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POLYACETYLENES FROM THE RABBITBRUSH, *CHRYSOTHAMNUS NAUSEOSUS*[*]

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Key Word Index—*Chrysothamnus nauseosus*; Compositae; rabbitbrush; new polyacetylenes; insect antifeedant substances; isolation; structure determination; ^{13}C NMR.

Abstract—Four new polyacetylenes, methyl *Z*,*Z*-10-acetoxymatricariate, methyl *Z*,*Z*-10-hydroxymatricariate, methyl 2(*Z*)-10-acetoxy-8,9-epoxydecen-4,6-diynoate and methyl 2(*Z*)-10-hydroxy-8,9-epoxydecen-4,6-diynoate, were isolated from the composite *Chrysothamnus nauseosus*. These compounds are naturally-occurring antifeedants of the Colorado potato beetle. The assigned structures rest on their spectroscopic properties as well as chemical interconversions.

INTRODUCTION

In a previous paper [1], we pointed out that the threat of increasing insecticide resistance in the Colorado potato beetle necessitates research on new approaches to its control. One of the promising new means of control is the use of antifeedants. Naturally-occurring antifeedants, i.e. secondary plant metabolites, would be preferable because they are least likely to be harmful to the environment.

As part of our investigation of insect control methods, we examined a number of sagebrush desert plant species, which are not attacked by the beetle, for antifeedant activity. Preliminary experiments demonstrated the strong antifeedant effect on the larvae of the Colorado potato beetle of rabbitbrush (*Chrysothamnus nauseosus*; Compositae, tribe Astereae). Antifeedant activity was determined by a choice test with third-instar Colorado potato beetle larvae using 14 mm diameter potato leaf disks coated with either a measured quantity of test solution or a solvent-blank solution [1].

RESULTS AND DISCUSSION

Using this bioassay, the activity of the $CHCl_3$ extract (fraction A) of rabbitbrush was largely confined to the $CHCl_3$ portion (fraction G) of a standard solvent–solvent partitioning scheme (see Experimental). Gel filtration of fraction G yielded two active antifeedant fractions, H and I. We report herein the structures of four new polyacetylenic compounds (methyl *Z*,*Z*-10-acetoxymatricariate (**1**), methyl *Z*,*Z*-10-hydroxymatricariate (**3**), methyl 2(*Z*)-10-acetoxy-8,9-epoxydecen-4,6-diynoate (**2**) and methyl 2(*Z*)-10-hydroxy-8,9-epoxydecen-4,6-diynoate (**4**)) separable by Si gel chromatography, which were the major components of fraction I. The structures of **1**–**4** were determined by spectral and chemical methods.

The UV spectra of **1** and **3** suggested the presence of an ene–diyne–ene chromophore while **2** and **4** were consistent with an ene–diyne part structure [2]. The presence of a diyne group was supported by the IR absorption near 2200 cm^{-1} and by four ^{13}C NMR resonances (singlets) in the 70–85 ppm region. The additional common spectral features of all four substances were a three-proton ^1H NMR singlet near δ 3.7, ^{13}C NMR resonances near 51 (*q*) and 164 ppm (*s*) and IR signals near 1725 and 1180 cm^{-1}. These data suggested the presence of a methyl ester group in compounds **1**–**4**.

Analysis of this data and the chemical formulae, obtained by high resolution mass spectrometry, indicated that **1**–**4** were matricaria ester derivatives. Polyacetylenes are common secondary metabolites of the Compositae and have been reported from a close relative of *C. nauseosus*, namely *Happlopappus brandegei* [2].

The geometry of the two olefinic bonds in **1** was determined by ^1H NMR chemical shift and coupling data [2, 3]. In **1**, H(2) and H(3) had identical chemical shifts (δ 6.22) and appeared as a singlet. The magnetic equivalence of H(2) and H(3) (δ 6.15) was also observed in methyl *cis*,*cis*-matricariate, (**5**) [2]. In the corresponding *trans*,*cis*-compound (**6**), H(2) (δ 6.25) and H(3) (δ 6.78) differed in chemical shift by 0.53 ppm [2]. Thus the chemical shift data indicated a *cis* C(2)-C(3) double bond. In the off-resonance decoupled carbon spectrum of **1**, C(2) and C(3) exhibited second-order coupling [4]. Computer simulation of the second-order pattern required that H(2) be coupled to

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[*] Part 2 in the series "Antifeedants for the Colorado Potato Beetle, *Leptinotarsa decemlineata*". For Part 1, see ref. [1].

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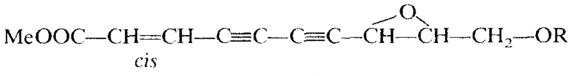
1 2 3 4 5 6 7 8 9 10

$$\mathrm{MeOOC{-}CH{=}CH{-}C{\equiv}CC{\equiv}CCH{=}CH{-}CH_2OR}$$

cis *cis*

1 R = Ac
3 R = H



$$\mathrm{MeOOC{-}CH{=}CH{-}C{\equiv}C{-}C{\equiv}C{-}\overset{\frown O \frown}{CH{-}CH}{-}CH_2{-}OR}$$

cis

2 R = Ac
4 R = H

$$\mathrm{MeOOC{-}CH{=}CH[C{\equiv}C]_2{-}CH{=}CH{-}Me}$$

cis *cis*

5

$$\mathrm{HOOC{-}CH{=}CH[C{\equiv}C]_2-CH{=}CH{-}Me}$$

trans *cis*

6

$$\mathrm{ROOCH{=}CH[C{\equiv}C]_2{-}CH{=}CH{-}CH_2{-}OH}$$

trans *trans*

7 R = H
8 R = Me

$$\mathrm{MeOOC{-}CH{=}CH[C{\equiv}C]_2{-}CH{=}CH{-}CH_2{-}OH}$$

trans *cis*

9

H(3) by 11 Hz and hence the C(2)–C(3) linkage has a *cis* configuration. H(8) (δ 5.78) was coupled to H(9) (δ 6.2) by 10.5 Hz, a value consistent with *cis* C(8)–C(9) geometry [3]. Additionally, C(8) exhibited three-bond coupling ($^3J_{\mathrm{CCCH}}$) with H(10) (Table 1) of 6 Hz. This value was consistent with a *cis* orientation of the C(8)–C(9) olefin [5].

Table 1. Carbon chemical shifts of polyacetylenes from *Chrysothamnus*^{a}

Carbon	Compound **1**	 **2**	 **3**	 **4**
1	164.0	164.4	164.8	164.5
2	121.3^{b}	121.6^{b}	122.0	121.3
3	131.1^{c}	132.7^{k}	131.2	132.5
4	78.5^{d}	70.1^{d}	78.7^{d}	70.0^{d}
5	84.2^{d}	84.0^{d}	85.1^{d}	84.2^{d}
6	80.8^{d,e}	80.7^{d,l}	82.1^{d}	81.2^{d}
7	79.3^{d}	74.5^{d,m}	(−)	74.3^{d}
8	110.7^{f}	44.1^{n,o}	109.0	44.5^{n}
9	140.7^{g}	55.5^{p}	146.6	58.2^{n}
10	61.8^{h}	63.3^{q}	61.1	61.7
Acetate carbonyl	170.0	170.5		
Methyl ester	51.7^{i}	51.7^{i}	51.8	51.8
Acetate methyl	20.3^{j}	20.6^{j}		

^{a}The values were recorded at 25.03 MHz and are in ppm downfield from TMS in $\mathrm{CDCl_3}$ solution; ^{b}*d*, $^1J_{\mathrm{CH}} = 168$ Hz; ^{c}*dd*, $^1J_{\mathrm{CH}} = 168$ Hz, $^2J_{\mathrm{CCH}} = 3$ Hz; ^{d}values within a column may be interchanged; ^{e}*d*, $^xJ_{\mathrm{CH}} = 12$ Hz; ^{f}*dt*, $^1J_{\mathrm{CH}} = 168$Hz, $^3J_{\mathrm{CCCH}} = 6$ Hz; ^{g}*d mult.*, $^1J_{\mathrm{CH}} = 164$ Hz, $^xJ_{\mathrm{CH}} = 5$ Hz; ^{h}*td*, $^1J_{\mathrm{CH}} =$ 150 Hz, $^3J_{\mathrm{CCCH}} = 10$ Hz; ^{i}*q*, $^1J_{\mathrm{CH}} = 148$ Hz; ^{j}*q*, $^1J_{\mathrm{CH}} =$ 128 Hz; ^{k}*d*, $^1J_{\mathrm{CH}} = 166$ Hz; ^{l}*d*, $^3J_{\mathrm{CCCH}} = 4$ Hz; ^{m}*d*, $^2J_{\mathrm{CCH}} = 12$ Hz, ^{n}values within a column may be reserved; ^{o}*d*, $^1J_{\mathrm{CH}} = 190$ Hz; ^{p}*ddd*, $^1J_{\mathrm{CH}} = 180$ Hz, $^2J_{\mathrm{CCH}} = 6{,}4$ Hz; ^{q}*td*, $^1J_{\mathrm{CH}} = 152$ Hz, $^xJ_{\mathrm{CH}} = 4$ Hz.

The IR (1745 cm^{-1}), carbon (170.0 and 20.3 ppm) and proton (3H singlet, δ 2.0) spectra suggested the presence of an acetate moiety in **1**. The proton chemical shift (δ 4.80) of H(10) as well as the carbon chemical shift of C(10) (61.9 ppm, *t*) required that the acetate be attached at this position. The one-bond coupling constant ($^1J_{\mathrm{CH}}$) of C(10) in the ^{13}C NMR of 150 Hz was also compatible with the attachment of an electronegative atom at this sp^2-hybridized center [4]. These data define **1** as methyl *Z*,*Z*-10-acetoxymatricariate.

Examination of the spectral data obtained for **3** indicated its close resemblance to **1**. The IR spectrum of **3** showed hydroxyl stretch (3600, 3400 cm^{-1}) and the absence of the acetate carbonyl band (1745 cm^{-1}) seen in **1**. The proton chemical shift of H(10) (δ 4.42) was a two-proton doublet which resonated at higher field in **3** than in **1**. This also indicated the absence of the acetate functionality. Treatment of **3** with acetic anhydride and pyridine yielded an acetate indistinguishable (IR, ^{1}H NMR, TLC, HPLC) from **1**. The ^{1}H NMR coupling constants (11 and 10.5 Hz) required a *cis* configuration of the two olefinic linkages [3]. Thus **3** was methyl *Z*,*Z*-10-hydroxymatricariate. The corresponding *E*,*E*-10-hydroxymatricaria acid (**7**) has been isolated from the sporophores of *Fistulina hepatica* [6] while methyl *E*,*E*- and *E*,*Z*-10-hydroxymatricariate, **8** and **9** respectively, have been isolated as a mixture from the culture filtrates of the fungus *Polyporus anthracophilus* [7].

High resolution mass spectrometry demonstrated **2** as a compound with molecular formula $\mathrm{C_{13}H_{12}O_5}$. Four of the five oxygen atoms were accounted for as a methyl ester (IR 1725 cm^{-1}; ^{13}C NMR 51.7 and 164.4 ppm; ^{1}H NMR 3H singlet, δ 3.79) and as an acetate ester (IR 1745 cm^{-1}; ^{13}C NMR 170.5 and 20.6 ppm; ^{1}H NMR 3H singlet, δ 2.10). The remaining oxygen atom was established as an epoxide by the presence of ^{13}C NMR signals, Table 1, at 44.1 (*d*, C(8)) and 55.5 ppm (*d*, C(9)) and mass spectral fragment ions at *m*/*e* 103, 146, 86 and 161. These ions resulted from cleavage of the epoxide ring. The epoxide carbon resonances occurred at unexpectedly high field. However as a substituent, the alkyne group is known to induce a diamagnetic shift of the α- and β-carbons [8]. For example, C(3) of 3-pentanol resonates at 74.5 ppm [9]. Replacement of the ethyl substituent by an ethynyl substituent yields 1-pentyn-3-ol and a corresponding 11.1 ppm upfield shift of C(3) to 63.4 ppm [9]. By analogy, an epoxy methine carbon adjacent to an alkyne linkage would be expected to resonate at higher field (*ca* 10 ppm) than one adjacent to alkane linkages. The epoxide assignment thus appears reasonable. Verification of the presence of an epoxide group was obtained by conversion of **1** into **2**. Treatment of **1** with less than one equivalent of *m*-chloroperbenzoic acid in $\mathrm{CH_2Cl_2}$ yielded, in addition to recovered **1**, **2** as the sole reaction product. Thus, the structure of **2** is established as methyl 2(*Z*)-10-acetoxy-8,9-epoxydecen-4,6-diynoate.

Compound **4**, $\mathrm{C_{11}H_{10}O_4}$, differed from **2** by $\mathrm{C_2H_2O}$. Support for **4** being the deacetyl derivative of **2** was found in the IR which now displayed absorption at 3600 cm^{-1} (hydroxy), in an upfield shift of the H(10) resonance by 0.47 ppm in the ^{1}H NMR, in a small upfield shift of C(10) (1.68 ppm) in the ^{13}C NMR [10]

Table 2. Threshold of inhibition of feeding

Test	Threshold level (μg/cm^2
Fraction I	40–70
Compound **1**	35–70
Compound **2**	<35
Compound **3**	<35
Compound **4**	<35

and in the concomitant absence of signals assignable to an acetate group. Treatment of **4** with acetic anhydride and pyridine yielded **2**, identified by TLC R_f value and HPLC retention volumes which were indistinguishable from a natural sample of **2**. Thus **4** is methyl 2(*Z*)-10-hydroxy-8,9-epoxydecen-4,6-diynoate.

The carbon chemical shift values for **1–4** are collated in Table 1. The acetylenic carbon resonances of compound **2** were assigned by measuring, in a gated decoupling experiment, the long-range carbon–proton coupling constants. Zeisberg and Bohlmann [11], in a study of symmetrical and unsymmetrical polyacetylenic compounds, observed that the long-range *sp*-hybridized carbon–proton coupling constants decrease in magnitude with an increase in the number of intervening bonds. Thus $^2J_{\equiv CCH}$ is greater than $^3J_{\equiv CCCH}$. The 74.5 ppm resonance of **2** exhibits a 12 Hz long-range coupling to the C(8) methine while the 80.7 ppm signal displays but 4 Hz long-range coupling to the C(8) methine. Thus the 74.5 ppm signal is assigned as C(7) and the 80.7 ppm resonance is assigned as C(6). The acetylenic carbon assignments of **4** follow from those in **2**. No unambiguous acetylene carbon assignments could be made for **1** or **3**.

Fraction I, which contained polyacetylenes **1–4**, inhibited feeding of third-instar Colorado potato beetle larvae at 40–70 μg/cm^2 (Table 2). The threshold level of **1** was 30–70 μg/cm^2 and less than 35 μg/cm^2 for **2**, **3** and **4**. Compounds **2** and **4** showed mild phytotoxicity in the leaf disk assay but no such toxicity was observed after 24 hr when **2** or **4** were applied to the leaves of greenhouse potato plants. We are continuing to examine the minor components of fraction I as well as acidic components of fraction H for additional feeding inhibitors.

EXPERIMENTAL

Isolation of **1–4**. *Chrysothamnus nauseosus* was collected 6 October 1978 in the sagebrush desert near Yakima, Washington. Dried and ground aerial parts (2.15 kg), were Soxhlet-extracted with CHCl$_3$. CHCl$_3$ extracts were washed with H$_2$O, dried (MgSO$_4$) and concd to a viscous oil, fraction A (314 g, 14% of dried plant material). Fraction A was dissolved in aq. MeOH (1 : 8, 1.5 l.) and extracted with petrol (3 × 0.5 l.) to yield an aq. MeOH fraction B and a petrol fraction C (66 g, 3.1% of dried plant). Fraction B was adjusted in concn to 1 : 4 aq. MeOH then extracted with CCl$_4$ (3 × 0.5 l.) to yield aq. MeOH fraction D and CCl$_4$-soluble fraction B (62 g, 3.4% of dried plant). Fraction D was then adjusted in concn to 1 : 3 aq. MeOH and extracted with CHCl$_3$ (3 × 0.5 l.) to yield after evapn aq. MeOH fraction F (40 g, 1.9% of dried plant) and CHCl$_3$ fraction G (123.8 g, 5.7% of dried plant). Gel filtration of fraction G (0.41 g) on Biobeads SX-2 (3.5 × 21 cm) in CHCl$_3$ yielded two active fractions H (104–144 ml, 0.27 g, 3.5% of dried plant) and I (145–192 ml, 0.042 g, 0.53% of dried plant). Step-gradient Si gel chromatography (89 g, 2.5 × 38 cm) (CHCl$_3$ to 2% MeOH in CHCl$_3$) of fraction I (0.461 g) yielded mixtures of **1** and **3** (301–499 ml, 0.208 g) and **2** and **4** (500–700 ml, 0.176 g). **1** and **3** were separated by HPLC (Si gel, 0.9 × 50 cm, CHCl$_3$) to give spectrally pure **1** (32.4–34.5 ml, 0.131 g, 0.15% of dried plant) and **3** (35.4–39.0 ml, 0.067 g, 0.08% of dried plant). **2** and **4** were separated by HPLC (Si gel, 0.9 × 50 cm, 1% MeOH in CHCl$_3$ to give spectrally pure **2** (28.2–32.4 ml, 0.127 g, 0.14% of dried plant) and **4** (35.4–39.6 ml, 0.036 g, 0.04% of dried plant).

Methyl 2(*Z*),8(*Z*)-10-*acetoxymatricaricate* (**1**). IR (neat) ν_{max} cm^{-1}: 2210, 2140, 1745, 1730, 1610, 1440, 1220, 1170, 1030, 820; UV λ_{max}^{MeOH} nm (ε): 329 (10 000), 308 (12 200), 289 (9300), 258 (16 500), 246 (18 000), 233 (15 500); ^{1}H NMR (90 MHz, CDCl$_3$): δ 6.22 (2H, *s*, C-2,3), 6.2 (1H, *m*, C(9)), 5.78 (1H, *dt*, *J* = 10.5, 1.5 Hz, C(8)), 4.80 (2H, *dd*, *J* = 6, 1.5 Hz C(10)), 3.73 (3H, *s*, OMe), 2.05 (3H, *s*, MeCO); MS (probe) *m/e* (rel. int.): M$^+$ 232 (9), 217 (3), 201 (2), 189 (4), 175 (3), 85 (21), 71 (35), 69 (14), 57 (56), 55 (16), 43 (100); high resolution MS *m/e* 232.0740 (calc. for C$_{13}$H$_{12}$O$_4$, 232.0736).

Methyl 2(Z)-10-*acetoxy*-8,9-*epoxydecen*-4,6-*diynoate* (**2**). IR ν_{max}^{Neat} cm^{-1}: 2240, 2150, 1745, 1725, 1610, 1440, 1220, 1180, 1040, 810; UV λ_{max}^{MeOH} nm (ε); 304 (9600), 287 (1100), 272 (7200), 285 sh (4000), 225 (21 600); ^{1}H NMR (90 MHz, CDCl$_3$): δ 6.30 (1H, *d*, *J* = 11 Hz, C(3) or (2)), 6.17 (1H, *d*, *J* = 11 Hz, C(2) or (3)), 4.40 (1H, *dd*, *J* = 12, 4.5 Hz, C(10)), 4.13 (1H, *dd*, *J* = 12, 6 Hz, C(10)), 3.79 (3H, *s*, OMe), 3.67 (1H, *d*, *J* = 4.5 Hz, C(8)), 3.37 (1H, *m*, C(9)), 2.10 (3H, *s*, MeCO); MS (probe) *m/e* (rel. int.): M$^+$ 248 (1), 217 (2), 205 (2), 189 (2), 188 (6), 175 (21), 162 (1), 161 (2), 146 (29), 131 (28), 103 (12), 87 (9), 86 (7), 43 (100); high resolution MS *m/e* 248.0700 (calc. for C$_{13}$H$_{12}$O$_5$, 248.0685).

Methyl 2(*Z*),8(*Z*)-10-*hydroxymatricarite* (**3**). Mp (uncorr.) 38.5–40.5°; IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3600, 3400, 2200, 2125, 1730, 1720, 1610, 1220, 1180, 760; UV λ_{max}^{MeOH} nm (ε): 330 (9500), 310 (11 500), 294sh (8800), 258 (16 800), 246 (18 500), 233 (15 100); ^{1}H NMR (90 MHz, CCl$_4$): δ 6.30 (1H, *m*, C(9)), 6.22 (2H, *s*, C(2), (3)), 5.68 (1H, *dt*, *J* = 10.5, 1.5 Hz, C(8)), 4.42 (2H, *dd*, *J* = 6.3, 1.5 Hz, C(10)), 3.77 (3H, *s*, OMe), 1.8 (1H, *br.s*, OH); MS (probe) *m/e* (rel. int.): M$^+$ 190 (97), 175 (62), 161 (100), 159 (54), 147 (54), 133 (16), 131 (54), 119 (46), 103 (68), 91 (52), 77 (75); high resolution MS *m/e* 190.0638 (calc. for C$_{11}$H$_{10}$O$_3$, 190.0630).

Methyl 2(Z)-10-*hydroxy*-8,9-*epoxydecen*-4,6-*diynoate* (**4**). Mp (uncorr.) 53.0–54.0° (CCl$_4$); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 2150, 1730, 1615, 1210, 1180, 1040, 810; UV λ_{max}^{MeOH} nm (ε): 307 (11 200), 288 (12 300), 273 (8100), 260sh (5300), 227 (2400); ^{1}H NMR (90 MHz, CDCl$_3$): δ 6.26 (1H, *d*, *J* = 11 Hz, C(3) or (2)), 6.15 (1H, *d*, *J* = 11 Hz, C(2) or (3)), 3.93 (2H, *dd*, *J* = 5.0, 2.5 Hz, C(10)), 3.74 (3H, *s*, OMe), 3.66 (1H, *d*, *J* = 3.8 Hz, C(8)), 3.37 (1H, *m*, C(9)); MS (probe) *m/e* (rel. int.): 206 (3), 205 (1), 192 (1), 191 (2), 189 (2), 188 (2), 175 (100), 149 (13), 147 (35), 146 (23), 133 (12), 131 (55); high resolution MS *m/e* 206.0590 (calc. for C$_{11}$H$_{10}$O$_4$, 206.0579).

Epoxidation of **1**. To a cooled (0°), magnetically stirred soln of **1** (18.55 mg, 0.08 mM) in CH$_2$Cl$_2$ (2 ml) was added *m*-chloroperbenzoic acid (*ca* 85% pure, 13 mg, 0.06 mM). The cooled mixture was stirred for 15 min, warmed to room temp. and stirred for 45 min longer. The mixture was diluted with Et_2O (15 ml) then extd sequentially with satd $NaHCO_3$, H_2O and satd aq. NaCl. The organic phase was dried and concd *in vacuo* to an oil (19 mg). ^1H NMR revealed the presence of **1** and **2**. HPLC (0.9×50 cm Si gel, $CHCl_3$) yielded analytically pure **1** (6.2 mg) and **2** (10 mg).

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