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7α-HYDROXY-SESQUITERPENE LACTONES FROM *DECACHAETA OVATIFOLIA*

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Key Word Index—*Decachaeta ovatifolia*; Compositae, Eupatorieae; sesquiterpene lactones; germacranolides; guaianolides; eudesmanolides.

Abstract—In addition to the known sesquiterpene lactone pinnatifidin, and the flavones 6-methoxyacacetin and 6-methoxyapigenin, the dichloromethane extract of the aerial parts of *Decachaeta ovatifolia* afforded four new sesquiterpene lactones: a germacranolide 7α-hydroxycostunolide, a guaianolide 4α,15-dihydro-7α-hydroxy-3-desoxyzaluzanin C and two eudesmanolides, 7α-hydroxysantamarine and 7α-hydroxyreynosin. The structure of 7α-hydroxycostunolide was confirmed by X-ray analysis.

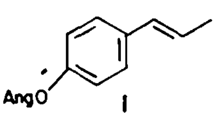
INTRODUCTION

Our interest in the chemotaxonomy of the tribe Eupatorieae led us to investigate the genus *Decachaeta* DC. (subtribe Hebecliniinae King and Robinson), a monotypic genus expanded by King and Robinson [1, 2] to include six additional species. Here we report from *Decachaeta ovatifolia* (DC.) King and Robinson four new sesquiterpene lactones all sharing the unusual 7-hydroxy structural feature; in addition, this species was found to contain a known sesquiterpene lactone and two known flavones. *Decachaeta ovatifolia* has previously been placed in both *Eupatorium* and *Ophryosporous* [1]. Little is known of the chemistry of allied taxa, but an earlier investigation of *Decachaeta thieleana* (Klatt.) King and Robinson reported the presence of only guaianolide sesquiterpene lactones [3, 4], while the three *Ophryosporous* (*sensu* King and Robinson) species that have been studied have yielded *p*-hydroxyacetophenone derivatives and anol derivatives (**1**) as well as one labdane diterpene [5, 6].

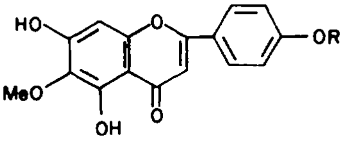
RESULTS AND DISCUSSION

The dichloromethane extract of the aerial parts of *Decachaeta ovatifolia* afforded four new sesquiterpene lactones (**5a**, **7**, **10a** and **12a**) and the three previously known compounds **2**–**4**.

Compound **5a** was isolated as colourless crystals by column and preparative TLC. The mass spectrum of compound **5a** showed a molecular ion at m/z 248 in accord with the formula $C_{15}H_{20}O_3$. ^{13}C NMR signals for one carbonyl and three double bonds, one of which was for an exocyclic methylene group (Table 2), suggested that a bicyclic structure was likely for **5a** since the formula required a total of six degrees of unsaturation. A prominent fragment in the MS at m/z 230 $[M - H_2O]^+$ and IR absorption at 3425 cm^{-1} indicated that the compound contained a hydroxyl group. In addition, the IR spectrum exhibited two strong absorptions at 1736 and 1720 cm^{-1} despite the ^{13}C NMR evidence that only a single carbonyl function was present in the molecule. We tentatively interpreted these data to mean that a single ester carbonyl existed in both a free and hydrogen bonded state. That this ester was actually an α,β-unsaturated-γ-lactone became clear from the following observations. In the ^1H NMR spectrum of **5a** two sharp singlets appeared at δ5.80 and 6.10. When **5a** was reduced with sodium borohydride, the product formed (**5b**) had a spectrum that lacked these signals and instead contained a methyl doublet at δ1.23, indicating that an exocyclic methylene group conjugated with a carbonyl had been reduced. Further, the IR absorptions in **5b** shifted to 1765 and 1778 (sh) cm^{-1} establishing that the carbonyl must be part of a γ-lactone. Thus, at this point only one degree of unsaturation remained unaccounted for in **5a**. Overall, both the ^1H and ^{13}C NMR spectra were remarkably similar to costunolide (**6**) (Tables 1 and 2); the principal differences in the ^1H NMR spectra are the doublet of triplets at δ2.68 and the appearance of the H-6 signal as a sharp doublet in **5a**, rather than a triplet and the multiplicity of the exocyclic methylene signals of the lactone ring. The latter two observations require a substituent at C-7. Since the formulae of **5a** and **6** differ only in the presence of a hydroxyl group in the former compound, and because no other prominent differences were observed in the ^1H NMR spectra of the two compounds, it was apparent that the hydroxyl group must be at C-7. The ^{13}C NMR spectrum of **5a** supported this conclusion with resonances observed at δ83.6 (*s*, C-7), 86.2 (*d*, C-6), 14.0 (*s*, C-11), 170.8 (*s*, C-12), and 120.3 (*t*, C-13) in close agreement with analogous 7-hydroxygermacradienolides from *Montanoa* [9]. Other deviations in the ^{13}C NMR spectrum of **5a** from those of the spectrum of **6** were in accord with predicted shifts caused by the hydroxyl substitution at C-7. All positions β to the hydroxyl group (C-6, C-8 and C-11) were found at lower field (*ca* 4 ppm), while the γ carbons C-5 and C-9 absorbed at higher field (*ca* 5 ppm). The position of the hydroxyl group also allows hydrogen bonding to occur between the hydroxyl and the lactone carbonyl, thus

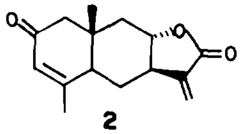


1



3 R = H

4 R = Me



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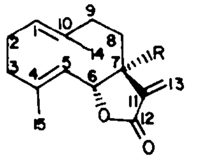
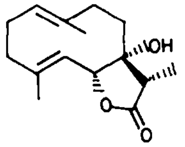
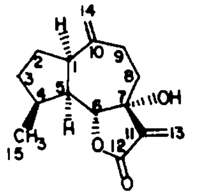


5a R = OH

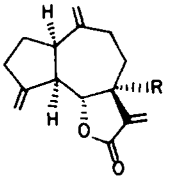
6 R = H



5b

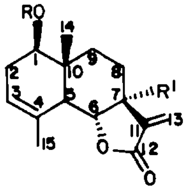


7



8 R = H

9 R = OH

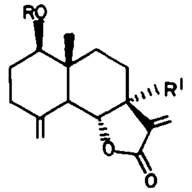


10a R = H, R^1 = OH

10b R = Ac, R^1 = OH

11a R = H, R^1 = H

11b R = Ac, R^1 = H



12a R = H, R^1 = OH

12b R = Ac, R^1 = OH

13 R = Ac, R^1 = H

accounting for the two IR absorptions*. In order to confirm the structure of **5a** as 7-hydroxycostunolide, an X-ray diffraction analysis was conducted. The results corroborated the proposed structure and the relative stereochemistry as depicted in the perspective drawing (Fig. 1). We tentatively assign the absolute stereochemistry of C-7 as *R*(α-OH) in accord with other sesquiterpene lactones of known absolute configuration. In the ^{1}H NMR spectrum, the doublet of triplets at δ2.68 can be assigned as H-9α since examination of Dreiding models shows that the 7α-hydroxy group is close enough to deshield this proton.

The second new compound (**7**), isolated as an amorphous solid in the MS showed a molecular ion at *m/z* 248 corresponding to a formula of $C_{15}H_{20}O_3$, as well as fragments at *m/z* 230 $[M - H_2O]^+$ and 215 $[M - H_2O - Me]^+$. The IR spectrum of **7** indicated the presence of an α-methylene-γ-lactone (1755 cm^{-1}) and a hydroxyl group (3430 cm^{-1}). The hydroxyl group was obviously at C-7 since the exomethylene protons displayed singlets at δ5.8 and 6.27 and the signal for H-6 was a doublet. Further, the ^{13}C NMR spectrum (Table 2) of **7** displayed a singlet at δ75.5 assignable to C-7 substituted with a hydroxyl group. Indeed, other carbon resonances in the spectrum were easily assignable to C-6, C-11, C-12 and C-13 of a lactone moiety similar to that found in **5a**, thus accounting for all the oxygen atoms required by the formula. The ^{1}H NMR spectrum (Table 1) of **7** also contained two broad singlets at δ4.98 and 5.02. ^{1}H NMR spin decoupling and COSY experiments established that **7** possessed a *trans*-lactonized, *cis*-fused guaianolide skeleton similar to that of dehydrocostus lactone (**8**) [11] as well as 7α-hydroxy-3-desoxyzaluzanin C (**9**) [10]. One notable difference between **7** and **9** was the replacement of the C-4 exocyclic methylene functioning with a methyl group in **7**. The methyl doublet at δ0.94 (*J* = 6.9 Hz) in **7** clearly represented H-15 (spin decoupling and COSY). NOE difference experiments showed that this methyl group must have a β configuration, since NOEs were observed for H-6 and to a lesser extent for H-2β, H-3 and H-14 when the methyl doublet was irradiated. H-5 and H-1 were unaffected, in marked contrast to the results for the same experiment performed on a similar guaianolide

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*Interestingly, the few known 7-hydroxylactones reported [9, 10] all have IR absorptions for the lactone carbonyl at even longer wavenumbers (1765–1775 cm^{-1}) than typical α,β-unsaturated-γ-lactones (1750–1755 cm^{-1}). No such double absorptions have previously been reported.

Table 1. ^{1}H NMR spectra of compounds **5a**, **6**, **7**, **10b**, **11b**, **12b** and **13** (200 MHz, TMS as int. standard)

H	**5a** Acetone-d_6	**5a** C_5D_5N/D_2O	**6** ($CDCl_3$)	**7** (500 MHz, $CDCl_3$)	**10b** ($CDCl_3$)	**11b** ($CDCl_3$)	**12b** ($CDCl_3$)	**13** ($CDCl_3$)
1	4.89 *br dd*	5.02	4.85 *br dd*	2.83 *dddd*	4.96 *dd*	4.90 *dd*	4.88 *dd*	4.80 *dd*
2				1.79 *m*†	2.49 *m*	2.47 *m*		
2′				2.00 *m*				
3				1.74 *m**†	5.37 *m*	5.35 *m*	2.33 *m*	
3′				1.65 *m**†				
4				2.35 *br dq*‡				
5	5.23 *br d*	5.64	4.75 *br d*	2.58 *dt*	3.07 *br d*		2.87 *br d*	
6	4.74 *d*	4.85	4.58 *dd*	4.14 *d*	4.07 *d*	4.1 *dd*	4.13 *d*	4.01 *t*
8				2.50 *ddd*				
8′				1.58 *dt*				
9	2.68 *br t*	2.98		2.33 *m*†				
9′				2.27 *m*†				
13a	6.10 *s*	6.45	6.28 *d*	5.80 *s*	6.17 *s*	6.08 *d*	6.18 *s*	6.1 *d*
13b	5.80 *s*	5.94	5.52 *d*	6.28 *s*	5.65 *s*	5.43 *d*	5.67 *s*	5.42 *d*
14	1.44 *br s*	1.42	1.43 *br s*	5.01 *br s*	0.99 *s*	0.97 *s*	0.92 *s*	0.90 *s*
14′				4.98 *br s*				
15	1.74 *br s*	1.72	1.72 *d*	0.93 *d*	1.82 *s*	1.85 *s*	4.88 *br s*	4.88 *br s*
15′							5.02 *br s*	5.02 *br s*
Ac					2.10 *s*	2.10 *s*	2.06 *s*	2.10 *s*

J (Hz) **5a**: 1, 2 = 10.6; 1, 2′ = 3.7, 5, 6 = 10; 5, 15 = 1.5; 9, 8 = 9, 9′ = 12.6; 9′, 8 = 2.1. **6**: 1, 2 = 12.1; 1, 2′ = 6.3; 5, 6 = 10; 5, 15 = 1.5; 6, 7 = 9; 7, 13a = 3.1; 7, 13b = 3.1. **7**: 1, 2 = 9; 1, 2′ = 8.5; 1, 5 = 11.1; 1, 14 = 1.5; 1, 14′ = 1.0; 4, 5 = 6.7; 4, 15 = 6.9; 5, 6 = 11.5; 8, 8′ = 13.5; 8, 9 = 4.0; 8, 9′ = 4.1; 8′, 9 = 13; 8′, 9′ = 4.5. **10b**: 1, 2 = 9.8; 1, 2′ = 6.9; 5, 6 = 12.2. **11b**: 1, 2 = 10.1; 1, 2′ = 6.3; 5, 6 = 12.2; 6, 7 = 6.3; 7, 13a = 7, 13b = 3.1. **12b**: 1, 2 = 9.4; 1, 2′ = 4.8; 5, 6 = 11.6. **13**: 1, 2 = 9.5; 1, 2′ = 4.7; 5, 6 = 6, 7 = 10.5; 7, 13a = 7, 13b = 3.1.

*Interchangeable.

†Signal obscured; chemical shift determined by COSY.

‡Signal partially overlapped; multiplicity determined by spin decoupling.

Table 2. ^{13}C NMR spectra of compounds **5a**, **6**, **7**, **8**, **9**, **10b** and **11b** (22.6 MHz as internal standard)

C	**5a** (acetone-d_6)	**6** (acetone-d_6)	**7** ($CDCl_3$)	**8*** ($CDCl_3$)	**9**† ($CDCl_3$)	**10b**‡ ($CDCl_3$)	**11b**‡ ($CDCl_3$)
1	128.7 *d*	128.7 *d*	44.6 *d*	47.5 *d*	46.14 *d*	§	76.6 *d*
2	27.2 *t*	26.7 *t*	27.8 *t*	30.2 *t*	30.03 *t*	29.67 *t*‖	29.4 *t*
3	40.6 *t*	41.62 *t*	35.1 *t*	32.5 *t*	32.86 *t*	121.3 *d*	120.6 *d*
4	138.0 *s*	137.9 *s*	36.1 *d*	150.9 *s*	150.38 *s*	133.1 *s*	133.1 *s*
5	122.5 *d*	127.5 *d*	43.3 *d*	51.9 *d*	45.9 *d*	43.05 *d*	50.8 *d*
6	86.2 *d*	82.2 *d*	86.0 *d*	85.1 *d*	87.89 *d*	82.06 *d*	81.0 *d*
7	83.6 *s*	50.98 *d*	75.5 *s*	45.0 *d*	75.71 *s*	75.5 *s*	50.8 *d*
8	32.4 *t*	28.5 *t*	36.9 *t*	30.9 *t*	36.21 *t*	26.86 *t*	21.0 *t*
9	35.2 *t*	39.9 *t*	34.3 *t*	36.2 *t*	34.1 *t*	29.79 *t*‖	34.0 *t*
10	142.8 *s*	141.45 *s*‖	143.5 *s*	148.9 *s*	142.74 *s*	39.34 *s*	39.6 *s*
11	146.0 *s*	141.9 *s*‖	150.1 *s*	139.5 *s*	151.79 *s*	142.6 *s*	138.6 *s*
12	170.8 *s*	170.5 *s*	170.0 *s*	170.0 *s*	169.94 *s*	170.7 *s*	170.3 *s*
13	120.3 *t*	119.1 *t*	122.6 *t*	119.9 *t*	122.75 *t*	118.8 *t*	117.0 *t*
14	16.0 *q*	16.3 *q*	111.5 *t*	112.4 *t*	111.54 *t*	23.28 *q*	23.2 *q*
15	17.7 *q*	17.4 *q*	15.1 *q*	109.4 *t*	108.79 *t*	11.77 *q*	12.3 *q*
Ac C=O						169.87 *s*	
Ac Me						21.07 *q*	

*Assignments of C-2 and C-3 interchanged from ref. [11].

†Assignments corrected from ref. [13].

‡Assignments by analogy to model compounds [18].

§Signal obscured by the solvent signals.

‖Assignments interchangeable within a column.

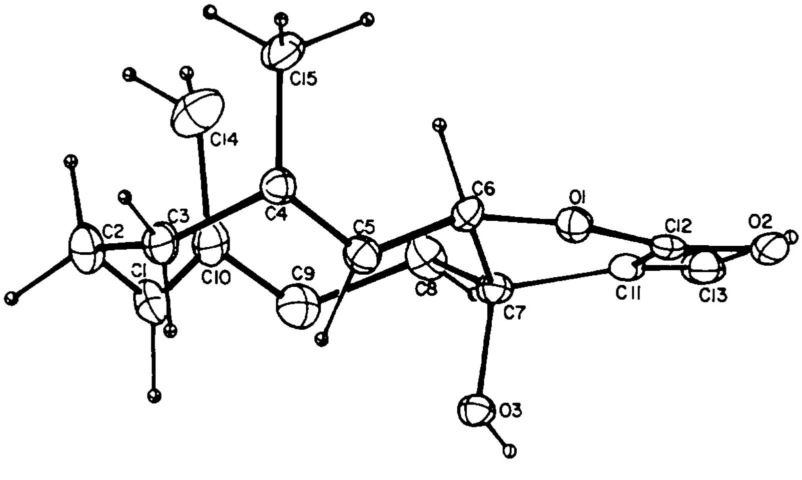


Fig. 1.

epimeric at C-4 [12]. Apart from expected shifts caused by the absence of the exocyclic double bond, the ^{13}C NMR spectrum of **7** was quite similar to that of **9** [13], with one exception. The reported assignments for C-8 and C-3 in **9** [13] must be interchanged in order to account for the effect of the C-7 hydroxyl group. Compound **7** is, therefore, 4α,15-dihydro-7α-hydroxy-3-desoxyzaluzanin C.

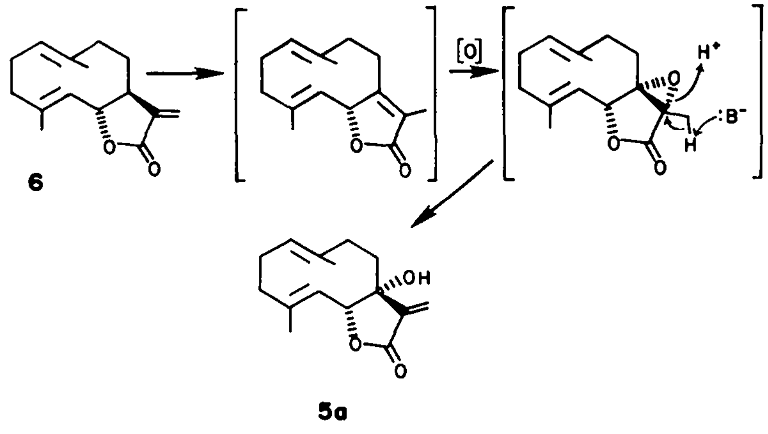
A third novel compound (**10a**) was isolated in small amounts; most of **10a** material obtained was mixed with another lactone and this mixture could be separated only after acetylation by prep. TLC. Before acetylation the ^{1}H NMR of the mixture indicated that no acetyl groups were present in either compound. However, the IR spectrum of some purified **10a** displayed absorptions at 3450, 3325 and 1740 cm^{-1} indicating that **10a** had at least one hydroxyl group and perhaps a lactone moiety similar to **5a** and **7**. The mass spectrum of the acetylation product of **10a** (**10b**) did not contain a molecular ion, but instead showed a peak at *m/z* 246 (base peak) which can be assigned to the $[M - HOAc]^+$ ion as well as fragments at *m/z* 228 $[M - HOAc - H_2O]^+$ and 213 $[M - HOAc - H_2O - Me]^+$. Compound **10b** again exhibited the lactone exomethylene protons as sharp singlets, and in addition the signal for H-6 was a doublet suggesting that C-7 must be substituted with a hydroxyl group. The signal for C-7 in the ^{13}C NMR spectrum (Table 3) appeared at δ75.5 and the remaining signals for the lactone ring were similar to those of **5a** and **7**.

The ^{1}H NMR spectrum of **10b** (Table 2) also showed two methyl signals in addition to the acetyl methyl, one a tertiary methyl singlet at δ0.99 and the second a vinylic methyl at δ1.82, suggesting a eudesmanolide skeleton for **10a**. This, together with the multiplicity of H-6, indicated the vinyl methyl was H-15 and that **10b** was 3,4-unsaturated. The signal of H-6 at δ4.07 was collapsed to a singlet by irradiation on the broad doublet at δ3.07 (H-5). A doublet of doublets observed at δ4.96 was assigned to the signal for the proton geminal to the acetoxyl group, its coupling with two vicinal protons indicating that the acetoxyl group could be at C-1, C-8 or C-9. Decoupling experiments established that the acetoxyl group was at C-1. To provide additional information about the structure an authentic sample of santamarine (**11a**) was acetylated. A comparison of the ^{1}H NMR (Table 1) and the ^{13}C NMR (Table 2) spectra of santamarine acetate (**11b**) and **10b** indicated that **11b** and **10b** were closely related. The coupling constants between H-1 and the two C-2 protons ($J = 6.3$, 10.1 Hz) in santamarine acetate (**11b**) were very similar to those in **10b** ($J = 6.9$, 9.8 Hz) suggesting that the C-1 acetoxyl group of **10b** had a β-configuration. Thus, **10b** can be formulated as the 7α-hydroxy derivative of santamarine acetate, and **10a** must be the 1β-hydroxy analog.

Compound **12a**, a minor constituent in the plant, was separated from **10a** as its acetylated product **12b**. The mass spectrum of **12b** showed fragments at *m/z* 246 $[M - HOAc]^+$, 228 $[M - HOAc - H_2O]^+$, 213 $[M - HOAc - H_2O - Me]^+$ as well as the base peak at *m/z* 43 $[Ac]^+$. A molecular ion was not observed.

The ^{1}H NMR spectrum (Table 2) of **12b** exhibited properties which indicated that **12b** was structurally related to **10b**. Compound **12b** also showed the exomethylene protons of the lactone moiety as sharp singlets (δ6.18 and 5.67) and the signal for H-6 as a sharp doublet indicating that **12b** again had C-7 substituted with a hydroxyl group. The ^{1}H NMR spectrum showed a broad doublet at δ2.87 assigned to H-5, this signal was collapsed to a broad singlet with irradiation of the sharp doublet of H-6 at δ4.13. In contrast to **10b**, **12b** lacked a vinyl methyl signal and instead contained two broadened singlets at δ5.02 and 4.88, suggesting the presence of an exocyclic methylene at C-4. Irradiation of the signal at δ5.02 sharpened the signal for H-5 as well as a complex multiplet at δ2.33, thus confirming the position of the exomethylene group. Further, the multiplet at 2.33 had to be one of the H-3 protons. The double of doublets at δ4.88, superimposed on one of the C-4 exomethylene signals, was assigned to the proton geminal to the acetoxy group. A comparison of ^{1}H NMR spectrum of **12b** with the ^{1}H NMR spectrum of reynosin acetate (**13**) (Table 2) showed that the signal at δ4.88 represented H-1 and that the acetoxy group must be β-oriented. Therefore, **12a** must be the 7α-hydroxy analog of reynosin.

The co-occurrence of compounds **5a**, **7**, **10a** and **12a**, and in particular the C-1 oxygen function of the latter two compounds, is suggestive of their biogenetic inter-



Scheme 1.

relationships. A possible biogenesis of the initial 7α-hydroxy compound, most likely the germacrolide **5a**, is presented in Scheme 1.

The unusual 7α-hydroxy lactones found in *D. ovatifolia* have been reported so far only from species of the unrelated genera *Montanoa* and *Podachaenium* (tribe Heliantheae), and *Thapsia* of the family Umbelliferae [9, 10, 14–16]. Nevertheless, the production of a guaianolide sesquiterpene lactone without an ester side chain (**7**) and particularly with the β-configuration of the C-4 methyl lends some support to placement of this species in *Decachaeta* along with *D. thieleana* (Klatt) King and Robinson and *D. scabrella* (B. L. Robinson) King and H. Robinson where similar compounds are found [3, 4; Miski *et al.*, unpublished]. In contrast, the type species of the genus, *D. haenkeana* DC., which is maintained as a separate subgenus by King and Robinson [1], does not contain sesquiterpene lactones. In addition, preliminary evidence suggests the genus *Ophryosporus*, as delimited by King and Robinson [1], is chemically distinct from *Decachaeta* [5, 6], in accord with the suggestion that the two genera are not closely allied. Further studies will be required to determine if other chemical characters can be found to define the genus *Decachaeta* and to understand the evolutionary significance of 7α-hydroxy lactones in the Eupatorieae. The particularly high molluscicidal activity of 7α-hydroxy lactones in comparison to other sesquiterpene lactones [13] gives additional importance to the search for similar compounds in related taxa.

EXPERIMENTAL

Air-dried and unground leaves and flowers (726 g) of *D. ovatifolia* collected in Michoacan, Mexico, 21 km south Uruapan on 15 November, 1983, by Fred Barrie (voucher Barrie, Ramamoorthy and Martinez 533 on deposit at University of Texas Herbarium) were extracted with CH_2Cl_2 and allowed to stand for 12 hr. The slurry was filtered and concd. The extract obtained (27 g) was separated by CC (silica gel) which was eluted with a hexane–EtOAc gradient with increasing amounts of EtOAc; 120 fractions were collected. From fractions 25–32 (25% EtOAc) 63 mg 7α-hydroxycostunolide (**5a**) were isolated as a crystalline solid. The mother liquor of these fractions and fractions 33–38 (27% EtOAc) showed on TLC (silica gel) the presence of **5a** and another compound. These fractions were evaporated to give a brown syrup (52 mg) which was separated on a Sephadex LH-20 column using as the solvent system hexane–CH_2Cl_2–MeOH (7:4:1). This column afforded an additional 18 mg **5a** (0.0112% dry wt) and 12 mg **7** (0.0017% dry wt). 7α-Hydroxycostunolide (**5a**) appeared blue–grey on a TLC plate (silica gel) after spraying with acidified vanillin reagent [17] and heating, while 4α,15-dihydro-7α-hydroxy-3-desoxyzaluzanin C (**7**) was bright blue after the same treatment.

From fraction 70 (45% EtOAc) 3 mg of **10a** were isolated; fractions 71–81 afforded **10a** mixed with another lactone; this mixture (19.7 mg) could only be partially separated before acetylation. The acetylated mixture was separated by repeated (×3) prep. TLC (silica gel, 0.5 mm, precoated E. Merck) developed with hexane–EtOAc (7:3). This separation yielded 6.2 mg **10b** and 9.2 mg of a mixture of **10b** and **12b**. Additional prep. TLC in the same solvent system afforded 3 mg **12b** and 4 mg **10b**.

7α-Hydroxycostunolide (**5a**). Mp 153° (dec.); IR ν_{max}^{KBr} cm^{-1}: 3425 (OH), 1736 (sh), 1720 (lactone C=O), 1660, 1395, 1290, 1270, 1180, 1100, 1060, 955; EIMS 70 eV (probe), *m/z* (rel. int.): 248 $[M]^+$ (2.95), 230 $[M-H_2O]^+$ (81.4), 215 $[M-H_2O-Me]^+$ (60), 121 (89.97), 109 (91.88), 91 (66), 81 (80.6), 55 (100).

Reduction of **5a** *with* $NaBH_4$. Compound **5a** (13 mg) was dissolved in 2 ml MeOH; then 20 mg $NaBH_4$ were added gradually and the soln was left 3 hr at room temp. After evaporation of solvent *in vacuo*, **5b** was worked-up in the usual manner.

7α-Hydroxy-11β,13-dihydrocostunolide (**5b**). Colourless gum. IR ν_{max}^{NaCl} cm^{-1}: 3450, 1778 (sh), 1765, 1452, 1270, 1195, 980; EIMS 70 eV (probe), *m/z* (rel. int.): 250 $[M]^+$ (7.8), 235 $[M-Me]^+$ (3.9), 232 $[M-H_2O]^+$ (2.9), 217 $[M-Me-H_2O]^+$ (6.1). ^1H NMR ($CDCl_3$, 200 MHz, TMS as int. standard): δ4.97 (*br d*, H-5), 4.87 (*br dd*, H-1), 4.68 (*d*, H-6), 2.49 (*q*, H-11), 1.72 (*br s*, H-15), 1.41 (*br s*, H-14), 1.23 (*d*, $J = 7$ Hz, H-13).

4α,15-Dihydro-7α-hydroxy-3-desoxyzaluzanin C (**7**). Mp 151–152°; IR ν_{max}^{KBr} cm^{-1}: 3430 (OH), 1755 (lactone C=O), 1665, 1635, 1165, 1050, 970; EIMS 70 eV (probe), *m/z* (rel. int.): 230 $[M-H_2O]^+$ (95.2), 215 $[M-H_2O-Me]^+$ (32.9), 202 $[M-H_2O-CO]^+$ (28.6), 120 (68.43), 109 (63.9), 91 (76.7), 81 (100).

7α-Hydroxysantamarine (**10a**). IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 3325 (OH), 1740 (lactone C=O), 1405, 1380, 1280, 1165, 1145, 1125, 1070, 1050, 1025, 980, 960, 985, 800.

7α-Hydroxysantamarine acetate (**10b**). Mp 210° (dec.); EIMS 70 eV, *m/z* (rel. int.): 246 $[M-OAc]^+$ (100), 228 [M – OAc

$- H_2O]^+$ (88.5), 213 $[228 - Me]^+$ (93), 219 (73.96), 91 (66.98), 55 (72.66), 43 (58.88).

7α-Hydroxyreynosin acetate (**12b**). Mp 199° (dec.); EIMS 70 eV, *m/z* (rel. int.): 246 $[M - OAc]^+$ (4.88), 228 $[M - OAc - H_2O]^+$ (63.2), 213 $[228 - Me]^+$ (32.29), 199 (79.94), 119 (9.16), 5 (9.16), 55 (18.5), 43 (100).

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