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ACETYLENES AND TERPENOIDS OF *BELLIS PERENNIS*

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Key Word Index—*Bellis perennis*; Asteraceae; daisy; essential oils; acetylenes; deca-4,6-diynoic acid; methyl deca-4,6-diynoate; 2,8-tetrahydromatricaria ester.

Abstract—The essential oils of leaves and flowers from *Bellis perennis*, the common daisy, have been investigated. Polyacetylenes were one of the major chemical classes (18–21%) mainly consisting of two new C_{10} acetylenic compounds which were identified, by spectroscopic and chemical means, as methyl deca-4,6-diynoate (2,8-tetrahydromatricaria ester) and deca-4,6-diynoic acid.

INTRODUCTION

Bellis perennis L., the common daisy, is a perennial herbaceous plant widely distributed in Europe. Traditionally it is used in the treatment of rheumatism and as an expectorant [1]. It has also been employed as a vulnerary and against ecchymoses in veterinary medicine. Furthermore, it has been shown that the plant possesses antifungal activity [2, 3]. We have analyzed the chemical composition of the essential oils from leaves and flowers of wild plants collected in Italy. Although there are several reports on the presence of saponins in the roots [4], the aerial organs have been little investigated [5] and there are no reports on the volatile compounds from this plant.

RESULTS AND DISCUSSION

The results of our study on the essential oils obtained from the leaves and the flowers of *B. perennis* are shown in Table 1. The components identified, amounting to 97% of the total, are grouped into chemical classes. The main bulk of the constituents in the two parts of the plant was made up of monoterpenes (47% and 62% from leaves and flowers, respectively) with β-myrcene (15.05% leaves; 28.43% flowers) and geranylacetate (11.99% leaves; 6.10% flowers) as the main volatiles. As shown, little variation was found in the compositional profile of the two plant organs, apart from the large amount of *cis*-3-hexenol (15.08%) in the leaves compared to the flowers (0.43%). The presence of *cis*-3-hexenol should not be regarded as unusual, however. Thus, C_6 leaf alcohols and aldehydes are widely distributed in fresh plant green tissues and are considered to be responsible for the typical 'green leaf odour' of grasses [6, 7].

Previous studies performed on the Asteraceae, have shown that the family is chemically very distinct with characteristic sesquiterpene lactones, pentacyclic triterpene alcohols, derivatives of caffeic acid and acetylenic compounds. Within the family, the tribe of Astereae is distinguished by the presence of typical polyacetylenes, polyenes and related substances and by the rarity or absence of sesquiterpene lactones [5].

As reported in Table 1, polyacetylenes represented abundant constituents also in the essential oils from *B. perennis* leaves (18%) and flowers (21%). After GC-EI-MS analyses of the total volatiles only minor polyacetylenic compounds could be identified, while identification of the major component **1** (13.87% and 15.04% in leaves and flowers, respectively) remained doubtful. CC separation of a total extract from the aerial organs of the plant led to the isolation of a fraction containing purified **1**, which was used for further spectroscopic investigations.

A characteristic IR absorption band at 1740 cm^{-1} was indicative of an ester group while a very weak absorption in the region 2230, 2152 cm^{-1} (C≡C) suggested the presence of a disubstituted acetylene. The ^1H and ^{13}C NMR spectra (Table 2) provided more insight into the molecular structure of **1**. A three-proton singlet at δ3.70 corroborated the presence of a methyl ester group. Moreover, the presence of a saturated fragment CH_3-$(CH_2)_2$- was suggested by the triplet signal at δ0.98, accounting for 3H, and the two signals at δ1.55 (2H, *tq*) and δ2.22 (2H, *tt*). The ^{13}C NMR spectrum showed the presence of 11 carbons. Absorptions for four quaternary carbons and one methoxyl group were found (Table 2). Further evidence for a structural fragment $-CH_2-C\equiv C-C\equiv C-CH_2-$ was also provided by the signals at δ2.22 and 2.58, in the ^1H NMR spectrum, corresponding to the methylene groups adjacent to acetylenic carbons. The assignment of acetylenic as well as methylene and methyl carbons were also confirmed by DEPT experiments (Table 2). Furthermore, MS fragmentation of **1** gave a molecular ion peak

Table 1. Composition (%) of essential oils from *B. perennis* leaves (L) and flowers (F)

Components	L	F	Detected in fraction¶
Aldehydes	**1.56**	**1.81**	
Hexanal	0.12	0.17	W, P_1
Heptanal	0.08	0.16	W, P_1
Nonanal	0.38	0.27	W, P_1
Decanal	0.08	*tr**	W, P_1
trans-2-Hexenal	0.06	0.14	W, P_1
2,4-Hexadienal	0.26	0.29	W, P_1
Heptadienal	0.01	0.02	W, P_1
Decadienal	*tr*	*tr*	P_1
Benzaldehyde	0.09	0.14	W, P_1
Phenylacetaldehyde	0.48	0.62	W, P_1
Alcohols	**16.59**	**1.69**	
Hexanol	0.27	0.08	W, P_1
Heptanol	0.01	*tr*	P_1
Octanol	0.10	*tr*	W, P_1
2-Ethyl-1-hexenol	0.06	*tr*	W, P_1
trans-2-Hexenol	0.58	0.20	W, P_1
cis-3-Hexenol	15.08	0.43	W, P_1
Oct-1-en-3-ol	0.26	*tr*	W, P_1
Benzylalcohol	0.11	0.24	W, P_1
2-Phenylethanol	*tr*	*tr*	P_1
Phytol	0.12	0.74	W, P_1
Ketones	**1.06**	**0.86**	
6-Methyl-5-hepten-2-one	*tr*	0.02	P_1
Oct-3-en-2-one	0.04	*tr*	W, P_1
Nonan-2-one	0.09	0.22	W, P_1
Pentadecan-2-one	0.34	0.14	W, P_1
Heptadecan-2-one	0.21	0.13	W, P_1
Pentadecan-2-one-6,10,14-trimethyl	0.38	0.28	W, P_1
Acetophenone	*tr*	0.07	W, P_1
Esters	**1.01**	**1.08**	
cis-3-Hexenylacetate	0.24	0.42	W, P_1
cis-3-Hexenyl-2-methylbutanoate	0.09	0.05	W, P_1
Octen-1-ol acetate	0.49	0.38	W, P_1
Methyl palmitate	0.03	0.07	W, P_1
Isopropyl palmitate	0.01	0.03	W, P_1
Methyl linoleate	0.05	0.04	W, P_1
Methyl linolenate	0.10	0.09	W, P_1
Hydrocarbons	**0.72**	**0.61**	
Undecane	0.41	0.35	W, N
Dodecane	0.03	*tr*	N
Tridecane	0.12	0.07	W, N
Tetradecane	*tr*	0.05	N
Hexadecane	0.11	0.10	W, N
Heptadecane	0.05	0.04	W, N
Octadecane	*tr*	*tr*	N
Monoterpenes	**47.36**	**61.93**	
α-Pinene	0.34	0.15	W, N
β-Pinene	4.10	4.05	W, N
β-Myrcene	15.05	28.43	W, N
Alloocimene	*tr*	*tr*	N
3-Carene	0.15	0.27	P_1
1,4-Cineole	*tr*	0.02	P_1
α-Terpinene	0.07	0.09	W, N
p-Cymene	*tr*	*tr*	N
Limonene	0.08	0.11	W, N
β-Phellandrene	1.30	1.16	W, N

Cont'd overleaf.

Table 1. *Contd.*

Components	L	F	Detected in fraction¶
1,8-Cineole	0.25	0.32	W, P_1
cis-Ocimene	*tr*	*tr*	N
trans-Ocimene	0.03	0.04	W, N
γ-Terpinene	*tr*	*tr*	N
cis-Linalooloxide	0.20	*tr*	W, P_1
trans-Linalooloxide	*tr*	*tr*	P_1
α-Terpinolene	0.03	*tr*	N
Linalool	0.54	1.19	W, P_1
1,3,8-*p*-Menthatriene	*tr*	*tr*	N
cis-Pinenehydrate	1.18	2.25	W, P_1
trans-Pinocarveol	0.05	*tr*	W, P_1
trans-Pinenehydrate	0.88	1.37	W, P_1
Camphor	0.60	0.71	W, P_1
Pinocarvone	0.03	0.05	W, P_1
Citronellal	0.25	0.07	W, P_1
Lavandulol	0.19	0.23	W, P_1
4-Terpineol	0.18	0.21	W, P_1
α-Terpineol	0.21	0.73	W, P_1
Dihydrocarveol	0.14	*tr*	W, P_1
cis-Piperitol	0.26	0.39	W, P_1
trans-Piperitol	0.51	0.69	W, P_1
trans-Carvenol	0.15	1.10	W, P_1
Nerol	0.22	0.20	W, P_1
cis-Carveol	0.05	0.10	W, P_1
Isogeraniol	*tr*	*tr*	P_1
Pulegone	0.52	0.32	W, P_1
Neral	0.02	*tr*	P_2
Piperitone	0.95	1.16	W, P_1
cis-Sabinenehydrate acetate	*tr*	0.04	P_1
Geraniol	1.51	0.46	W, P_1, P_2
Linalyl acetate	0.21	0.05	W, P_1
cis-Verbenyl acetate	*tr*	*tr*	P_1
Geranial	0.36	0.38	W, P_1
Geranic acid methyl ester	0.82	1.10	W, P_1
Thymol	0.12	0.01	W, P_1, P_2
trans-Verbenyl acetate	*tr*	*tr*	P_1
cis-Pinocarveyl acetate	0.37	0.25	W, P_1
trans-Pinocarveyl acetate	0.09	0.02	W, P_1
Sabinyl acetate	0.99	0.30	W, P_1
Dihydrocarveyl acetate	0.19	0.20	W, P_1
Lavandulyl acetate	0.06	0.15	W, P_1
α-Terpinenyl acetate	0.07	0.10	W, P_1
Neryl acetate	1.65	7.31	W, P_1
Geranyl acetate	11.99	6.10	W, P_1
Geranilacetone	0.06	0.04	W, P_1
Neryl propionate	*tr*	*tr*	P_1
Geranyl propionate	0.12	0.01	W, P_1
Neryl angelate	*tr*	*tr*	P_1
Geranyl angelate	0.01	*tr*	P_1
Sesquiterpenes	**3.25**	**1.71**	
δ-Elemene	0.01	*tr*	N
α-Cubebene	0.09	0.02	W, N
Naphthalene-1,2,3,4,4a,7-hexahydro-1,6-Dimethyl-4-(1-methylethyl)	*tr*	*tr*	N
α-Ylangene	*tr*	*tr*	N
α-Copaene	0.16	0.10	W, N
β-Patchoulene	0.08	0.11	W, N
β-Bourbonene	0.12	0.07	W, N
β-Cubebene	0.10	0.15	W, N

Cont'd overleaf.

Table 1. *Contd.*

Components	L	F	Detected in fraction¶
β-Caryophyllene	0.39	0.14	W, N
Aromadendrene	0.02	0.03	W, N
α-Himachalene	0.15	0.10	W, N
α-Humulene	0.10	0.08	W, N
cis-β-Farnesene	0.32	0.12	W, N
allo-Aromadendrene	*tr*	*tr*	N
γ-Muurolene	0.26	0.10	W, N
Curcumene-*ar*	*tr*	*tr*	N
β-Selinene	*tr*	*tr*	N
δ-Selinene	*tr*	*tr*	N
α-Selinene	*tr*	*tr*	N
Germacrene B	0.05	*tr*	W, N
α-Longipinene	*tr*	0.01	N
α-Muurolene	*tr*	*tr*	N
α-Farnesene	0.16	0.05	W, N
γ-Cadinene	0.46	0.30	W, N
2,4,6-Trimethylazulene	*tr*	*tr*	N
δ-Cadinene	0.43	0.08	W, N
4,5,9,10-Dehydroisolongifolene	0.16	0.01	W, N
Neophytadiene	0.19	0.24	W, N
Torreyol	*tr*	*tr*	P_1
Poliacetylenes	**18.27**	**20.73**	
Methyl deca-4,6-diynoate	13.87	15.04	W, P_1
Lachnophyllum ester	2.83	3.53	W, P_1
Matricaria ester†	0.16	0.23	W, P_1
Matricaria ester†	0.07	0.10	W, P_1
Deca-4,6-diynoic acid	1.03	1.40	W. A
Lachophyllum acid	0.31	0.43	W, A
Diterpenes			
Abietatriene	*tr*	*tr*	N
Acids	**2.34**	**2.56**	
Octanoic acid	*tr*	*tr*	A
Nonanoic acid	*tr*	*tr*	A
Decanoic acid	*tr*	*tr*	A
Undecanoic acid	*tr*	*tr*	A
Lauric acid	0.68	0.35	W, A
Tridecanoic acid	*tr*	*tr*	A
Myristic acid	0.22	0.40	W, A
Pentadecanoic acid	*tr*	*tr*	A
Palmitic acid	1.06	1.21	W, A
Heptadecanoic acid	*tr*	*tr*	A
Stearic acid	0.10	0.18	W, A
Hexandicarboxilyc acid	*tr*	*tr*	A
Palmitoleic acid	*tr*	*tr*	A
Linoleic acid	0.08	0.10	W, A
Linolenic acid	0.20	0.32	W, A
Benzoic acid	*tr*	*tr*	A
Phenylacetic acid	*tr*	*tr*	A
Coumaric acid	*tr*	*tr*	P_2, A
Miscellaneous	**1.98**	**2.15**	
1,2,3-Trimethylbenzene	0.01	*tr*	N
trans-Decahydronaphtalene	*tr*	*tr*	N
Naphthalene	*tr*	*tr*	N
3,5-Dimethylphenol	0.03	0.05	W, P_2
Naphthalene-1,2-dihydro-1,1,6-trimethyl	*tr*	*tr*	N
p-Vinylguaiacol	0.23	0.19	W, P_2
Amethole	*tr*	0.01	P_2

Cont'd overleaf.

Table 1. *Contd.*

Components	L	F	Detected in fraction¶
Eugenol	0.02	0.06	W, P_2
β-Damascenone	0.10	0.16	W, P_1
β-Ionone	0.36	0.19	W, P_1
2,3-Dihydrobenzofurane	0.92	1.24	W, P_1, P_2
Dihydroactinidiolide	0.30	0.25	W, P_1
cis-Cyclododecene	0.01	*tr*	N
Unidentified	**2.72**	**1.87**	
MW = 182	1.34	1.10	W, P_1
MW = 182	0.20	0.11	W, P_1
MW = 182	0.10	0.08	W, P_1
MW = 182	0.43	0.34	W, P_1
Monoterpene $C_{10}H_{16}O$	0.05	0.10	W, P_1
Sesquiterpene $C_{15}H_{24}$	0.02	0.14	W, N
Diterpene $C_{20}H_{32}$	*tr*	*tr*	N
Total %	96.86	96.99	

*tr: traces ($\leq 0.01\%$); $> 0.01\%$ quoted to nearest 0.01%.

¶W, whole essential oil; N, non polar fraction; P_1, P_2 polar fractions (see text); A, acid fraction.

†Isomers not identified.

Table 2. ^1H and ^{13}C NMR spectral data of acetylene **1** ($^{10}CH_3$–$^9CH_2$–$^8CH_2$–$^7C\equiv^6C$–$^5C\equiv^4C$–$^3CH_2$–$^2CH_2$–$^1COOCH_3$)

H		C	*J* (Hz)	DEPT
10	0.98 *t* [7.0]	1	171.88	C
9	1.55 *tq* [7.0]	2	32.78	CH_2
8	2.22 *tt* [7.0; 1.0]	3	15.02	CH_2
2, 3	2.58 *m*	4	74.77	C
OMe	3.70 *s*	5	65.95	C
		6	64.98	C
		7	78.08	C
		8	21.03	CH_2
		9	21.64	CH_2
		10	13.34	CH_3
		OMe	51.76	CH_3

at *m/z* 178, consistent with a molecular formula of $C_{11}H_{14}O_2$, and a base peak at *m/z* 91 corresponding to a $[C_7H_7]^+$ ion derived by loss of a $(C_2H_4 + CO_2CH_3)$ group from the parent ion to give a $[CH_3CH_2CH_2C\equiv C-C\equiv C-]^+$ fragment. On the basis of the above spectroscopic data, compound **1** was identified as methyl deca-4,6-diynoate (2,8-tetrahydromatricaria ester), a hydrogenated relative to matricaria ester, never reported previously as a natural product. The synthesis of methyl deca-4,6-diynoate is, however, described in the literature, although only the UV data were used to characterize the product [8].

To obtain an unequivocal structural elucidation of natural compound **1**, we prepared synthetic **1** (see Experimental). The chromatographic behaviour and spectroscopic features (MS, NMR, UV) of synthetic **1** were superimposable on those of the natural methyl deca-4,6-diynoate obtained by us from the epigeal parts of *B. perennis*. Two products, **3** and **4**, were formed along with synthetic **1**. Their spectroscopic data allowed the identification of **3** as deca-4,6-diyne and **4** as dimethyl octa-3,5-diyn-1,8-dioate (Experimental, Tables 3 and 4).

Finally, GC and GC-MS analysis of the acid fraction (after treatment with CH_2N_2; see Experimental) ob-

Table 3. ^1H and ^{13}C NMR spectral data of acetylene **3** ($^{10}CH_3$–$^9CH_2$–$^8CH_2$–$^7C\equiv^6C$–$^5C\equiv^4C$–$^3CH_2$–$^2CH_2$–$^1CH_3$)

H		C	*J* (Hz)
1, 10	0.98 *t* [7.0]	1	13.29
2, 9	1.51 *tq* [7.0]	2, 9	21.90
3, 8	2.22 *tt* [7.0; 1.0]	3, 8	21.02
		4, 7	77.29
		5, 6	65.22

Table 4. ^1H and ^{13}C NMR spectral data of acetylene **4** (CH_3OCO–$^9CH_2$–$^8CH_2$–$^7C\equiv^6C$–$^5C\equiv^4C$–$^3CH_2$–$^2CH_2$–$^1COOCH_3$)

H		C	*J* (Hz)
2, 3, 8, 9	2.58 *m*	1	171.77
OMe	3.72 *s*	2, 9	32.84
		3, 8	14.85
		4, 7	75.57
		5, 6	65.83
		OMe	51.75

tained by CC fractionation of the oil, revealed the presence of a component showing the same chromatographic elution time and identical fragmentation pattern as **1**. This compound was identified as deca-4,6-diynoic acid (**2**). Both compounds are reported here, to the best of our knowledge, for the first time.

Polyacetylenes are common constituents of several higher plants and fungi [9–13]. C_{10} polyacetylenes seem to be typical of the Astereae, with matricaria ester (methyl deca-2,8-dien-4,6-diynoate) as the most widespread compound [9, 14]. Over the years, a number of dehydrogenated acetylenes related to matricaria ester have been isolated from natural sources, in contrast, among the hydrogenated derivatives, only *cis*-8-dihydro matricaria ester has been found to occur frequently as a natural product [7–9]. Thus the finding of compounds **1** and **2** enlarge the series of the hydrogenated relatives of matricaria ester. Their isolation from *B. perennis*, however, should not be regarded as completely unexpected. It is, in fact, consistent with previous studies which established the presence of deca-4,6-diynoic acid diesters in *B. perennis* root extracts [15, 16].

EXPERIMENTAL

General. TLC: silica gel 60F254. Compounds were visualized by heating at 120° after spraying with vanillin (1% EtOH)–H_2SO_4 (5% EtOH) reagent. Polyacetylenes were detected by inspection under UV light. CC: silica gel 60H, 230–400 mesh; IR: KBr discs; UV: hexane; ^1H and ^{13}C NMR: 300 MHz, $CDCl_3$ with TMS as int. standard. Multiplicities and the assignment of ^{13}C chemical shifts were made with the aid of DEPT. FID-GC: a DB5-bonded phase fused silica capillary column (30 m; 0.32 mm i.d.; 0.25 μm film thickness) with the following program: 40° (5 min), 4° min to 280° (20 min). Injector and detector port were kept at 290°. The splitless mode (1 μl) injection was used. He was the carrier gas with a head pressure of 12.0 psi. Data were processed with the aid of a computing integrator. GC-EI-MS: DB5 (as above) and OV1 capillary column (25 m; 0.25 mm i.d.; 0.25 μm film thickness) directly inserted into the ion source. Analytical conditions were the same as for GC. MS: 40–500 amu, 1 scan sec^{-1}; ionizing electron energy, 70 eV; electron current, 0.3 mA; ion source, 200°; vacuum, 10^{-5} torr.

Plant material. Wild flowering plants of *Bellis perennis* L. were collected in the surroundings of Pavia (Italy). Only the aerial parts were used for the extraction of essential oils.

Extraction of the essential oils. Flowers (40 g) and leaves (70 g) were steam distilled separately for 1 hr. The distillate was saturated with NaCl, extracted with distilled Et_2O, dried overnight with Na_2SO_4 and then concentrated under vacuum to give 2.1 and 3.0 mg of essential oil from flowers and leaves, respectively. The organic extracts were analyzed directly by GC and GC-MS.

Fractionation of the essential oils. The oils were subjected to gradient elution CC. Pentane was used to recover the non-polar fraction (N) containing terpenes, aliphatic and aromatic hydrocarbons. Successive elution with Et_2O afforded esters, aldehydes, alcohols and oxygenated terpenes (P_1). Phenols were identified in the fraction (P_2) obtained with Et_2O–MeOH (9:1). Finally, Et_2O–MeOH–AcOH (89:10:1) gave the acidic fraction (A). Solvent was removed by distillation using a rotary evaporator. All the eluted fractions were analyzed by GC and GC-MS. Fraction A was methylated with CH_2N_2 prior to GC and GC-MS.

Identification of the essential oil components. Authentic reference compounds, peak matching library search, as well as published mass spectra [17–20] were used for identification.

Isolation and purification of methyl deca-4,6-diynoate (**1**). About 14 kg of flowers and leaves from *B. perennis* were steam distilled together as described above to yield 407 mg of essential oils. The extract on CC using the same solvent system as previously described gave four fractions: N, 225 mg, 55% of the total oil; P_1, 160 mg, 39%; P_2, 3 mg, 0.7% and A, 6 mg, 2%. Pure **1** (14.0 mg) was obtained when the solvent mix was approximately 5% Et_2O. All the eluted fractions were analyzed by GC and GC-MS. The acid fraction was methylated with CH_2N_2 before GC and GC-MS. Compound **1** was also submitted to IR, UV and NMR for identification.

Synthesis of **1**. Pent-4-yn-1-oic acid (0.95 g, 9.7 mmol) was treated with CH_2N_2 to give the corresponding methyl ester which was then reacted at room temp. with pent-1-yne (1.01 g, 14.8 mmol), in a soln of NH_4Cl (3.3 g), CuCl (21 g) and 0.6 ml 2M ammonia in 75 ml H_2O [8]. The reaction mixture was mechanically stirred for 2 hr and then extracted with Et_2O. Synthetic compound **1** was purified from the by-products **3** and **4** by CC. UV, GC-MS and NMR spectra were acquired for **1**, **3** and **4**. Synthetic and natural compound **1** were also submitted to co-chromatography.

Methyl deca-4,6-diynoate (**1**). UV λ_{max} nm (ε): 225 (460), 237 (357), 253 (208), 287 (53); closely resembles UV spectral data reported in reference [8]. IR ν_{max} cm^{-1}: 2230, 2152 (C≡C–C≡C), 1740 (C=O); EI-MS *m/z* (rel. int.): $[M^+, C_{11}H_{14}O_2]$ 178 (58), $[M-Me]^+$ 163 (6), $[M-C_2H_4]^+$ 150 (42), $[M-OCH_3]^+$ 147 (31), $[M-C_3H_7]^+$ 135 (39), $[M-CO_2CH_3]^+$ 119 (36), 107 (92), 103 (39), $[M-C_2H_4-CO_2CH_3]^+$ 91 (100), 77 (81), 63 (50), 51 (33); NMR: Table 2.

Deca-4,6-diyne (**3**). UV λ_{max} nm (ε): 225 (391), 239 (373), 253 (221); EI-MS *m/z* (rel. int.): $[M^+, C_{10}H_{14}]$ 134 (55), 119 (6), 117 (9), 115 (4), 105 (24), 103 (21), $[M-C_3H_7]^+$ 91 (100), 79 (40), 77 (59), 63 (31); ^1H and ^{13}C NMR: Table 3.

Dimethyl octa-3,5-diyn-1,8-dioate (**4**). UV λ_{max} nm (ε): 225 (821), 253 (302), 275 (288), 287 (342); EI-MS *m/z* (rel. int.): $[M^+, C_{12}H_{14}O_4]$ 222 (6), 207 (4), 194 (68), 191 (39), 179 (22), 163 (53), 149 (36), $[M-CH_2CH_2CO_2CH_3]^+$ 135 (50), 121 (76), 103 (65), 91 (85), 77 (100); ^1H and ^{13}C NMR: Table 4.

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