (1) and a completely substituted A-ring for rheediaxanthone B. The presence of the C(1) hydroxy-group being already established, the nature of the other substituents was deduced by the following signals in the ^1H n.m.r. spectrum of rheediaxanthone B: (*a*) three olefinic protons as an ABX system and a *gem*-dimethyl group as a singlet (δ 1.76), characteristic of a αα-dimethylallyl chain; (*b*) two methyl singlets (δ 1.70 and 1.38) and a methyl doublet (δ 1.30) showing vicinal coupling (δ 7 Hz) with a one-proton quartet (δ 4.40), attributed to an ααβ-trimethyldihydrofuran ring.[15-17] From the above results the angular structure (2), or the corresponding linear one, can be assigned to rheediaxanthone B.

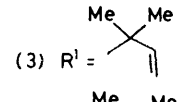
To provide further information, rheediaxanthone B was refluxed with HCO_2H; under these conditions an αα-dimethylallyl chain adjacent to a phenolic hydroxy usually cyclizes to generate a trimethyl-dihydrofuran.[12,15] In our case, from this reaction three products were obtained. The main product, m.p. 207—208 °C, $[\alpha]_D = -34.5°$, had lost the αα-dimethylallyl chain, as evidenced by the mass spectrum, M^+ at m/z 328, and by the ^1H n.m.r. spectrum, in which the signals of the chain are replaced by an aromatic singlet. The chemical shift (δ 6.12) of the generated aromatic proton can be

assigned [18] either to C(2)-H or to C(4)-H, leaving the structural problem practically unsolved, but the angular structure (5) becomes the most likely one on the basis of the remarkable differences of the physical constants compared to those of the known [13] linear isomer (toxyloxanthone C; m.p. 290—291 °C; $[\alpha]_D = +59°$).

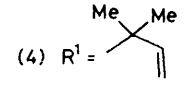




(2) R^1 = $R^2 = R^3 = H$



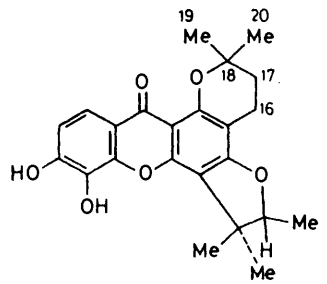
(3) R^1 = R^2 = Ac, R^3 = H



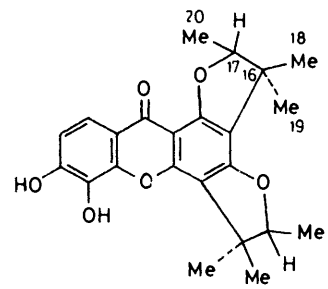
(4) R^1 = $R^2 = R^3$ = Ac

(5) $R^1 = R^2 = R^3 = H$

The other two products obtained from HCO_2H treatment were the fully cyclized compounds (6) and (7), whose ^1H n.m.r. spectra lacked the chelated hydroxy-group signal. Compounds (6) and (7) were obtained in better yield than the deprenylated one (5) by the action of 30% trifluoroacetic acid in chloroform overnight at room temperature; their formation definitively assigns the angular structure (2) to rheediaxanthone B, which was also confirmed by ^{13}C n.m.r. data comparison (see below). The difficult acetylation of the C(1)-OH under



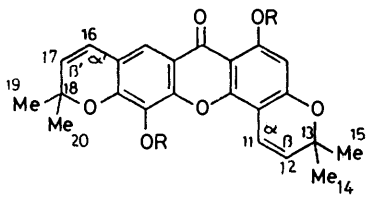
(6)



(7)

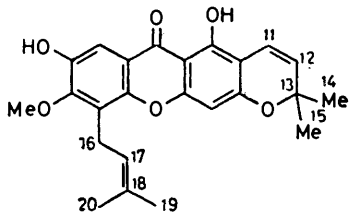
severe conditions may now be explained by the presence of the αα-dimethylallyl chain on C(2), as has been previously suggested.[10] The pyrano-compound (6) needs further comment: at first sight, its formation may appear unexpected, but we must consider the presence, in the reaction mixture, of compound (5) and of an active prenyl unit in a strong acid; these conditions, normally used in *C*-prenylation on aromatic substrates, may produce a C(2)-γγ-dimethylallyl intermediate, which subsequently cyclizes to (6) (*cf. e.g.* ref. 19). Structure (7) was assigned to rheediaxanthone C, also optically active, by comparison with compound (7), obtained from rheediaxanthone B.

Normally compounds isolated from plants and containing a trimethyl-dihydrofuran ring are considered probable artefacts of the true natural product, owing to cyclization of an αα-dimethylallyl chain on the adjacent phenolic hydroxy-group during chromatographic purification. The optical activity should exclude this possibility for rheediaxanthone B, but not for rheediaxanthone C; moreover, while the first product was certainly detected (t.l.c.) in the crude extract, the presence of the latter one was obscured by impurities. In conclusion, rheediaxanthone B is a true natural product, while some doubt still remains for rheediaxanthone C. To the best of our knowledge, only toxyloxan-



(8) R = H

(9) R = Ac



(10)

thone C has been previously reported [13] to be optically active.

The fourth pigment of *Rheedia benthamiana*, present in minor amount, was the optically inactive rheediaxanthone A, $C_{23}H_{20}O_6$ (M^+ at *m/z* 392). The u.v.–visible spectrum showed striking similarities to those of 1,3,5,6-tetraoxygenated xanthones with an extended chromophore, such as macluraxanthone (1) and jacareubin,[6,7] and the lack of change after addition of NaOAc (see Experimental section) indicated that both the C(3)-OH and C(6)-OH were not free. In the ^1H n.m.r. spectrum the presence of signals for two 2,2-dimethyl-2*H*-pyran rings, and of one-proton singlets at δ 13.15 [C(1)-OH], δ 7.37 (H^8) and 6.15 (H^2 or H^4) left only two possibilities, structure (8) or the isomeric one having pyran rings in a linear sequence, for rheediaxanthone A. The fomer one was preferred on the basis of the upfield shift (0.33 p.p.m.) of the aromatic proton (H^2) of ring A in the ^1H n.m.r. spectrum in [$^2H_6$]pyridine, showing its *ortho*-relationship with the C(1)-OH.[20] Additional support was provided by the ^1H n.m.r. spectrum of diacetyl-

rheediaxanthone A (9), which did not show the upfield shift expected for H_α in the alternative linear structure, as a consequence of the acetylation of the *peri*-C(1)-OH.[21]

^{13}C N.m.r. spectral data for the xanthones isolated and some of their derivatives are given in the Table, together with those of manglexanthone (10), previously isolated [22] from *Tovomita mangle* G. Mariz.

Compounds (1), (2), (5), (6), and (7) present an identical substitution pattern in ring B, as confirmed by the similarity of the C-13 shifts for C(5)—C(8). The chemical shift of the carboxy-group is diagnostic of C(1) in the SFORD spectrum of triplets at δ 30.5 and 16.5, whereas in (7) the signals of the dihydro-furan ring are coupled.

Structure (8) for rheediaxanthone A is confirmed by comparison of ring-A chemical shifts with the corresponding ones of (1), and in particular of (10). These differences cannot be attributed to the use of a different solvent (see chemical shifts of xanthone in $CDCl_3$ and in [$^2H_6$]DMSO [23]). The assignments of the pyran-ring olefinic carbons were made on the basis of corresponding values for (1) and (10), and similar models.[25]

^{13}C N.m.r. assignments [a]

	(1)	(2)	(5)	(6)	(7)	(8) [b]	(10) [c]
C(1)	157.7 [d]	163.7 [d]	165.1 [d]	155.6	159.2 [d]	166.5	159.4 [d]
C(2)	103.9 [e]	111.4	92.8	100.0	115.2 [e]	98.1	103.5 [e]
C(3)	155.3 [d]	161.9 [d]	163.3 [d]	160.9	158.2 [d]	162.1 [d]	156.4 [d]
C(4)	112.5	112.9 [e]	112.6	116.2	114.5 [e]	100.6	94.3
C(4a)	154.4 [d]	150.6	152.3	152.8	152.3	159.5 [d]	156.5 [d]
C(4b)	145.6	145.8	145.9	145.0	145.4	145.8	147.4 [f]
C(5)	132.5	132.5	132.6	132.3	132.3	133.0	123.1
C(6)	151.3	151.7	152.0	150.2	150.6	150.9	152.2
C(7)	112.7	112.6	112.7	112.0	111.9	118.2	147.7 [f]
C(8)	115.3	116.1	115.9	116.1	115.9	120.9	107.1
C(8a)	112.5	113.1 [e]	113.0	112.1	113.9 [e]	113.4	115.5
C(9)	180.1	180.1	179.6	173.4	173.1	179.5	179.4
C(9a)	102.1 [e]	102.3	102.2	105.6	102.4	102.2	102.3 [e]
C(11)	114.9	42.8	43.2	44.0	43.0 [f]	111.8	114.5
C(12)	127.1	89.3	90.3	90.2	90.2 [g]	131.0	127.8
C(13)	77.5	20.8	21.0	21.5	21.0 [h]	77.3 [e]	78.1
C(14)	27.1	25.2	25.1	25.6	25.1 [i]	27.7	28.0
C(15)	27.1	14.2	14.1	14.3	14.3 [j]	27.7	28.0
C(16)	40.3	40.2		16.5	43.3 [f]	114.8	22.6
C(17)	29.3	28.3		30.5	90.6 [g]	126.5	121.6
C(18)	29.3	28.3		75.2	21.3 [h]	77.6 [e]	130.5
C(19)	150.0	148.1		26.6	25.4 [i]	27.7	25.5
C(20)	107.2	108.4		26.6	14.4 [j]	27.7	17.8

[a] Chemical shifts in δ relative to $SiMe_4$; solvent [$^2H_6$]DMSO, unless otherwise noted. [b] In [$^2H_6$]DMSO–$CDCl_3$ (1 : 1). [c] δ (OMe) at 60.3. [d,e,f,g,h,i,j] In the same column, signals having the same letter may be interchanged.

substitution: formation of hydrogen-bonds shifts C(9) to *ca.* δ 180 whereas in xanthone it resonates at δ 176.1.[23] As confirmation, in compounds (6) and (7) C(9) is found to distinctly higher field. Comparison between the ^{13}C spectral data of (5) and those of toxyloxanthone C, reported by J. F. Castelao *et al.*,[23] confirms the non-identity of these compounds: the carbons of ring A show several differences, *e.g.* the aromatic methine is at δ 92.8 in (5) against δ 89.3. Furthermore in toxyloxanthone C signals at δ 102.7 and 116.1 were assigned to C(2) and C(9a), respectively. On the basis of the constancy of the C(9a) δ-value in the compounds examined, in particular (1) and (10), and by analogy with similar models,[24,25] we propose to reverse these assignments. On the contrary, other assignments are in good agreement, allowing for the different substitution of ring A.

In several assignments, analyses of coupled spectra were used in order to resolve ambiguities: *i.e.* C(6), C(5), and C(4a) show the expected splitting caused by a *meta*-hydrogen ($^3J_{CH}$), as well as C(4) in (5). The remaining uncertainties are not crucial to structural elucidations.

Thus the structure of (6) is confirmed by the presence

Finally, in (10) the 6 position for the methoxy-group was confirmed by its chemical shift, the *ortho-ortho*-disubstituted OMe carbon resonating at δ >60, instead of the normal value of δ 55—58.[26]

EXPERIMENTAL

U.v. spectra (EtOH) were recorded on a Beckmann Acta III, and i.r. spectra on a Perkin-Elmer 247, spectrophotometer, ^{13}C n.m.r. spectra on a Varian XL 100 operating at 25.2 MHz and ^1H n.m.r. spectra on a Varian EM 360 spectrometer. Mass spectra were run on an AEI 12 instrument at 70 eV. For optical rotations a Perkin-Elmer 141 apparatus was used. Column chromatography was performed on MN Kieselgel.

Plant Material.—The roots of *Rheedia benthamiana* Pl. Triana were collected in north-eastern Brazil (Municipio São Lourenço da Mata, Pernambuco) and identified by Dr. Marcelo de Ataide Silva (Instituto de Pesquisas agronomicas, Recife, Brazil). A voucher sample is kept in the Herbarium of Instituto de Antibioticos (Recife) under the cipher 4825.

Extraction and Purification.—The root bark (1.2 kg) was extracted twice with cold EtOH to give an orange-brown residue (250 g). The crude extract was dissolved in acetone, hexane was added, and the insoluble material discarded by centrifugation. The soluble portion was evaporated and

purified on a silica-gel column with benzene containing increasing quantities of ethyl acetate. Rheediaxanthone A (150 mg), macluraxanthone (1.1 g), rheediaxanthone B (1.4 g), and rheediaxanthone C (0.5 g) were successively eluted. Every xanthone was again purified by further chromatography or crystallization.

Macluraxanthone (1) crystallized from benzene–ethyl acetate, m.p. 181—183 and 204—206 °C (lit.,[7] m.p. 181—182 and 205—206 °C); $\lambda_{max.}$ 240, 284, 340, and 380 (sh) nm (log ε 4.23, 4.63, 4.19, and 3.94); δ ([$^2H_6$]acetone) 13.83 (1 H, s), 7.56 (1 H, d, *J* 8 Hz, H-8), 6.97 (1 H, d, *J* 8 Hz, H-7), 6.67 (1 H, d, *J* 10 Hz, H_α), 6.75—6.27 (1 H, X part of ABX system), 5.66 (1 H, d, *J* 10 Hz, H_β), 5.17—4.73 (2 H, AB part of ABX), 1.75 (6 H, s), and 1.50 (6 H, s); *m/z* 394 (M^+, 50%), 379 (100), 378 (68), 365 (8), 353 (10), 351 (12), 338 (8), and 182 (7).

Rheediaxanthone B (2), yellow-green crystals from benzene–ethyl acetate, m.p. 208—211 °C, $[\alpha]_D$ −27.3 (*c* 0.8, acetone) (Found: C, 69.75; H. 6.25. $C_{23}H_{24}O_6$ requires C, 69.68; H, 6.10%); $\lambda_{max.}$ 255, 290, and 333 nm (log ε 4.60, 4.02, 4.29); (+AcONa) 375; (+AcONa–H_3BO_3) 357; (+MeONa *) 374; (+$AlCl_3$ after 8 h [9]) 355 nm; $\nu_{max.}$ (KBr) 1 650, 1 620, 1 600, 1 560, 1 470, 1 420, 1 380, 1 340, 1 290, 1 180, 1 160, 1 110, 1 095, 1 060, 970, 935, 905, 880, 820, and 800 cm^{-1}; δ ([$^2H_6$]acetone) 14.30 (1 H, s), 7.63 (1 H, d, *J* 8 Hz, H-8), 6.97 (1 H, *J* 8 Hz, H-7), 6.55—6.08 (1 H, X part of ABX), 5.05—4.68 (2 H, AB part of ABX), 4.47 (1 H, q, *J* 7 Hz), 1.57 (9 H, s), 1.40 (3 H, d, *J* 7 Hz), and 1.33 (3 H, s); δ (C_5D_5N) 14.88 (1 H, s), 7.93 (1 H, d, *J* 8 Hz, H-8), 7.13 (1 H, d, *J* 8 Hz, H-7), 6.80—6.33 (1 H, X part of ABX), 5.23—4.87 (2 H, AB part of ABX), 4.40 (1 H, q, *J* 7 Hz), 1.76 (6 H, s), 1.70 (3 H, s), 1.38 (3 H, s), and 1.30 (3 H, d, *J* 7 Hz); *m/z* 396 (M^+, 50%), 381 (100), 380 (63), 367 (14), 355 (32), 341 (25), and 325 (11).

Acetylation with pyridine–acetic anhydride overnight at room temperature afforded the yellow diacetyl-derivative (3), m.p. 167—169 °C (CH_2Cl_2–heptane); δ ($CDCl_3$) 13.65 (1 H, s), 8.10 (1 H, d, *J* 8.5 Hz, H-8), 7.13 (1 H, *J* 8.5 Hz H-7), 6.55—6.07 (1 H, X part of ABX), 5.05—4.70 (2 H, AB part of ABX), 4.40 (1 H, q, *J* 7 Hz), 2.38 (3 H, s), 2.32 (3 H, s), 1.56 (6 H, s), 1.48 (3 H, s), 1.37 (3 H, d, *J* 7 Hz), and 1.23 (3 H, s).

Refluxing (3) (20 h) in Ac_2O–AcONa, standard work-up, and chromatographic separation gave unreacted (3) and the light yellow triacetyl-derivative (4) in 50% yield, m.p. 152—153 °C (CH_2Cl_2–heptane); δ ($CDCl_3$) 8.10 (1 H, d, *J* 8.5 Hz, H-8), 7.13 (1 H, d, *J* 8.5 Hz, H-7), 6.50—6.02 (1 H, X part of ABX), 5.10—4.73 (2 H, AB part of ABX), 4.45 (1 H, q, *J* 7 Hz), 2.41 (3 H, s), 2.38 (3 H, s), 2.33 (3 H, s), 1.55 (9 H, s), 1.40 (3 H, d, *J* 7 Hz), and 1.28 (3 H, s).

Action of Acids on Rheediaxanthone B.—(*a*) Rheediaxanthone B (120 mg) was refluxed for 45 min in HCO_2H. The reaction mixture was separated on a silica-gel column: the deprenylated rheediaxanthone (5) (78 mg) was eluted with benzene–ethyl acetate (8 : 2); the cyclo-derivatives (6) (20 mg) and (7) (12 mg) were eluted with benzene–ethyl acetate (1 : 1).

(*b*) Rheediaxanthone B (105 mg) in $CHCl_3$ containing 30% trifluoroacetic acid was left at room temperature for 16 h. The mixture was evaporated and separated as above to yield unreacted (2) (10 mg), (5) (18 mg), (6) (32 mg), and (7) (40 mg).

Deprenylated rheediaxanthone (5), m.p. 207—208 °C (ethyl acetate–heptane); $[\alpha]_D$ −34.5 (*c* 0.7, acetone); $\lambda_{max.}$ 255, 289, and 331 nm (log ε 4.62, 4.05, 4.27); (+$AlCl_3$) 358 nm; $\nu_{max.}$ 1 650, 1 620, 1 600, and 1 580 cm^{-1}; δ ([$^2H_6$]acetone) 13.46 (1 H, s), 7.63 (1 H, d, *J* 8 Hz, H-8), 6.98 (1 H, d, *J* 8 Hz, H-7), 6.12 (1 H, s, H-2), 4.52 (1 H, q, *J* 7 Hz), 1.65 (3 H, s), 1.43 (3 H, d, *J* 7 Hz), and 1.35 (3 H, s); δ (C_5D_5N) 14.0 (1 H, s), 7.87 (1 H, d, *J* 8 Hz, H-8), 7.13 (1 H, d, *J* 8 Hz, H-7), 6.40 (1 H, s, H-2), 4.47 (1 H, q, *J* 7 Hz), 1.70 (3 H, s), 1.37 (3 H, s), and 1.32 (3 H, d, *J* 7 Hz); *m/z* 328 (M^+, 27%), 313 (100), 298 (14), 285 (17), 269 (5), 257 (6), and 149 (11).

Cyclo-derivative (6), m.p. 258—261 °C (CH_2Cl_2–heptane); $[\alpha]_D$ −25.7 (*c* 0.6, acetone); $\lambda_{max.}$ 254, 291, and 320 nm (log ε 4.71, 4.17, and 4.34); $\nu_{max.}$ (KBr) 1 630—1 600 and 1 560 cm^{-1}; δ ($CDCl_3$) 7.70 (1 H, d, *J* 8 Hz, H-8), 7.0 (1 H, d, *J* 7 Hz, H-7), 4.47 (1 H, q, *J* 7 Hz), 2.68 (2 H, t, *J* 6.5 Hz), 1.80 (2 H, t, *J* 6.5 Hz), 1.63 (3 H, s), and 1.45—1.30 (12 H); *m/z* 396 (M^+, 40%), 381 (100), 353 (7), 341 (43), 325 (46), 313 (12), 311 (13), 297 (7), 285 (10), and 183 (7).

Cyclo-derivative (7), m.p. 207—209 °C (CH_2Cl_2), $[\alpha]_D$ −16.3 (*c* 0.5, acetone); for spectral data see rheediaxanthone C.

Rheediaxanthone C (7), light yellow crystals (from CH_2Cl_2–heptane), m.p. 260—263 °C; $[\alpha]_D$ −24.3 (*c* 0.91, acetone) (Found: C, 69.8; H, 6.2. $C_{23}H_{24}O_6$ requires C, 69.68; H, 6.10%); $\lambda_{max.}$ 256, 290, and 319 nm (log ε 4.66, 4.13, 4.27); (+AcONa) 348; (+AcONa–H_3BO_3) 341; (+MeONa*) 355; (+$AlCl_3$) 319 nm; $\nu_{max.}$ (KBr) 1 640—1 600, 1 520, 1 470, 1 430, 1 380, 1 370, 1 320, 1 200, 1 130, 1 090, 1 055, 970, 930, 860, 830, and 800 cm^{-1}; δ ([$^2H_6$]acetone) 7.53 (1 H, d, *J* 8 Hz, H-8), 6.89 (1 H, d, *J* 8 Hz, H-7), 4.53 and 4.43 (2 H, q, *J* 7 Hz, partially superimposed), and 1.63—1.15 (18 H); δ (C_5D_5N) 8.0 (1 H, d, *J* 8 Hz, H-8), 7.10 (1 H, d, *J* 8 Hz, H-7), 4.50 (2 H, q, *J* 7 Hz), 1.73 (3 H, s), 1.38 (9 H, s), and 1.23 (6 H, d, *J* 7 Hz); *m/z* 396 (M^+, 25%), 381 (100), 351 (6), 313 (11), and 198 (4).

Rheediaxanthone A (8), yellow crystals (from benzene–ethyl acetate), m.p. 259—261 °C (Found: C, 70.35; H, 5.20. $C_{23}H_{20}O_6$ requires C, 70.40; H, 5.14%); $\lambda_{max.}$ 278, 335, and 385(sh) nm (log ε 4.77, 4.06, 3.82); (+AcONa) unaltered; (+MeONa) 400; (+$AlCl_3$) 425 nm; $\nu_{max.}$ (KBr) 1 640, 1 560, 1 490, 1 470, 1 425, 1 405, 1 395, 1 370, 1 325, 1 300, 1 260, 1 240, 1 190, 1 145, 1 120, 1 100, 925, 880, and 800 cm^{-1}; δ ([$^2H_6$]acetone) 13.15 (1 H, s), 7.37 (1 H, s, H-8), 6.90 (1 H, d, *J* 10 Hz, H_α), 6.50 (1 H, d, *J* 10 Hz, H_α'), 6.15 (1 H, s, H-2), 6.00 (1 H, d, *J* 10 Hz, H_β), 5.70 (1 H, d, *J* 10 Hz, H_β'), 1.47 (6 H, s), and 1.44 (6 H, s); δ (C_5D_5N) 13.70 (1 H, s), 7.63 (1 H, s, H-8), 7.00 (1 H, d, *J* 10 Hz, H_α), 6.43 (1 H, s, H-2), 6.40 (1 H, d, *J* 10 Hz, H_α'), 5.63 (1 H, d, *J* 10 Hz, H_β), 5.47 (1 H, d, *J* 10 Hz, H_β'), 1.40 (6 H, s), and 1.27 (6 H, s); *m/z* 392 (M^+, 26%), 377 (100), 362 (4), 361 (10), 347 (8), 203 (8), and 182 (30).

Acetylation with pyridine–acetic anhydride overnight at room temperature afforded the diacetyl derivative (9), white crystals (from CH_2Cl_2–heptane), m.p. 208—210 °C; δ ($CDCl_3$) 7.70 (1 H, s, H-8), 6.66 (1 H, d, *J* 10 Hz, H_α), 6.40 (1 H, s, H-2), 6.34 (1 H, d, *J* 10 Hz, H_α'), 5.63 (2 H, d, *J* 10 Hz, H_β, H_β'), 2.43 (6 H, s), 1.47 (6 H, s), and 1.44 (6 H, s); δ ([$^2H_6$]acetone) 7.83 (1 H, s, H-8), 6.73 (1 H, d, *J* 10 Hz, H_α), 6.50 (1 H, d, *J* 10 Hz, H_α'), 6.43 (1 H, s, H-2), 5.83 (2 H, d, *J* 10 Hz, H_β, H_β'), 2.42 (3 H, s), 2.32 (3 H, s), 1.47 (6 H, s), and 1.43 (6 H, s).

One of us (J. S. B. C.) thanks the Conelho Nacional de Pesquises, Brazil, for a fellowship.

[0/780 *Received*, 22*nd May*, 1980]

* The yellow solution becomes colourless in a few hours.

REFERENCES

[1] J. C. Roberts, *Chem. Rev.*, 1961, **61**, 591.
[2] I. Carpenter, H. D. Locksley, and F. Scheinmann, *Phytochemistry*, 1969, **8**, 2013.
[3] C. M. Andrade da Mata Rezende, and O. R. Gottlieb, *Biochem. Systematics*, 1973, **1**, 111.
[4] K. Hostettmann and H. Wagner, *Phytochemistry*, 1977, **16**, 821.
[5] R. Braz Filho, G. Cavalcante de Magalhães, and O. R. Gottlieb, *Phytochemistry*, 1970, **9**, 673.
[6] M. L. Wolfrom, F. Komitsky, jun., G. Fraenkel, J. H. Looker, E. E. Dickey, P. McWain, A. Thompson, P. M. Mundell, and O. M. Windrath, *J. Org. Chem.*, 1964, **29**, 692.
[7] M. L. Wolfrom, E. E. Dickey, P. McWain, A. Thompson, J. H. Looker, O. M. Windrath, and T. Komitsky, jun., *J. Org. Chem.*, 1964, **29**, 689.
[8] S. P. Gunasekera, S. Selliah, and M. U. S. Sultanbawa, *J.C.S. Perkin I*, 1975, 1539.
[9] R. Alves de Lima and G. Delle Monache, *Rend. Acad. Naz. dei XL (Roma)*, 1977—8, (V), **3**, 181.
[10] M. L. Wolfrom, F. Komitsky, jun., and P. M. Mundell, *J. Org. Chem.*, 1965, **30**, 1088.
[11] B. Jackson, H. D. Locksley, and F. Scheinmann, *J. Chem. Soc.* (*C*), 1966, 178.
[12] H. D. Locksley, I. Moore, and F. Scheinmann, *J. Chem. Soc.* (*C*), 1966, 2265.
[13] V. H. Deshpande, A. V. Rama Rao, M. Varadan, and K. Venkataraman, *Indian J. Chem.*, 1973, **11**, 518.
[14] A. A. Lins Mesquita, D. De Barros Corrêa, O. R. Gottlieb, and M. Taveira Magalhães, *Anal. Chim. Acta*, 1968, **42**, 311.
[15] E. D. Burling, A. Jefferson, and F. Scheinmann, *Tetrahedron*, 1965, **21**, 2553.
[16] H. D. Locksley and I. G. Murray, *J. Chem. Soc.* (*C*), 1971, 1332.
[17] H. D. Locksley, A. J. Quillinan, and F. Scheinmann, *J. Chem. Soc.* (*C*), 1971, 3804.
[18] D. Barraclough, H. D. Locksley, F. Scheinmann, M. Taveira Magalhães, and O. R. Gottlieb, *J. Chem. Soc.* (*B*), 1970, 603.
[19] F. Delle Monache, O. G. De Lima, J. F. De Mello, G. Delle Monache, and G. B. Marini Bettolo, *Gazzetta*, 1973, **103**, 779.
[20] F. Delle Monache, M. Marquina Mac-Quhae, F. Ferrari, and G. B. Marini Bettolo, *Tetrahedron*, 1979, **35**, 2143 and refs. cited therein.
[21] A. Arnone, G. Cardillo, L. Merlini, and R. Mondelli, *Tetrahedron Letters*, 1967, 4201.
[22] M. Marta, F. Delle Monache, G. B. Marini Bettolo, D. Andrade Lyra, J. F. De Mello, and O. G. De Lima, *Gazzetta*, 1976, **106**, 651.
[23] J. F. Castelão, jun., O. R. Gottlieb, R. A. De Lima, A. A. Lins Mesquita, H. E. Gottlieb, and E. Wenkert, *Phytochemistry*, 1977, **16**, 735.
[24] M. Sum b. Hj. Idris, A. Jefferson, and F. Scheinmann, *J.C.S. Perkin I*, 1977, 2158.
[25] E. Wenkert and H. E. Gottlieb, *Phytochemistry*, 1977, **16**, 1811.
[26] T. Nakano, J. Alonso, R. Grillet, and A. Martin, *J.C.S. Perkin I*, 1979, 2107.