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CHEMICAL INVESTIGATION OF THE GENUS *RHEEDIA*, IV.[1] THREE NEW XANTHONES FROM *RHEEDIA BRASILIENSIS*[2]

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ABSTRACT.—The structures of three new prenylated xanthones, isolated from the root bark extract of *Rheedia brasiliensis*, were established as 4″,5″-dihydro-1,5-dihydroxy-6′,6′-dimethylpyrano (2′,3′:6,7)-4″,4″,5″-trimethylfurano (2″,3″:3,4) xanthone (**1**); 1,3,5-trihydroxy-6′,6′ dimethylpyrano (2′,3′:6,7)-4-(1,2-dimethylprop-2-enyl) xanthone (**2**); and 1,3,5,6-tetrahydroxy-4-(1,1-dimethylprop-2-enyl)-7-(3-methylbut-2-enyl) xanthone (**3**).

Following our examination (1-3) of the genus *Rheedia*, which has afforded several prenylated xanthones, we have studied the C_6H_6 extract of the root bark of *Rheedia brasiliensis* (Martius) Pl. and Tr. A preliminary tlc comparison showed the main components to be the same as those in the roots of *Rheedia benthamiana* Pl. and Tr. (1) and *Rheedia gardneriana* Pl. and Tr. (2), *i.e.*, rheediaxanthone B (1) and a polyprenylated benzophenone, whose structure will be the object of a future communication. Extended cc and plc afforded the known macluraxanthone, rheediaxanthones A and C (1), rheediachromenoxanthone, isorheediaxanthone B (2), 8-deoxygartanin, and pyranojacareubin (3)—all described in our previous papers. Three new xanthones, whose structure determination is the object of this paper, have been isolated.

RESULTS AND DISCUSSION

Tlc on silica gel with C_6H_6-EtOAc (9:1) separated the three compounds: $C_{23}H_{22}O_6$ (Rf=0.65), $C_{23}H_{22}O_6$ (Rf=0.50), and $C_{23}H_{24}O_6$ (Rf=0.45), to which the structures **1, 2,** and **3** were attributed, respectively. The pmr spectra disclosed, in addition to the common signals of two isolated aromatic H and a chelated OH, the following prenyl substituents: a 2,2-dimethyl-2H-pyran ring and a 2,3-dihydro-2,3,3-trimethylfuran ring in **1**; a 2,2-dimethyl-2H-pyran ring and a 1,1-dimethylprop-2-enyl chain in **2**; a 3-methylbut-2-enyl and a 1,1-dimethylprop-2-enyl chain in **3**.

All the compounds showed a 1,3,5,6-tetraoxygenated xanthone chromophore (Table 1), conjugated with the pyran ring in the former two (shoulder at 365 nm in the uv spectrum) (2). Ring B substitution pattern in compounds **1** and **2** was determined by comparison of their pmr resonances and those of the derivatives **1a, 2a,** and **2b** with the signals of analogous pyranoxanthones and their acetylderivatives (1-3).

An immediate shift of the uv maximum with $AlCl_3$ (4) in the spectrum of the three compounds was consistent with the presence of an isolated H-2 proton (high field singlet in the pmr spectrum); the chemical shift of this proton was similar but underwent a larger paramagnetic shift with C_5D_5N (5) in compounds **2** and **3**, in accordance with the presence of a free 3-OH (shift with AcONa of the uv maximum). The furan

[1]For part II of the series, see Delle Monache, *et al.* (3).

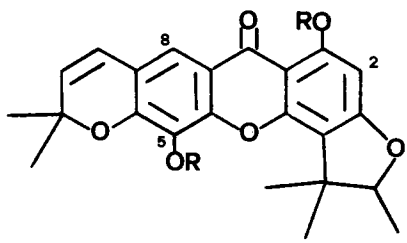
[2]A preliminary communication was presented at the Second International Conference on Chemistry and Biotechnology of Biologically Active Natural Products held in Budapest, 15-19 August 1983.

TABLE 1. Uv Spectra (MeOH) of 1,3,5,6-Tetraoxygenated Xanthones from the Genus *Rheedia* [λ max (log ε)]

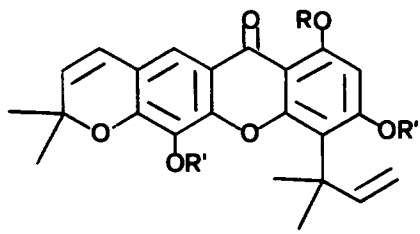
Xanthone	Reference	Conjugated		
Macluraxanthone	1	284(4.63)	340(4.19)	380sh(3.94)
Rheediaxanthone A	1	278(4.77)	335(4.06)	385sh(3.82)
Pyranojacareubin	3	288,296(4.71)	346(4.10)	395sh(3.72)
1		286(4.50)	326(4.35)	363sh(3.92)
2		277(4.62)	327(4.11)	364sh(3.88)
		Not conjugated		
Rheediaxanthone B	1	255(4.60)	290(4.02)	332(4.29)
Rheediaxanthone C	1	265(4.66)	290(4.13)	319(4.27)
Isorheediaxanthone B	2	256(4.68)	288(4.25)	332(4.43)
3		253(4.55)	288(4.02)	328(4.30)

ring in **1** must therefore be closed at C-4; similarly, the propenyl chain was placed at C-4 for **2** and **3**, this assignment being in agreement with the *gem*-dimethyl resonance values: δ 2.11 and 2.05 in C_5D_5N, respectively (2).

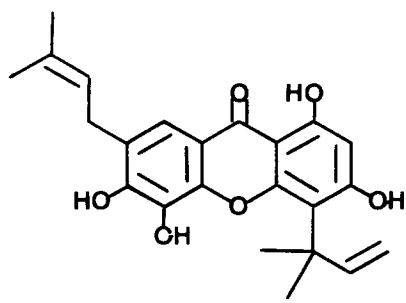
The shifts of the uv maxima with $AcONa/H_3BO_3$ and $AlCl_3/HCl$ (6) finally evidenced two *ortho*-dihydroxy groups (in 5 and 6 positions) in the compound **3**, while the loss of 56 mu from the base peak $M\text{-}CH_3^{\neg+}$ in the mass spectrum (7) confirmed the placement of the γ,γ-dimethylallyl chain at C-7. On the basis of the above considerations, the structures **1, 2,** and **3** were assigned to the three xanthones. Compound **2** was



1 R=H
1a R=$COCH_3$



2 R=R′=H
2a R=H R′=$COCH_3$
2b R=R′=$COCH_3$



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linked to compound **1** by conversion of the former into the latter. During the cc separation, some fractions of **2**, on checking by tlc, were contaminated by traces of **1**, which was absent in previous eluates. Transformation of **2** into **1** in the presence of SiO_2 was postulated and confirmed experimentally. A pure sample of **2** gave on $SiO_2/CHCl_3$ a mixture of **1** and **2** in a few days, and after 3 months, the conversion was almost complete. Compound **1** is probably not an artifact because it was present in the original extract and showed optical activity, but is formation from **2** (in the presence of SiO_2) may account for the measured low α-value.

The action of stronger acids on **2** was also investigated after consideration of the results obtained with rheediaxanthone B (2). Compound **2** with TFA yielded a mixture of four (at least) substances whose structures were nevertheless determined. The less polar products were identified with compound **1** and the two isomeric chromanoxanthones **4** and **5**, whose structures followed from consideration of pmr spectra in CD_3COCD_3 and C_5D_5N (5) and uv spectra with additives (4, 6).

Structure **6** was attributed to a third polar isomeric chromanoxanthone by the same considerations (summarized in Table 2). With HCOOH, **2** gave the same products as with TFA plus a second polar compound, whose structure was determined as **7**. The product **7**, $C_{18}H_{16}O_6$ (MW 326), still contains the pyran moiety on the ring B, but the two *meta*-coupled protons in the pmr spectrum are evidently H-2 and the new H-4, originated by the elimination of the α,α-dimethylallyl chain (1, 2).

TABLE 2. Comparison of Spectral Data of the Isomeric Chromanoxanthones Yielded by Action of Acids on Compound **2**

	Reference	4	5	6
Shift induced in the uv spectrum by $AlCl_3$	4,6	immediate	delayed	no shift
Shift induced in the uv spectrum by AcONa	4	no shift	no shift	bathochromic
δ(CD_3COCD_3) of ring A isolated H		6.14	6.42	6.41
δ(C_5D_5N)-δ(CD_3COCD_3)	5	+0.36	+0.10	+0.36
Shift induced by C_5D_5N on αCH_2	4	diamagnetic	paramagnetic	paramagnetic

Compounds **3** and **2** were also linked chemically, the former giving the latter as the main product on boiling with DDQ in C_6H_6.

Finally, we want to emphasize the presence in the mass spectra of these diprenylated xanthones of several doubly charged ions. Particularly when the prenyl substituents are cyclized, very intense peaks are found at *m/z* values corresponding with doubly charged ions formed by the losses of two radicals (Me+Me or Me+C_4H_7).

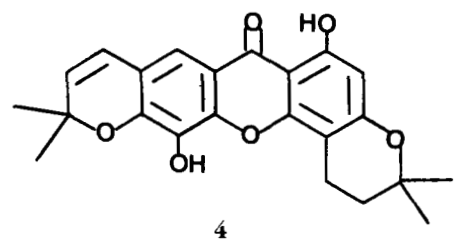
EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Elemental analyses were in agreement with molecular formulas. Mps were determined by means of a Kofler hot plate and are uncorrected. Spectra were recorded with the following instruments: uv, Beckmann Acta III; pmr, Varian EM 360; ms, AEI MS-12. Absorbents used were from E. Merck (plc and tlc) and Macherey-Nagel (cc).

PLANT MATERIAL.—Root bark of *R. brasiliensis* was collected in Northeastern Brazil (S. Lourenço, Pernambuco) and identified by Alda Chiappetta (Departamento de Antibioticos, U.F.Pe., Recife).

EXTRACTION AND SEPARATION OF THE XANTHONES.—Extraction with hot C_6H_6 of the root bark of the plant (43 g) gave a residue (4.5 g), which was fractionated on a silica gel coumn with hexane-EtOAc, 4:1.

Each fraction was rechromatographed over silica gel with $CHCl_3$ or C_6H_6-EtOAc mixtures. The pure xanthones were finally obtained by plc and by crystallization.



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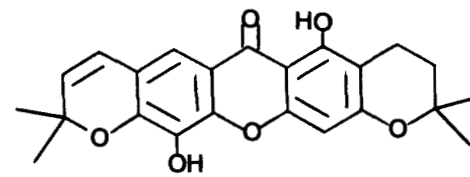

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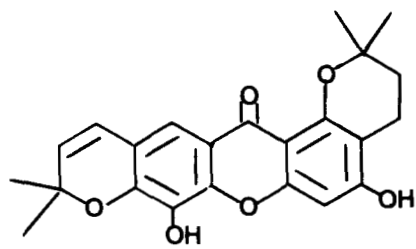

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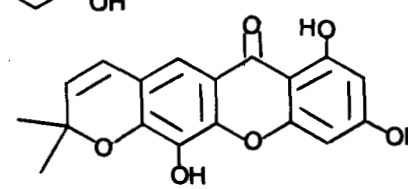

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Macluraxanthone, rheediaxanthones A, B, and C (1), rheediachromenoxanthone, isorheediaxanthone B (2), 8-deoxygartanin, and pyranojacareubin (3) were isolated and identified by comparison with authentic samples. The three new xanthones (**1, 2,** and**3**) were isolated in low yield.

4",5"-Dihydro-1,5-dihydroxy-6',6'-dimethylpyrano (2',3':6,7)-4",4",5"-trimethylfurano (2",3":3,4)-xanthone: (**1**, 60 mg); $C_{23}H_{22}O_6$, mp 194-195° (Et_2O-hexane), $[\alpha]^{20}D=-6$ (0.4, $CHCl_3$); pmr δ ($CDCl_3$): 12.10 (1H, br, ex. D_2O, 1-OH), 7.42 (1H, s, H-8), 6.40 (1H, d, $J=10$ Hz, H-4'), 6.20 (1H, s, H-2), 5.70 (1H, d, $J=10$ Hz, H-5'), 5.10 (1H, br, ex. D_2O, 5-OH), 4.53 (1H, q, $J=7$ Hz, H-5"), 1.59+1.32 (3H+3H, s+s, 4"-Me_2), 1.50 (6H, s, 6'-Me_2), 1.41 (3H, d, $J=7$ Hz, 5'-Me); Δδ=δ (C_5D_5N)-δ ($CDCl_3$): H-8 (+0.26), H-2 (+0.28), H-4' (+0.05), H-5' (−0.05); uv λ max (MeOH): in Table 1; (AcONa and MeONa): 280, 331, 362 sh: ($AlCl_3$): 250, 292, 364, 419; ms *m/z* (rel. int.): 394 (M^+, 31), 393 (9), 379 (M-Me, 100), 363 (9), 351 (10), 349 (14), 295 (9), 197 (M/2, 7), 189 (10), 182 (M-2Me/2, 28), 174 (13), 168 (13), 154 (M-2Me-CO/2, 34).

Diacetylderivative, (**1a**): $C_{27}H_{26}O_8$, mp 162-163° (Et_2O-hexane); pmr δ ($CDCl_3$): 7.68 (1H, s, H-8), 6.39 (1H, s, H-2), 6.34 (1H, d, $J=10$ Hz, H-4'), 5.64 (1H, d, $J=10$ Hz, H-5'), 4.54 (1H, q, $J=7$ Hz, H-5"), 2.45+2.43 (3H+3H, s+s, 2×COMe), 1.58+1.28 (3H+3H, s+s, 4"-Me), 1.44 (6H, s, 6'-Me), 1.42 (3H, d, $J=7$ Hz, 5"-Me).

1,3,5-Trihydroxy-6',6'-dimethylpyrano (2',3':6,7)-4-(1,1-dimethylprop-2-enyl)-xanthone: (**2**, 160 mg); $C_{23}H_{22}O_6$, mp 188-189° (Et_2O-hexane); pmr δ ($CDCl_3$): 13.20 (1H, s, ex. D_2O, 1-OH), 7.50 (1H, br, ex. D_2O, 3-OH), 7.38 (1H, s, H-8), 6.96-6.30 (1H, A part of AXY), 6.39 (1H, d, $J=10$ Hz, H-4'), 6.24 (1H, s, H-2), 5.80 (1H, br, ex. D_2O, 5-OH), 5.67 (1H, d, $J=10$ Hz, H-5'), 5.54-5.14 (2H, XY part of AXY), 1.73 (6H, s, propenyl-Me_2), 1.50 (6H, s, 6'-Me_2); Δδ=δ (C_5D_5N)-δ ($CDCl_3$): H-8 (+0.24), H-2 (+0.42), H-4' (+0.02), H-5' (−0.07), propenyl-Me_2 (+0.38), 6'-Me_2 (−0.26); uv λ max (MeOH): in Table 1; (AcONa): 274, 368; ($AlCl_3$): 247, 288, 363, 402 sh; ms *m/z* (rel. int.): 394 (M+, 39), 393 (15), 379 (M-Me, 100), 363 (5), 351 (6), 349 (9), 295 (3), 197 (M/2, 3), 189 (4), 182 (M-2Me/2, 10), 174 (4), 168 (3), 154 (M-2Me-CO/2, 6).

Acetylderivatives: **2** (35 mg) was left in pyr/Ac_2O for 3 days; standard work gave a mixture of two products, separated by plc ($CHCl_3$): *3,5-Diacetylderivative.* (**2a,** 14 mg): $C_{27}H_{26}O_8$, mp 219-221° (Et_2O-hexane); pmr δ ($CDCl_3$): 12.60 (1H, s, ex. D_2O, 1-OH), 7.71 (1H, s, H-8), 6.54-6.00 (1H, A part of

AXY), 6.40 (1H, d, J=10 Hz, H-4'), 6.36 (1H, s, H-2), 5.72 (1H, d, J=10 H-5'), 5.05-4.70 (2H, XY part of AXY), 2.38 (3H, s, 5-OCOMe), 2.20 (3H, s, 3-OCOMe), 1.61 (6H, s, propenyl-me_2), 1.47 (6H, s, 6'-Me_2). *1,3,5-Triacetylderivative,* (**2b,** 26 mg); $C_{29}H_{28}O_9$, mp 165-166° (Et_2O-hexane); pmr δ ($CDCl_3$): 7.71 (1H, s, H-8), 6.60 (1H, s, H-2), 6.56-6.04 (1H, A part of AXY), 6.38 (1H, d, J=10 Hz, H-4'), 5.70 (1H, d, J=10 Hz, H-5'), 5.08-4.70 (2H, XY part of AXY), 2.41 (3H, s, 1-OCOMe), 2.38 (3H, s, 5-OCOMe), 2.20 (3H, s, 3-OCOMe), 1.64 (6H, s, propenyl-Me_2), 1.43 (6H, s, 6'-Me_2).

Action of acids on compound **2**: Compound **2** (40 mg) was left in $CHCl_3$ (3.6 ml) and TFA (0.4 ml) overnight. The reaction mixture on plc ($CHCl_3$-MeOH, 99:1) was separated in two fractions: the former (15 mg) on plc (C_6H_6×2) gave compounds **1**,**4**, and **5**; the latter (20 mg) on plc ($CHCl_3$-MeOH, 98:2) gave compound **6**.

Compound **2** (60 mg) was held at reflux in HCOOH (6 ml) for 45 min. The mixture was separated on silica gel column in two fractions ($CHCl_3$ and $CHCl_3$-MeOH, 98:2): the former (25 mg) gave on plc (C_6H_6×2) the products **1**, **4**, and **5**, while the latter (30 mg) yielded compounds **6** and **7**.

1,5-Dihydroxy-6',6'-dimethyl-2H-pyran (2',3': 6,7)-6'',6''-dimethyl-2H, 4H-pyran (2'',3'': 3,4)-xanthone, (**4**): $C_{23}H_{22}O_6$, mp 188-190° (Et_2O); pmr δ (CD_3COCD_3): 7.45 (1H, s, H-8), 6.60 (1H, d, J=10 Hz, H-4'), 6.14 (1H, s, H-2), 5.92 (1H, d, J=10 Hz, H-5'), 2.92 (2H, t, J=6 Hz, 4''-CH_2), 1.93 (2H, t, J=6 Hz, 5''-CH_2), 1.50 (6H, s, 6'-Me_2), 1.39 (6H, s, 6''-Me_2); Δδ=δ (C_5D_5N)-δ (CD_3COCD_3): H-8 (+0.30), H-2 (+0.36), H-4 (−0.10), H-5' (−0.24), 4''-CH_2 (−0.09), 5''-CH_2 (−0.28); uv λ max (MeOH): 274 (log ε 4.70), 330 (4.18), 364 sh (3.74); ($AlCl_3$ immediate): 245, 253, 287, 362, 416 sh; (MeONa) 280, 332, 380 sh; ms *m/z* (rel. int.): 394 (M^+, 43), 393 (23), 379 (M-Me, 100), 339 (M-C_4H_7, 32), 337 (34), 233 (M-Me-C_4H_8, 39), 295 (8), 197 (M/2, 4), 189.5 (M-Me/2, 8), 182 (M-2Me/2, 38), 175 (M-Me-CHO/2, 9), 162 (M-Me-C_4H_7/2, 49).

1,5-Dihydroxy-6',6'-dimethyl-2H-pyran (2',3': 6,7)-6'',6''-dimethyl-2H, 4H-pyran (2'',3'': 2,3)-xanthone, (**5**): $C_{23}H_{22}O_6$, mp 202-204° (Et_2O); pmr δ (CD_3COCD_3): 7.44 (1H, s, H-8), 6.58 (1H, d, J=10 Hz, H-4'), 6.42 (1H, s, H-4), 5.90 (1H, d, J=10 Hz, H-5'), 2.70 (2H, t, J=6 Hz, 4''-CH_2), 1.89 (2H, t, J=6 Hz, 5''-CH_2), 1.49 (6H, s, 6'-Me_2), 1.38 (6H, s, 6''-Me_2); Δδ=δ (C_5D_5N)-δ (CD_3COCD_3): H-8 (+0.30), H-4 (+0.10), H-4' (−0.09), H-5' (−0.23), 4''CH_2 (+0.03), 5''-CH_2 (−0.24); uv λ max (MeOH); 276 (log ε 4.70), 332 (4.18), 372 sh (3.78); ($AlCl_3$ after 20 min.): 243, 252 sh, 287, 365, 414 sh; (MeONa): 282, 329, 380 sh; ms *m/z* (rel. int.): 394 (M^+, 50), 393 (27), 379 (M-Me, 100), 339 (M-C_4H_7, 20), 337 (27), 323 (M-Me-C_4H_8, 65), 295 (8), 197 (M/2, 4), 189.5 (M-Me/2, 7), 182 (M-2M/2, 20), 175 (M-Me-CHO/2, 11), 168 (M-2Me-CO/2, 7), 162 (M-Me-C_4H_7/2, 60).

3,5-Dihydroxy-6',6'-dimethyl-2H-pyran (2',3': 6,7)-6'',6''-dimethyl-2H, 4H-pyran (2'',3'': 1,2)-xanthone, (**6**): $C_{23}H_{22}O_6$, mp 306-306° ($CHCl_3$-MeOH); pmr δ (CD_3COCD_3): 7.37 (1H, s, H-8), 6.52 (1H, d, J=10 Hz, H-4'), 6.41 (1H, s, H-4), 5.82 (1H, d, J=10 Hz, H-5'), 2.70 (2H, t, J=6 Hz, 4''-CH_2), 1.83 (2H, t, J=6 Hz, 5''-CH_2), 1.46 (6H, s, 6'-Me_2), 1.39 (6H, s, 6''-Me_2); Δδ=δ (C_5D_5N)-δ (CD_3COCD_3): H-8 (+0.55), H-4 (+0.34), H-4' (−0.09), H-5' (−0.25), 4''-CH_2 (+0.18), 5''-CH_2 (−0.09); uv λ max (MeOH and $AlCl_3$): 275 (log ε 4.70), 306 (4.18), 356 sh (3.87); (AcONa): 275, 350; (MeONa): 283, 330, 356; ms *m/z* (rel. int.): 394 (M^+, 30), 393 (7), 379 (M-Me, 100), 339 (M-C_4H_7, 24), 337 (39), 323 (M-Me-C_4H_8, 66), 295 (6), 197 (M/2, 4), 189.5 (M-Me/2, 8), 182 (M-2Me/2, 24), 175 (M-Me-CHO/2, 18), 168 (M-2Me-CO/2, 12), 162(M-Me-C_4H_7/2, 75).

1,3,5-Trihydroxy-6',6'-dimethyl-2H-pyran (2',3':6,7)-xanthone, (**7**): $C_{18}H_{14}O_6$, mp 315° ($CHCl_3$-MeOH); pmr δ (CD_3COCD_3); 7.42 (1H, s, H-8), 6.57 (1H, d, J=10 Hz, H-4'), 6.45 (1H, d, J=2 Hz, H-4), 6.22 (1H, d, J= Hz, H-2), 5.86 (1H, d, J=10 Hz, H-5'), 1.49 (6H, s, 6'-Me_2); Δδ=δ (C_5D_5N)-δ (CD_3COCD_3): H-8 (+0.21), H-4 (+0.25), H-2 (+0.41), H-4' (−0.09), H-5' (−0.18); uv λ max (MeOH): 273 (log ε 4.46), 330 (3.95), 366 sh (3.72); ($AlCl_3$); 241, 250 sh, 283, 361, 402 sh; (AcONa): 273, 290 sh, 350; (MeONa): 260 sh, 232, 268; ms *m/z* (rel. int): 326 (M^+, 45), 325 (20), 311 (M-Me, 100), 309 (M-OH, 4), 297 (M-CHO, 5), 282 (M-Me-CHO, 3), 163 (M/2, 3), 155.5 (M-Me/2, 19), 154.5 (M-OH/2, 8).

1,3,5,6-Tetrahydroxy-4 (1,1-dimethylprop-2-enyl)-7 (3-methylbut-2-enyl)-xanthone: (**3**, 35 mg), $C_{23}H_{24}O_6$, mp 173-174° (Et_2O-hexane); pmr δ (CD_3COCD_3): 13.40 (1H, s, ex. D_2O, 1-OH), 7.46 (1H, s, H-8), 6.90-6.30 (1H, A part of AXY), 6.26 (1H, s, H-2), 5.32 (1H, m, CH=), 5.32-4.72 (2H, XY part of AXY), 3.42 (2H, d, J=7 Hz, CH_2), 1.72 (12H, br s, 4×Me); Δδ=δ (C_5D_5N)-δ (CD_3COCD_3): H-8 (+0.55), H-2 (+0.44), CH_2 (+0.28), propenyl-me_2 (+0.33), butenyl-Me_2 (−0.04); uv λ max (MeOH): in Table 1; (AcONa): 254, 376; (MeONa): 248 sh, 262, 392; (AcONa/H_3BO_3): 264, 358; ($AlCl_3$): 238 sh, 271, 398; ($AlCl_3$/HCl): 238, 268, 350; ms *m/z* (rel. int.): 396 (M^+, 51), 395 (8), 381 (M-Me, 100), 379 (M-OH, 15), 367 (5), 363 (3), 355 (14), 353 (10), 341 (M-C_4H_7, 15), 325 (M-Me-C_4H_8, 27), 311 (11), 297 (14), 295 (3), 285 (13), 273 (13), 198 (M/2, 3), 183 (M-2Me/2, 4), 163 (M-MeC_4H_7/2, 6), 161 (M-OH-C_4H_7/2, 6).

Oxidation of compound **3**: Compound **3** (20 mg) and DDQ (11 mg) were held at reflux 1 h in anhydrous C_6H_6. The residue on plc (CH_2Cl_2×2) gave as main products compound **2** (8 mg) and unaltered **3**(6 mg).

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