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POLYHYDROXYAGAROFURAN DERIVATIVES FROM *RZEDOWSKIA TOLANTONGUENSIS**

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Key Word Index—*Rzedowskia tolantonguensis*; Celastraceae; dihydroagarofuran sesquiterpene; ; rzedowskins A, B, C and D; structure determination.

Abstract—The structures of Rzedowskins A, B, C and D, new sesquiterpenes of the polyhydroxyagarofuran-type and constituents of *Rzedowskia tolantonguensis*, were established by chemical and spectroscopic methods.

INTRODUCTION

Rzedowskia tolantonguensis Medrano belongs in a new genus of Celastraceae in Mexico; the genus *Rzedowskia* was discovered recently by Medrano *et al.* [1]. This paper describes the chemical study of this shrub to obtain additional evidence to support the Botanical classification. The ocurrences of compounds of the polyhydroxyagarofuran-type is common in other Celastraceae species [2].

RESULTS AND DISCUSSION

From a methanolic extract of aerial parts of the plant were isolated rzedowskins A, B, C and D (**1a–d**). Rzedowskin A (**1a**) was the least polar compound (TLC) and it was obtained as white crystals, mp 210°. The UV spectrum of **1a** showed absorptions at 202, 218 and 265 nm consistent with an aromatic structure. The IR spectrum showed hydroxyl and carbonyl esters bands. Its ^{1}H NMR spectrum showed two doublet signals at δ4.03 and 3.53 (J = 1.5 Hz) and a simple broad signal at δ7.3 (5H) which were assigned to the protons of an epoxycinnamic system (–O–C(=O)–CH–CH–C_6H_5). The mass spectrum of **1a** revealed the ion m/z 517 $[M-15]^+$ due to the loss of a methyl group of the gem dimethyl grouping [3] while the peak at m/z 369 $[M-163]^+$ could be explained by the loss of the fragment O–C(=O)–CH–CH–C_6H_5.

The position and orientation of the three esters groups in **1a** were established by their chemical shifts, coupling constants and the multiplicity of the signals related to base protons (Table 1). The double signal at δ5.5 (1H, $J_{1\beta,2\alpha}$ = 11 Hz) was assigned to H-1, the proton base of the epoxycinnamate ester, which has a *trans*-diaxial interaction with H-2 [4]. The signal centred at δ4.9 (*ddd*, $J_{1\beta,2\alpha}$ = 11 Hz, $J_{2\alpha,3\beta}$ = 11 Hz, $J_{2\alpha,3\alpha}$ = 6 Hz) was assigned to H-2, the acetate base proton. The other acetyl group was on C-9, since the double doublet signal at δ4.76 ($J_{8\alpha,9\alpha}$ = 6 Hz, $J_{8\beta,9\alpha}$ = 2 Hz) was due to H-9, which had a β-equatorial orientation. The doublet signal at δ4.38 (simplified with D_2O) was attributed to H-6 with the β-axial orientation, which is lightly coupled to H-7 equatorial.

The rzedowskins B and C (**1b** and **1c**, respectively) were isolated as white solids. The IR spectra of both materials showed absorptions for hydroxyl, carbonyl ester and conjugated double bond with an aromatic ring. Their ^{1}H NMR spectra showed epoxycinnamate signals and two olefinic protons at δ7.66 and 6.36. (*d* J = 16 Hz) which were attributed to a *trans*-cinnamate group. The mass spectra of these compounds revealed the ion of m/z 131 due to the fragment C_6H_5–CH=CH–C≡O$^+$. Thus, **1b** and **1c** were recognised as mixtures of the cinnamate and epoxycinnamate esters and it was not possible to separate these by conventional methods. Both mixtures have an hydroxyl group at C–2, as shown by the ^{1}H NMR signal at δ3.6. The difference between **1b** and **1c** is the hydroxyl group at C-6 in **1b** (δ4.35) and the acetyl group on the some position in **1c** (δ5.45). In both mixtures H-1 appeared as a simple signal at δ5.75 and H-9 was seen as a double of doublets at δ4.98. An ozonolysis reaction of **1c** mixture was tried without success but an increase in the proportion of epoxycinnamate compound was observed (^{1}H NMR evidence). The ^{13}C NMR spectra of **1c** and Mortonol B (**7**) [5] were compared and the carbons signals were assigned according to Table 2.

Oxidation of **1b** and **1c** with Jones reagent afforded **2b** and **2c**, respectively. The IR spectra of both later compounds showed tertiary hydroxyl bands (3500 cm^{-1}). The IR spectrum of **2b** showed absorption bands at 1770 and 1720 cm^{-1} indicating the presence of cyclopentanone and cyclohexanone, respectively. The ^{13}C NMR spectrum of **2b** showed the C-2 signal at δ201.66 *s* (Table 2).

The acetylation of **1b** with pyridine and acetic anhydride afforded **3a**, which was shown to be identical with

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Table 1. ^{1}H NMR spectral data of **1a-d** (δ from TMS in $CDCl_3$, 80 MHz)*

	1a	1b	1c	1d
H-1	5.56 *d* (11)	5.28 *d* (11)	5.36 *d* (11)	5.46 *d* (11)
H-2	4.9 *ddd* (11,11,6)	3.63 *m*†	3.6 *m*†	3.66 *ddd* (11,11,6)
H-6	4.38 *d*‡	4.35 *d*‡	5.45 *br s*	5.61 *br s*
H-9	4.76 *dd* (2,6)	4.78 *dd* (2,6)	4.76 *dd* (2,6)	4.85 *dd* (2,6)
H-12	1.66 *s*	1.60 *s*	1.60	1.51¶
H-13	1.52 *s*	1.51 *s*	1.52 *s*	1.52 *s*¶
H-14	1.43 *s*	1.45 *s*	1.50 *s*	1.40 *s*
H-15	1.33 *s*	1.33 *s*	1.39 *s*	1.36 *s*
6-OAc	2.00 *s*		2.01 *s*	
9-OAc	1.96 *s*	2.05 *s*	1.91 *s*	1.94 *s*
H-aromatic	7.3 *br s*	7.3 *m*	7.3 *m*	7.4 *m*§
H_α	4.03 *d* (1.5)	6.36 *d* (16)‖	6.36 *d* (16)‖	6.35 *d* (16)
H_β	3.53 *d* (1.5)	7.66 *d* (16)‖	7.66 *d* (16)‖	7.69 *d* (16)

*The coupling constants in Hz are in parentheses.
†With D_2O *dt* (J = 11,6).
‡With D_2O broad singlet.
§With D_2O β-nicotinic system signals H-2′ 9.03 d (1.5), H-4′ 8.45 *dt* (1.5, 8), H-6′ 8.76 dd (1.5,4), H-5 overlapped by aromatic signals.
‖Further epoxycinnamate system signals at δ3.53 and 4.03 *d* (1.5).
¶Interchangeable.

Table 2. ^{13}C NMR spectral data of **1c**, **2b** and mortonol B (**7**) (δ from TMS, in $CDCl_3$, 20.1, MHz)

C	1c	2b	7
1	72.72 *d*	79.92 *d*	72.08 *d*
2	67.58 *d*	201.06 *s*	68.99 *d*
3	49.10 *t*	54.82 *t*	44.37 *t*
4	84.64 *s*	85.40 *s*	70.95 *s*
5	91.17 *s*	91.37 *s*	85.77 *s*
6	76.20 *d*	76.95 *d*	211.04 *s*
7	57.87 *d*	57.73 *d*	55.34 *d*
8	48.59 *t*	49.24 *t*	33.14 *t*
9	79.63 *d*	72.70 *d*	72.23 *d*
10	51.63 *s*	53.19 *s*	55.84 *s*
11	71.00 *s*	74.42 *s*	78.55 *s*
12	21.48 *q*	21.41 *q*	22.24 *q*
13	24.89 *q*	24.97 *q*	23.63 *q*
14	20.24 *q*	20.17 *q*	17.88 *q*
15	29.74 *q*	29.73 *q*	29.62 *q*
α	145.66 *d*	146.14 *d*	
β	118.05 *d*	117.38 *d*	
MeCO	170.24 *s*	169.98 *s*	170.21 *s*
MeCO	20.99 *q*	20.62 *q*	20.76 *q*
insat. CO*	165.94 *s*	165.36 *s*	
PhCO			164.79 *s*

*Cinnamate ester carbonyl.

1a. The same reaction for **1c** afforded **3b**. The esterification involved principally the C-2 hydroxyl substituent under the mild conditions employed. In this way the triesters **3c** and **3e** were prepared in an attempt to obtain crystals for X-ray analysis. However, appropriate crystals were not obtained. The tetraesters **3d** and **3f** were obtained as minor products.

Jones oxidation of **3a** afforded **4** indicating that the hydroxyl group on C-6 is not esterified. Dehydration of **3b** ($SOCl_2$–pyridine) afforded **5**. Basic hydrolysis ($KHCO_3$–MeOH) of **1b** and **1c** gave the same compound **6**. The mass spectrum of **6** showed the base peak at *m/z* 43 and its IR spectrum showed the typical absorption bands of hydroxyl and carbonyl ester groups. The ^{1}H NMR spectrum revealed a simple signal at δ2.18, which was assigned to the acetate group and a double doublet signal at 4.83 which was assigned to H-9. For this reason, the cinnamate and epoxycinnamate groups must be linked to C-1 in all rzedowskins.

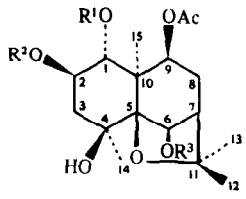
The rzedowskin D (**1d**) was an alkaloid, its IR spectrum revealed hydroxyl and carbonyl ester groups and *trans*-cinnamate double bond absorption bands and a pyrimidic ring band (1590 cm^{-1}) [6]. The mass spectrum revealed an ion at *m/z* 570 $[M]^+$ (0.1) and it corresponded to molecular formula $C_{32}H_{37}NO_9$. The mass spectral peaks at *m/z* 131 (100) and 106 (42) revealed the presence of cinnamate and β-nicotinate groups, respectively. ^{1}H NMR spectrum of **1d**, which was very similar to the spectrum of **1c**, showed the H-6 signal at δ5.61 the proton base of the nicotinate group. The remaining aromatic signals confirm the presence of carboxypiridine heterocycle (δ9.3, 8.7 and 8.45).

Rzedowskins A, B, C and D have a β-dihydroagarofurane structure and their relative stereochemistry is represented by structures **1a–d**. It is interesting to note the absence of oxidation of the C-14 methyl group and also that some of these compounds are epoxy derivatives.

During the preparation of this paper a report appeared about the same plant which also described the isolation of **1d** [7].

EXPERIMENTAL

Mps: uncorr. Column chromatography: silica gel 70–230 mesh (Merck); TLC: silica gel 60 F_{254} (Merck); flash chromato-

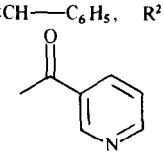


1a R^1 = OC—CH(O)—CH—C_6H_5; R^2 = Ac, R^3 = H

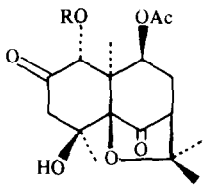
1b R^1 = OC—CH(O)—CH—C_6H_5 and OC—CH=CH—C_6H_5; R^2 = R^3 = H

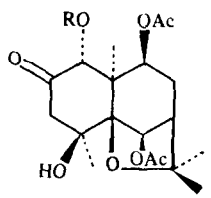
1c R^1 = OC—CH(O)—CH—C_6H_5 and OC—CH=CH—C_6H_5, R^2 = H; R^3 = Ac

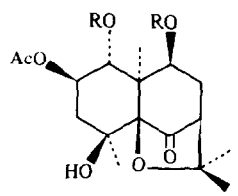
1d R^1 = OC—CH=CH—C_6H_5; R^2 = H; R^3 =



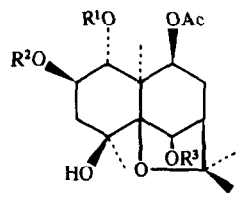
6 R^1 = R^2 = R^3 = H







2b R = OC—CH(O)—CH—C_6H_5 **2c** R = OC—CH=CH—C_6H_5 **7** R = OC—C_6H_5



3a R^1 = OC—CH(O)—CH—C_6H_5 and OC—CH=CH—C_6H_5; R^2 = Ac; R^3 = H

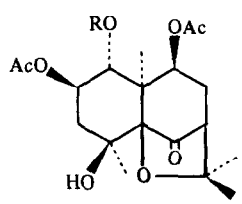
3b R^1 = OC—CH(O)—CH—C_6H_5 and OC—CH=CH—C_6H_5; R^2 = R^3 = Ac

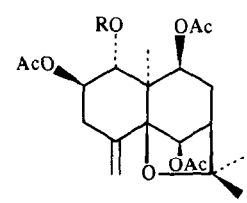
3c R^1 = OC—CH(O)—CH—C_6H_5 and OC—CH=CH—C_6H_5; R^2 = OCC_6H_5; R^3 = H

3d R^1 = OC—CH(O)—CH—C_6H_5 and OC—CH=CH—C_6H_5; R^2 = R^3 = OCC_6H_5

3e R^1 = OC—CH(O)—CH—C_6H_5 and OC—CH=CH—C_6H_5; R^2 = OC-*p*-C_6H_4-Br; R^3 = H

3f R^1 = OC—CH(O)—CH—C_6H_5 and OC—CH=CH—C_6H_5; R^2 = R^3 = OC-*p*-C_6H_4-Br





4 R = OC—CH(O)—CH—C_6H_5 **5** R = OC—CH=CH—C_6H_5

graphy: silica gel 230–400 mesh (Merck). Removal of volatile solvent was always performed under red. pres. Mass spectra were determined by EI (70 eV).

Isolation of rzedowskins. *R. tolantonguensis* was collected in July, 1981, in Barrancas de Tolantongo, Ixmiquilpan (Hidalgo, México). Voucher specimens (321901) of the plant were identi-

fied by Dr F. González-Medrano, Departamento de Botánica, Instituto de Biología, UNAM, México. Dried aerial parts of the plant (2.3 kg) were extracted with MeOH at room temp for 12 hr. The MeOH extract was concd to minimum volume, dissolved in H_2O and percolated through Celite. The H_2O soln was extracted with $CHCl_3$. An aliquot (3 g) of $CHCl_3$ extract (360 g) was chromatographed on a silica gel column. Elution with hexane–EtOAc (6:1) gave **1a** as white crystals mp 210° (128 mg, from hexane–Me_2CO), UV λ_{max}^{MeOH} nm (log ε): 202 (4.03), 218 (4.05), 265 (3.00); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3530, 3450, 1750; MS, *m/z* (rel. int): 517 $[M-15]^+$ (3.2), 369 (15), 191 (20), 173 (23), 91 (64), 43 (100). Elution of the column with hexane-EtOAc (1:1) separated the material into three fractions: Fr. A (**1a** and **1b**, 313 mg), Fr. B (**1a**, **1b** and **1c**, 1.05 g) and Fr. C (**1b** and **1c**, 200 mg). The EtOAc eluate afforded **1d** as white crystals, mp 143–145° (60 mg), UV λ_{max}^{MeOH} nm (log ε): 203 (4.30), 218 (4.41), 222 (4.38), 2.68 (3.30); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3560, 1725, 1646, 1593; MS, *m/z* (rel. int): 579 $[M]^+$ (0.1), 561 $([M-18]^+$ (0.2), 564 $[M-15]^+$ (0.2), 131 (100), 124 (20), 106 (42), 43 (40). Fr. B was rechromatographed on silica gel. The fractions eluted with hexane–EtOAc (1:1) afforded **1b** as a white solid, one spot by TLC analysis; mp 110°; UV λ_{max}^{MeOH} nm (log ε): 218 (3.96), 275 (3.60), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 1740, 1650; MS *m/z* (rel. int.): 475 $[M-15]^+$ (2.5), 327 (18), 131 (68), 91 (66), 43 (100). The same elution gave **1c**, as a white solid, mp 196°; UV λ_{max}^{MeOH} nm (log ε): 202 (4.07), 215 (4.11), 220 (4.06), 278 (4.16), 298 (3.85); IR $\nu_{max}^{CHCl_3}$ cm^{-1}; 3500, 1740, 1720, 1642; MS *m/z* (rel. int.): 517 $[M-15]^+$ (1.2), 369 (18), 131 (100), 103 (28), 91 (47), 43 (33).

Oxidation of **1b**. Compound **1b** (100 mg) in Me_2CO (5 ml) on an ice bath was treated with Jones reagent (2 ml) for 10 min, then the mixture was extracted with EtOAc. Removal of the solvent gave **2b**, which was crystallized from hexane–Me_2CO (95 mg), mp 120°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3530, 1770, 1750, 1740, 1720, 1050; ^1H NMR (80 MHz, $CDCl_3$): δ1.13 (3H, *s*), 1.33 (3H, *s*), 1.60 (3H, *s*), 1.66 (3H, *s*); 2.09 (3H, *s*, OAc), 2.96 (1H, *d*, part of AB system, J_{gem} = 12 Hz, H-3), 3.46 (1H, *d*, *J* = 2 Hz) and 4.16 (1H, *d*, *J* = 2 Hz) epoxydic ring, 4.98 (1H, *dd*, $J_{8\alpha,9\alpha}$ = 2 Hz, $J_{8\beta,9\alpha}$ = 6 Hz, H-9), 5.8 (1H, *s*, H-1), 7.3 (5H, *s*, H-aromatic).

Oxidation of **1c**. Compound **1c** (500 mg) was treated as for **1b**. After the work up, the product was purified by flash chromatography (hexane–EtOAc 1:1) which was crystallized from MeOH (152 mg), mp 222–224°, UV λ_{max}^{MeOH} nm (log ε): 202 (4.03), 217 (4.03), 278 (3.00); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3520, 1740, 1720, 1640, 1380; ^1H NMR (80 MHz, $CDCl_3$): δ1.30 (6H, *s*, H-12 and H-13), 1.62 (6H, *s*, H-14 and H-15), 1.97 (3H, *s*, OAc), 2.14 (3H, *s*, OAc), 3.03 (1H, *d*, *J* = 12, H-3), 4.98 (1H, *dd*, *J* = 2, 6 Hz, H-9), 5.53 (1H, *s*, H-6), 5.70 (1H, *s*, H-1), 6.31 (1H, *d*, *J* = 16Hz) and 7.62 (1H, *d*, *J* = 16Hz) and 7.15 and 7.50 (5H, *m*) *trans*-cinnamate group: MS *m/z* (rel.int.): 514 $[M]^+$ (0.8), 472 $[M-42]^+$, 454 $[M-60]^+$ (2), 324 (3), 131 (78), 103 (39), 77 (14), 43 (100).

Acetylation of **1b**. Compound **1b** (80 mg) was treated with pyridine (1 ml) and Ac_2O (1 ml) for 1 hr on a steam bath. The product was crystallized from hexane–Me_2CO (40 mg) and was identical with **1a** by direct comparison of physical and spectroscopic data.

Acetylation of **1c**. Compound **1c** was acetylated as for **1b** to afford **3b**, mp 110°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3530, 1740, 1630; ^1H NMR (80 MHz, $CDCl_3$): δ1.43 (6H, *s*), 1.49 (6H, *s*), 1.83 (3H, *s*, OAc), 1.95 (3H, *s*, OAc), 2.10 (3H, *s*, OAc), 2.97 (1H, D_2O exchangeable), 3.53 (1H, *d*, *J* = 1.5 Hz) and 4.06 (1H, *d*, *J* = 1.5 Hz) epoxydic ring, 4.77 (1H, *dd*, *J* = 2.6 Hz, H-9), 4.97 (1H, *t*, *J* = 11 Hz, H-2), 5.46 (1H, *s*, H-6), 5.52 (small signal) (1H, *d*, $J_{1\beta,2\alpha}$ = 11 Hz, H-1, proton base of epoxy-cinnamate group), 5.6 (1H, *d*, $J_{1\beta,2\alpha}$ = 11 Hz, H-1, proton base of cinnamate group), 6.38 (1H, *d*, *J* = 16 Hz) and 7.64 (1H, *d*, *J* = 16 Hz) and 7.15–7.50 (5H, *m*) *trans*-cinnamate group; MS *m/z* (rel. int.): 499 $[M-59]^+$ (1), 456 (3), 438 (4), 378 (15), 131 (100), 43 (48).

Benzoylation of **1b**. To a soln of **1b** (100 mg) in pyridine (1 ml) was added benzoyl chloride (0.5 ml). After 30 min, the reaction mixture was poured into H_2O and extracted with EtOAc. An oil was obtained which was purified by chromatography on a column of silica gel. The first product eluted, **3d**, was obtained as a crystalline solid, mp 170°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3520, 1750, 1720, 1640; ^1H NMR (80 MHz, $CDCl_3$): 1.98 (3H, *s*, OAc), 3.63 and 4.08 epoxydic ring, 4.98 (1H, *dd*, *J* = 2.6, H-9), 5.12 (1H, *ddd*, $J_{1\beta,2\alpha}$ = 11 Hz, $J_{2\alpha,3\beta}$ = 11 Hz, $J_{2\alpha,3\alpha}$ = 4 Hz, H-2), 5.58 (1H, *s*, H-6), 5.80 (1H, *d*, *J* = 11 Hz, H-1, proton base of epoxycinnamate group), 5.85 (1H, *d*, *J* = 11 Hz, H-1, proton base of cinnamate group), 6.46 (1H, *d*, *J* = 16 Hz) and 7.80 (1H, *d*, *J* = 16 Hz) and 8.16, 7.96 and 7.5 (*m*, H-aromatic). A more polar second product **3c** was obtained as a solid, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3520, 1750, 1720, 1640; ^1H NMR (80 MHz, $CDCl_3$): δ1.81 (3H, *s*, OAc), 3.30 (1H, *m*, D_2O exchangeable), 3.58 and 4.05 epoxydic ring, 4.98 (1H, *dd*, *J* = 2.6 Hz, H-9), 5.12 (1H, *ddd*, *J* = 11,11,4 Hz, H-2), 5.78 (1H, *d*, *J* = 11 Hz, H-1), 7.05 and 8.02 (H-aromatic).

p-Bromobenzoyl derivative of **1b**. Compound **1b** (100 mg) was treated with pyridine and *p*-bromobenzoyl chloride. The work-up was realized in the usual way. The reaction product was chromatographed on silica gel, to give **3f** (33 mg) and **3e** (8 mg). Compound **3f**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3520, 1750, 1720, 1640, 1600; ^1H NMR (80 MHz, $CDCl_3$): δ1.85 (3H, *s*, OAc), 3.59 and 4.07 epoxydic ring, 4.9 (1H, *dd*, *J* = 2.6 Hz, H-9), 5.08 (1H, *ddd*, *J* = 11, 11, 6 Hz, H-2), 5.58 (1H, *s*, H-6), 5.75 (1H, *d*, *J* = 11 Hz, H-1) and 7.65 (*m*, H-aromatic).

Oxidation of **3a**. The compound **3a** was treated with Jones reagent in the usual way (*vide supra*). A crystalline product was obtained from hexane–Me_2CO, mp 192–194°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3530, 1765, 1750, 1650; ^1H NMR (80 MHz, $CDCl_3$): δ1.26 (6H, *s*), 1.55 (3H, *s*), 1.73 (3H, *s*), 1.96 (3H, *s*, OAc), 2.01 (3H, *s*, OAc), 3.58 and 4.20 epoxydic ring, 4.91 (2H, *m*, H-2 and H-9), 5.61 (1H, *d*, *J* = 11 Hz, H-1, proton base of epoxycinnamate group) 5.64 (small signal) (1H, *d*, *J* = 11 Hz, H-1), proton base of cinnamate group), 6.40 (1H, *d*, *J* = 16 Hz) and 7.3 (1H, *d*, *J* = 16 Hz) and 7.3 (*m*, H-aromatic).

Dehydration of **3b**. To a soln of **3b** (380 mg) in pyridine, on the ice bath, was added $SOCl_2$ (2 ml) and the reaction mixture was allowed to stand at room temp. for 30 min. The reaction mixture was poured on to ice and neutralized with NaOH soln. The mixture was then extracted with EtOAc. The reaction product was purified by prep. TLC (hexane–EtOAc 7:3), mp 216–217°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1750, 1710, 1640, 1380; ^1H NMR (80 MHz, $CDCl_3$): δ1.28 (3H, *s*), 1.43 (3H, *s*), 1.58 (3H, *s*), 1.83 (3H, *s*, OAc), 2.00 (3H, *s*, OAc), 2.11 (3H, *s*, OAc), 4.86 (2H, *m*, H-2 and H-9), 4.90 (1H, *s*, H-11), 5.18 (1H, *s*, H-11), 5.31 (1H, *s*, H-6), 5.85 (1H, *d*, *J* = 11 Hz, H-1), 6.43 (1H, *d*, *J* = 16 Hz) and 7.67 (1H, *d*, *J* = 16 Hz) and 7.47 (5H, *m*, aromatic); MS, *m/z* (rel. int.): 556 $[M]^+$ (1.1), 540 (0.10), 498 (3), 131 (49), 91 (75), 43 (100).

Hydrolysis of **1b**. To a soln of **1b** (100 mg) in MeOH (5 ml) was added a soln of $KHCO_3$ in MeOH with stirring. The reaction mixture was allowed to stand at room temp for 48 hr. The reaction mixture was then extracted with EtOAc. The EtOAc extract was washed with a 5% HCl (3 times) then with H_2O and concentrated under red. pres. The reaction product **6** was purified by preparative TLC (EtOAc), to give an oily product; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3560, 3500, 3420, 1720; ^1H NMR (80 MHz, $CDCl_3$): δ1.1, 1.50, 1.51 and 1.63 (12 H, 4 *s*), 2.18 (3H, *s*, OAc), 3.0 (1H, *m*, exchangeable with D_2O), 3.36 (1H, *m*, exchangeable with D_2O), 3.6 (1H, *m*, H-2), 3.96 (1H, *d*, *J* = 11 Hz, H-1), 4.33 (1H, *d*, *J* = 4 Hz, H-6), 4.83 (1H, *dd*, *J* = 6.2, Hz, H-9); MS *m/z* (rel. int.): 329 $[M-15]^+$ (5), 326 (0.3), 311 (0.3), 287 (5), 269 (53), 43 (100). The basic hydrolysis of **1c** afforded the same compound **6**.

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