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NEW SESQUITERPENES AND ACETYLENES FROM *ATHANASIA* AND *PENTZIA* SPECIES*

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Key Word Index—*Athanasia* sp.; *Pentzia* sp.; Compositae; furansesquiterpenes; guaianolide; eremophilenic acid; acetylenic acids.

Abstract—Chemical investigation of several *Athanasia* and *Pentzia* species afforded in addition to known compounds a new furansesquiterpene, a new guaianolide related to matricarin, two biogenetically interesting acetylenic acids and an eremophilenic acid. The structures were elucidated by spectroscopic methods. The delimitation of the South African genera *Athanasia*, *Pentzia* and *Matricaria* is discussed. From the observed constituents it is suggested that some species should be transferred from *Athanasia* to *Pentzia* or vice versa and that the South African *Matricaria* species are possibly better placed in *Pentzia*.

INTRODUCTION

Species of the two South African genera *Athanasia* and *Pentzia*, tribe Anthemideae, are morphologically so similar that delimitation of the two groups is very difficult. However, previous investigations show the two genera may be easily separated on chemical grounds. Thus, in nine *Athanasia* species [2, 3] typical furansesquiterpenes and no acetylenes were found, whereas in *Pentzia* species acetylenic compounds, very similar to those of *Tanacetum* species [4, 5] were characterized. It was therefore of interest to investigate *Athanasia* and *Pentzia* spp. further to see whether these chemical differences are valid as taxonomic markers for the two genera.

RESULTS AND DISCUSSION

The results of the present survey of *Athanasia* and *Pentzia* spp. are summarized in Table 1. It may be seen that the roots of *Athanasia grandiceps* Hilliard et Burtt. contain the furansesquiterpenes **1** and **2**, previously isolated from other *Athanasia* species [3], while the aerial parts afford in addition to large quantities of **1** and *p*-hydroxyacetophenone (**3**) a further furan derivative with the molecular formula $C_{15}H_{22}O_4$. Both the ^1H-NMR data and the MS fragmentation pattern are in agreement with structure **4** (see Table 2 and Scheme 1), which we have named athanagrandione and is closely related to **1**.

Pentzia pinnatifida Oliv. has been transferred by O. Hilliard [6] to *Athanasia* on the basis of morphological data. The roots contain besides γ-humulene (**5**) the furan ketones **2** and **6**, while the aerial parts afford **5** together

Table 1. Sesquiterpenes and acetylenes found in *Athanasia* and *Pentzia* spp.

Species	Furan-sesquiter-penes	Ses-quiter-penes	Sesquiter-pene lactones	Acetylenes
Athanasia calva				**8–10**,
roots		**13**		**14–16**, **18**
A. coronopifolia				
aerial parts*			**12**	
roots†				**8**, **9**
A. grandiceps				
aerial parts*	**1**, **4**			
roots	**1**, **2**			
A. leucoclada				
aerial parts	**2** + uni- **2** dent.			
roots				
A. thodei				
aerial parts		**32**, **34**	**31**, **36**, **37**	**8**(*c* + *t*)
roots				**8**(*c* + *t*), **26**
A. woodii				
aerial parts	**2**			
roots	**2**			
P. cooperi				
aerial parts		**38**		**28**, **39**
roots				**8**, **15**, **39**, **40**
P. incana				
aerial parts				**27**
P. pinnatifida				
aerial parts	**2** (*c* + *t*)	**5**, **7**		
roots	**2** (*c* + *t*)	**5**, **6**		
P. tenella				
aerial parts				**14**, **27–29**
roots				**14**, **27–29**

* also contains **3**.
† also contains **11**.
c = *cis*, *t* = *trans*.

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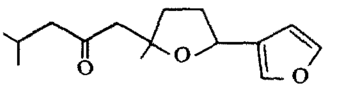
* Part 135 in the series "Naturally Occurring Terpene Derivatives"; for part 134 see: Bohlmann, F. and Le Van, N., *Phytochemistry* 17, 570.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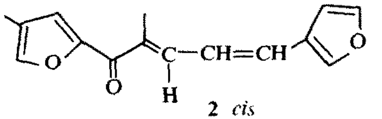
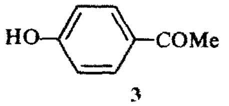


2 *cis*
trans



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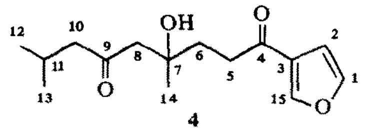

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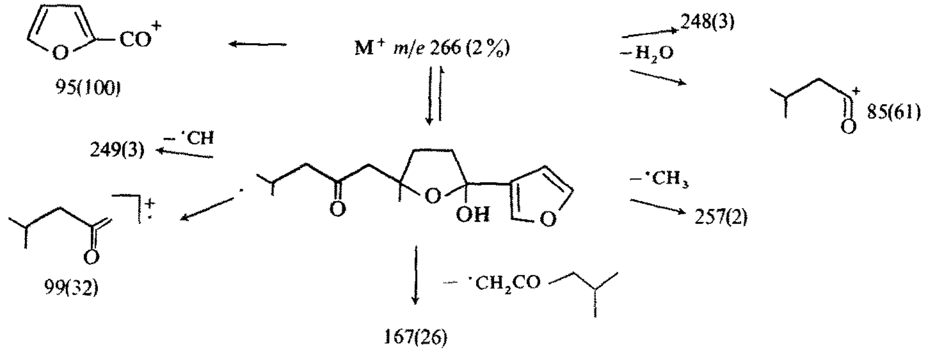

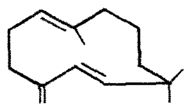
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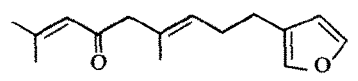
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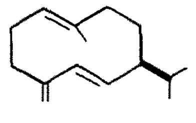
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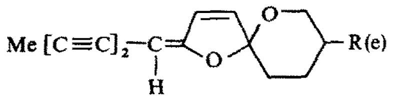
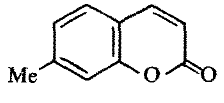


8: R = H **9**: R = Ac **10**: R = OH



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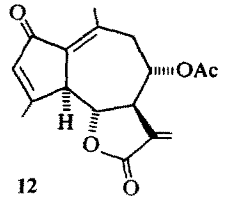

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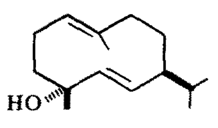


13

with germacrene D (**7**) and *cis*- and *trans*-**2**. Thus, the present results strongly support the morphological data.

The roots of *A. leucoclada* (DC) Harv. also contain *cis*- and *trans*-**2**, but in addition the aerial parts produce small amounts of a complex mixture of furansesquiterpenes, which however could not be identified adequately.

The roots of *A. coronopifolia* Harv. synthesize the spiroketal enolethers **8** and **9** together with herniarin (**11**) while the aerial parts afford, besides **3**, a sesquiterpene lactone with molecular formula $C_{17}H_{18}O_5$, the physical properties of which are in agreement with a 11,12-dehydromatricarin (**12**) (see Table 3). The configurations at C-5, 6, 7 and 8 clearly follow from the observed coupling constants in the ^{1}H-NMR spectrum of **12**. Signals were assigned by double resonance experiments. The chemical constituents of this species suggest its transfer to *Pentzia*.

Table 2. ^{1}H-NMR data of **4** ($CDCl_3$).

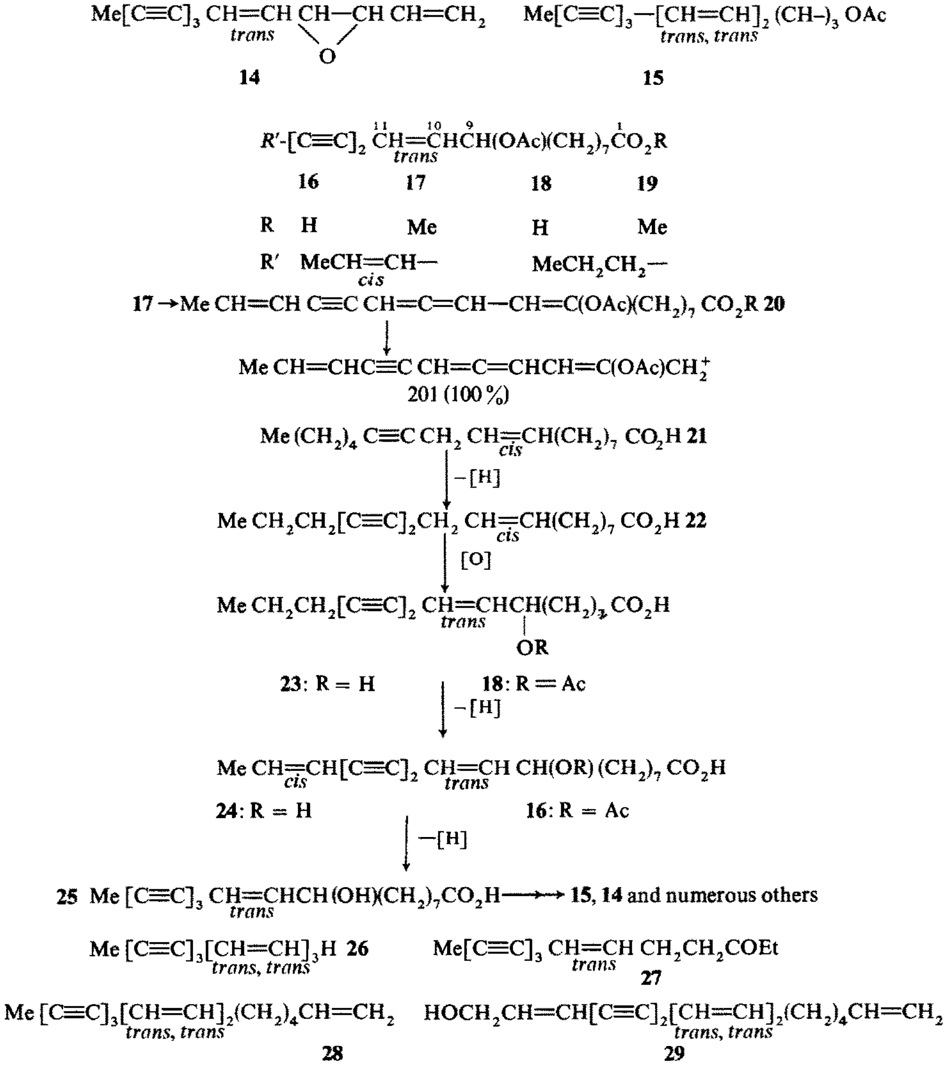
1-H	*dd* 7·44	10-H	*d* 2.32
2-H	*dd* 6.78	11-H	*dqq* 2.14
5-H	*m* 2.95 *m* 2·87	12,13-H	*d* 0.94
6-H	*m* 1.98 *m* 1.85	14-H	*s* 1.23
8-H	*s* 2.60	15-H	*dd* 8.09
		OH	*s*(*br*) 4.16

J(Hz): 1,2 = 1.5; 1,15 = 1; 2,15 = 2; 10,11 = 11,13 = 7.

Table 3. ^{1}H-NMR data of **12** ($CDCl_3$).

3-H	*dq* 6.20	9β-H	*dd* 2.47
5α-H	*d*(*br*) 3·52	13-H	*d* 6.23
6β-H	*dd* 3.72	13-H	*d* 5.66
7α-H	*ddddd* 3.27	14-H	*s*(*br*) 2.45
8β-H	*ddd* 4.92	15-H	*s*(*br*) 2.34
9α-H	*dd* 2.73	OAc	*s* 2.16

J(Hz): 3,5 = 3,15 = 1; 5,6 = 6,7 = 7,8 = 10; 7,13 = 3.5; 7,13 = 3; 8β,9α = 10; 8β,9β = 2; 9α,9β = 13



$Me[C{\equiv}C]_3\,\underset{trans}{CH{=}CH}\,CH{-}CH\,CH{=}CH_2$ (CH–CH bridged by O) **14**

$Me[C{\equiv}C]_3{-}\underset{trans,\,trans}{[CH{=}CH]_2}\,(CH{-})_3\,OAc$ **15**

$R'{-}[C{\equiv}C]_2\,\overset{11}{C}H\underset{trans}{=}\overset{10}{C}H\overset{9}{C}H(OAc)(CH_2)_7\overset{1}{C}O_2R$

	16	**17**	**18**	**19**
R	H	Me	H	Me
R′	$Me\underset{cis}{CH{=}CH}{-}$		$MeCH_2CH_2{-}$	

17 → $Me\,CH{=}CH\,C{\equiv}C\,CH{=}C{=}CH{-}CH{=}C(OAc)(CH_2)_7\,CO_2R$ **20**

$\downarrow$

$Me\,CH{=}CHC{\equiv}C\,CH{=}C{=}CHCH{=}C(OAc)CH_2^+$

201 (100%)

$Me\,(CH_2)_4\,C{\equiv}C\,CH_2\,CH\underset{cis}{=}CH(CH_2)_7\,CO_2H$ **21**

$\downarrow -[H]$

$Me\,CH_2CH_2[C{\equiv}C]_2CH_2\,CH\underset{cis}{=}CH(CH_2)_7\,CO_2H$ **22**

$\downarrow [O]$

$Me\,CH_2CH_2[C{\equiv}C]_2\,CH\underset{trans}{=}CHCH(OR)(CH_2)_7\,CO_2H$

23: R = H **18**: R = Ac

$\downarrow -[H]$

$Me\,CH\underset{cis}{=}CH[C{\equiv}C]_2\,CH\underset{trans}{=}CH\,CH(OR)\,(CH_2)_7\,CO_2H$

24: R = H **16**: R = Ac

$\downarrow -[H]$

25 $Me\,[C{\equiv}C]_3\,CH\underset{trans}{=}CHCH(OH)(CH_2)_7CO_2H \longrightarrow$ **15, 14** and numerous others

$Me\,[C{\equiv}C]_3\underset{trans,\,trans}{[CH{=}CH]_3}H$ **26**

$Me[C{\equiv}C]_3\,CH\underset{trans}{=}CH\,CH_2CH_2COEt$ **27**

$Me\,[C{\equiv}C]_3\underset{trans,\,trans}{[CH{=}CH]_2}(CH_2)_4CH{=}CH_2$ **28**

$HOCH_2CH{=}CH[C{\equiv}C]_2\underset{trans,\,trans}{[CH{=}CH]_2}(CH_2)_4CH{=}CH_2$ **29**

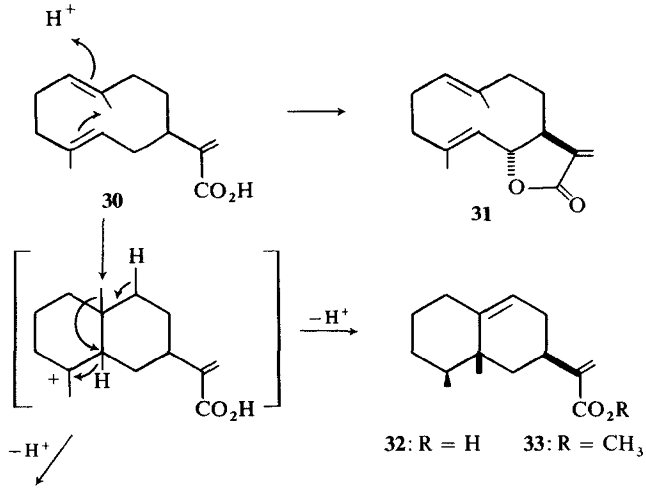
Similarly, the chemistry of *A. calva* Hutch. indicates that this species also might be better placed in the genus *Pentzia*. Thus the roots contain the acetylenes **8–10**, **14** and **15** together with the hydroxygermacrene **13** and two acids, which could not be separated adequately as such nor in their ester form. The spectral data of the acids, however, (see Table 3) clearly show that they are acetylenic acids **16** and **18**, though in the mass spectrum of **16** and **17** the base peak is formed by loss of $^{\cdot}(CH_2)_6CO_2R$ and not $^{\cdot}(CH_2)_7CO_2R$ as expected. Most probably this is because of a rapid hydrogen transfer from C-9 to C-13 involving a six membered ring, so that loss of $^{\cdot}(CH_2)_6CO_2R$ from the resulting allene **20** is then easily explained. We named **16** athanacalvic acid. The isolation of **16** and **18** is of biogenetic interest in that we may indicate that crepininic acid (**21**), the common precursor of all acetylenes in the Compositae [4], is first transformed via **22** to **23**. The next step is most probably a *cis*-elimination of hydrogen at C-16 and C-17 as in the formation of **16** from **18**. The final dehydrogenation of **24** gives the triyne **26**, which has been shown to be a very common precursor for all acetylenes with such end groups [4] (examples are **14**, **15** and **26–28**). As shown by feeding experiments, the labelled *trans*-isomer of **24** is not transformed to the triynes.

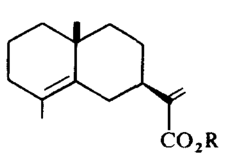
The roots of *A. thodei* Bolus also contain **8** together with the *trans*-isomer and traces of **26**, the precursor of **14** [4], while the aerial parts afford besides *cis*- and *trans*-**8**, two sesquiterpene acids, which could be separated only as

Table 4. ^{1}H-NMR data of **16–19** ($CDCl_3$)

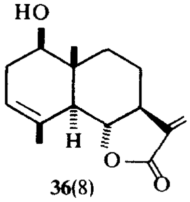
	16	17	18	19
2-H	*t* 2·34	*t* 2.30	*t* 2.34	*t* 2.30
3,8-H	*m* 1.61	*m* 1.61	*m* 1.61	*m* 1.61
4–7-*H*	*m* 1.31	*m* 1.28	*m* 1.31	*m* 1.28
9-*H*	*dt* 5.28	*dt* 5.29	*dt* 5.24	*dt* 5.25
10-H	*dd* 6.17	*dd* 6.18	*dd* 6.13	*dd* 6.13
11-H	*d*(*br*) 5.76	*d*(*br*) 5.78	*d*(*br*) 5.68	*d*(*br*) 5.70
16-H	*d*(*br*) 5.50	*d*(*br*) 5.57	*t* 2.30	*t* 2.30
17-H	*dq* 6.20	*dq* 6.19	*m* 1.61	*m* 1.61
18-H	*dd* 1.92	*dd* 1.92	*t* 1.00	*t* 1.00
OCH_3	—	*s* 3.66	—	*t* 3.66

J(Hz): 2,3 = 7.5; 8,9 = 9,10 = 6.5; 10,11 = 16; 16,17 = 10.5; 16,18 = 1.5; 17,18 = 7.





34: R = H 35: R = CH$_3$



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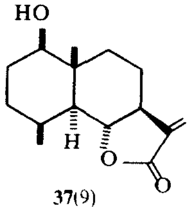

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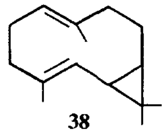

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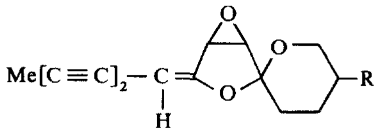
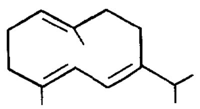


39: R = H 40: R = OH



41

methyl esters using silver nitrate coated plates. The less polar ester is identical with the methyl ester of isocostic acid (**35**) [7]. The structure of the second ester must be **33**, as shown by NMR data (see Table 5). The naturally occurring compound therefore has the structure **32**, which is the first eremophilene derivative to be isolated from a member of the tribe Anthemideae. Most probably both acids, **32** and **34**, are formed from the unknown acid **30**, which must be the precursor of costunolide (**31**) also present in the aerial parts together with the known lactones **36** and **37**. The constituents isolated from this species also indicate that it would be better placed in *Pentzia*.

Table 5. ^{1}H-NMR data of **33** (CDCl$_3$)

		Δ*			Δ*
1α-H	*d*(*br*) 1.93	0.12	8β-H	*dd*(*br*) 1.96	0.6
1β-H	*dd*(*br*) 2.21	0.09	9-H	*ddd* 5.36	0.18
2,3-H	*m* 1.25–1.6		13-H	*s*(*br*) 6.18	1.35
4α-H	*ddq* 1.77	0.27	13-H	*dd* 5.51	0.50
6α-H	*d*(*br*) 1.90	0.65	14-H	*s* 0.93	0.16
6β-H	*dd* 1.11	0.43	15-H	*d* 0.82	0.18
7α-H	*dd*(*br*) 2.74	0.86	OCH$_3$	*s* 3.76	1.17
8α-H	*d*(*br*) 2.08	0.5			

* Δ—values after addition of 0.2 equivalents of Eu(fod)$_3$.
J(Hz): 1α,2β = 13; 1β,2α = 13; 1,9 = 1.5; 3α,4α = 5; 3β,4α = 11; 4α,15 = 7; 6α,6β = 13; 6α,7α = 2; 6β,7α = 13; 7α,13 = 1; 7α,8α ~ 2; 7α,8β = 13, 8α,8β = 16, 8α,9 = 6.

Both the roots and the aerial parts of *A. woodii* (Thell.) Hilliard contain **2** whilst in the roots germacrene C (**41**) is also present. The roots and the aerial parts of *Pentzia tenella* DC contain **14** and **26–29**. The roots of *Pentzia cooperi* Harv. produce **8**, **15**, **39** and **40**. while the aerial parts contain **28**, bicyclogermacrene **38** and **39**. The aerial parts of *Pentzia annua* DC, synthesize only **15** and those of *P. incana* O. Kuntz **27**, linalolacetate and a mixture of unidentified sesquiterpene lactones.

CONCLUSIONS

If we consider the previous surveys of *Athanasia* and *Pentzia* spp. it would appear that only those species which synthesize furansesquiterpenes may be considered as true *Athanasia* sp., while those which produce spiroketal enolethers with a six membered ring such as **8** or compounds biogenetically related to C$_{14}$-acetylenes belong to the genus *Pentzia* [10]. Sesquiterpene lactones may also be typical of *Pentzia* species (e.g. **5**), as they have not so far been found in any *Athanasia* taxa. Furthermore it is suggested that most of the South African *Matricaria* species should be included in the genus *Pentzia*, as they contain the same or very similar acetylenes to those of *Pentzia* species and none of the C_{13}-acetylenes which are typical of the European *Matricaria* species [4]: *M. globifera* Fenzl. [11], *M. suffructicosa* L. (= *Pentzia suffructicosa* (L.) Hutch. *ex* Merxm. [5], *M. nigellaefolia* DC. [10, 11], *M. pilulifera* Fourc. [10], *M. grandiflora* Fenzl. [10], *M. zuurbergensis* Oliv. [12], *M. multiflora* Fenzl. (= *Pentzia elegans* DC) [5]. A taxonomic revision of the genera *Athanasia*, *Pentzia* and *Matricaria* is obviously needed, which would take into consideration the new chemical data. Previous results also suggest a close relationship of the South African *Pentzia* and *Matricaria* spp. with *Tanacetum* [4].

EXPERIMENTAL

IR: Beckman IR 9, CCl_4. ^1H-NMR: Bruker WH 270, TMS as internal standard, δ-values; MS: Varian MAT 711, 70 eV; optical rotation. Perkin–Elmer polarimeter, $CHCl_3$. The air dried plant material, collected in South Africa, was extracted with Et_2O–petrol 1:2 and the resulting extracts were separated first by column chromatography (Si gel, act. grade II) and further by TLC (Si gel, GF 254) using Et_2O–petrol mixtures as solvents. Known compounds were identified by comparison of their IR-, NMR- and UV-spectra with those of authentic material.

Athanasia grandiceps Hilliard et Burtt. (voucher 77/121): 150 g roots afforded 80 mg **1** and 80 mg **2**, while from 350 g aerial parts 1.6 g **1**, 40 mg **4** (Et_2O–petrol 1:1) and 60 mg **3** were obtained.

Athanasia pinnatifida (Oliv.) Hilliard (voucher Hilliard 5578): 200 g roots afforded 70 mg **5**, 5 mg **6**, 250 mg **2** and 20 mg *trans*-**2**, while 250 g aerial parts yielded 50 mg **7**, 50 mg **5**, 150 mg **2** and 150 mg *trans*-**2**.

Athanasia leucoclada (DC) Harv. (voucher 77/231): 230 g roots afforded 35 mg **2** and 10 mg *trans*-**2** while from 70 g aerial parts only traces of unidentified furans were obtained.

'*Athanasia*' *coronopifolia* Harv. (voucher 77/272): 200 g roots afforded 40 mg **8**, 5 mg **9** and 5 mg **11**. 150 g aerial parts yielded 25 mg **12** (Et_2O–petrol 1:1) and 20 mg **3**.

'*Athanasia*' *calva* Hutch (voucher 77/164): 640 g roots yielded 5 mg **14**, 5 mg **15**, 30 mg **8**, 500 mg **9**, 50 mg **10**, 120 mg **13**, 300 mg **16** and **18** (3:1) and 100 mg of a complex triterpene mixture. 170 g aerial parts only afforded 100 mg of unidentified triterpenes.

Pentzia tenella DC. (voucher 73/75): 10 g roots afforded 2.5 mg **27**, 3 mg **14**, 1 mg **29** and 1 mg **28**, while 500 g aerial parts yielded 14 mg **28**, 1 mg **14**, 4 mg **27** and 4 mg **29**.

'*Athanasia*' *thodei* Bolus (voucher 77/271): 15 g roots afforded 0.1 mg **26**, 20 mg **8** and 100 mg *trans*-**8**, while 200 g aerial parts yielded 300 mg **8** and *trans*-**8** (1:1), 0.5 mg **32** and **34** (1:1) (Et_2O–petrol 1:10), 20 mg **31**, 10 mg **36** and 6 mg **37**.

Athanasia woodii (Thell.) Hilliard (voucher 77/135): 210 g roots afforded 20 mg **41** and 350 mg **2** while 85 g aerial parts yielded 10 mg **2**.

Pentzia cooperi Harv. (voucher 77/251): 60 g roots afforded 5 mg **15**, 30 mg **8**, 40 mg **39** and 3 mg **40**, while 260 g aerial parts yielded 100 mg **38**, 50 mg **28** and 80 mg **39**.

Pentzia incana O. Kuntze (voucher 73/156): 100 g aerial parts yielded 1 mg **27**, 100 mg linalolacetate and 20 mg of a mixture of unidentified sesquiterpene lactones.

Pentzia annua DC (voucher 73/107): 150 g aerial parts afforded 1 mg **15**.

Athanagrandion (**4**): Colourless oil. IR: OH (hydrogen bonded) 3560; $>$C=O 1705; furanketone 1690, 1570, 1517, 875 cm^{-1}. MS: M^+ *m/e* 266.152 (2%) (calc. for $C_{15}H_{22}O_4$ 266.152) $[\alpha]_D$ $-0.7°$ ($c = 2.8$).

11,13-*Dehydromatricarin* (**12**): Mp 146° (Et_2O–petrol). IR: γ-methylene lactone 1785, 1650; OAc 1750, 1233; C=C—CO 1700, 1623 cm^{-1}. MS: M^+ *m/e* 302.115 (60%) (calc. for $C_{17}H_{18}O_5$ 302.115); $-H_2C{=}C{=}O$ 260 (25); —AcOH 242 (100); 242 $-{}^{\cdot}CH_3$ 227 (43); 242 —CO 214 (25); 242 $-{}^{\cdot}CHO$ 213 (18); 214 $-{}^{\cdot}CH_3$ 199 (41); H_3CCO^+ 43 (84)

$$[\alpha]^{\lambda}_{24^\circ} = \frac{\begin{array}{cccc}589 & 578 & 546 & 436\,\text{nm}\end{array}}{\begin{array}{cccc}+120.8 & +126.5 & +144.6 & +254.4^\circ\end{array}} (c = 1.0).$$

Athanacalvic acid (**16**); Colourless oil, not free from **18**. IR: CO_2H 3400–2500, 1710; OAc 1745, 1235; *trans* CH=CH 1635, 955 cm^{-1}. MS: M^+ *m/e* 330.183 (5%) (calc. for $C_{20}H_{26}O_4$); $-H_3C\ CO^{\cdot}$ 287 (30); —AcOH 270 (31); $-{}^{\cdot}(CH_2)_6\ CO_2H$ 201.092 (100) (calc. for $C_{13}H_{13}O_2$ 201.092); 201 $-H_2C{=}C{=}O$ 159 (48); $C_{10}H_9^+$ 129 (45); $C_{10}H_8^+$ 128 (37); $C_9H_7^+$ 115 (63); $H_3C\ CO^+$ 43 (90).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{\begin{array}{ccc}589 & 578 & 546\,\text{nm}\end{array}}{\begin{array}{ccc}-77.1 & -81.4 & -95.5^\circ\end{array}} (c = 2.5).$$

16,17-*Dihydroathanacalvic acid* (**18**): Colourless oil, not free from **16**. IR: CO_2H 3400–2500, 1710; OAc 1745, 1235; *trans* CH=CH 1635, 955 cm^{-1}. MS: M^+ *m/e* 332.188 (6%) (calc. for $C_{20}H_{28}O_4$ 332.188); —AcOH 272 (41); $-{}^{\cdot}(CH_2)_6\ CO_2H$ 203 (40); $H_3C\ CO^+$ 43 (100).

100 mg of **16** and **18** in 2 ml Et_2O were esterified with diazomethane. The resulting esters were partially separated by TLC (Et_2O–petrol 1:3). **17**: IR: CO_2CH_3 1735; OAc 1743, 1240; C≡C 2240, 2210; *trans* CH=CH 3035, 1635, 955 cm^{-1}. MS: M^+ *m/e* 344 (8%); $-H_3C\ CO^{\cdot}$ 301 (34); $-{}^{\cdot}(CH_2)_6\ CO_2CH_3$ 201 (100); $C_{10}H_9^+$ 129 (44); $C_{10}H_8^+$ 128 (37); $C_9H_7^+$ 115 (57); $H_3C\ CO^+$ 43 (95). **18**: IR: CO_2CH_3 1735; OAc 1745; 1240; C≡C 2240; *trans* CH=CH 1635, 955 cm^{-1}. MS: M^+ *m/e* 346 (6%); $-{}^{\cdot}(CH_2)_6\ CO_2CH_3$ 203 (38); $H_3C\ CO^+$ 43 (100).

Eremophil-9(10), 11(13)-*dien*-12-*oic acid* (**32**): Colourless oil, not separated from **34**. 100 mg **32** and **34** (1:1) were esterified with diazomethane and the resulting esters were separated on a silver nitrate coated plate (Et_2O–petrol 1:10). The more polar fraction was **33**, colourless oil. IR: C=C CO_2R 1724, 1625 cm^{-1}. MS: M^+ *m/e* 248.178 (55%) (calc. for $C_{16}H_{24}O_3$ 248.178); $-{}^{\cdot}CH_3$ 233 (100); $-CH_3OH$ 216 (27); 216 $-{}^{\cdot}CH_3$ 201 (59); 201 —CO 178 (60).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{\begin{array}{cccc}589 & 578 & 546 & 436\,\text{nm}\end{array}}{\begin{array}{cccc}-0.9 & -1.1 & -1.2 & -2.2^\circ\end{array}} (c = 1.74).$$

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