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NEW GERMACRANOLIDES AND OTHER SESQUITERPENE LACTONES FROM *DICOMA* SPECIES*

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Key Word Index—*Dicoma anomala* subsp. *anomala*; *D. anomala* subsp. *cirsioides*; *D. schinzii*; *D. zeyheri*; *D. macrocephala*; Compositae; Mutisieae; sesquiterpene lactones; germacranolides; eudesmanolide; guaianolide; acetylenic compounds.

Abstract—Two subspecies of *Dicoma anomala* afforded, in addition to known compounds, an eudesmanolide, a guaianolide and four germacranolides, the latter being closely related 8, 12-lactones. *D. schinzii* gave three new germacranolides and *D. zeyheri* a pair of isomeric acetylenic compounds. The structures were elucidated by highfield ^{1}H NMR spectroscopy. The chemotaxonomic situation of this genus is discussed briefly.

INTRODUCTION

So far the investigations of *Dicoma* species have shown that highly oxygenated germacranolides may be typical for this genus [1, 2]. We have now studied the constituents of further species, which again afforded germacranolides and some other lactones. The structural elucidation of these compounds is discussed in this paper.

RESULTS AND DISCUSSION

A re-investigation of the roots of *Dicoma anomala* Sond. subsp. *cirsioides* (Harv.) Willd. afforded, in addition to stigmasterol, sitosterol and lupenone, the eudesmanolides **1** [3], **2** and **4** [4] as well as the guaianolides **5** [5] and **6**. The structure of **2** clearly followed from the ^{1}H NMR spectrum (Table 1), especially when it was compared with those of **1** and **4**. Some signals, however, were different from those of 11β, 13-dihydrotubiferin **3** [4]. The β-orientation of the 11-methyl group followed from the observed coupling $J_{7,11}$. The ^{1}H NMR spectrum of **6** (Table 1) was very similar to that of **5**. The presence of a 9α-hydroxy group followed from the downfield shift of H-14 and the coupling $J_{8,9}$. This was confirmed by spin decoupling which allowed the assignment of all signals. The corresponding 9-*O*-angelate was isolated from *Zinnia* species [6], and as expected the couplings $J_{8,9}$ were nearly the same. The aerial parts gave germacrene D, lupeol, taraxasterol and four sesquiterpene lactones, the germacran-8,12-olides **8–11**. The ^{1}H NMR spectra at room temperature showed broadened, ill-defined signals. However, at elevated temperatures nearly all signals could be assigned by spin decoupling (Table 2). Obviously, all the lactones were 15-hydroxy-14-acetoxygermacranolides with one additional ester group, the nature of which also followed from the typical signals, though the relative position of the ester groups could not be established by partial hydrolysis. **11** was a 3-hydroxy-2-methyl-

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

	2	**6**
H-1	6.69 *d*	3.78 *dd*
H-2	5.90 *d*	2.49 *d*(*br*) 2.75 *dd*
H-4	2.58 *dq*	—
H-5	2.08 *dd*	3.26 *dddd*
H-6	4.21 *dd*	3.95 *dd*
H-7	2.12 *dddd*	3.37 *dddd*
H-8α	1.60 *m*	2.40 *ddd*
H-8β	1.68 *ddd*	1.67 *ddd*
H-9	1.77 *m*	4.63 *ddd*
H-11	2.64 *dq*	—
H-13	1.22 *d*	6.33 *d* 5.62 *d*
H-14	1.18 *s*	5.09 *s* 4.67 *d*
H-15	1.37 *d*	6.27 *d*(*br*) 5.88 *d*(*br*)

J (Hz): compound **2**: 1, 2 = 10; 4, 5 = 11; 4, 15 = 7.5; 5, 6 = 6, 7 = 10.5; 7, 8α = 4; 7, 8β = 10; 7, 11 = 7; 8α, 8β = 13; 8β, 9α = 10; 8β, 9β = 4; compound **6**: 1, 2 ~ 1; 1, 2′ = 8.5; 1, 5 = 9; 2, 2′ = 18; 5, 6 = 6, 7 = 9.5; 5, 15 = 2.7; 7, 8α = 3; 7, 8β = 11; 7, 13 = 3.5; 7, 13′ = 3; 8α, 8β = 14; 8α, 9β = 8β, 9β = 3.

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*Part 439 in the series "Naturally Occurring Terpene Derivatives". For Part 438, see Bohlmann, F. and Gupta, R. K. (1982) *Phytochemistry* **21** (in press).

Table 2. ^{1}H NMR spectral data of compounds **8–16** (400 MHz, $CDCl_3$, TMS as int. standard)

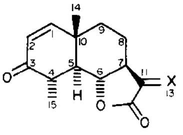
	8	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
H-1	5.25 *dd*(*br*)	5.27 *dd*(*br*)	5.25 *dd*(*br*)	5.28 *dd*(*br*)	5.38 *dd*(*br*)	5.38 *dd*(*br*)	5.53 *dd*(*br*)	5.51 *dd*(*br*)	5.18 *m*
H-2	2.44 *m*	2.44 *m*	2.44 *m*	2.44 *m*	2.44 *m*	2.43 *m*	2.39 *m*	2.38 *m*	2.34 *m*
H-2′	2.35 *m*	2.35 *m*	2.35 *m*	2.35 *m*	2.35 *m*	2.36 *m*			
H-3	2.62 *ddd*	2.65 *ddd*	2.62 *ddd*	2.60 *ddd*	2.63 *ddd*	2.59 *ddd*	2.66 *ddd*	2.66 *ddd*	2.65 *ddd*
H-3′	2.15 *ddd*	2.17 *ddd*	2.15 *ddd*	2.15 *ddd*	2.10 *ddd*	2.15 *ddd*	2.14 *ddd*	2.14 *ddd*	2.14 *m*
H-5	4.92 *d*(*br*)	4.94 *d*(*br*)	4.93 *d*(*br*)	4.92 *d*(*br*)	4.81 *d*(*br*)	4.91 *d*(*br*)	4.85 *m**	4.96 *d*(*br*)	4.90 *d*(*br*)
H-6	5.12 *dd*	5.17 *dd*	5.14 *dd*	5.22 *dd*	4.76 *dd*	4.53 *dd*		4.65 *dd*	4.83 *dd*
H-7	3.02 *dddd*	3.05 *dddd*	3.03 *dddd*	3.05 *dddd*	2.76 *m*	2.71 *m*	2.76 *m*	2.80 *m*	2.77 *m*
H-8	5.05 *dd*(*br*)	5.00 *dd*(*br*)	5.00 *dd*(*br*)	5.17 *dd*(*br*)	1.75 *ddd* 2.34 *ddd*	1.73 *ddd* 2.37 *ddd*	2.06 *m* 2.23 *ddd*	2.05 *m* 2.25 *d*(*br*)	
H-9	2.72 *d*(*br*)	2.77 *d*(*br*)	2.72 *d*(*br*)	2.74 *d*(*br*)	4.28 *d*(*br*)	4.29 *d*(*br*)	5.31 *dd*	5.31 *dd*	
H-9′	2.44 *m*	2.44 *m*	2.44 *m*	2.47 *m*					
H-13	6.34 *d*	6.33 *d*	6.33 *d*	6.36 *d*	6.30 *d*	6.31 *d*	6.32 *d*	6.33 *d*	6.29 *d*
H-13′	5.79 *d*	5.75 *d*	5.76 *d*	5.80 *d*	5.63 *d*	5.64 *d*	5.58 *d*	5.59 *d*	5.56 *d*
H-14	4.58 *d*(*br*)	4.69 *d*(*br*)	4.62 *d*(*br*)	4.65 *d*(*br*)	4.56 *d*(*br*)	4.58 *d*(*br*)	4.62 *dd*	4.60 *d*(*br*)	4.66 *d*(*br*)
H-14′	4.43 *d*(*br*)	4.52 *d*(*br*)	4.42 *d*(*br*)	4.49 *d*(*br*)	4.47 *d*(*br*)	4.35 *d*(*br*)	4.42 *d*(*br*)	4.40 *d*(*br*)	4.37 *d*(*br*)
H-15	4.22 *d*(*br*)	4.25 *d*(*br*)	4.23 *d*(*br*)	4.19 *s*(*br*)		4.70 *d*(*br*)	4.22 *d*(*br*)	4.62 *d*(*br*)	4.24 *d*(*br*)
H-15′	4.13 *d*(*br*)	4.14 *d*(*br*)	4.12 *d*(*br*)		4.25 *s*(*br*)	4.69 *d*(*br*)	4.12 *d*(*br*)	4.50 *d*(*br*)	4.11 *d*(*br*)
OCOR	2.08 *s*	6.85 *qq*	2.4 *m*	2.45 *dq*	2.52 *qq*	2.54, 2.62 *qq*	2.54 *qq*	2.55 *qq*	6.10 *s*(*br*)
		1.80 *dq*	1.67 *ddq*	3.90 *dq*	1.14 *d*	1.15, 1.16 *d*	1.16 *d*	1.17 *d*	5.60 *dq*
		1.83 *dq*	1.48 *ddq*	1.26 *d*	1.16 *d*	1.21 *d*(6H)	1.165 *d*	1.175 *d*	1.95 *dd*
			0.90 *t*	1.18 *d*					
			1.14 *d*						
OAc	2.05 *s*	2.04 *s*	2.04 *s*	2.08 *s*			2.07 *s*	2.11, 2.08 *s*	

*In $C_6D_6/CDCl_3$: H-5 4.59 *d*(*br*), H-6 4.64 *dd*; *J* (Hz): compounds **8–11**: 1, 2 = 11.5; 1, 2′ = 5; 2, 3 = 5; 2′, 3 = 2; 2, 3′ = 4; 2′, 3′ = 4; 3, 3′ = 13; 5, 6 = 9.5; 6, 7 = 8; 7, 8 ~ 5; 7, 13 = 3.2; 7, 13′ = 3; 7, 8 ~ 9; 7, 8′ ~ 7; 8, 9′ = 8; 9, 9′ = 13; 14, 14′ = 12.5; 15, 15′ = 14; compounds **12–16**: 1, 2 = 12; 1, 2′ = 5; 2, 3 = 2′, 3 ~ 3; 2, 3′ = 12; 2′, 3′ = 5; 3, 3′ = 13; 5, 6 = 10; 6, 7 = 9; 7, 8 = 10; 7, 8′ ~ 2; 7, 13 = 3.5; 7, 13′ = 3; 8, 9 ~ 10; 8, 9′ ~ 2; 8, 8′ = 14; 14, 14′ = 12.5; 15, 15′ = 13.5; OTigl: 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.3; OMebu: 2′, 3′ = 3′, 4′ = 7; $3'_1, 3'_2$ = 14; 2′, 5′ = 7; OCOCH(Me)CH(OH)Me: 2′, 3′ = 3′, 4′ = 2′, 5′ = 7; OMeacr: 3′, 4′ = 1.

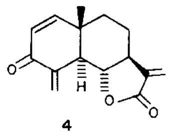
butyrate as could be deduced from the doublet quartets at δ 2.45 and 3.90 as well as from the two doublets at δ 1.26 and 1.18. The flexibility of the ring system and the couplings $J_{7,8}$ indicated the presence of 8, 12-lactones, while the chemical shifts of H-1 and H-5 required *trans*-double bonds. The 6α-orientation of the ester groups followed from the couplings $J_{5,6}$ and $J_{6,7}$. Accordingly, **8–11** were closely related to artemisiifolin and to a diacetate, which had been isolated from *D. anomala* subsp. *cirsioides* [1]. However, the configuration of the 1, 10-double bond was erroneously presented as *trans* [1]. As in the latter case, the H-1 signal was shifted downfield [1, 2]. Similarly, 14-oxo-dicomanolide [1] also has a 1, 10-*cis*-double bond (**23** and **24**). The constituents of the collections from Natal and Transvaal therefore differed noticeably.

The aerial parts of *D. anomala* Sond. subsp. *anomala* afforded phytol, lupeol and its acetate, germacrene D and also **8**, **10** and **11**, while the roots gave no definite compounds.

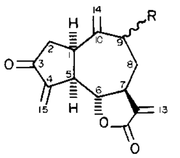
The roots of *D. schinzii* O. Hoffm. afforded taraxasterol, lupeol and its acetate together with their Δ 12-isomers and the eudesmanolides **1**, **3** and **4**, while the aerial parts gave in addition to lupeol three further germacranolides, the isobutyrates **12–14**, all closely related to albicolide [7]. The structure of **12** followed from the ^{1}H NMR spectrum (Table 2). Irradiation at δ 2.76 showed that this signal was that of H-7 as the typical methylene lactone doublets collapsed to singlets, the double doublet at δ 4.76 to a doublet and the threefold doublets at δ 1.75 and 2.34 to double doublets. Further spin decoupling allowed the assignment of all signals. The stereochemistry at C-9 followed from the couplings observed, while the relative position of the isobutyrate residue followed from the chemical shifts of H-14. The ^{1}H NMR spectral data of **13** were close to those of **12** (Table 2). However, the signals of H-15 were shifted downfield and signals of an additional isobutyrate residue were visible. Furthermore, a small shift of the H-14 signals indicated the usual conformation of germacranolides with both, C-14 and C-15 above the plane. Compound **14** was a germacranolide with an acetate group. The ^{1}H NMR spectral data of **14** (Table 2) differed from those of **12** in the chemical shift of H-9 indicating that the acetate was at C-9. Furthermore, the H-1 signal was shifted downfield by δ 0.25, which could be an indication of a 1,10-*cis*-double bond. However, acetylation of **12** afforded the diacetate **15**, where the H-1 signal showed nearly the same chemical shift showing that the downfield shift was due to the effect of the 9β-acetoxy group. As partial saponification of **14** was not successful, the relative position of the isobutyrate could not be established. The proposed position seemed to be likely as all the other esters had a C_4-ester group at C-14. A re-investigation of the roots of *D. zeyheri* Sond. afforded β-farnesene, α-humulene, 5 mg **7** [8], 20 mg **19**, 1 mg **20**, 1 mg **21**, 20 mg **22** and a mixture of **17** and **18**, which could not be separated. The spectral data, however, showed that the isomers differed only in the stereochemistry



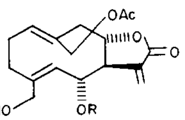
1 X = CH_2
2 X = β-Me, H
3 X = α-Me, H



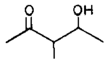
4

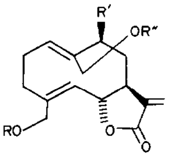


5 R = H
6 R = α-OH
7 R = β-OH

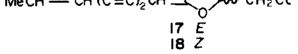


8 R = Ac
9 R = Tigl
10 R = Mebu

11 R =


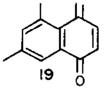


	12	13	14	15	16
R	H	*i* Bu	H	Ac	H
R'	OH	OH	OAc	OAc	H
R''	*i* Bu	*i* Bu	*i* Bu	*i* Bu	Meacr

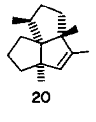


$MeCH\overset{trans}{=}CH(C\equiv C)_2CH=$ (furan) CH_2Cl

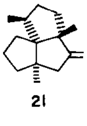
17 *E*
18 *Z*



19



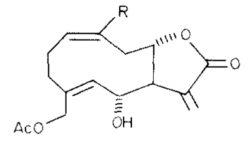
20



21

$Me(CH_2)_{10}CH=C=CH(CH_2)_3CO_2H$

22



23 R = CH_2OAc
24 R = CHO

of the 5, 6-double bond. The molecular formula ($C_{13}H_{11}OCl$) and the ^1H NMR spectrum (see Experimental) indicated the presence of the cyclized acetylenes which were obviously formed via the corresponding chlorohydrine. As in similar cases, the *Z*-isomer showed a more downfield shifted H-6 signal. The aerial parts gave no characteristic compounds except **22** [9]. The roots of *D. macrocephala* DC afforded lupeol and its acetate as well as taraxasterol, while the aerial parts gave germacrene D, lupeol and its acetate as well as their Δ 12-isomers, cycloartenol, taraxasterol and minute amounts of **16** as followed from the ^1H NMR spectrum (Table 2), which was similar to those of known albicolide derivatives. As irradiation of the H-1 signal sharpened the signals of the methylene group, which were more downfield, the ester group was at C-14.

The chemistry of the genus *Dicoma* showed that highly oxygenated germacranolides, especially those with O-functions at C-14 and C-15, may be typical, though *D. zeyheri* is an exception. Further investigations may show whether the chemistry of this genus really differs from that of other genera of the subtribe Gochnatiinae, where some sesquiterpene lactones have been reported [2].

EXPERIMENTAL

The air-dried plant material, collected in Feb. 1981 in Transvaal, was extracted with Et_2O-petrol (1:2), and the resulting extracts were separated by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing the ^1H NMR spectra with those of authentic material. Vouchers were deposited in the Botanic Research Institute, Pretoria.

Dicoma anomala subsp. *cirsioides* (voucher 81/201). The roots (245 g) afforded 10 mg stigmasterol, 2 mg sitosterol, 5 mg lupenone, 2 mg **1**, 3 mg **2** (Et_2O-petrol, 3:1), 2 mg **4**, 1 mg **5** and 1 mg **6** (C_6H_6–CH_2Cl_2–Et_2O, 5:5:1), while the aerial parts (140 g) gave 2 mg germacrene D, 5 mg lupeol, 2 mg taraxasterol, 2 mg **8**, 3 mg **9**, 7 mg **10** and 2 mg **11** [lactones separated by TLC (C_6H_6–CH_2Cl_2–Et_2O, 5:5:1, several times)].

Dicoma anomala subsp. *anomala* (voucher 81/225). The roots (30 g) gave no characteristic compounds, while the aerial parts (30 g) afforded 2 mg germacrene D, 5 mg lupeol, 2 mg of its acetate, 2 mg phytol, 1 mg **8**, 1 mg **10** and 3 mg **11**.

Dicoma schinzii (voucher 81/51). The roots (22 g) afforded 5 mg lupeol and 1 mg of its Δ 12-isomer, 2 mg lupeyl acetate and 1 mg of its Δ 12-isomer, 10 mg taraxasterol, 1 mg **1**, 2 mg **3** and 1 mg **4**, while the aerial parts (170 g) gave 100 mg lupeol, 8 mg **12**, 1.4 mg **13** and 10 mg **14** (separated by TLC, C_6H_6–CH_2Cl_2–Et_2O, 5:5:1, several times).

Dicoma zeyheri (voucher 81/257). The roots (80 g) afforded 5 mg β-farnesene, 1 mg α-humulene, 5 mg **7**, 5 mg **17** and **18** (*ca* 1:4) (Et_2O-petrol, 1:20), 20 mg **19**, 1 mg **20**, 1 mg **21** and 20 mg, **22**, while the aerial parts (105 g) gave 25 mg **22**.

Dicoma macrocephala (voucher 81/180). The roots (20 g) afforded 15 mg lupeol, 5 mg of its acetate and 10 mg taraxasterol, while the aerial parts (220 g) gave 3 mg germacrene D, 30 mg lupeol, 15 mg lupeyl acetate and 5 mg of its Δ 12-isomer, 5 mg cycloartenol, 25 mg taraxasterol and 1 mg **16** (C_6H_6–CH_2Cl_2–Et_2O, 5:5:1, several times).

11α, 13-*Dihydrotubiferin* (**2**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1790 (γ-lactone), 1680 (C=CC=O); MS *m/z* (rel. int.): 248.141 $[M]^+$ (60) ($C_{15}H_{20}O_3$), 220 $[M-CO]^+$ (42), 215 $[220-Me]^+$ (10), 192 $[220-CO]^+$ (34), 177 $[192-Me]^+$ (18), 69 (100); $[\alpha]_D \sim +30^\circ$ ($c = 0.15$, $CHCl_3$).

9α-*Hydroxy-dehydrozaluzanin C* (**6**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1705 (C=C–C=O); MS *m/z* (rel. int.): 260.115 $[M]^+$ (4) ($C_{15}H_{16}O_4$), 242 $[M-H_2O]^+$ (4), 214 $[242-CO]^+$ (6), 55 (100); $[\alpha]_D + 30^\circ$ ($c = 0.06$, $CHCl_3$).

14-*Acetoxyartemisiifolin*-6-O-*acetate* (**8**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 1775 (γ-lactone), 1740, 1240 (OAc); MS *m/z* (rel. int.): 304.131 $[M-HOAc]^+$ (1) ($C_{17}H_{20}O_5$), 244 $[304-HOAc]^+$ (6), 226 $[244-H_2O]^+$ (7), 55 (100).

14-*Acetoxyartemisiifolin*-6-O-*tiglate* (**9**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1740 (OAc), 1710 ($C{=}CCO_2R$); MS *m/z* (rel. int.): 404 $[M]^+$ (0.5), 304.131 $[M-HOAng]^+$ (3) ($C_{17}H_{20}O_5$), 244 $[304-HOAc]^+$ (6), 226 $[244-H_2O]^+$ (5), 83 $[C_4H_7CO]^+$ (100);

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+18 \quad +20 \quad +23 \quad +41} \quad (c = 0.23,\ \text{CHCl}_3).$$

14-*Acetoxyartemisiifolin*-6-O-[2-*methylbutyrate*] (**10**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1750 (OAc), 1730 (CO_2R); MS *m/z* (rel. int.): 406 $[M]^+$ (0.5), 304.131 $[M-RCO_2H]^+$ (3) ($C_{17}H_{20}O_5$), 244 $[304-HOAc]^+$ (6), 226 $[244-H_2O]^+$ (6), 85 $[C_4H_9CO]^+$ (40), 57 $[85-CO]^+$ (100);

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+41 \quad +44 \quad +50 \quad +89} \quad (c = 0.5,\ \text{CHCl}_3).$$

14 - *Acetoxyartemisiifolin* - 6 - O - [2 - *methyl* - 3 - *hydroxybutyrate*] (**11**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1750 (OAc, COOR): MS *m/z* (rel. int.): 304.131 $[M-RCO_2H]^+$ (8) ($C_{17}H_{20}O_5$), 244 $[304-HOAc]^+$ (14), 226 $[244-H_2O]^+$ (14), 101 $[RCO]^+$ (34), 83 $[101-H_2O]^+$ (71), 57 (100);

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+22 \quad +26 \quad +30 \quad +57} \quad (c = 0.17,\ \text{CHCl}_3).$$

9β-*Hydroxy*-14-*isobutyryloxyalbicolide* (**12**). Colourless gum, IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3610 (OH), 1770 (γ-lactone), 1730 (CO_2R); MS *m/z* (rel. int.): 350 $[M]^+$ (0.2), 262.121 $[M-RCO_2H]^+$ (20) ($C_{15}H_{18}O_4$), 244 $[262-H_2O]^+$ (12), 226 $[244-H_2O]^+$ (8), 71 $[C_3H_7CO]^+$ (100);

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-3.6 \quad -3.6 \quad -4.1 \quad -5.6} \quad (c = 0.76,\ \text{CHCl}_3).$$

Acetylation (Ac_2O, 4-pyrolidinopyridine [10], $CHCl_3$) afforded the diacetate **15**, colourless gum; ^1H NMR see Table 2.

9β-*Hydroxy*-14-*isobutyryloxyalbicolide*-15-O-*isobutyrate* (**13**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1740 (CO_2R); MS *m/z* (rel. int.): 333 $[M-RCO_2]^+$ (20), 332 $[M-RCO_2H]^+$ (1), 244.109 $[332-RCO_2H]^+$ (6) ($C_{15}H_{16}O_3$), 71 $[C_3H_7CO]^+$ (100).

9β-*Acetoxy*-14-*isobutyryloxyalbicolide* (**14**). Colourless gum, IR $\nu_{\max}^{CCl_4}$, cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1740 (OAc, CO_2R); MS *m/z* (rel. int.): 304.131 $[M-RCO_2H]^+$ (1.5) ($C_{17}H_{20}O_5$), 244 $[304-HOAc]^+$ (16), 226 $[244-H_2O]^+$ (17), 71 $[C_3H_7CO]^+$ (100);

$$[\alpha]_{24°}^{\lambda}=\frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+17 \quad +18 \quad +20 \quad +20}\ (c = 1.0,\ CHCl_3).$$

14-*Methacryloylalbicolide* (**16**). Colourless gum, IR $\nu_{\max}^{CCl_4}$, cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1720 ($C{=}CCO_2R$); MS *m/z* (rel. int.): (CI, isobutane): 333 $[M+1]^+$ (3), 247 $[333-RCO_2H^+]$ (47), 229 $[247-H_2O]^+$ (100).

5E- *and* 5Z-*zeyherin* (**17** and **18**). Colourless gum, UV $\lambda_{\max}^{Et_2O}$ nm: 334; IR $\nu_{\max}^{CCl_4}$, cm^{-1}: 2220, 2140 ($C{\equiv}C$), 1630 ($C{=}C$); MS *m/z* (rel. int.): 218.050 $[M]^+$ (48) ($C_{13}H_{11}OCl$), 169 $[M-CH_2Cl]^+$ (100), 115 $[C_9H_7]^+$ (14); ^1H NMR ($CDCl_3$): H-1 3.59 and 3.60 *dd*; H-1′ 3.66 and 3.78 *dd*; H-2 5.42 and 5.48 *dddd*; H-3 6.53 *dd*; H-4 6.76 *dd*; H-6 5.02 and 4.69 *s*(*br*); H-11 5.60 *d*(*br*); H-12 6.30 *dq*; H-13 1.82 and 1.81 *dd* [*J*(Hz): 1.1′ = 11; 1, 2 = 1, 2′ = 6; 2, 3 = 2, 4 = 2; 3, 4 = 6.5; 11, 12 = 16; 12, 13 = 7].

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