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# SESQUITERPENES AND ACETYLENES FROM *ARGYRANTHEMUM ADAUCTUM* SSP. *JACOBAEIFOLIUM*

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**Key Word Index**—*Argyranthemum adauctum*; Compositae; acetylenic compounds; frutescin derivatives; sesquiterpenes; bisabolene derivative; 8-isovaleryloxymyrcene.

**Abstract**—The roots of *Argyranthemum adauctum* ssp. *jacobaeifolium*, a rare endemic from Gran Canaria, afforded two new derivatives of the aromatic acetylene frutescin and 8-isovaleryloxymyrcene, while the aerial parts gave a new bisabolol derivative. Furthermore several known compounds were isolated. The structures were elucidated by high field $^1$H NMR spectroscopy and a few chemical reactions.

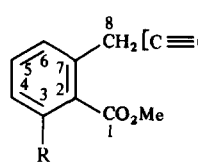
The roots of *Argyranthemum adauctum* (Link) Humphries ssp. *jacobaeifolium* (Schultz Bip) Humphries afforded the *cis-trans* isomeric spiroketal enolether poly-yneacetates [1], a thiophene amide [2] and frutescin **2** [3]. Furthermore two compounds were present which were closely related to **2** as shown by the spectral data. The molecular formula of the less polar compound was $C_{14}H_{12}O_2$ while that of the more polar one was $C_{14}H_{12}O_3$. The $^1$H NMR spectra (Table 1) clearly showed that the second compound had phenolic hydroxyl in the *ortho* position to a carbonyl group ($\delta$10.26, *s*). All other signals were close to those of **2**. Accordingly, the new compound was the corresponding desmethyl derivative **3**. The $^1$H NMR spectral data of the second compound were also close to those of **2**. However, in agreement with the molecular formula only one methoxy signal was visible. The aromatic signals clearly showed that the 3-methoxy group was missing thus the structures of this acetylenic compound was **1**. While **3** obviously is the precursor of **2**, [4], **1** must be the result of reduction of the proposed intermediate in the biogenesis of **3** [4]. The roots also contained a minute amount of a monoterpene derivative. The $^1$H NMR spectrum (see Experimental) clearly showed that we were dealing with 8-isovaleryloxymyrcene (**4**). Thus the $^1$H NMR spectrum was close to that of myrcene and the observed shift differences favoured a C-8 position of the oxygen function; its structure followed from the typical $^1$H NMR signals.

The aerial parts afforded **2**, syringenin isobutyrate and the sesquiterpene lactones balchanine [5], reynosin [6], 8α-acetoxyreynosin [7] and tulipinolide [8] as well as a small amount of a sesquiterpene alcohol, the bisabolene derivative **5**. The structure of **5** followed from the molecular formula and the $^1$H NMR spectrum (Table 2) and could be established by reduction of bisabolone (**7**) [9] which afforded the epimers **5** and **6**. Inspection of

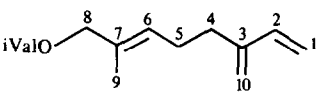
Table 1. $^1$H NMR spectral data of compounds **1** and **3** (400 MHz, $CDCl_3$, TMS as internal standard)

| | 1 | 3 |
|---|---|---|
| H-3 | 7.94 *dd* | — |
| H-4 | 7.32 *br dd* | 6.93 *dd* |
| H-5 | 7.50 *ddd* | 7.37 *dd* |
| H-6 | 7.66 *br d* | 7.05 *dd* |
| H-8 | 4.10 *br s* | 3.93 *br s* |
| H-13 | 1.93 *t* | 1.92 *t* |
| OMe | 3.90 *s* | 3.99 *s* |
| OH | — | 10.26 *s* |

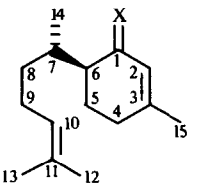
*J* (Hz): 3, 4 = 4, 5 = 5, 6 = 8; 3, 5 = 2; 4, 6 = 1; 8, 13 = 1.




R
**1** H
**2** OMe
**3** OH




**4**




X
**5** αOH, H
**6** βOH, H
**7** O

Table 2. $^1$H NMR spectral data of compounds **5** and **6** (400 MHz, $CDCl_3$, TMS as internal standard)

| | 5 | 6 |
|---|---|---|
| H-1 | 4.08 *br d* | 4.14 *br t* |
| H-2 | 5.40 *br s* | 5.62 *br d* |
| H-10 | 5.14 *tqq* | 5.13 *tqq* |
| H-12 | 1.63 *br s* | 1.63 *br s* |
| H-13 | 1.70 *br s* | 1.70 *br s* |
| H-14 | 0.86 *d* | 0.99 *d* |
| H-15 | 1.70 *br s* | 1.71 *br s* |

*J* (Hz): 7, 14 = 7; 9, 10 = 7; 10, 12 = 10, 13 = 1; compound **5**: 1, 2 ~ 2; 1, 6 = 8; compound **6**: 1, 2 = 1, 6 = 5.

models showed that the coupling of H-1 agreed with the proposed stereochemistry. The chemistry of this species shows relationships to *Argyranthemum frutescens* [3, 4] where, however, no sesquiterpene lactones were reported.

## EXPERIMENTAL

The fresh plant material (grown from seeds from the Botanical Garden, Oslo, Norway, voucher 68/75) was extracted with $Et_2O$–petrol, 1:2 (12 hr room temp) and worked-up in the usual fashion. The CC fractions (100 ml) of the root extract were as follows: 1 (petrol), 2 ($Et_2O$–petrol, 1:10), 3 ($Et_2O$–petrol, 1:3), 4 ($Et_2O$–petrol, 1:1), 5 ($Et_2O$) and 6 ($Et_2O$–MeOH, 20:1). TLC of fraction 2 (always $SiO_2$, PF 254; $Et_2O$–petrol, 1:10, detection by UV 255 nm) 2 mg **4** ($R_f$ 0.70), 2 mg **1** ($R_f$ 0.52) and 3 mg **2** ($R_f$ 0.48). TLC of fraction 3 ($Et_2O$–petrol, 1:3) gave 4 mg *cis* and 3 mg *trans* spiroketal enol ether poly-yn acetate, 2 mg **1** and 2 mg **3** ($R_f$ 0.42). Fraction 4 on TLC ($Et_2O$–petrol, 1:1) gave 7 mg 6-[thienyl-2] sorbic acid isobutyl amide. Fractions 5 and 6 gave no characteristic compounds. The fractions (50 ml) of the extract of the aerial parts (100 g) were as follows: 1 (petrol), 2 ($Et_2O$–petrol, 1:10), 3 ($Et_2O$–petrol, 1:3) 4 ($Et_2O$–petrol, 1:1) 5 ($Et_2O$) and 6 ($Et_2O$–MeOH, 20:1). TLC of fraction 2 ($Et_2O$–petrol, 1:10) gave 2 mg syringenin isobutyrate, TLC of fraction 3 ($Et_2O$–petrol, 1:3) afforded 5 mg **2** ($R_f$ 0.70) and 2 mg **5**, ($R_f$ 0.62). TLC of fraction 4 ($Et_2O$–petrol 3:1) gave 2 mg tulipinolide, 1 mg 8α-acetoxyreynosine ($R_f$ 0.50), 2 mg balchanine and 5 mg reynosin ($R_f$ 0.45) (the latter two not separated). Fractions 5 and 6 gave no characteristic compounds. Known compounds were identified by their 400 MHz $^1$H NMR spectra. Quantities were determined by weight.

*3-Desmethoxyfrutescin* (**1**). Colourless crystals, mp 78–79° (petrol), IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 1736 ($CO_2R$), 1600, 1570 (Ph); MS *m/z* (rel. int.): 212.083 $[M]^+$ (59) ($C_{14}H_{12}O_2$), 197 $[M-Me]^+$ (20), 181 $[M-OMe]^+$ (52), 180 $[M-MeOH]^+$ (37), 152 $[M-HCO_2Me]^+$ (100).

*3-O-Desmethylfrutescin* (**3**). Colourless crystals, mp 88–89° (petrol), IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3500–2700 (OH, hydrogen bonded), 1670 ($CO_2R$, hydrogen bonded), 1615, 1580 (Ph); MS *m/z* (rel. int.): 228.079 $[M]^+$ (17), ($C_{14}H_{12}O_3$), 213 $[M-Me]^+$ (8), 196 $[M-MeOH]^+$ (100), 181 $[196-Me]^+$ (8).

*8-Isovaleryloxymyrcene* (**4**). Colourless oil (no impurities detectable in the 400 MHz $^1$H NMR spectrum), IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 1735 ($CO_2R$); MS *m/z* (rel. int): 236.178 $[M]^+$ (2) ($C_{15}H_{24}O_2$), 134 $[M-RCO_2H]^+$ (20), 85 $[C_4H_9CO]^+$ (56), 57 $[85-CO]^+$ (100); $^1$H NMR ($CDCl_3$): 5.06 *d* (H-1, *J* = 11 Hz), 5.23 *d* (H-1′, *J* = 17 Hz), 6.36 *dd* (H-2, *J* = 17, 11 Hz), 5.44 *t* (H-6, *J* = 6 Hz), 4.58 *br s* (H-8), 1.75 *br s* (H-9), 4.99 *br s* (H-10), 5.03 *br s* (H-10′); OiVal: 2.20 *d* (*J* = 7 Hz), 2.05 *m*, 0.95 *d* (*J* = 7 Hz).

*1α-Hydroxybisabol-2,10-diene* (**5**). Colourless oil (no impurities detectable in the 400 MHz $^1$H NMR spectrum), IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3600 (OH), 905 (C=CH); MS *m/z* (rel. int.): 222.198 $[M]^+$ (5) ($C_{15}H_{26}O$), 204 $[M-H_2O]^+$ (38), 161 $[204-C_3H_7]^+$ (22), 119 $[C_8H_{11}]^+$ (100), 93 $[204-C_8H_{15}]^+$ (81), 82 $[C_7H_{10}]^+$ (78), 69 $[C_5H_9]^+$ (87).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{+9 \quad +10 \quad +17 \quad +25} \text{CHCl}_3;\ c = 0.97$$

*Partial synthesis of* **5**. To 10 mg **7** in 2 ml $Et_2O$ 10 mg $LiAlH_4$ were added. After 5 min usual work-up afforded by TLC ($Et_2O$–petrol, 1:3) 2 mg **6** and 6 mg **5**, identical with the natural compounds, were obtained.

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