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POLYACETYLENES FROM THE *ARTEMISIA* 'VULGARES' GROUP

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Key Word Index—*Artemisia* 'Vulgares' group, Asteraceae, Anthemideae; polyacetylenes, spiroacetal enol ethers.

Abstract—Comparative phytochemical analyses on polyacetylenes within *Artemisia vulgaris* and closely related species ('Vulgares' group) resulted in a comprehensive survey of typical derivatives. Apart from already known structures several hitherto unknown compounds were characterized. The stereochemistries of two rather common polyacetylenic hydrocarbons have been re-examined and the structures of five further derivatives have been elucidated by spectroscopic methods

INTRODUCTION

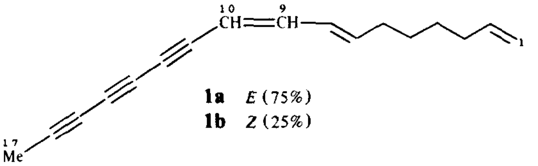
The accumulation of polyacetylenes represents a typical biogenetic trend within the Asteraceae (Compositae). Especially rich in these compounds are the tribes Heliantheae, Cynareae and Anthemideae [1] The polyacetylene pattern of the tribe Anthemideae clearly deviates from the others, especially by the formation of bicyclic spiroacetal ethers and open chain derivatives of the dehydromatricaria ester and artemisia ketone type In order to determine the biogenetic trends within the genus *Artemisia*, a great number of different species has been analysed. It has been shown that the distribution of different types of polyacetylenes is of special chemotaxonomic significance [2]. Based on the available data it became apparent that especially *Artemisia vulgaris* L. and its closely related East Asiatic and North American species ('Vulgares' group) [3] represents a rich source of many different polyacetylenes, sometimes accumulated in considerable amounts. Because of their phenotypical plasticity many members of the 'Vulgares' exhibit a broad morphological diversity. Hence, all attempts to segregate the different species still remains a taxonomic problem. A more recent comparative investigation on characteristic polyacetylenes of a representative set of the 'Vulgares' group has been carried out in order to demonstrate to what extent different acetylene patterns may contribute to a more natural grouping [4].

As a result of that screening, five hitherto unknown polyacetylenic derivatives have been isolated. Their structure elucidation is described in the present paper. In addition, the isomers of 'centaur X3' (**1**) and the 'trienetriyne' (**2**), both widely distributed within the 'Vulgares' [2], were re-examined and unambiguously identified

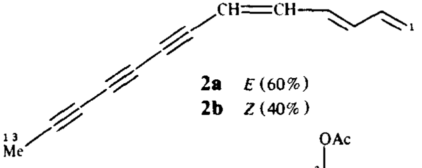
RESULTS AND DISCUSSION

The petrol/diethylether extracts of 17 East Asiatic and 11 North American species of the 'Vulgares' group were analysed for characteristic polyacetylenes. Altogether 23 different polyacetylenes were isolated [4] from which 18 structures have already been described previously [1, 5, 6]. In the following, these already known structures are listed together with original references, as the newly characterized compounds **1b**, **2b** and **3–7** should be seen within the entire systematic framework of related co-occurring constituents (for details concerning the distribution patterns see ref. [4]).

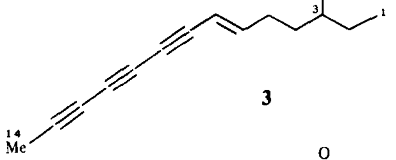
The already known polyacetylenes found in 'Vulgares' consisted of eight very characteristic open chain derivatives of the methyltriyne type [1] with variable chain lengths. C_{17}: (*E*,*E*)-1,7,9-heptadecatriene-11,13,15-triyne = centaur X_3 (**1a**) [7, 8]; C_{14} (*E*,*E*)-4,6-tetradecadiene-8,10,12-triyn-1-ol [9], its acetate [10], and (*E*)-6-tetradecene-8,10,12-triyn-3-one = 'artemisia ketone' [7]; C_{13}: (*E*,*E*)-1,3,5-tridecatriene-7,9,11-triyne (**2a**) [11] and its 3,4-epoxide = 'pontica epoxide' [10]; C_{10}: (*E*)- and



1a *E* (75%)
1b *Z* (25%)



2a *E* (60%)
2b *Z* (40%)



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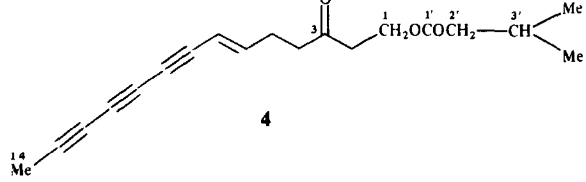

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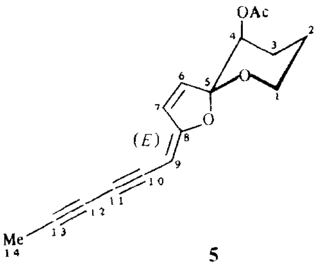
(*Z*)-2-decene-4,6,8-triynoic acid methylester = 'dehydromatricaria ester' [7, 12, 13]. Three cyclic derivatives, the C_{10} lactone (*Z*)-5-(hexa-2,4-diynylidene)-2,5-dihydrofuran-2-one [14], related to 'dehydromatricaria ester', and the rather rare cyclic C_{14} derivatives ichthyotheriol and ichthyotheriol acetate [15] were isolated as well.

Another type of polyacetylenic derivatives frequently found in the 'Vulgares' group is represented by spiroacetal enol ethers with an oxolene five-ring in *spiro* connection to an oxane six-ring (dioxaspiro[4,5]decene-system). In addition to the newly isolated compounds **5**–**7**, five further closely related and already described derivatives have been detected, namely the (*Z*)- and (*E*)-parent compound of type **5** without an OAc group at C-4 [16, 17], the precursor of the spiroacetal enol ether *syn*-epoxides **6**, **7** with $R^1 = R^2 = H$ [5], and two analogous *anti*-epoxides with the 6,7-epoxide ring directed towards C-4 (*anti* to the oxane oxygen) with $R^1 = R^2 = H$ and R^1 = OAc, $R^2 = H$ [18, 19]. Finally, two thiophene derivatives have also been isolated, the widespread thienylmethylene-dioxaspiro[4, 5]decene [6, 20] and its less common dimer which was reported recently [6].

The following discussion of the new compounds is divided into three sections. The first deals with the isomers of hydrocarbons **1** and **2**, the second includes the structure elucidation of the two open chain C_{14} derivatives **3** and **4** closely related to 'artemisia ketone', and the third presents the spiroacetal enol ether derivatives **5**–**7**.

Triene-triynes **1 (a, b)** *and* **2 (a, b)**

The hydrocarbons **1** and **2** are usually obtained as hardly separable isomeric mixtures. The dominant and clearly assigned all-*trans* (*E*,*E*)-isomer is in most cases contaminated with a second mono-*cis* [8] isomer, which was presumed to be the (7*Z*,9*E*)-isomer for **1** [1, 8, 21] and the (3*Z*,5*E*)-isomer for **2** [1]. Later, the (7*E*,9*Z*)-isomer for **1** was mentioned together with the (7*E*,9*E*)-isomer, however, no further comments were given [22]. In all the other numerous papers where the isolation of the triene-triyne hydrocarbons is reported, structure presentations with undefined (*Z*)- or (*E*)-stereochemistries of the double bonds are used. This uncertainty in the literature is the reason that these simple and often isolated compounds will be discussed in some detail.



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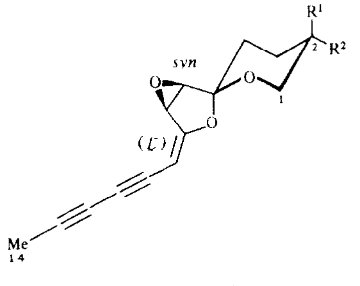
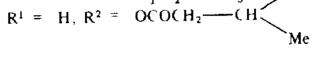


6 R^1 = OAc, R^2 = H



7 $R^1 = H$, $R^2 = \overset{1}{O}C\overset{2}{O}CH_2{-}\overset{3}{C}H(\overset{4}{Me})Me$

A close inspection of the 250 MHz ^1H NMR spectra of the isomeric mixtures **1** and **2** showed that the corresponding isomers are distinguished by a (*Z*) or (*E*) configuration of the double bond next to the triyne grouping. This results in a mixture of (7*E*,9*E*) and (7*E*,9*Z*) for **1**, and in a mixture of (3*E*,5*E*) and (3*E*,5*Z*) for **2**. The most striking evidence is furnished by the doublets of the olefinic protons next to the triyne unit. For compound **1**, this characteristic *d* is found at δ 5.50 with $J = 15.5$ Hz [**1a**, (*E*,*E*)] and at δ 5.32 with $J = 10.5$ Hz [**1b**, (7*E*,9*Z*)] in a ratio of 75 : 25 in favour of the dominant (*E*,*E*)-isomer. The corresponding figures for compound **2** are δ 5.63, $J = 15.5$ Hz [**2a**, (*E*,*E*)] and δ 5.45, $J = 10.5$ Hz [**2b**, (3*E*,5*Z*)] in a ratio of 3 : 2 in favour of the (*E*,*E*)-isomer.

Based on previous observations from polyacetylenic alkamides, a double bond near the centre of the molecule and in direct conjugation to at least two conjugated triple bonds tends to isomerize easily (compare the compounds reported in ref [23]). This spontaneous photo-isomerization, which also seems to be the case for compounds **1** and **2**, may be the reason for the often described co-occurrence of corresponding isomers. Using the experience from similar coupling systems [23], all resonances in the spectra of mixtures **1a** + **b** and **2a** + **b** could be assigned.

In the spectrum of **1a** + **b** the most downfield resonance is the *dd* for H-9 of the (*E*,*E*)-isomer (**1a**), the most downfield signal for **2a** + **b** is the *dd* for H-5 of the (*E*,*E*)-isomer (**2a**). Due to the anisotropy of the neighbouring triple bond this is expected for the protons of an (*E*)-configurated double bond in a β position relative to this triple bond (comp. [23]). In the case of two (or more) double bonds next to triple bonds with a (*Z*) configurated double bond directly conjugated to the triple bonds, the γ protons are expected to be shifted to relatively low-field (comp. [23]). The resonance for H-8 of **1b** is found at δ 6.55 (*dd*) and for H-4 of **2b** at 6.75 ppm. A further informative signal belongs to the β-proton of the (*E*,*Z*)-isomers **1b** and **2b**, because the *dd* with $J = 10.5$ and 10.5 Hz degenerates to a characteristic pseudo triplet found at δ 6.60 for H-9 of **1b** and also at δ 6.60 for H-5 of **2b**. Finally, the proposed (7*E*,9*E*)- and (7*E*,9*Z*) configurations in the isomers of **1** are supported by the coincidence of resonance signals for the two isomers **1a** and **1b** for all protons along the carbon chain from C-1 to C-7 (Table 1). This is by no means compatible with different configurations of the C-7, C-8 double bond. On the other hand, it is interesting to note that the terminal methyl groups of the **a** and **b** isomers of **1** and **2** show slightly different chemical shifts ($\Delta\delta_{b-a} = 0.01$ ppm) and are well suited to estimate the isomeric ratios simply by the signal heights.

To complete the discussion on these wide-spread and often isolated highly unsaturated hydrocarbons it should be mentioned that due to the easily occurring (*E*)-(*Z*)-photoisomerization, it is difficult to arrive at any conclusions concerning the original distribution of isomers in the living plants.

Table 1 ^{1}H NMR data for compounds **1** (**a** **b** = 3 1), **2** (**a** **b** = 3 2), and **3**–**7** (250 MHz, CDCl$_3$)

	1		**2**						
H	**a**	**b**	**a**	**b**	**3**	**4**	**5**	**6**	**7**
1	*cis*: 4 95 *br d* *trans* 5 01 *br d*		5 20–5 40 *m*		0 89 *t*	4.34 *t*	ax 4.03 *ddd* eq. 3 88 *dm*	3 98 ‖ 4 03 ‖	ax. 3.69 *dd** eq· 3.97 *dd*
2	5 80 *ddt*		6 25–6.45 *m*		1 57 *dq*	2.73 *t*	~1 52 *m*	eq 4 91 *m*¶	ax 4.91 *dddd*
3	2 00–2 15 *m*		6 25–6 45 *m*		4 82 *tt*†	—	~2 00 *m*	~2.0 *m* (1H)	~2 10 *m* (1H)
4	1 42 *m*		6 48 *dd*	6 75 *dd*	1 64 *dt*‡	2 56 *t*	eq· 4.79 *dd**	1.3–1 6 *m* (3H)	1.8–1.9 *m* (3H)
5	1 42 *m*		6 79 *dd*	6 60 *dd**	2 17 *dt*‡	2 45 *dt*‡	—	—	—
6	2 00–2 15 *m*		5 63 *d*	5 45 *d*	6.36 *dt*	6 34 *dt*	6 28 *dd*§	3.88 *d*	3 87 *d*
7	5 90 *dt*		—		5 52 *d*	5 54 *d*	6 72 *d*	4 34 *d*	4 32 *d*
8	6 11 *dd*	6 55 *dd*	—		—	—	—	—	—
9	6 73 *dd*	6 60 *dd**	—		—	—	5 04 *br s*	5 16 *br s*	5 19 *br s*
10	5 50 *d*	5 32 *d*	—		-		—	—	—
13	—		2 01 *s*	2 02 *s*	—	—	—	—	—
14	—		—		2 00 *s*	2 00 *s*	2 00 *s*	2.00 *s*	2.00 *s*
17	2 00 *s*	2 01 *s*	—		—	—	—	—	—
2′	—		—		2.05 *s*	2.17 *d*	2 13 *s*	2 13 *s*	2.18 *d*
3′	—		—		-	2 06 *m*	—	—	2 10 *m*
4′	—		—		—	0 95 *d*	—	—	0 96 *d*

Coupling constants (Hz) **1** 1*c*,1*t* < 2, 1*c*,2 = 10, 1*t*,2 = 17, 2,3 = 7; 6,7 = 7.5; 7,8 = 15 5, 8,9 = 10.5, **1a**. 9,10 = 15 5, **1b** 9,10 = 10.5 **2** 3,4 = 15 5, 4,5 = 10 5, **2a** 5,6 = 15 5, **2b** 5,6 = 10.5 **3**· 1,2 = 5,6 = 7; 2,3 = 3,4 = 4,5 = 6.5, 6,7 = 16. **4**· 1,2 = 2,3 = 6; 4,5 = 7 5, 5,6 = 2′,3′ = 3′,4′ = 7; 6,7 = 16 **5** 1ax, 1eq = 1ax,2ax = 11, 1ax,2eq = 3ax,4eq = 3eq,4eq = 2, 6,7 = 6 **6**. 1ax,1eq = 12, 6,7 = 3 **7** 1ax,1eq = 1ax,2ax = 2ax,3ax = 10.5, 1eq,2ax = 2ax,3eq = 5 2, 6,7 = 3, 2′,3′ = 3′,4′ = 7

*Pseudo *t*

‡Pseudo q

†Pseudo quintet

§Additional long range coupling of 2 Hz

‖ Essentially a close and broad AB system $J(\mathrm{A,B}) = 12$ Hz, $J(\mathrm{1ax,2eq}) \sim J(\mathrm{1eq,2eq}) < 3$ Hz

¶One broad resonance $W_{1/2} = 6$ Hz (all 4 vicinal coupling constants < 3 Hz)

Open chain C$_{14}$-derivatives 3 *and* 4

The C$_{14}$ methyltriyne compounds **3** and **4** are both closely related to the widespread 'artemisia ketone'. Compound **3** is the acetate of the corresponding 'artemisia alcohol' which was isolated from several species of the tribus Anthemideae [1, 9]. The bifunctional 3-oxo-1-isovalerate **4** may be formed in the course of the biosynthetic pathway leading from 4,6-tetradecadiene-8,10,12-triyn-1-ol ('C$_{14}$-alcohol') to 'artemisia ketone'. The 1,3-diol corresponding to **4** (with an additional conjugated C-4, C-5 double bond; tetradeca-4,6-diene-8,10,12-triyne-1,3-diol) was postulated to be an important biogenetic link between the 'C$_{14}$-alcohol' and 'artemisia ketone' [1, 24] In the 'Vulgares' group both the 'C$_{14}$-alcohol' and 'artemisia ketone' were present in considerable amounts, the compounds **3** and **4**, however, were found only as minor constituents (cf. Experimental).

The structures of **3** and **4** followed from the ^{1}H NMR spectra and were confirmed by mass determination and other spectroscopic data (see Experimental). The NMR spectrum of **3** (see Table 1) is very similar to the spectrum of 'artemisia ketone' and especially to its lithium aluminium hydride reduction product ('artemisia alcohol'). The ester is indicated by the COOMe singlet at δ 2 05 and the proton at C-3 which appears as a sharp quintet (*tt* with J = 6.5 and 6.5 Hz) In the ^{1}H NMR spectrum of **4** the isovalerate ester is indicated by the characteristic 2′ protons (*d* for 2H at δ 2 17), the H-3′ (*m*) and the two 4′-Me groups (*d* for 6H at δ 0 95). Because of the sharp triplet for 2H at δ4.34 indicating a –CH$_2$–CH$_2$–O–CO– arrangement, the ester must be derived from a primary alcohol. The methylene groups next to the carbonyl group at C-3 show up as triplets at δ 2.73 (H-2) and 2.56 (H-4). The assignments and the bond sequence of both chains (alcohol and acid component) were confirmed by decoupling experiments.

Spiroacetal enol ethers 5–7

Compound **5** is an acetyloxy derivative of the well known (*E*)-configurated 'six-ring' spiroacetal enol ether [17]. However, the oxidation at C-4 of the oxane ring is unusual (in most cases further incorporation of oxygen takes place at C-2, compare compounds **6**, **7** and refs [17, 19]). The ^{1}H NMR spectrum of **5** is very similar to that of the already described axial C-2-acetate [17], except for the striking difference of the coupling pattern of the –OCH$_2$– (C-1) protons. The axial C-2-acetates are characterized by an ABX pattern for the methylene protons next to oxygen with large geminal and small vicinal coupling constants (e.g. acetate **6**). However, the acetate **5** shows an ABXY pattern typical for O–CH$_2$–CH$_2$ in a six ring chair (cf. Table 1). The proton at δ4.79 (geminal to the –OCOMe group) appears as a narrow pseudo-triplet showing only two small vicinal couplings of the eq-ax, eq-eq type; this is only compatible with an axial –OCOMe group at C-4.

In a recent publication, we have reported on the isolation, structure determination and absolute configuration of a new polyacetylenic spiroacetal enol ether with an additional epoxide ring in *syn* arrangement relative to the oxane ring of the spiro system [5]. Now we have found two further substituted compounds belonging to this series, the axial C-2-acetate **6** and the equatorial C-2-isovalerate **7**

In the ^{1}H NMR spectra of **6** and **7** the spiroketal enol ether part of the molecule is partially very similar to the spectrum of the parent compound ($R^1 = R^2 = H$, comp. [5]), however, the coupling patterns of the protons geminal to –OCOR are conclusive for substitution at C-2 The >CH(OCOR) proton of **6** appears as a rather narrow multiplet (or very broad pseudo-singlet with $W_{1/2} = 6$ Hz, therefore eq H and ax-OCOR), the C-1 protons (–OCH$_2$) appear as the close AB part of a ABX system with a large geminal and several very small vicinal couplings In the spectrum of compound **7**, the proton >CH(OCOR) shows up as a very broad group of seven lines orginating from a *dddd* with $J = 10.5$, 10 5, 5 2, 5 2 Hz (therefore ax H and eq –OCOR group). The C-1 methylene protons of **7** are well separated and show a ABX pattern with a *dd* for the equatorial C-1 proton at δ3 97 ($J_{gem} = 10\ 5$ Hz and $J_{vic\ ax-eq} = 5.2$ Hz) and a *dd* (pseudo *t*) for the axial C-1 proton at δ3 69 ($J_{gem} = 10\ 5$ Hz and $J_{vic\ ax-ax} = 10\ 5$ Hz) These data indicate a sequence –O–CH$_2$–CH(OCOR)–CH$_2$– in the oxane six-rings of both compounds **6** and **7** The isovalerate moiety of **7** is also clear from the corresponding 2′-4′ proton resonances (cf Table 1). The mass spectra (high resolution MS and several characteristic fragments, comp Experimental and ref. [25]) confirmed the derived structures Almost identical chiroptical data ($[\alpha]_D$ and CD spectra) of **6** and **7** compared to the parent compound ($R^1 = R^2 = H$ [5]) proved identical absolute configurations for the *spiro* and epoxide carbon positions C-5, C-6, and C-7 within the *syn* epoxide series of the spiroacetal enol ethers.

EXPERIMENTAL

Plant material. The new compounds were isolated from four different species *A carruthii* Wood ex Carruth (AR-926) cult, U S A, Utah, HB Provo, achenes originally from Utah, U S A Clear Creek Canyon, Sevier County, 1800 m, leg E D McArthur, *A cf opulenta* Pamp (AR-873/B) cult, UdSSR, HB Wladiwostok, *A selengensis* Turcz (AR-1185) cult, North Corea, HB Kim Il Sungis (Pyongyang), *A vulgaris* L (AR-1182) transpl, Italy, South Tyrol, Vinschgau, Prod am Stilfserjoch, 900 m, leg B Wallnofer All species were cultivated under field conditions in the Botanical Garden of the University of Vienna Numbers in parentheses refer to the experimental cultivations Voucher specimens are deposited at the herbarium of the Institute of Botany, University of Vienna (WU)

Fresh air-dried underground parts were cut into small pieces and extracted with Et$_2$O–petrol (60–80°) (1 2) for 48 hr at room temp The resulting extract was separated first by CC silica gel, increasing polarity of eluents starting with petrol and changing gradually to pure Et$_2$O and further by TLC (Merck Kieselgel 60 F$_{254}$, petrol–Et$_2$O)

The amounts of compounds given below refer to 100 g air dried underground parts (comp ref [4]) AR-926 contained 35 mg of compound **3** ('artemisia alcohol acetate'), the main polyacetylenic constituent in this plant was 'artemisia ketone' (60 mg) From AR-873/B the hydrocarbons **1** and **2**, together with the spiroether acetate **5** could be isolated in amounts of *ca* 5–10 mg, the dominant polyacetylene was the parent compound of **5** (without acetyloxy group) AR-1185 contained 4 mg **1**, 6 mg **2**, 7 mg *syn*-epoxyspiroether acetate **6**, 48 mg *syn*-epoxyspiroether isovalerate **7**, and 63 mg of (*E*)-*syn*-epoxyspiroether (parent compound of **6** and **7**) 'Artemisia ketone isovalerate' (**4**) was isolated from AR-1182 as a minor constituent (*ca* 2 mg) together with large amounts of centaur X$_3$ (**1**) and 'artemisia ketone' (in the order of 50 mg)

(E)-6-*Tetradecene*-8,10,12-*triyn*-3-*yl ethanoate* ('*artemisia acetate*') (**3**) Colourless oil, $[\alpha]_D^{20} = +17^\circ$, $[\alpha]_{436}^{20} = +43^\circ$ (CHCl$_3$, $c = 0\ 4$), IR $\nu_{max}^{CCl_4}$ cm^{-1} 2962 *s*, 2927 *s*, 2873 *m*, 2851 *m*, 2223 *m*, 2199 *w*, 1734 *vs*, 1616 *w*, 1459 *m*, 1442 *m*, 1373 *s*, 1235 *vs*, 1187 *m*, 1134 *m*, 1113 *m*, 1084 *m*, 1017 *s*, 949 *s*, 606 *w*, UV $\lambda_{max}^{Et_2O}$ nm (ε) 329 (14 400), 307 (20 400), 288 (15 600), 272 (9 600), 257 (6 000), 242 (120 000), 230 (75 000), CD λ^{Et_2O} nm ($\Delta\varepsilon$) 328 (+0 18), 308 (+0 22), 290 (+0 20), 273 (+0 12), 243 (+0 7), 231 (+0 5), MS (70 eV, 100°) m/z 242 $[M]^+$ (6%), 183 $[M-HOAc]^+$ (15), 182 (97), 167 (33), 166 (29), 165 (46), 154 (18), 153 (61), 152 (78), 149 (20), 141 (29), 140 (84), 139 (60), 127 (39), 115 (32), 101 (18), 43 (100), HR MS observed 242 131, $C_{16}H_{18}O_2$ requires 242 1307

(E)-3-*Oxo*-6-*tetradecene*-8,10,12-*triynyl*-3-*methylbutanoate* ('*artemisia ketone isovalerate*') (**4**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 2951 *s*, 2920 *s*, 2866 *m*, 2325 *w*, 2222 *m*, 1734 *s*, 1720 strong shoulder, 1458 *m*, 1366 *m*, 1292 *m*, 1181 *m*, 1165 *m*, 1095 *m*, 952 *m*, UV $\lambda_{max}^{Et_2O}$ nm (ε) 329 (14 500), 307 (20 500), 288 (16 000), 272 (10 500), 257 (7 500), 242 (120 000), 231 (77 000), MS (70 eV, 100°) m/z 298 $[M]^+$ (5%), 196 (11), 168 (18), 167 (27), 166 (34), 153 (52), 152 (48), 141 (38), 140 (58), 139 (51), 115 (43), 89 (21), 63 (18), 43 (100), HR MS observed 298 157, $C_{19}H_{22}O_3$ requires 298 1569

trans-(E)-10-*Acetyloxy*-2-(2,4-*hexadiynylidene*)-1,6-*dioxaspiro* [4 5] *dec*-3-*ene* (**5**) Colourless oil, $[\alpha]_D^{20} = -18^\circ$, $[\alpha]_{436}^{20} = -36^\circ$ (CHCl$_3$, c 0 1), IR $\nu_{max}^{CCl_4}$ cm^{-1} 2951 *m*, 2924 *m*, 2883 *w*, 2849 *w*, 2139 *w*, 1743 *s*, 1628 *m*, 1574 *w*, 1465 *w*, 1438 *w*, 1380 *w*, 1368 *m*, 1282 *m*, 1268 *m*, 1232 *s*, 1189 *s*, 1155 *w*, 1147 *w*, 1095 *m*, 1085 *s*, 1068 *w*, 1050 *m*, 1012 *m*, 990 *m*, 949 *w*, 916 *w*, 899 *m*, 628 *w*, 605 *w*, UV $\lambda_{max}^{Et_2O}$ nm (ε) 316 (19 600), 265 (6 000), 236 (13 400), 222 (15 500), CD λ^{Et_2O} nm ($\Delta\varepsilon$) 352 (+0 20), 310 (−0 45), 285 (−0 50), 243 (−1 7), 234 (−1 4), MS (70 eV, 90°) m/z 272 $[M]^+$ (15%), 212 $[M-MeCOOH]^+$ (11), 159 (20), 71 (100), HRMS observed 272 105, $C_{16}H_{16}O_4$ requires 272 1048

(+)-(3S,4R,5S,8R)-(E)-8-*Acetyloxy*-3,4-*epoxy*-2-(2,4-*hexadiynylidene*)-1,6-*dioxaspiro*[4 5]*decane* (**6**) Colourless oil, $[\alpha]_D^{20} = +12^\circ$, $[\alpha]_{436}^{20} = +26^\circ$ (CHCl$_3$, c 0 1), IR $\nu_{max}^{CCl_4}$ cm^{-1} 2948 *m*, 2920 *m*, 2848 *m*, 2148 *w*, 1736 *s*, 1648 *s*, 1451 *w*, 1438 *w*, 1384 *m*, 1370 *m*, 1358 *w*, 1293 *w*, 1279 *m*, 1233 *s*, 1186 *s*, 1169 *w*, 1137 *m*, 1107 *m*, 1082 *w*, 1058 *w*, 1016 *s*, 965 *w*, 942 *w* 922 *w*, 893 *m*, 853 *m*, 683 *w*, UV $\lambda_{max}^{Et_2O}$ nm (ε) 293 (15 000), 279 (18 000), 266 (13 000), 253 (sh, 7400), 225 (31 000); CD λ^{Et_2O} nm ($\Delta\varepsilon$) 310 (−1 00), 295 (+2 45), 279 (+4 55), 265 (+4 4), 253 (+2 7), 240 (sh, +1 3), MS (70 eV, 110°) m/z 288 $[M]^+$ (9%), 184 (7), 125 (14), 124 $[(cyc\ C_5H_6O)=CH-CHO]^+$ (76), 123 (12), 111 (21), 109 (16), 104 $[Me-(C\equiv C)_2-CH=CO]^+$ (13) (ref [25]), 102 (12), 99 (11), 97 (34), 95 (41), 43 (100), HRMS observed 288 100, $C_{16}H_{16}O_5$ requires 288 0997 ^{13}C NMR (CDCl$_3$, 250 MHz, δ) 170 5 (C=O), 163 5 (C-8), 105.4 (C-5), 86 1 (C-9), 79 9 and 69.3 (–C≡), 66 1 and 66 0 (C-1, C-2), 58 8 (C-7), 52 3 (C-6), 25 5 (C-4), 22 1 (C-3), 21 2 (C-2′), 4 6 (C-14)

(+)-(3S,4R,5S,8S)-(E)-3.4-*Epoxy*-8-*isovaleryloxy*-2-(2,4-*hexadiynylidene*)-1,6-*dioxaspiro* [4 5]*decane* (**7**). Colourless oil, $[\alpha]_D^{20} = +10^\circ$, $[\alpha]_{436}^{20} = +24^\circ$ (CHCl$_3$, c 0 1), IR $\nu_{max}^{CCl_4}$ cm^{-1} 2952 *s*, 2920 *s*, 2866 *m*, 2847 *m*, 2147 *w*, 1733 *s*, 1648 *s*, 1462 *m*, 1450 *m*, 1432 *m*, 1411 *w*, 1383 *m*, 1366 *m*, 1357 *m*, 1334 *w*, 1320 *w*, 1308 *w*, 1280 *s*, 1261 *m*, 1239 *s*, 1210 *w*, 1194 *s*, 1181 *s*, 1165 *m*, 1139 *s*, 1118 *w*, 1093 *s*, 1020 *s*, 958 *w*, 934 *m*, 904 *m*, 857 *s*, 688 *w*, UV

$\lambda_{max}^{Et_2O}$ nm (ε) 293 (14 500), 278 (17 200), 266 (12 200), 253 (*sh*, 6 400), 243 (weak sh, 3 800), 224 (28 600); CD λ^{Et_2O} nm ($\Delta\varepsilon$) 310 (−1 35), 295 (+2.08), 278 (+4 35), 264 (+4 15), 253 (+2.8), 245 (sh, +1.4); MS (70 eV, 120°) *m/z* 330 $[M]^+$ (10%), 124 [(cyc C_5H_6O)=CH–CHO]$^+$ [25] (100), 104 [Me–$(C\equiv C)_2$–CH=CO]$^+$ [25] (14), 102 (20), 95 (27), HRMS· observed 330 147, $C_{19}H_{22}O_5$ requires 330 1467. ^{13}C NMR ($CDCl_3$, 250 MHz, δ) 172 2 (C=O), 163 1 (C-8), 104 7 (C-5), 86 2 (C-9), 79 9 and 69 2 (–C=), 66.3 (C-2), 65 1 (C-1), 58 4 (C-7), 52 3 (C-6), 43 4 (C-2′), 29.5 (C-4), 25.7 (C-3′), 24 0 (C-3), 22 3 (C-4′), 4 6 (C-14)

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