131. New Irregular Monoterpenes in *Artemisia vulgaris*

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Dedicated to Professor *George Büchi* on the occasion of his 60th birthday

(13.V.81)

Summary

A gas chromatographic investigation of the steam distilled oil of the herb of *Artemisia vulgaris* led to the identification of 21 irregular monoterpenes of non-head-to-tail isoprenoid skeleton. The spectral data of some of these compounds are discussed. The structures of eight new irregular monoterpenes are given.

Introduction. – *Artemisia vulgaris*, the common mugwort, is a perennial shrub growing wild and abundantly all over the temperate and cold temperate zones. Two different essential oils of this plant are known. One is an extract of the roots that has been analyzed by different groups [1] [2] and contains interesting poly-acetylenic compounds. The other is the steam distillate of the herb, called 'Armoise', highly appreciated in fine perfumery for its herbal, aromatic green odour, where the burning freshness of thujone is combined with a rich hay-like undertone. Several analyses of this oil have already been described ([3] [4] and ref. cit. therein).

Results and discussion. – The present investigation of a steam distillate of Moroccan origin furnished new results, especially in the series of the non-head-to-tail monoterpenes. 'Armoise' contains 30% of camphor and 35% of thujone and isothujone. The remaining 35% of the oil is a complicated mixture of volatile compounds, mostly monoterpenes. Twenty-six known bicyclic monoterpenes have been found. We also identified twenty-one non-head-to-tail isoprenoid monoterpenes (representing 5% of the oil) having either artemisia or santolina skeletons (see **1–21** in *Scheme 1*).

Of these irregular monoterpenes 5,6-epoxy-3,3,6-trimethyl-1-hepten-4-one ('epoxy-artemisia ketone'; **3**), 3-methyl-1-(1,1-dimethyl-2-propenyl)-2-butenyl propionate (artemisyl propionate; **6**), (2*E*)-2,5-dimethyl-4-vinyl-2,5-hexadienyl propionate (lyratyl propionate; **12**), (2*Z*)-2,5-dimethyl-4-vinyl-2,5-hexadienyl acetate ((*Z*)-lyratyl acetate; **16**), 5-methyl-2-methylidene-3-vinyl-4-hexenyl acetate (**17**), 1,1,4-trimethyl-2-vinyl-3-pentenyl acetate (santolinyl acetate; **19**), 1,1,4-trimethyl-3-oxo-2-vinyl-4-pentenyl acetate (**20**), and the two diastereoisomers of

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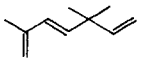
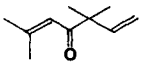
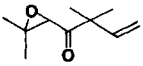
Scheme 1. *Irregular monoterpenes in* Artemisia vulgaris



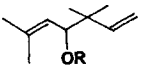
Artemisia triene **1**



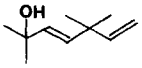
Artemisia ketone **2**



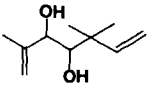
'Epoxy-artemisia ketone' **3**



R = H Artemisia alcohol **4**
R = $COCH_3$ **5**
R = COC_2H_5 **6**



Yomogi alcohol **7**



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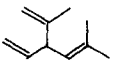
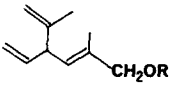
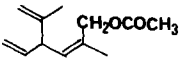


Santolina triene **9**



R = H Lyratol **10**
R = $COCH_3$ **11**
R = COC_2H_5 **12**
R = $COCH(CH_3)_2$ **13**
R = $COCH(CH_3)C_2H_5$ **14**
R = $COCH_2CH(CH_3)_2$ **15**



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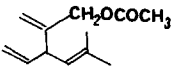

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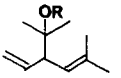
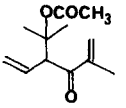


R = H Santolina alcohol **18**
R = $COCH_3$ **19**



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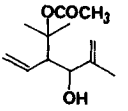

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3-hydroxy-1,1,4-trimethyl-2-vinyl-4-pentenyl acetate (**21a,21b**) are new compounds[1]).

Recently, *Segal et al.* described the isolation of some similar irregular monoterpene alcohols in *Artemisia herba alba* [5]. The biogenetic origin of these structures has been widely discussed ([6] [7] and ref. cit. therein).

The artemisia group. Artemisia triene (**1**) [10], artemisia ketone (**2**), artemisia alcohol (**4**) and its acetate **5** are known products [8] [9]. We identified the epoxide

[1]) For the synthesis and spectral data of the new products see exper. part.

3 of artemisia ketone for the first time in nature. Its ^{1}H-NMR. spectrum is extremely simple: four singlets for four methyl groups, one singlet for an ether proton, and one *ABC*-pattern for a vinyl group. The mass spectrum indicates a molecular weight of 168 ($C_{10}H_{16}O_2$).

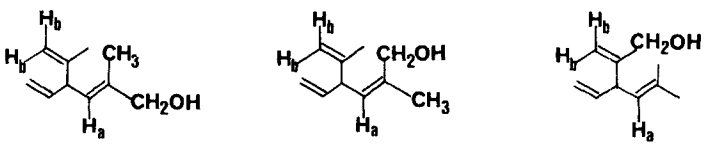
It is noteworthy that the mass spectrum of the known yomogi alcohol (**7**) [10] represents a mixture of the dehydration product, artemisia triene (**1**), and the alcohol itself, so the proportions of the fragments vary considerably, depending on the condition of the source of the mass spectrometer.

The compounds 2,2-dimethyl-3-buten-1-ol (**22**), 2,2-dimethyl-3-butenal (**23**) and 2,2-dimethyl-3-butenoic acid (**24**), also present in the steam distillate, can be considered as degradation products of artemisia compounds, **24** being the main constituent of the acid fraction, **22** and **23** being present only in traces.

The santolina group. In the series derived from santolina triene (**9**) [10], lyratol (**10**) and its acetate **11** [11] [12] predominate (0.5 and 1% of the entire oil); lyratyl propionate (**12**) could be isolated for a ^{1}H-NMR. spectrum, whereas the higher esters [13] were detected in traces only by GLC./MS. We identified the (*Z*)-lyratyl acetate (**16**), but not its parent alcohol **25**. (*Z*)-Acetate **16** showed the same mass spectrum as the (*E*)-acetate **11**, but had a lower retention time in capillary GLC. using *UCON* as stationary phase. To a small peak, which appeared under the same GLC. conditions between (*Z*)- and (*E*)-lyratyl acetate, structure **17** was attributed based on its mass spectrum; this was proven by subsequent synthesis of **17**. This new santolina compound is closely related to the lyratols and also exhibits similar MS. and ^{1}H-NMR. spectra.

We characterized compounds **11**, **16** and **17** as the corresponding alcohols **10**, **25** and **26**, respectively *(Scheme 2)*. Decoupling experiments in the 360-MHz-

Scheme 2



10 **25** **26**

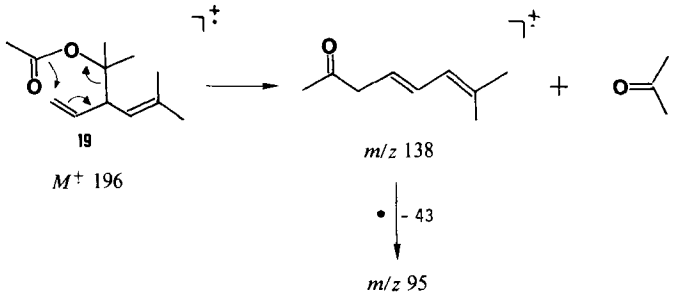
^{1}H-NMR. spectra distinguished between the isomers **10** and **26**: irradiating at H_a, one methyl group decoupled in **10**, and two methyl groups decoupled in **26**, whereas irradiation at H_b decoupled one methyl group in **10**, and none in **26**. Isomers **10** and **25** show different chemical shifts for the methyl group at the tri-substituted double bond (1.72 ppm for **10** and 1.85 ppm for **25**). The acetates prepared from **10**, **25** and **26** were identical with the acetates **11**, **16** and **17**, respectively, of the natural fraction, according to mass spectra and retention times in capillary GLC.

The structure of our santolina alcohol (**18**), prepared by the method described in [14] [15], was proved by ^{1}H-NMR. spectroscopy. Its fragmentation pattern in the

MS. does not correspond to the data reported for santolina alcohol in [16], but to the ones given there for 2,7-dimethyl-4,6-octadien-2-ol (data in [16] are probably confused).

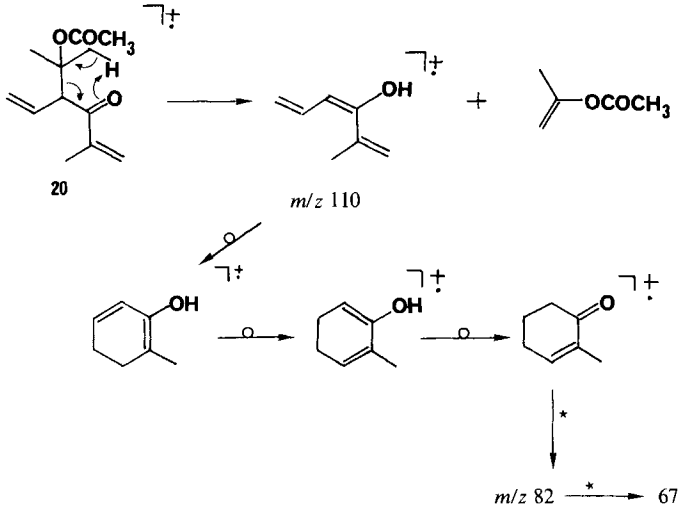
The mass spectrum of santolinyl acetate (**19**) does not follow the pattern that might be expected for monoterpene acetates, the fragment *m/z* 138 usually pointing to a molecular ion M^+ 198 and not 196. This might be the reason why **19** was not yet identified as natural product. We propose the following mechanism for the fragmentation of **19** to explain the loss of 58 mass units from M^+ *(Scheme 3).*

Scheme 3



The acetate **20**, which might be the photooxygenation product of santolinyl acetate (**19**), is present to the extent of 0.5% in 'Armoise', but its isolation was difficult because it decomposed almost entirely during the separation procedure. We deduced its structure from the ^{13}C-NMR. spectrum, where we clearly identified an ester and a ketone function (170.3 and 200.9 ppm). In the ^{1}H-NMR. spectrum

Scheme 4



the chemical shift (1.9 ppm) of the acetate methyl group is at higher field than expected which can be explained by the shielding effect of the keto group. The chemical shift of H–C(2) is extremely high (a doublet at 4.8 ppm) indicating its highly unsaturated surroundings. The MS. of **20** has the main peaks at *m/z* 69 and 41 caused by the fission of the C(2)–C(3) bond, and important fragments at *m/z* 110 and 82 that might be formed according to the fragmentation in *Scheme 4.*

The interesting fact that the identified irregular monoterpenes are highly oxidized may be due to the enzymatic and nonenzymatic transformations during the drying of the herb prior to extraction.

We thank Dr. *A. F. Thomas* and Dr. *B. Maurer* (Firmenich SA) for helpful discussions.

Experimental Part

(With the collaboration of *Christine Gagliardi*)

General. Direct coupling of the gas chromatograph to a mass spectrometer (GLC./MS.): A *Carlo Erba* Fractovap GI 450 equipped with a capillary column coated with *UCON* HB 5100 (50 m, 0.3 mm) is combined with a *Varian MAT 112* mass spectrometer (electron energy 70 eV, ionisation temp. 210°). Packed column for isolation by trapping: *Carlo Erba Fractovap GT 450* with a column filled with *SP 1000* on *Chromosorb G*, 80–100 mesh, acid washed (2.7 m/4 mm). ^{1}H-NMR. spectra were recorded on a *Hitachi Perkin-Elmer R-24A* (60 MHz), a *Bruker HFX 90/15"* (90 MHz) or a *Bruker WH 360* (360 MHz) instrument, using $CDCl_3$ as solvent and tetramethylsilane (=0 ppm) as internal standard. ^{13}C-NMR. spectra were measured on a *Bruker WH 360* at 90.5 MHz. Abbreviations: *s* = singlet, *d* = doublet, *t* = triplet, *qa* = quadruplet, *m* = multiplet, *J* = spin-spin coupling constant (Hz). Column chromatography was performed on a 9:1 mixture of silica gel *Merck* 60 and silica gel *Merck* 'less than 0.08' using as solvent a hexane/ether gradient.

Analysis. – By distillation 1 kg of a steam-distilled oil of Morrocan *Artemisia vulgaris* was roughly separated in three parts: Part I (407 g) up to 80°/12 Torr, Part II (550 g) up to 66°/0.28 Torr and residu III (40 g). Fractions I and II were each carefully redistilled in a spinning-band column to furnish 20 subfractions which were further divided by silica gel chromatography. Then direct capillary GLC./MS. coupling was used to identify known products with the aid of our internal spectra file and product collection. The structures of unknown compounds were established by GLC. trapping and further spectral analysis (^{1}H-NMR., ^{13}C-NMR.), and proved by synthesis. In all cases an exact match of retention times (using *Kováts'* method [17]) and of the spectral data between the compound *ex* 'Armoise' and the reference sample was obtained.

Syntheses. – They were performed with the kind collaboration of Dr. *C. Tarchini*, Dr. *F. Näf*, Dr. *K. H. Schulte-Elte* and *B. Egger.*

2,2-Dimethyl-3-butenoic acid (**24**). To a *Grignard* reagent prepared from 1.25 g of Mg, 6.7 g of 1,1-dimethyl-2-propenyl chloride and 50 ml of ether, CO_2 gas was added for 30 min at RT. to yield, after work-up, 1 g of **24**, b.p. 83°/10 Torr. – ^{1}H-NMR. (90 MHz): 1.3 (*s*, 6 H); 5.05, 5.22 and 6.07 (*ABC*-system, 3 H). – MS.: 114 (8, M^+), 69 (100), 41 (98), 99 (42), 27 (32), 53 (22).

2,2-Dimethyl-3-buten-1-ol (**22**). In 1000 ml of ether, 42 g of **24** were reduced with 12 g of $LiAlH_4$ to give 21 g of **22**, b.p. 40°/10 Torr. – ^{1}H-NMR. (60 MHz): 1.0 (*s*, 6 H); 3.3 (br. *s*, 2 H); 4.8–6.0 (*ABC*-system, 3 H). – MS.: 100 (0, M^+), 41 (100), 69 (81), 77 (22), 55 (15), 27 (13), 82 (4).

2,2-Dimethyl-3-butenal (**23**). A solution of 2 g of **22** in 20 ml of CH_2Cl_2 was treated with 6.46 g of pyridinium chromate in 40 ml of CH_2Cl_2 for 180 min at RT. (s. [18]) to give 0.43 g of **23**, b.p. 60°/200 Torr. – ^{1}H-NMR. (60 MHz): 1.2 (*s*, 6 H); 5.0–6.0 (*ABC*-system, 3 H); 9.4 (*s*, 1 H). – MS.: 98 (7, M^+), 69 (100), 41 (98), 43 (47), 55 (42), 27 (33), 83 (23).

5,6-Epoxy-3,3,6-trimethyl-1-hepten-4-one ('epoxy-artemisia ketone'; **3***).* Artemisia ketone (**2**) was prepared as described in [8] or [9]. A mixture of 0.45 g of **2** in 5 ml of MeOH, 1 ml of H_2O_2-solution (30%) and 0.3 ml of 6N NaOH was stirred for 4 h at 0° to give 0.3 g of **3**, b.p. 75°/10 Torr. – ^{1}H-NMR.

(360 MHz): 1.0 (*s*, 3 H); 1.18 (*s*, 3 H); 1.20 (*s*, 3 H); 1.42 (*s*, 3 H); 3.7 (*s*, 1 H); 5.27 and 5.95 (*ABC*-system, 3 H). – MS.: 168 (0.5, M^+), 41 (100), 69 (87), 43 (54), 83 (16), 96 (16), 27 (14), 111 (6), 153 (6), 126 (5).

1,1,4-Trimethyl-2-vinyl-3-pentenyl acetate (Santolinyl acetate; **19***).* Santolina alcohol (**18**) was prepared according to [15]. A mixture of 3.5 g of **18**, 6.86 g of acetic anhydride, 6.58 g of triethylamine and 0.448 g of 4-(dimethylamino)pyridine [19] was stirred for 24 h. After work-up 3.7 g of **19** were isolated, b.p. 81°/10 Torr. – ^{1}H-NMR. (90 MHz): 1.41 (*s*, 3 H); 1.43 (*s*, 3 H); 1.66 (*s*, 3 H); 1.75 (*s*, 3 H); 1.96 (*s*, 3 H); 3.54 (*t*, 1 H); 4.9–5.2 (*m*, 3 H); 5.6–6.0 (*m*, 1 H). – MS.: 196 (0, M^+), 43 (100), 95 (56), 59 (40), 93 (38), 121 (35), 79 (23), 138 (16).

3-Hydroxy-1,1,4-trimethyl-2-vinyl-4-pentenyl acetate (**21**). A mixture of 0.5 g of **19**, 50 ml of pyridine, and 100 mg of rose bengale was oxygenated at RT. in a conventional irradiation apparatus [20] with a UV. mercury lamp of 125 Watt. After 6 h, 45 ml of O_2 were absorbed. Then 1 ml of dimethyl sulfide was added, the pyridine was distilled off and rose bengale removed by filtration on *Celite*. The mixture contained 50% of **19** and 50% of the two diastereoisomers **21a** and **21b** which could not be separated by prep. GLC. – ^{1}H-NMR. (360 MHz; **21a/21b**): 1.16 (*s*, 3 H); 1.21 (*s*, 3 H); 1.66 (*d*, 3 H); 2.06 (*s*, 3 H); 2.50 (*m*, 1 H); 4.90 (br. *s*, 1 H); 5.00 (br. *s*, 1 H); 5.12 and 5.48 (*ABC*-system, 3 H); 5.34 (*d*, 1 H). – MS. (**21a**; obtained by GLC./MS.): 212 (0, M^+), 43 (100), 79 (51), 94 (35), 82 (28), 59 (17), 67 (12). MS. (**21b**; obtained by GLC./MS.): 212 (0, M^+), 43 (100), 79 (73), 94 (38), 82 (27), 59 (18), 67 (12).

1,1,4-Trimethyl-3-oxo-2-vinyl-4-pentenyl acetate (**20**). With a solution of 16 ml of *Jones'* reagent in 12 ml of acetone [21] 500 mg of the preceding reaction mixture **19/21** were oxidized to **20**, which was isolated by prep. GLC. – ^{1}H-NMR. (360 MHz): 1.50 (*s*, 3 H); 1.52 (*s*, 3 H); 1.88 (*s*, 3 H); 1.92 (*s*, 3 H); 4.79 (*d*, 1 H); 5.18 and 5.90 (*ABC*-system, 3 H); 5.80 (*s*, 1 H); 6.05 (*s*, 1 H). – ^{13}C-NMR. (90 MHz): 200.9 (*s*); 170.3 (*s*); 145.3 (*s*); 133.9 (*d*); 125.1 (*t*); 119.6 (*t*); 83.8 (*s*); 56.3 (*d*); 24.8 (*qa*); 23.7 (*qa*); 20.9 (*qa*); 17.9 (*qa*). – MS.: 210 (0, M^+), 43 (100), 41 (86), 69 (78), 82 (70), 95 (20), 110 (15), 59 (14), 135 (6), 150 (5), 122 (2), 168 (0.2).

5-Methyl-2-methylidene-3-vinyl-4-hexenyl acetate (**17**). Using the method of *Johnson* [22], 10 g of 5-methyl-2,4-hexadien-1-ol, 100 g of ethyl orthoacetate and 0.4 g of propionic acid were heated for 1 h at 138° with continuous distillation of the ethanol formed: 9.5 g of *ethyl 5-methyl-3-vinyl-4-hexenoate* (**27**), b.p. 80°/10 Torr. – ^{1}H-NMR. (60 MHz): 1.25 (*t*, 3 H); 1.7 (*s*, 3 H); 2.35 (*d*, 2 H); 3.55 (*m*, 1 H); 4.1 (*qa*, 2 H); 4.8–6.0 (*ABC*-system, 3 H); 5.2 (*d*, 1 H).

Ester **27** was reduced with $LiAlH_4$ in ether to *5-methyl-3-vinyl-4-hexen-1-ol* (**28**). – ^{1}H-NMR. (60 MHz): 1.6 (*s*, 3 H); 1.7 (*s*, 3 H); 1.7 (*m*, 2 H); 3.2 (*m*, 1 H); 3.7 (*t*, 2 H); 4.8–6.0 (*m*, 4 H).

Alcohol **28** was oxidized with CrO_3 in pyridine [23] to *5-methyl-3-vinyl-4-hexenal* (**29**). – ^{1}H-NMR. (60 MHz): 1.65 (*s*, 3 H); 2.45 (*d*×*t*, 2 H); 3.5 (*m*, 1 H); 4.8–6.0 (*m*, 4 H); 9.7 (*t*, 1 H).

For 3 h 3 g of **29** were treated at 80° with 2.2 g of formaline (40%), 1.8 g of piperidine and 20 ml of 1N HCl following the method of *Mannich* (s. [24]) to give 1.9 g of *5-methyl-2-methylidene-3-vinyl-4-hexenal* (**30**). – ^{1}H-NMR. (90 MHz): 1.65 (*d*, 3 H); 1.72 (*d*, 3 H); 4.2 (*m*, 1 H); 4.8–6.0 (*m*, 4 H); 6.0 and 6.25 (2 *s*, 2 H); 9.48 (*s*, 1 H). – MS.: 150 (16, M^+), 135 (100), 79 (94), 41 (92), 91 (78), 67 (73), 107 (63).

Aldehyde **30** was reduced to *5-methyl-2-methylidene-3-vinyl-4-hexen-1-ol* (**26**) with $LiAlH_4$ in ether. – ^{1}H-NMR. (90 MHz): 1.65 and 1.75 (2 *s*, 6 H); 3.72 (*t*, 1 H); 4.1 (*d*, 2 H); 5.0–6.0 (*m*, 6 H). – MS.: 152 (1, M^+), 119 (100), 41 (79), 91 (76), 79 (66), 67 (11), 55 (51).

The desired **17** was obtained from **26** with Ac_2O in 4-(dimethylamino)pyridine [19]. – ^{1}H-NMR. (60 MHz): 1.8 and 1.9 (*s*, 6 H); 2.2 (*s*, 3 H); 3.8 (*m*, 1 H); 4.65 (*s*, 2 H); 5.1–6.0 (*m*, 6 H). – MS.: 194 (0.1, M^+), 43 (100), 119 (90), 91 (61), 41 (42), 79 (28), 105 (20), 134 (17).

(Z)-Lyratol (=(2Z)-2,5-dimethyl-4-vinyl-2,5-hexadien-1-ol; **25***).* Lyratol (**10**) was prepared by the method described in [12]; **25** was isolated as small impurity of **10** by prep. GLC. – ^{1}H-NMR. (90 MHz): 1.70 (*s*, 3 H); 1.85 (*d*, 3 H); 3.65 (*t*, 1 H); 4.11 (*s*, 2 H); 4.76 (*s*, 2 H); 5.0 (*m*, 2 H); 5.33 (*d*, 1 H); 5.6–6.0 (*m*, 1 H).

(Z)-Lyratyl acetate (**16**). It was obtained as impurity in the synthesis of lyratyl acetate (**11**) from **10** (s. **26**→**17**), and identified only by GLC./MS. coupling. – MS.: 194 (0, M^+), 43 (100), 119 (61), 91 (33), 79 (23), 105 (15), 134 (13).

Lyratyl propionate (**12**). Lyratol (**10**) was treated with propionic anhydride and triethylamine as usual to give **12**. – ^{1}H-NMR. (360 MHz): 1.08 (*t*, 3 H); 1.68 (*d*, 3 H); 1.72 (*d*, 3 H); 2.37 (*qa*, 2 H); 3.60 (*t*, 1 H); 4.51 and 4.79 (2 *s*, 2 H); 5.05 and 5.80 (*ABC*-system, 3 H); 5.46 (*d*, 1 H). – MS.: 208 (0, M^+), 57 (100), 119 (48), 29 (45), 91 (24), 79 (16), 41 (16).

Artemisyl propionate (**6**). It was prepared from **4** as above (**10**→**12**). – ^{1}H-NMR. (60 MHz): 1.0 (*s*, 3 H); 1.2 (*t*, 3 H); 1.75 (br. *s*, 6 H); 2.3 (*qa*, 2 H); 4.8–6.1 (*m*, 4 H). – MS.: 210 (0.1, M^+), 85 (100), 57 (83), 141 (45), 29 (25), 41 (15), 95 (4).

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