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EUDESMANOLIDES AND COSTIC ACID DERIVATIVES FROM *FLOURENSIA MACROPHYLLA*

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Key Word Index—*Flourensia macrophylla*, Compositae, sesquiterpenes, costic acid derivatives, eudesmanolides

Abstract—The aerial parts of *Flourensia macrophylla* afforded, in addition to compounds similar to those from other *Flourensia* species, four new eudesmanolides and five derivatives of costic acid The structures were elucidated by ^{1}H NMR spectroscopy The chemotaxonomic aspects are discussed briefly

INTRODUCTION

The genus *Flourensia* (Compositae, tribe Heliantheae) was placed by Stuessy [1] in the subtribe Helianthinae but later was transferred together with *Encelia* to the large subtribe Ecliptinae [2]. The chemistry of these two genera shows close relationships by the co-occurrence of a large variety of *p*-hydroxyacetophenone derivatives [3, 4] Furthermore from *Flourensia* species several flavanoids were reported [4–8], oxygenated lupane derivatives [4, 9] and especially costic acid derivatives [7–9], which seem to be characteristic So far, however, no sesquiterpene lactones were isolated which are widespread in the subtribe Ecliptinae We now have studied the constituents of *Flourensia macrophylla* Blake from Peru The results are discussed in this paper

RESULTS AND DISCUSSION

The aerial parts of *F macrophylla* afforded, in addition to widespread compounds several lupane derivatives, a large variety of *p*-hydroxyacetophenone derivatives (see Experimental) and several costic acid derivatives (**5**–**10**) as well as alantolactone and four new derivatives of the latter (**1**–**4**) Compound **1**, molecular formula $C_{20}H_{20}O_3$, showed ^{1}H NMR spectral data which were in part close to that of alantolactone (Table 1) All signals could be assigned by spin decoupling The presence of a 9α-hydroxy group followed from the downfield shifts of the H-1α and H-5 signals and the absence of the characteristic pairs of H-9 doublets These were replaced by a broadened singlet at δ3 84 which was transformed to a sharp doublet by irradiation of a broadened singlet at 1 83, indicating that the broadening was due to a coupling with a hydroxyl proton The corresponding signal (1 83) therefore disappeared on deuterium exchange

The spectroscopic data of **2** showed that an isomer of **1** was present Again all signals, which were separated completely in the 400 MHz spectrum (Table 1), could be assigned by spin decoupling. The equatorial orientation of the 9-hydroxy group could be deduced from the upfield shifts of the H-1α and H-5 signals, the downfield shift of the H-1β signals, if compared with those of **1**, and from the coupling $J_{8,9}$

Table 1 ^{1}H NMR spectral data of compounds **1**–**4** (400 MHz, $CDCl_3$, TMS as int standard)

	1	**2**	**3**	**4**
H-1α	1 86 *ddd*	1 20 *ddd*	1 60 *m*	—
H-1β	1 31 *br d*	2 07 *br d*	1 75 *m*	—
H-2α	1 69 *m*	1 66 *br d*	1 75 *m*	2 62 *m*
H-2β	1 60 *ddddd*	1 49 *ddddd*	1 60 *m*	2 73 *m*
H-3α	1 99 *br ddd*	1 96 *br ddd*	1 97 *m*	2 36 *m*
H-3β	2 33 *br d*	2 32 *br d*	2 35 *br d*	2 39 *m*
H-5α	2 33 *br d*	1 87 *br d*	2 44 *br d*	2 18 *br d*
H-6α	1 74 *ddd*	1 71 *ddd*	2 14 *ddd*	1 88 *ddd*
H-6β	1 35 *ddd*	1 34 *ddd*	1 67 *ddd*	1 60 *ddd*
H-7α	3 20 *br ddd*	3 07 *ddddd*	3 49 *ddddd*	2 94 *br ddd*
H-8α	4 41 *dd*	4 57 *dd*	4 69 *d*	4 60 *ddd*
H-9α	—	3 49 *d*	—	2 00 *br dd*
H-9β	3 84 *br s*	—	—	2 37 *dd*
H-13	6 16 *d*	6 14 *d*	6 27 *d*	6 17 *d*
H-13′	5 62 *d*	5 62 *d*	5 70 *d*	5 62 *d*
H-14	0 82 *s*	0 81 *s*	1 01 *s*	1 11 *s*
H-15	4 80 *ddd*	4 80 *ddd*	4 94 *ddd*	5 07 *br s*
H-15′	4 46 *ddd*	4 48 *ddd*	4 62 *ddd*	4 77 *br s*
OH	1 83 *br s*	2 17 *d*	—	—

J (Hz) Compounds **1** and **2** 1α, 1β = 1α, 2β = 13 5, 1α, 2α = 4 5, 1β, 2β = 4, 2α, 2β = 2β, 3α = 13 5, 2α, 3α = 5, 2β, 3β = 4, 3α, 3β = 13, 3α, 15 = 3α, 15′ = 5α, 15 = 5α, 15′ = 15, 15′ = 1 5, 5α, 6α = 3, 5α, 6β = 12 5, 6α, 6β = 14 5, 6α, 7α = 7 5, 6β, 7α = 12 5, 7α, 8α = 5 5, 7α, 13 = 1, 7α, 13′ = 1 2, compound **1** 8α, 9β = 2 2, compound **2** 8α, 9α = 4 5, 9, OH = 11, compound **3** 3α, 15 = 3α, 15′ = 5α, 15 = 5α, 15′ = 15, 15′ = 1 5, 5α, 6α = 3, 5α, 6β = 12 5, 6α, 7α = 8 5, 6α, 6β = 14, 6β, 7α = 11, 7α, 8α = 7 5, 7α, 13 = 7α, 13′ = 2, compound **4** 5α, 6α = 2 5, 5α, 6β = 12 5, 6α, 6β = 14, 6α, 7α = 6 5, 6β, 7α = 12 5, 7α, 8α = 8α, 9α = 4 5, 7α, 13 = 1 2, 7α, 13′ = 0 9, 8α, 9β = 2, 9α, 9β = 16 5

The molecular formula and the IR spectrum of **3** clearly indicated that a ketolactone was present The ^{1}H NMR spectrum (Table 1) clearly showed that the keto group was at C-9 Accordingly, the H-8 signal now was a doublet Again all signals could be assigned by spin decoupling, but those of H-1 and H-2 were overlapped multiplets

The molecular formula of **4** indicated that this lactone was an isomer of **3** The keto group was at C-1 as followed from the ^{1}H NMR spectrum (Table 1) which showed pronounced downfield shifts of the H-9α signal if compared with that of alantolactone Spin decoupling allowed the assignment of all signals though those of H-2 and H-3 were overlapped, not first order signals A downfield shift of the H-14 signal and no drastic shifts of H-15 excluded a 3-position of the keto group The presence of *cis*-8,12-eudesmanolides (**1–4**) also followed from the Cotton effects of **2–4**, if the Geissman rule was applied [10]

The structures of **6–10**, which were purified as their methyl esters **6a–10a**, again followed from the ^{1}H NMR spectral data (Table 2) and the molecular formulae Compound **6** obviously was an isomer of 1-oxo-costic acid [4] The position of the keto group followed from the splitting and the downfield shift of the H-8 signals, while the splitting of H-7 showed that the residue at C-7 was equatorial orientated though the H-7 signal was broadened due to the overlapping of the H-6 signals causing a none first order system This also was visible from the H-5 signal which showed no clear *trans*-diaxial coupling However, the similarity of the signals with those of costic acid and related compounds excluded a different stereochemistry at C-5

The ^{1}H NMR spectrum of **7a** showed that a costic acid derivative was present with a 9α-hydroxy group, while from that of **8a** a 9β-hydroxy group could be deduced (Table 2) Accordingly, the H-9 signal showed small couplings in the spectrum of **7a** while in that of **8a** a 11 Hz coupling for *trans*-diaxial protons were visible The axial hydroxy group in **7a** caused a considerable downfield shift of the H-1α and H-5 signals which together with the observed coupling $J_{5,6\beta}$ showed that a *trans*-decalin derivative was present Again all signals were assigned by spin decoupling, except the signals of H-2 and H-6α which were overlapped multiplets in the spectra of **7a** and **8a** Reaction of the free acid **8** with tosyl chloride in pyridine led to the lactone **11** which supported the *cis*-orientation of the 9-hydroxyl group and the 7-acrylic acid side chain (see ^{1}H NMR Table 3)

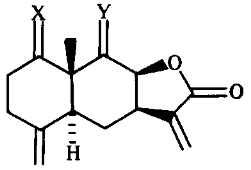
The molecular formulae of **9a** and **10a** again showed that we were dealing with a pair of isomers Inspection of the ^{1}H NMR spectra (Table 2) showed further that **9a** had vicinal hydroxyl groups As $J_{7,8}$ and $J_{8,9}$ both were small the substituents at C-7–C-9 were *cis*-orientated while a large coupling $J_{6\beta,7}$ indicated an equatorial C-7 residue Hence the stereochemistry of **9a** was as shown Acid catalysed transesterification of **9a** afforded the lactone **12** with a rearranged double bond (^{1}H NMR see Table 3) The ^{1}H NMR spectrum of **10a** clearly showed that the methyl ester of 1β,9β-dihydroxy costic acid was present as all signals could be assigned by spin decoupling, only those of H-2α, H-5α and H-8α forming a multiplet As both low field double doublets (H-1 and H-9) showed a large coupling the equatorial orientation of the hydroxyl groups was established

The chemistry of *F macrophylla* is close to that of *F*

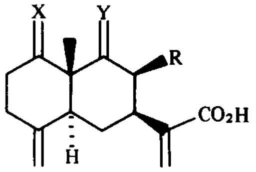
Table 2 ^{1}H NMR spectral data of compounds **6a–10a** (400 MHz, $CDCl_3$ TMS as int standard)

	6a	**7a**	**8a**	**9a**	**10a**
H-1α	1 64 *ddd*	1 91 *ddd*	1 27 *ddd*	1 27 *m*	3 81 *dd*
H-1β	1 83 *br d*	1 23 *br d*	1 96 *br d*	1 97 *br d*	—
H-2α	1 76 *br d*	1 67 *m*	1 71 *m*	1 66 *m*	1 82 *m*
H-2β	1 53 *ddddd*	1 60 *m*	1 57 *m*	1 56 *m*	1 58 *dddd*
H-3α	1 96 *br ddd*	2 01 *br ddd*	2 00 *br ddd*	1 99 *m*	2 10 *br ddd*
H-3β	2 31 *br d*	2 29 *br d*	2 32 *br d*	2 32 *br d*	2 31 *ddd*
H-5α	2 26 *br dd*	2 40 *br d*	1 89 *br d*	1 90 *br d*	1 82 *m*
H-6α	1 82 *m*	1 64 *m*	1 64 *m*	1 36 *br d*	1 67 *br d*
H-6β		1 37 *ddd*	1 31 *ddd*	1 81 *ddd*	1 32 *ddd*
H-7α	2 91 *br dddd*	3 00 *br dddd*	2 65 *br dddd*	2 86 *br ddd*	2 63 *br dddd*
H-8α	2 34 *dd*	1 74 *dddd*	1 85 *dddd*	4 06 *dd*	1 82 *m*
H-8β	2 79 *dd*	1 84 *ddd*	1 53 *ddd*	—	1 52 *ddd*
H-9α	—	—	3 52 *dd*	3 38 *d*	3 86 *dd*
H-9β	—	3 57 *dd*	—	—	—
H-13	6 25 *br s*	6 18 *br s*	6 19 *br s*	6 39 *br s*	6 20 *br s*
H-13′	5 66 *br s*	5 57 *br s*	5 61 *br s*	5 76 *br s*	5 60 *br s*
H-14	1 09 *s*	0 76 *s*	0 78 *s*	0 90 *s*	0 80 *s*
H-15	4 88 *ddd*	4 75 *ddd*	4 76 *ddd*	4 79 *ddd*	4 82 *ddd*
H-15′	4 63 *ddd*	4 45 *ddd*	4 48 *ddd*	4 56 *ddd*	4 53 *ddd*
OMe	3 78 *s*	3 76 *s*	3 76 *s*	3 78 *s*	3 76 *s*

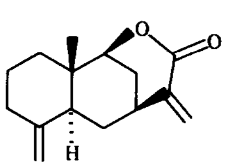
J (Hz) Compound **6a** 1α, 1β = 1α, 2β = 2α, 2β = 2β, 3α = 3α, 3β = 12 5, 1α, 2α = 3 5, 1β, 2β = 2β, 3β = 4, 3α, 15 = 3α, 15′ = 5α, 15 = 5α, 15′ = 15, 15′ = 1 5, 5α, 6α = 6 5, 5α, 6β = 8, 6α, 7 = 7, 8α = 4, 6β, 7 = 7, 8β ~ 12, 7α, 8α = 4, 7α, 8β = 8α, 8β = 13, compounds **7a–9a** 1α, 1β = 1α, 2β = 13, 1α, 2α = 4 5, 2α, 3α = 5, 2β, 3α = 3α, 3β = 13, 3α, 15 = 3α, 15′ = 5α, 15 = 5α, 15′ = 15, 15′ = 1 5, 5α, 6β = 12, 6α, 6β = 13 5, 6α, 7α = 7α, 8α = 4, 6α, 8α = 1 5, 6β, 7α = 7α, 8β = 8α, 8β = 12 5, (compound **7a** 8α, 9β = 8β, 9β = 3, compound **8a** 8α, 9α = 4, 8β, 9α = 11, compound **9a** 7α, 8α = 8α, 9α = 3 5), compound **10a** 1α, 2α = 4 5, 1α, 2β = 11, 2α, 2β = 2β, 3α = 3α, 3β = 13, 2α, 3α = 2β, 3β = 5, 3α, 15 = 3α, 15′ = 5α, 15 = 5α, 15′ = 15, 15′ = 1 5, 5α, 6β = 6α, 6β = 6β, 7α = 7α, 8β = 8α, 8β = 12 5, 6α, 7α = 7α, 8α = 4, 8α, 9α = 4 5, 8β, 9α = 11 5



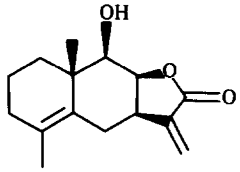
	1	**2**	**3**	**4**
X	H_2	H_2	H_2	O
Y	αOH,H	βOH,H	O	H_2



	5	**6***	**7***	**8***	**9***	**10***
X	O	H_2	H_2	H_2	H_2	βOH,H
Y	H_2	O	αOH H	βOH,H	βOH,H	βOH,H
R	H	H	H	H	OH	H



11



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* **6a** — **10a** are the corresponding methylesters

Table 3 ^{1}H NMR spectral data of compounds **11** and **12** (400 MHz, $CDCl_3$, TMS as int standard)

	11	**12**
H-1α	1 43 *ddd*	1 3–1 6 m
H-1β	1 63 *br d*	
H-2α	1 70 *m*	
H-2β		
H-3α	2 02 *m*	1 97 *m*
H-3β	2 32 *br d*	
H-5α	1 98 *br d*	—
H-6α	2 17 *ddd*	2 73 *dd*
H-6β	1 41 *ddd*	2 05 *dd*
H-7α	3 01 *dddddd*	3 03 *ddddd*
H-8α	2 19 *ddd*	4 53 *dd*
H-8β	1 89 *ddd*	—
H-9α	4 38 *ddd*	3 61 *dd*
H-13	6 34 *d*	6 16 *d*
H-13′	5 49 *br s*	5 59 *d*
H-14	0 78 *s*	1 12 *s*
H-15	4 78 *ddd*	1 69 *br s*
OH	—	2 05 *d*

J (Hz) Compound **11** 1α, 1β = 13 5, 1α, 2α = 6, 1α, 2β = 12, 3α, 3β = 13, 3α, 15 = 3α, 15′ = 5α, 15 = 5α, 15′ = 15, 15′ = 1 5, 5α, 6α = 5, 5α, 6β = 6α, 6β = 14, 6α, 7α = 11 5, 6β, 7α = 7α, 8α = 7α, 8β = 7α, 9α = 8α, 9α = 8β, 9α = 3, 7α, 13 = 7α, 13′ = 1, 8α, 8β = 14 5, compound **12** 6α, 6β = 13 5, 6α, 7α = 7, 6β, 7α = 11 5, 7α, 8α = 6, 7α, 13 = 7α, 13′ = 1 5, 8α, 9α = 4, 9α, OH = 8

heterolepis [4] in the cooccurrence of several prenylated *p*-hydroxyacetophenone derivatives, a prenylated flavanone, lupane derivatives and the costic acid derivatives However, eudesmanolides have been isolated for the first time from a *Flourensia* species though the costic acids derivatives surely are the precursors of these sesquiterpene lactones Similar lactones have been isolated from several genera from the Ecliptinae Though this subtribe is somewhat diverse taxonomically [2], these findings again support the placing of *Flourensia* and *Encelia* in this subtribe Further investigations may show whether the chemistry can support a further separation of this large subtribe

EXPERIMENTAL

The aerial parts (400 g), (voucher RMK 9027, collected in January 1982 in Peru) were extracted with Et_2O–petrol, 1 2 (2 hr, room temp), and the extract obtained (50 g) was worked-up in the usual fashion CC separation of 5 g extract afforded fractions as follows 1 (petrol, 100 ml), 2 (Et_2O–petrol, 1 10 and 1 3, each 100 ml), 3 (Et_2O–petrol, 1 1, 100 ml), 4 (Et_2O and Et_2O–MeOH, 10 1, each 100 ml) TLC (petrol) of fraction 1 afforded 5 mg germacrene D, 3 mg α- and 3 mg γ-curcumene Repeated TLC (always SiO_2 PF 254, Et_2O–petrol, 1 3, detection by UV, 255 nm) of fraction 2 gave 35 mg euparin (R_f 0 61), 10 mg euparin methyl ether (R_f 0 57), 15 mg 3α-angeloyloxy-6-hydroxy tremetone (R_f 0 42), 3 mg of the corresponding methyl ether, 60 mg 8-angeloyloxy-8-desoxo-euparin methyl ether (R_f 0 42), 3 mg 6-acetyl-8-(3,3-dimethyl allyl)-2,2-dimethylchromene (R_f 0 40), 3,5-*bis*-(3,3-dimethylallyl)-4-hydroxy acetophenone (R_f 0 38), 15 mg 20,29-epoxylupenone [4] (R_f 0 37), 15 mg 20,29-epoxylupeol [9]

(R_f 0 33), 15 mg 30-hydroxylupenone [4] (R_f 0 30), 5 mg alantolactone (R_f 0 28) and 60 mg 4-hydroxyacetophenone (R_f 0 20) Repeated TLC (Et_2O–petrol, 1 1) of fraction 3 afforded (increasing polarity) 25 mg alantolactone (R_f 0 50), 5 mg 20,29-epoxylupenone (R_f 0 57), a mixture of **5** [4] and **6** (R_f 0 52) (separation after addition of CH_2N_2 gave 50 mg **5a** [4] (R_f 0 60) and 200 mg **6a** (R_f 0 58), (TLC Et_2O–petrol, 1 2)), 40 mg 4-hydroxyacetophenone (R_f 0 30) and a mixture of **3** and **4** (R_f 0 25), which by TLC (C_6H_6–CH_2Cl_2–Et_2O, 5 5 1) gave 60 mg **3** (R_f 0 50) and 20 mg **4** (R_f 0 45), as well as a mixture of 5 mg **1** and 20 mg 5,3′-dihydroxyisobarachin-7-*O*-methyl ether [4] (R_f 0 2), which was separated by HPLC (RP 8, MeOH–H_2O, 7 3, detection UV and refractometer, **1** R_t 5 5 min) Repeated TLC (Et_2O–petrol, 3 1) of fraction 4 afforded 20 mg **5** (R_f 0 70), 100 mg (R_f 0 68) **6**, 60 mg **3** (R_f 0 67), 20 mg **4** (R_f 0 67), 5 mg 5,3′-dihydroxyisobarachin-7-*O*-methyl ether (R_f 0 66), 15 mg **1** (R_f 0 63), 200 mg scopoletin-(3′-methyl-but-2′-en-1′-yl)-ether (R_f 0 66), 20 mg **7** (R_f 0 60), 20 mg **8** (R_f 0 57), 200 mg scoparone (R_f 0 50), 400 mg **2** (R_f 0 30), 10 mg **9** (R_f 0 20), 10 mg **10** (R_f 0 18) and 300 mg scopoletin (R_f 0 17) **7–10** were further purified after addition of CH_2N_2 as their methyl esters **7a–10a** [TLC for **7a** (R_f 0 52) and **8a** (R_f 0 48) Et_2O–petrol, 1 1 and 3 1 for **9a** (R_f 0 45) and **10a** (R_f 0 40)] Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material Quantities were determined by weight

9α-Hydroxyalantolactone (**1**) Colourless oil, which could not be induced to crystallize, IR $\nu_{\max}^{CCl_4}$ cm^{-1} 3600 (OH), 1775 (γ-lactone), MS m/z (rel int) 248 141 $[M]^+$ (3) (calc for $C_{15}H_{20}O_3$ 248 141), 230 $[M - H_2O]^+$ (62), 215 $[230 - Me]^+$ (15), 202 $[230–CO]^+$ (10), 134 $[C_{10}H_{14}]^+$ (100), 119 $[134 - Me]^+$ (58)

9β-Hydroxyalantolactone (**2**) Colourless crystals, mp 171°, IR $\nu_{\max}^{CHCl_3}$ cm^{-1} 3600 (OH), 1770 (γ-lactone), MS m/z (rel int) 248 141 $[M]^+$ (57) (calc for $C_{15}H_{20}O_3$ 248 141), 230 $[248 - H_2O]^+$ (48), 215 $[230 - Me]^+$ (14), 202 $[230 - CO]^+$ (16), 134 (28), 105 (61), 95 (100), 91 (94), 79 (92), CD (MeCN) $\Delta_{\varepsilon_{260}} = -1\ 3$

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\mathrm{nm}}{+78 \quad +82 \quad +93 \quad +160}\ (\mathrm{CHCl_3},\ c\ 1\ 9)$$

9-Oxo-alantolactone (**3**) Colourless crystals, mp 118°, IR $\nu_{\max}^{CCl_4}$ cm^{-1} 1780 (γ-lactone), 1715 (C=O), MS m/z (rel int) 246 126 $[M]^+$ (61) (calc for $C_{15}H_{18}O_3$ 246 126), 218 $[M - CO]^+$ (19), 203 $[218 - Me]^+$ (28), 107 (70), 105 (51), 93 (96), 91 (85), 79 (100), CD (MeCN) $\Delta\varepsilon_{309} = +1\ 7$, $\Delta\varepsilon_{258} = -2\ 0$

1-Oxo-alantolactone (**4**) Colourless crystals, mp 164°, IR $\nu_{\max}^{CCl_4}$ cm^{-1} 1780 (γ-lactone), 1715 (C=O), MS m/z (rel int) 246 126 $[M]^+$ (100) (calc for $C_{15}H_{18}O_3$ 246 126), 218 $[M - CO]^+$ (12), 191 (36), 190 (37), 107 (52), 105 (47), 92 (63), 91 (78), 79 (77), 53 (94), CD (MeCN) $\Delta\varepsilon_{302} = +0\ 7$, $\Delta\varepsilon_{260} = -1\ 9$

9-Oxo costic acid (**6**) Isolated as its methyl ester **6a**, colourless crystals, mp 46°, IR $\nu_{\max}^{CCl_4}$ cm^{-1} 1720 (C=CCO$_2$R), 1705 (C=O), MS m/z (rel int) 262 157 $[M]^+$ (100) (calc for $C_{16}H_{22}O_3$ 262 157), 230 $[M - MeOH]^+$ (27), 202 $[230 - CO]^+$ (24), 187 $[202 - Me]^+$ (20), 107 (57), 95 (67), 93 (80), 79 (81)

9α-Hydroxy costic acid (**7**) Isolated as its methyl ester **7a**, colourless oil, IR $\nu_{\max}^{CCl_4}$ cm^{-1} 3600 (OH), 1720, 1650 (C=CCO$_2$R), MS m/z (rel int) 264 $[M]^+$ (2), 246 162 $[M - H_2O]^+$ (100) (calc for $C_{16}H_{22}O_2$ 246 162), 231 $[246 - Me]^+$ (18), 214 $[246 - MeOH]^+$ (20), 186 $[214 - CO]^+$ (25), 171 $[186 - Me]^+$ (38), 145 $[171 - C_2H_2]^+$ (41), 91 (64), 79 (63)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\mathrm{nm}}{+9 \quad +10 \quad +11 \quad +17}\ (\mathrm{CHCl_3},\ c\ 0\ 35)$$

9β-Hydroxy costic acid (**8**) Isolated as its methyl ester **8a**, colourless oil, IR $\nu_{\max}^{CCl_4}$ cm^{-1} 3600 (OH), 1720, 1650 (C=CCO$_2$R), MS m/z (rel int) 264 172 $[M]^+$ (6 5) (calc for $C_{16}H_{24}O_3$ 264 172), 246 $[M - H_2O]^+$ (32), 232 $[M - MeOH]^+$ (21), 204 $[232 - CO]^+$ (41), 91 (100), 79 (98)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\mathrm{nm}}{+16 \quad +17 \quad +19 \quad +22}\ (\mathrm{CHCl_3},\ c\ 0\ 83)$$

To 10 mg **8** (containing **7**) in 0 5 ml pyridine 12 mg tosyl chloride was added After standing at room temp for 20 hr, TLC (Et_2O–petrol, 3 1) gave 5 mg **11**, IR $\nu_{\max}^{CCl_4}$ cm^{-1} 1730 (δ-lactone), MS m/z (rel int) 232 146 $[M]^+$ (51) (calc for $C_{15}H_{20}O_2$ 232 146), 217 $[M - Me]^+$ (11), 204 $[M - CO]^+$ (16), 145 (41), 95 (64), 91 (81), 53 (100)

8β,9β-Dihydroxy costic acid (**9**) Isolated as its methyl ester **9a**, colourless crystals, mp 53°, IR $\nu_{\max}^{CCl_4}$ cm^{-1} 3600 (OH), 1725, 1650 (C=CCO$_2$R), MS m/z (rel int) 280 168 $[M]^+$ (8) (calc for $C_{16}H_{14}O_4$ 280 168), 262 $[M - H_2O]^+$ (34), 247 $[262 - Me]^+$ (64), 230 $[262 - MeOH]^+$ (28), 215 $[247 - MeOH]^+$ (44), 187 $[215 - CO]^+$ (28), 102 (71), 95 (71), 81 (74), 55 (100)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\mathrm{nm}}{+34 \quad +43 \quad +51 \quad +83}\ (\mathrm{CHCl_3},\ c\ 0\ 35)$$

5 mg **9a** in 0 5 ml Me_2CO containing a drop of H_2SO_4 after standing 15 min at room temp afforded by TLC (Et_2O–petrol, 2 1, two developments) 3 mg **11**, colourless oil, ^{1}H NMR see Table 3

1β,9β-Dihydroxy costic acid (**10**) Isolated as its methyl ester **10a**, colourless oil, IR $\nu_{\max}^{CCl_4}$ cm^{-1} 3600 (OH), 1725, 1650 (C=CCO$_2$R), MS m/z (rel int) 280 168 $[M]^+$ (2 5) (calc for $C_{16}H_{24}O_4$ 280 168), 262 $[M - H_2O]^+$ (18), 244 $[262 - H_2O]^+$ (20), 230 $[262 - MeOH]^+$ (19), 202 $[230 - CO]^+$ (24), 121 (78), 91 (81), 79 (80), 55 (100)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\mathrm{nm}}{+17 \quad +20 \quad +22 \quad +33}\ (\mathrm{CHCl_3},\ c\ 0\ 7)$$

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REFERENCES

1 Stuessy, T F (1977) *The Biology and Chemistry of the Compositae* (Heywood, V H, Harborne, J B and Turner, B L, eds) p 635 Academic Press, London

2 Robinson, H (1981) *Smithsonian Contribution of Botany* **51**, 48

3 Bohlmann, F and Grenz, M (1977) *Chem Ber* **110**, 295

4 Bohlmann, F and Jakupovic, J (1979) *Phytochemistry* **18**, 1189

5 Dillon, M O, Mabry, T J, Besson, E, Bouillant, M L and Chopin, J (1976) *Phytochemistry* **15**, 1085

6 Rao, M M, Kingston, D G I and Spittler, T D (1970) *Phytochemistry* **9**, 227

7 Dillon, M O and Mabry, T J (1977) *Phytochemistry* **16**, 1318

8 Guerreiro, E, Kavka, J, Giordarno, O and Gros, E G (1979) *Phytochemistry* **18**, 1235

9 Rodriguez-Hahn, L and Rodriguez, J (1977) *Rev Latinoam Quim* **3**, 148

10 Stocklin, W, Waddell, T G and Geissman, T A (1970) *Tetrahedron* **26**, 2397