Phytochemistry, Vol. 21, No. 10, pp. 2531–2535, 1982.
Printed in Great Britain.

0031-9422/82/102531-05$03.00/0

SESQUITERPENES AND A DIMERIC SPIROKETONE FROM *CINERARIA FRUTICULORUM**

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(*Received* 16 *October* 1981)

Key Word Index—*Cineraria fruticulorum*; *C. parvifolia*; Compositae; sesquiterpenes; spathulenol derivatives; γ-humulene derivatives; cinalbicol derivatives; new carbon skeleton; dimeric spiroketone; hydroxymyrtenol.

Abstract—The aerial parts of *Cineraria fruticulorum* afforded in addition to known compounds three spathulenol derivatives, a hydroxymyrtenol and an oxo-humulene, while the roots gave in addition to known compounds a further humulene derivative, three cinalbicol derivatives, a sesquiterpene with a spirodienone moiety and its dimer. From *C. parvifolia* only known compounds were isolated which, however, confirmed previous results on this genus. The structures were elucidated by spectroscopic methods and a few chemical transformations.

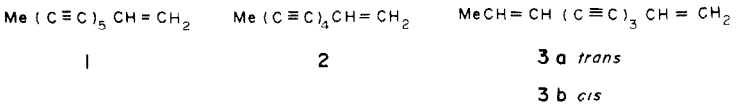
INTRODUCTION

So far the investigation of representatives of the South African genus *Cineraria* (Compositae, tribe Senecioneae) have shown that in addition to unusual C_{11}-acetylenes with different degrees of unsaturation rearranged eremophilanes may be characteristic for this genus [1]. We now have studied the constituents of two further species. Again both species afforded C_{11}-acetylenes and several rearranged eremophilanes as well as nine new sesquiterpenes, a dimeric one and a new monoterpene. The structure elucidation of these compounds is discussed in this paper.

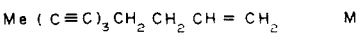
RESULTS AND DISCUSSION

The aerial parts of *C. fruticulorum* afforded phytol, linolenic acid, the acetylenes **1**, **2**, **3a**, **3b**, **4a**, **5a**, **5b** and **6** [1], **8**, 2, 4, 6-trimethoxycinnamyl alcohol (**25**) and new sesquiterpenes, γ-humulene-9-one (**13**) and the spathulenol derivatives **10–12**, while the roots gave sitosterol, stigmasterol, γ-humulene, curcumene, **1**, **6**, hydroxymyrtenol (**8**), **13–15**, **19–21** [1], three further cinalbicol derivatives (**16–18**) as well as the spiro compound **26** and its dimer **29**. The structure of **8** clearly followed from the ^{1}H NMR spectral data and those of the corresponding diacetate **9** (Table 1), especially when compared with those of myrtenol and verbenol, respectively. A pair of four-fold doublets at δ4.09 and 4.03 in the spectrum of **8** indicated the allylic CH_2OH group. These signals were shifted downfield in the spectrum of the diacetate as well as a three-fold doublet at δ4.36, obviously due to the proton under the second allylic hydroxyl. Spin decoupling allowed the assignment of all signals. The absolute configuration was not determined. The ^{1}H NMR spectra of **10–12** (Table 2) were in part similar to that of spathulenol. The position of the second hydroxyl of **10a** followed from the signal of the proton under the hydroxyl which was coupled with H-7 as could be shown by spin decoupling. In deuteriobenzene all signals could be assigned, though some were overlapped multiplets. The spectrum of the corresponding diacetate **10b** supported the structure. The stereochemistry at C-8 followed from the coupling constant $J_{7,8}$. The spectra of **11a** and the corresponding triacetate **11b** (Table 2) showed that one methyl was replaced by CH_2OH (δ3.76*d* and 3.67*d*). If the deshielding effects of this group were considered the CH_2OH group had to be placed α-orientated at C-11 as both cyclopropane signals were shifted downfield when compared with the shifts of **10a**. Furthermore the observed shifts of the methyl signals in the spectra of **11a** and **11b** supported this assignment. The spectral data of **12** (Table 1) clearly showed that the CH_2OH group was replaced by an aldehyde group. Again the observed shift differences of H-6 and H-7 excluded a 4-position of the additional oxygen function. Furthermore in the latter case in the mass spectrum a strong fragment $[M-CHO]^+$ should be observed. The ^{1}H NMR spectral data of **13** and **14** (Table 3) were in part close to those of γ-humulene. The presence of a 9-keto group caused in the spectrum of **13** a strong downfield shift of the H-1 signal, indicating a conjugated keto group which was supported by the IR band at 1670 cm^{-1}. Spin decoupling allowed the assignment of nearly all signals. Though the signals of H-2, H-3, H-7 and H-8 were unresolved multiplets, **13** seemed to be the only possible structure. The ^{1}H NMR spectrum of **14** clearly showed that the 1.10-double bond was missing. Accordingly now, the H-10 signal was visible, which was coupled with a methyl doublet, and in the IR spectrum a carbonyl bond at 1710 cm^{-1} appeared. The stereochemistry at C-10, however, could not be determined. The ^{1}H NMR spectra of the cinalbicol

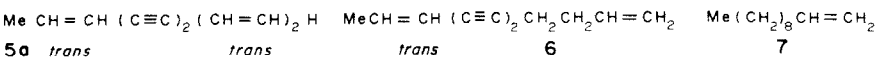
*Part 429 in the series "Naturally Occurring Terpene Derivatives". For Part 428 see Bohlmann, F., Singh, P. and Jakupovic, J. (1982) *Phytochemistry* **21**, 2122.



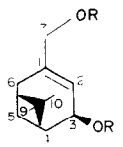
1 2 3a *trans* 3b *cis*



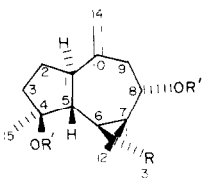
4a 4b



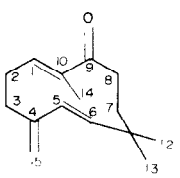
5a *trans trans* 5b *trans cis* 6 7



8 R = H
9 R = Ac



10a R = Me, R′ = H
10b R = Me, R′ = Ac
11a R = CH_2OH, R′ = H
11b R = CH_2OAc, R′ = Ac
12 R = CHO, R′ = H



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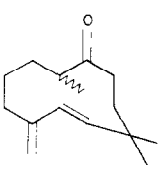

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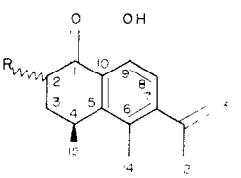
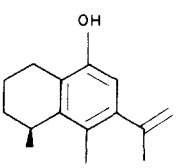


15 R = H
16 R = α-OH
17 R = β-OH
18 R = β-OAc



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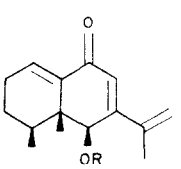
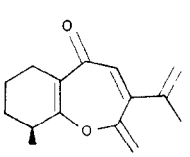


20 R = Ac
21 R = Ang



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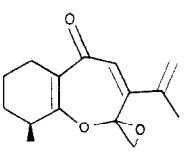

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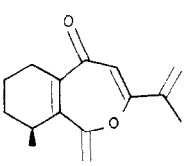

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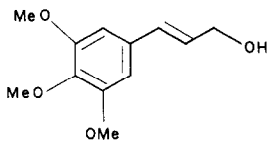

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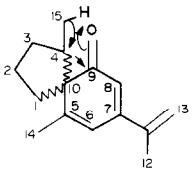
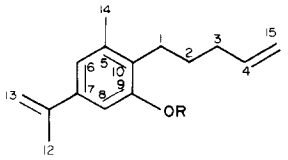
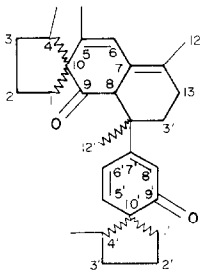


26*

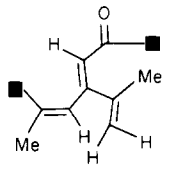


27* R = H
28* R = Ac

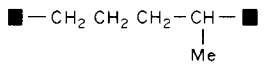


29*

* Numbering as in eremophilanes



A



B

derivatives **16–18** (Table 4) were close to that of **15**. Obviously **16** and **17** were epimers, which, however, could not be separated. Spin decoupling allowed the assignment of all signals. The 2-position of the hydroxyl group directly followed from the ^{1}H NMR spectrum. The couplings of H-2 showed that the hydroxyl was equatorial in both epimers indicating a different conformation. The couplings of H-3 allowed an assignment of the relative stereochemistry in **16** and **17**. The H-3β-signal in the spectrum of **17** clearly showed the presence of two axial–axial couplings and that of H-3α the expected two axial, equatorial couplings. This required the proposed stereochemistry. The H-2 and H-3 couplings in the spectrum of **18** indicated a 2β-acetoxy group as $J_{2,3}J_{2,3'}$, $J_{3,4}$ and $J_{3',4}$ were nearly identical. Models showed that this required a changed conformation compared with that proposed for **17**, probably due to the missing hydrogen bond. The structure of **26** followed from the molecular formula, the fragmentation pattern, the ^{1}H NMR spectral data (Table 5), spin decouplings and chemical transformations. A carbonyl band at 1655 cm^{-1} clearly indicated the presence of a dienone. This was supported by the chemical shifts and the couplings of the olefinic protons and the olefinic methyls. Spin decoupling led to the sequences **A** and **B**, which only could be combined in structure **26**. **26** we have named cinera-5,7,11-trien-9-one. The stereochemistry at C-4 and C-10 was not determined. The molecular formula of **29** showed that this diketone was a dimer and the ^{1}H NMR spectral data (Table 5) supported the presence of a formal Diels–Alder adduct of **26** to itself. While the signals in part were nearly the same as those of **26** several new ones in combination with the results of spin decoupling led to the proposed structure. A broadened singlet at δ3.32 obviously was the signal of H-6 as it coupled with an olefinic methyl (1.72) and with the olefinic signal at δ6.42, which itself coupled with an olefinic methyl (1.85). The remaining olefinic methyl (1.93) was coupled with an olefinic proton (6.05), which itself was coupled with the remaining olefinic signal δ5.57. Inspection of a model showed that the upfield shift of the latter may be due to the shielding effect of the 9-keto group. Though not all signals could be assigned, the proposed structure seemed to be very likely. Heating of **26** at 120° did not yield the dimer **29**, which therefore surely was no artefact, but afforded by a 1.5-H-shift the rearranged phenol **27** (see chemical structures), which on acetylation gave **28** as clearly followed from the ^{1}H NMR spectrum (Table 5). This also supported the structure of **26**. Accordingly the latter is one of the few examples of a triterpene formed by dimerization of a sesquiterpene. Of course the stereochemistry at the asymmetric centers could not be determined.

The roots of *C. parvifolia* afforded eremophilene, **2**, **3a**, **4a**, **4b**, **19**, **20**, **21** [1] and **22–24** [1], while the

Table 1. ^{1}H NMR spectral data of compounds **8** and **9** (400 MHz, $CDCl_3$, TMS as internal standard)

	8	**9**
H-2	5.60*dddd*	5.62*dddd*
H-3	4.36*dddd*	5.40*dddd*
H-4	2.22*dddd*	2.27*dddd*
H-5	2.33*ddd*	2.36*ddd*
H-5′	1.35*d*	1.49*d*
H-6	2.17*ddd*	2.18*ddd*
H-7	4.03*dddd*	4.48*dddd*
H-7′	4.09*dddd*	4.53*dddd*
H-9	1.37*s*	1.37*s*
H-10	0.88*s*	0.92*s*
OAc	—	2.05*s*
		2.08*s*

J (Hz): 2, 3 = 2, 7 = 2, 7′ = 2, 6 = 2, 4″ = 3, 7 = 6, 7 ~ 1.5; 3, 4 = 4, 5 = 4, 6 = 5, 6 ~ 5; 5, 5′ = 9; 7, 7′ = 13.

Table 2. ^{1}H NMR spectral data of compounds **10a–12** (400 MHz, $CDCl_3$, TMS as internal standard)

	11a	**11b**	**10a**	**10b**	**12**(C_6D_6)
H-1	1.90*m*	1.83*m*	1.9*m*	1.85*m*	1.90*m*
H-2	2.15*m*		2.13*m*		1.95*m*
H-2′	1.85*m*				1.70*m*
H-3	1.78*m*	2.2–1.6*m*	1.9–1.55*m*	2.1–1.55 *m*	1.55*m*
H-3′	1.70*m*				1.28*m*
H-5	1.34*dd*	1.18*dd*	1.20*dd*	1.25*m*	1.22*dd*
H-6	0.78*dd*	0.88*dd*	0.61*dd*	0.75*dd*	0.70*dd*
H-7	0.98*dd*	1.13*dd*	0.79*dd*	0.90*dd*	0.91*dd*
H-8	3.58*ddd*	4.60*ddd*	3.50*ddd*	4.55*ddd*	3.88*ddd*
H-9	2.55*dd*	2.54*dd*	2.55*dd*	2.53*dd*	2.49*dd*
H-9′	2.42*dd*	2.37*dd*	2.41*dd*	2.40*dd*	2.31*dd*
H-12	1.25*s*	1.18*s*		1.08*s*	0.98*s*
H-13	3.76*d*	4.33*d*	1.13*s*	1.10*s*	9.62*s*
H-13′	3.67*d*	4.08*d*			
H-14	4.88*br s*	4.90*br s*	4.83*br s*	4.89*br s*	4.92*br s*
H-14′				4.88*br s*	4.88*br s*
H-15	1.34*s*	1.57*s*	1.28*s*	1.63*s*	1.14*s*
OAc				2.06*s*	
				2.28*s*	

J (Hz): 1, 5 = 5, 6 = 11; 6, 7 = 9.5; 7, 8 = 9; 8, 9 = 1.5; 8, 9′ = 11; 9, 9′ = 13; 13, 13′ = 12.5.

aerial parts gave squalene, lupeol and its Δ^{12} isomer, stigmasterol, sitosterol, phytol, linolenic acid, nerolidol, **2**, **6**, **7**, **19–22** and **24**. The chemistry of these two *Cineraria* species again showed that rearranged eremophilanes and C_{11}-acetylenes are characteristic for this genus. Though the genus surely is closely related to *Senecio* [2] the chemistry is typically different [3].

EXPERIMENTAL

The air-dried plant material, collected in February 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). Several compounds were solids, but due to the small amounts of material no correct mp can be given. Known compounds were identified by comparing the ^{1}H NMR spectra with those of authentic material. Vouchers were deposited in the Botanic Research Institute, Pretoria.

C. fruticulorum *Hutch. et Taylor* (*voucher* 81/83). The aerial parts (170 g) afforded 3 mg phytol, 150 mg linolenic acid, 2 mg **1**, 4 mg **2**, 7 mg **3a**, 8 mg **3b**, 10 mg **4a**, 10 mg **5a**, 10 mg **5b**, 10 mg **6**, 8 mg **8** (Et_2O-petrol, 1:1), 2 mg **13** (Et_2O–petrol, 1:10) and 2 mg **25**, while the roots (65 g) gave 5 mg stigmasterol, 5 mg sitosterol, 5 mg curcumene, 6 mg **1**, 2 mg **6**, 3 mg **8**, 10 mg γ-humulene, 3 mg **13**, 0.5 mg **14** (Et_2O–

Table 3. ^{1}H NMR spectral data of compounds **13** and **14** (400 MHz, $CDCl_3$, TMS as internal standard)

	13	**14**
H-1	6.52*tq*	
H-5	5.44*d*	5.47*d*
H-6	6.06*d*	5.92*d*
H-7	1.52*br t*	1.5*m*
H-8	2.52*m*	2.42*ddd*
H-8′		2.15*ddd*
H-10	—	2.75*ddq*
H-12	1.03*s*	1.06*s*
H-13		1.08*s*
H-14	1.77*d*	1.02*d*
H-15	5.00*br s*	4.87*br s*
H-15′	5.02*br s*	4.89*br s*

J (Hz): 5, 6 = 16; 7, 8 ~ 6; compound **13**: 1, 2 = 8.5; 1, 14 = 1.5; compound **14**: 1, 10 = 10; 1′, 10 = 3; 7, 8 = 11; 7, 8′ = 7; 7′, 8 = 7′, 8′ = 1.5; 8, 8′ = 15; 10, 14 = 7.

Table 4. ^{1}H NMR spectral data for compounds **16–18** (400 MHz, $CDCl_3$ TMS as internal standard)

	16	**17**	**18**
H-2	4.69*dd*	4.30*dd*	5.48*dd*
H-3	2.38*ddd*	2.56*ddd*	2.45*ddd*
H-3′	2.20*ddd*	1.80*ddd*	2.16*ddd*
H-4	3.42*ddq*	2.32*ddq*	3.35*ddq*
H-8	6.65*s*	6.66*s*	6.66*s*
H-12	2.00*br s*	2.01*br s*	2.00*br s*
H-13	5.20*dq*	5.20*dq*	5.20*dq*
H-13′	4.84*dq*	4.86*dq*	4.87*dq*
H-14	2.20*s*	2.22*s*	2.20*s*
H-15	1.40*d*	1.35*d*	1.38*d*
OAc	—	—	2.18*s*
OH	11.43	11.90	11.95

J (Hz): Compound **16**: 2, 3 = 6; 2, 3′ = 13; 3, 3′ = 13.5; 3, 4 = 6; 3′, 4 = 8.5; 4, 15 = 7; 8, 13 = 12, 13 = 1.5; compound **17**: 2, 3 = 6; 2, 3′ = 11; 3, 3′ = 13.5; 3, 4 = 2.5; 3′, 4 = 9; 4, 15 = 7; 8, 13 = 12, 13 = 1.5; compound **18**: 2, 3 = 5.5; 3, 3′ = 14.5; 3, 4 = 5.5; 3′, 4 = 5; 4, 15 = 7; 8, 13 = 12, 13 = 1.5.

Table 5. ^{1}H NMR spectral data of compounds **26**, **28** and **29** (400 MHz, $CDCl_3$, TMS as internal standard)

	26	**28**	**29***
H-1	—	2.50*m*	—
H-2$_1$	1.95*m*	1.55	—
H-2$_2$	2.05*m*		—
H-3$_1$		2.15*m*	—
H-3$_2$	1.55*m*		
H-4	2.43*ddq*	5.84*ddt*	—
H-6	6.40*dq*	6.94*d*	6.42*br s*
H-6′	—	—	6.05*br s*
H-8	6.01*br s*	7.16*s*	3.32*br s*
H-8′	—	—	5.57*br s*
H-12	2.02*dd*	2.34*s*	1.85*br s*
H-12′	—	—	1.37*s*
H-13$_1$	5.64*br s*	5.33*br s*	—
H-13$_2$	5.35*br s*	5.04*dq*	—
H-14	2.04*d*	2.10*dd*	1.72*br s*
H-14′	—	—	1.93*br s*
H-15	0.84*d*	5.06*ddt* 5.00*ddt*	1.12*d*
H-15′	—	—	0.80*d*
OAc	—	2.32*s*	—

*All other signals were overlapping multiplets between 2.4 and 1.3.

J (Hz): Compound **26**: 3, 4 = 4, 15 ~ 7; 6, 8 = 6, 14 ~ 1.5; 12, 13 = 1; compound **28**: 3, 4 = 6.5; 4, 15 = 17; 4, 15′ = 10; 6, 14 = 1; 8, 13′ = 12, 13 ~ 1.5; 15, 15′ = 1.5; compound **29**: 4, 15 = 4′, 15′ = 7.

petrol, 1:10), 10 mg **15**, 4 mg **16** and **17** (*ca* 3:2) (Et_2O–petrol, 1:1), 2.5 mg **18** (Et_2O–petrol, 3:1), 1 mg **19**, 2 mg **20**, 5 mg **21**, 5 mg **26** (Et_2O–petrol, 1:10) and 1 mg **29** (same solvent).

C. parvifolia *Burtt. Davy* (*voucher* 81/100). The roots (60 g) afforded 2 mg eremophilene, 2 mg **2**, 12 mg **4a**, 3 mg **4b**, 3 mg **6**, 3 mg **19**, 2 mg **20**, 5 mg **21**, 5 mg **22**, 2 mg **23** and 7 mg **24**, while the aerial parts (210 g) gave 5 mg squalene, 15 mg lupeol and its Δ^{12}-isomer, 5 mg sitosterol, 10 mg stigmasterol, 3 mg phytol, 5 mg nerolidol, 10 mg **2**, 5 mg **6**, 15 mg **7**, 5 mg **19**, 2 mg **20**, 10 mg **21**, 7 mg **22** and 7 mg **24**.

3β-*Hydroxymyrtenol* (**8**). Colourless solid, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3620 (OH), 1610 (C = C); MS *m/z* (rel. int.): 150.104 [M − H_2O]$^+$ (6) ($C_{10}H_{14}O$), 135 [150 − Me]$^+$ (42), 117 [135 − H_2O]$^+$ (23), 79 (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-48 \quad -54 \quad -64 \quad -106} (CHCl_3, c0.24).$$

5 mg **8** was acetylated with Ac_2O–4-dimethylaminopyridine (0.5 hr, 50°). TLC (Et_2O–petrol, 3:1) afforded 4 mg **9**, colourless oil. ^{1}H NMR see Table 1.

8α-*Hydroxyspathulenol* (**10a**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1635 (C=C); MS *m/z* (rel int.): 236.178 [M]$^+$ (2) ($C_{15}H_{24}O_2$), 218 [M − H_2O]$^+$ (9), 203 [218 − Me]$^+$ (9), 200 [218 − H_2O]$^+$ (8), 185 [200 − Me]$^+$ (9), 55 [C_4H_7]$^+$ (100); $[\alpha]_D = -0.5°$ ($CHCl_3$, *c*0.39). 3 mg **10a** were transformed to the diacetate **10b** (Ac_2O–4-dimethylaminopyridine, 1 hr, 50°), colourless gum. ^{1}H NMR see Table 2.

8α, 13-*Dihydroxyspathulenol* (**11a**). Colourless solid, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1630 (C=C); MS *m/z* (rel. int.): 252 [M]$^+$ (1), 234 [M − H_2O]$^+$ (0.5), 216 [234 − H_2O]$^+$ (12), 201 [216 − Me]$^+$ (6), 55 [C_4H_7]$^+$ (100); $[\alpha]_D = -2.7°$ ($CHCl_3$, *c*0.15). 3 mg **11a** were transformed to the triacetate **11b** (s.a.), colourless gum, MS *m/z* (rel. int.): 378.204 [M]$^+$ (0.3) ($C_{21}H_{30}O_6$), 319 [M − OAc]$^+$ (9), 318 [M − HOAc]$^+$ (2), 258 [318 − HOAc]$^+$ (5), 198 [258 − HOAc]$^+$ (43), 146 [$C_{11}H_{14}$]$^+$ (100), 131 [146 − Me]$^+$ (61), 55 (79).

8α-*Hydroxy*-13-*oxo*-*spathulenol* (**12**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740 (CHO); MS *m/z* (rel. int.): 250.157 [M]$^+$ (4) ($C_{15}H_{22}O_3$), 232 [M − H_2O]$^+$ (6), 217 [232 − Me]$^+$ (7), 203 [232 − CHO]$^+$ (9), 199 [217 − H_2O]$^+$ (12), 57 [C_4H_9]$^+$ (100); $[\alpha]_D = -25°$($CHCl_3$, *c*0.1).

9-*Oxo*-γ-*humulene* (**13**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1670, 1615 (C=CC=O); MS *m/z* (rel. int.): 218.177 [M]$^+$ (52) ($C_{15}H_{22}O$), 203 [M − Me]$^+$ (33), 175 [203 − CO]$^+$ (32), 133 (100), 93 (98), 91 (94); $[\alpha]_D = -102°$ ($CHCl_3$, *c*1.05).

9-*Oxo*-1, 10-*dihydro*-γ-*humulene* (**14**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1710 (C=O); MS *m/z* (rel. int.): 220.193 [M]$^+$ (41) ($C_{15}H_{24}O$), 205 [M − Me]$^+$ (22), 177 [205 − CO]$^+$ (38), 93 (100); $[\alpha]_D = -32°$ ($CHCl_3$, *c*0.05).

2α- *and* β-*hydroxy*-1-*oxocinalbicol* (**16** and **17**). Colourless, unseparated gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3520, 3300–2800 (OH), 1640 (C=O), 1610, 1550 (aromatic); MS *m/z* (rel. int.): 246.126 [M]$^+$ (100) ($C_{15}H_{18}O_3$), 228 [M − H_2O]$^+$ (94), 213 [228 − Me]$^+$ (16), 200 [228 − CO]$^+$ (31), 185 [200 − Me]$^+$ (32);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-272 \quad -269 \quad -264 \quad -144} (CHCl_3, c0.37).$$

2β-*Acetoxy*-1-*oxocinalbicol* (**18**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400–2800 (OH), 1750 (OAc), 1640 (C=O); MS *m/z* (rel. int.): 288.133 [M]$^+$ (22) ($C_{17}H_{20}O_4$), 246 [M − ketene]$^+$ (100), 228 [M − HOAc]$^+$ (3); $[\alpha]_D = -343°$ ($CHCl_3$, *c*0.25).

Cinera-5,7,11-*trien*-9-*one* (**26**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1655, 1630, 1620, 1520 (dienone), 915 (C=CH_2); MS *m/z* (rel. int.): 216.157 [M]$^+$ (41) ($C_{15}H_{20}O$), 201 [M − Me]$^+$ (27), 187 [M − CHO]$^+$ (12), 173 [201 − CO]$^+$ (15), 173 [M − C_3H_7]$^+$ (24), 161 [M − C_4H_7]$^+$ (100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+375 \quad +408 \quad +546 \quad +2286} (CHCl_3, c0.5).$$

5 mg **26** in 0.5 ml C_6D_6 was heated in a sealed tube for 30 min at 200°. TLC (Et_2O–petrol, 3:1) gave 2 mg **27**, which on acetylation yielded 2 mg **28**, colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1765 (PhOAc); MS *m/z* (rel. int.): 258.162 [M]$^+$ (12) ($C_{17}H_{22}O_2$), 216 [M − ketene]$^+$ (32), 161 [216 − C_4H_7]$^+$ (100).

Bis-*cineradienone* (**29**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720 (C=O), 1670 (C=CCO); MS *m/z* (rel. int.): 432.303 [M]$^+$ (48) ($C_{30}H_{40}O_2$), 417 [M − Me]$^+$ (11), 404 [M − CO]$^+$ (3), 389 [404 − Me]$^+$ (2), 376 [404 − CO]$^+$ (6), 361 [376 − Me]$^+$ (2), 217 [$C_{15}H_{21}O$]$^+$ (58), 216.151 [$C_{15}H_{20}O$]$^+$ (45), 201 [216 − Me]$^+$ (32), 173 [201 − CO]$^+$ (50), 161 [216 − C_4H_7]$^+$ (100).

Acknowledgements—We thank Dr. B. de Winter and Miss M. Welman, Botanic Research Institute, Pretoria, for their help during collection and identification of the plant material and the Deutsche Forschungsgemeinschaft for financial support.

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