Tetrahedron Vol. 49, No 31, pp 6805-6820, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

Branched Long Chain Alkyl Methyl Ethers: A New Class of Lipids from Spider Silk

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(*Received in Germany* 2 *April* 1993)

Abstract: Long chain methyl branched 1-methoxyalkanes, a new class of ether lipids, have been identified from silk of the spider *Linyphia triangularis* (Araneae: Linyphiidae) by use of gas chromatographic retention indices, GC/MS investigations, and chemical modifications. Methyl groups are predominantly located at C-2, and ω–3 or ω–2 positions, respectively. Chain length varies between C_{24} and C_{32}. The synthesis of representative compounds is reported.

INTRODUCTION

It is well known that the webs of spiders are largely made up of proteins. In recent years it became evident that in addition to the fibroin several other classes of chemicals like glycoproteins, inorganic salts, amino acids, and ionic forms of small biogenic amines or sulfur compounds occur on spider silk (for references see[1,2]). No attention has so far been given to lipids on the silk. In the following we will report on the identification and synthesis of a new class of lipids from the silk of *Linyphia* spiders.

RESULTS AND DISCUSSION

During our work on pheromones of spiders[3] we analyzed CH_2Cl_2 extracts of silk from *Linyphia triangularis* by GC/MS. The gas chromatogram of an extract of twenty clean webs (ca. 1 mg silk, see Fig. 1) shows the large number of compounds occurring.

Several late eluting peaks showed mass spectra (see Fig. 2) with a characteristic fragment of $m/z = 45$ which showed to be consistent with the formula C_2H_5O as determined by high resolution mass spectroscopy. All other major signals in the spectra of each of the unknown compounds did not contain oxygen and represented typical alkyl fragments. Reaction of an extract with MSTFA did not affect the unknowns thus excluding the presence of hydroxy groups. Therefore, it seemed likely that these compounds were 1-methoxyalkanes (alkylmethyl ethers) which exhibit prominent ions at $m/z =$ 45 in their mass spectra due to α-cleavage next to the methoxy group. The highest visible prominent fragment is formed by loss of methanol from the molecular ion. By comparison with authentic samples

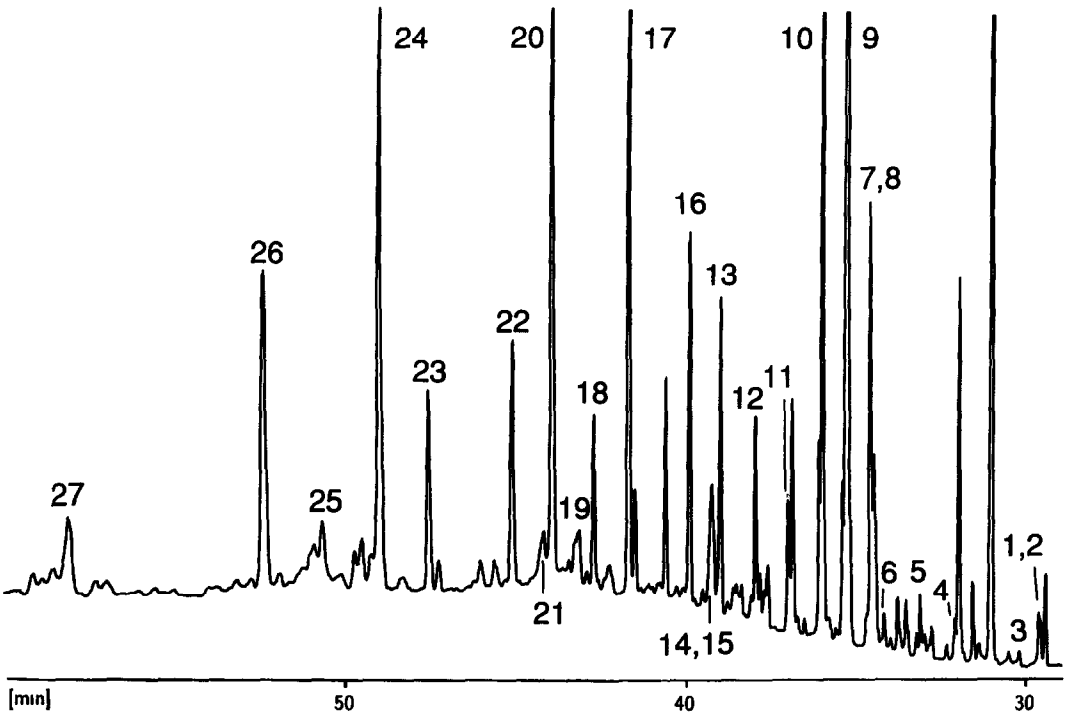


Figure 1: Gas chromatogram of a CH_2Cl_2 extract from silk of *L. triangularis*. Numbers refer to Table 2.

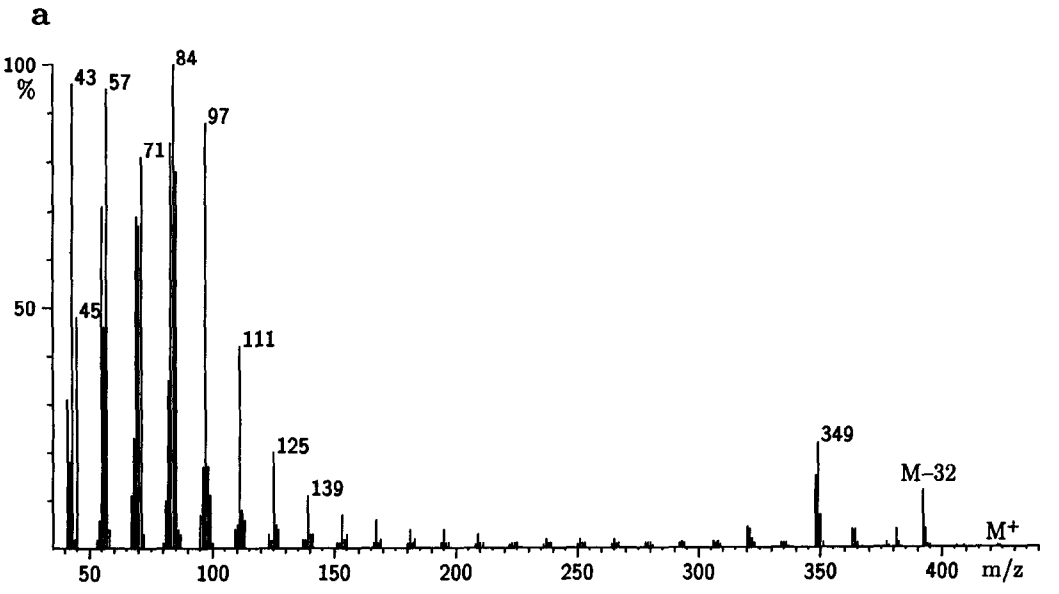


Figure 2: Mass spectra of silk lipids: a) 1-methoxy-24-methylheptacosane; b) 1-methoxy-2,24-dimethylheptacosane; c) 1-methoxy-2,14,18-trimethylheptacosane (from natural extract, ions C according to Fig. 3).

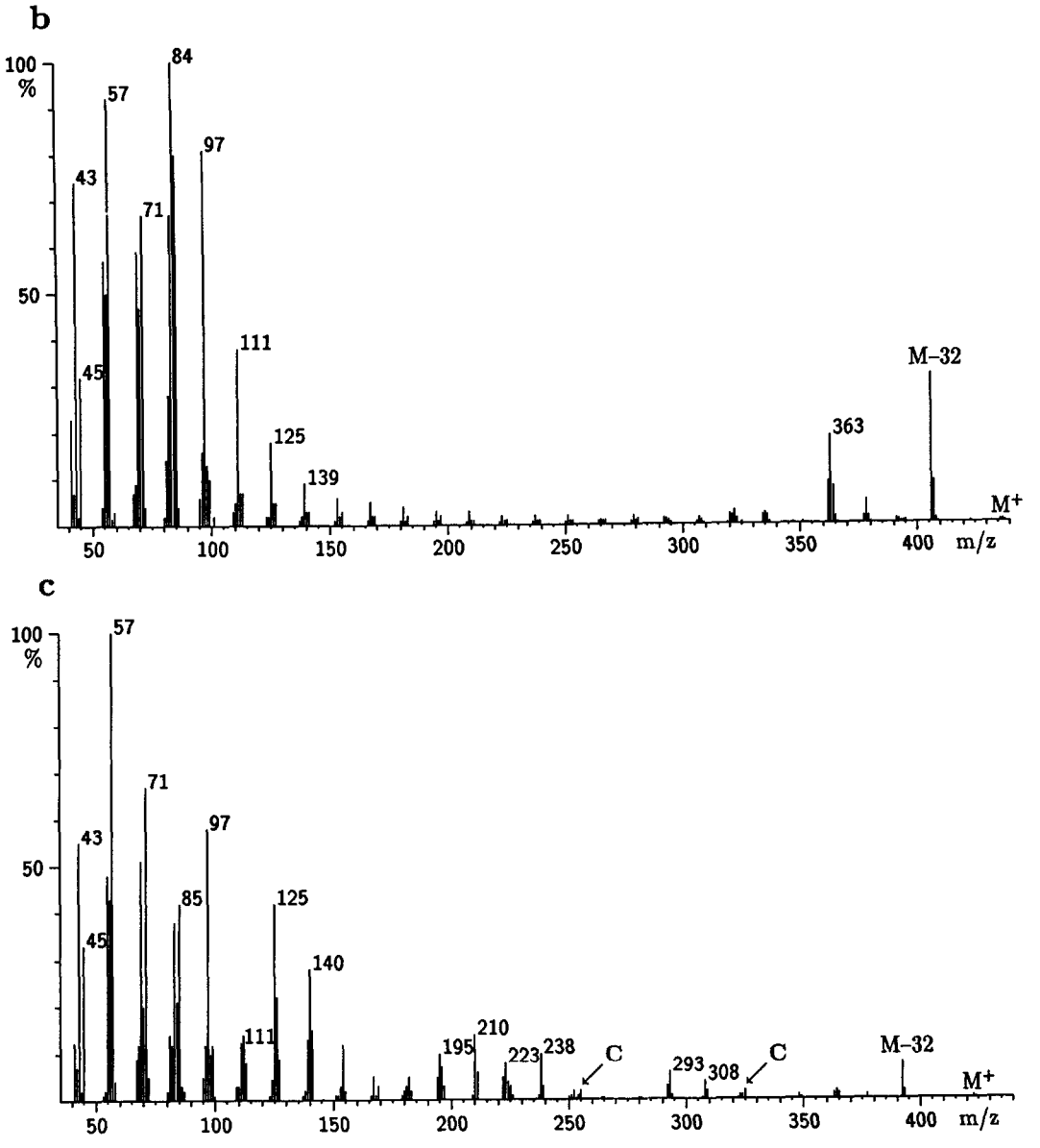


Figure 2 continued.

it became evident that these compounds are not simple *n*-1-methoxyalkanes. Therefore, the 1-methoxyalkanes were considered to contain methyl branchings, as encountered often in cuticular hydrocarbons of insects.[4]

The branching positions of the methyl groups in the different compounds were determined by the concept described as follows: Mass spectra of long chain 1-methoxyalkanes bearing methyl groups at the ω–1, ω–2 or ω–3 positions have been published.[5] Direct determination of internal branching positions from the mass spectra of the 1-methoxyalkanes, only, is difficult, because methanol is easily eliminated from the molecule to form an alkene, which shows more or less unspecific fragmentation. The general mass-spectroscopic fragmentation pattern of branched 1-methoxyalkanes is depicted in Fig. 3. It is deduced from the analyses of the mass spectra of several methyl branched 1-methoxyalkanes which have been synthesized as reference compounds (see below).

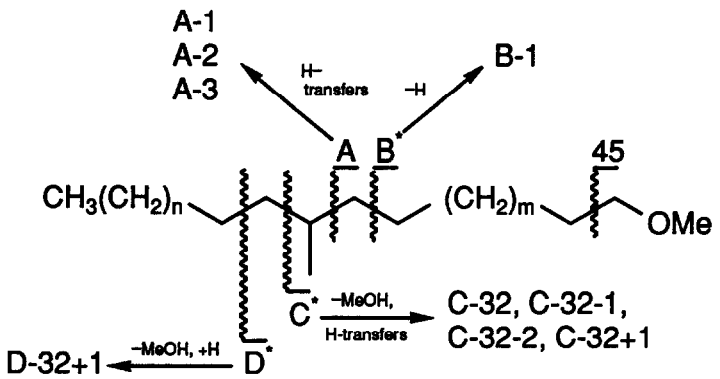


Figure 3: Mass-spectroscopic fragmentation pattern of internally branched 1-methoxymethylalkanes. *: Ions not observed in the mass spectra, but see text.

Prominent ions in the higher mass range are expected to arise from α- and β-cleavage next to the methyl branching. Nevertheless, due to H-transfers and loss of methanol, only the following fragment ions can be observed: A cluster of peaks formed by A ($m/z = C_{n+5}H_{2(n+5)+1}$) and respective ions with 1, 2 or 3 mass units less, and the ion B–1 ($m/z = C_{n+6}H_{2(n+6)}$) include the alkyl chain of the molecule. Fragment ions derived from the opposite site have lost methanol and form a cluster of peaks including C–32 ($m/z = C_{m+6}H_{2(m+6)-1}$), C–32–1, C–32+1, and C–32+2, and an additional ion D–32+1 ($m/z = C_{m+7}H_{2(m+7)}$). The resulting peak groups A/B–1 and C–32/D–32+1 do not allow to assign which part of the molecule they include, because both groups belong to the same homologue series of ions, and the relative intensities of the different ions within a cluster seem to depend more from their m/z values than from their origin. The ion C, which still contains the methoxy group, does not appear in monomethyl 1-methoxyalkanes but occurs in low to moderate abundance in some dimethyl- and in trimethyl 1-methoxyalkanes. As a consequence branching positions of monomethyl 1-methoxyalkanes can not be derived from their mass spectra, while it is possible in some dimethyl- and in trimethyl compounds because of the occurrence of the significant ion C.

Table 1: Experimental I Increments of Heptacosane Derivatives.

	R–CH_2–OMe	R–CO_2Me	R–CH_3
FG	232	336	0
(*ω*–2)-*Me*	75	75	73
(*ω*–3)-*Me*	59	58	57[12]
2-*Me*	39	30	63
10-*Me*	31	32	34[12]
12-*Me*	31	32	32[12]

It thus seems desirable to convert the 1-methoxyalkanes into compounds which show a different mass spectroscopic fragmentation pattern and thus allows the determination of branching positions in monomethyl 1-methoxyalkanes. This can be achieved by transformation of the methyl ethers to the corresponding methyl esters. Such a selective transformation is attainable using RuO_4 which oxidizes only the methylene group adjacent to the ether oxygen atom.[6] Basing on the reported conditions, a new microprocedure using RuO_4 was developed, furnishing high yields of methyl esters in the oxidation of natural extracts. The formation of the expected esters also confirms the natural compounds to be 1-methoxyalkanes. Small amounts of formates were also formed from the major components (< 3%). Monomethyl branching positions in methyl esters can be determined from their mass spectra,[7,8] while problems arise especially in complex mixtures for polymethyl branched methyl esters because of low abundance of the ions formed by branching induced fragmentation.[9] Obviously the mass spectroscopic behavior of 1-methoxyalkanes and the corresponding methyl esters complement one another, allowing identification of the esters if the number of methyl branchings in the unknown compounds is known.

On the other hand, it is not always possible to distinguish whether a mass spectrum represents a mono-, di-, or trimethyl 1-methoxyalkane or methyl ester. The use of retention indices (I),[10] which has been shown to be very helpful in the determination of branching positions and numbers of methyl groups along the chain in hydrocarbons,[11,12] can be used for this purpose. Corresponding I values can be calculated (I_c) according to equation 1, by adding increments for a functional group (*FG*), and methyl groups (Me_i, i indicating the position of the methyl group along the chain) to the base value of the respective unbranched hydrocarbon (N, e. g. 2700 for a C_{27} carbon chain). The values of Me_i vary with the position of the methyl groups in the chain, and were obtained, as those for *FG*, by measuring I of reference compounds (see Tab. 1).

$$I_c = N + FG + \sum Me_i \tag{1}$$

The applicability of this method for polymethyl branched ethers and esters was proven by measuring the I values of 1-methoxy-2,10,24-trimethylheptacosane (**11**) and the corresponding methyl ester, and comparing them with respective calculated values I_c. The difference of only 2 or 3 units between the observed and the calculated values underlines the usefulness of this method.

Final prove for the correctness of the identifications basing on the methods described above was obtained by conversion of the 1-methoxyalkanes to hydrocarbons which allow determination of

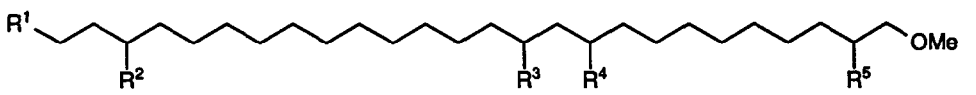
Table 2: 1-Methoxyalkanes Identified in Silk Extracts of *Linyphia triangularis*[a]

	Compound	I	C
1	1-methoxy-2,12-dimethyltricosane	2606	m
2	1-methoxy-2,14-dimethyltricosane	2606	t
3	1-methoxy-2,20-dimethyltricosane	2625	t
4	1-methoxy-22-methyltetracosane	2706	t
5	1-methoxy-2,22-dimethyltetracosane	2743	t
6	1-methoxy-22-methylpentacosane	2790	t
7	1-methoxy-2,12-methylpentacosane	2804	m
8	1-methoxy-2,14-methylpentacosane	2804	m
9	1-methoxy-2,22-dimethylpentacosane	2832	M
10	1-methoxy-2,14,18-trimethylpentacosane	2839	M
11	1-methoxy-24-methylhexacosane **1**	2905	m
12	1-methoxy-2,24-dimethylhexacosane	2947	m
13	1-methoxy-24-methylheptacosane **6**	2990	m
14	1-methoxy-2,14-dimethylheptacosane	3005	m
15	1-methoxy-2,16-dimethylheptacosane	3005	m
16	1-methoxy-2,24-dimethylheptacosane **9**	3032	m
17	1-methoxy-26-methyloctacosane	3107	M
18	1-methoxy-2,26-dimethyloctacosane	3145	m
19	1-methoxy-18-methylnonacosane	3162	t
20	1-methoxy-26-methylnonacosane	3192	M
21	1-methoxy-2,18-dimethylnonacosane	3205	t
22	1-methoxy-2,26-dimethylnonacosane	3230	m
23	1-methoxy-28-methyltriacontane	3308	m
24	1-methoxy-2,28-dimethyltriacontane	3348	M
25	1-methoxy-28-methylhentriacontane	3392	t
26	1-methoxy-2,28-dimethylhentriacontane	3430	M
27	1-methoxy-2,30-dimethyldotriacontane	3548	m

a) Numbers refer to peaks in Fig. 1; I: Retention index; C: concentration; M: major component of the silk extracts; m: minor component; t: trace component.

branching positions by analysis of mass-spectroscopic fragmentation patterns and I values.[12,13] This derivatization could be achieved by transforming the methoxy alkanes into iodides using trimethylsilyl iodide, followed by reduction to hydrocarbons with lithium aluminum hydride or to deuterated hydrocarbons with the corresponding deuteride. Mass spectroscopic analyses of the iodides did not show the presence of any ions indicative for the determination of methyl branching positions in the spectra. Despite some superposition with hydrocarbons originally present in the extract, many assignments could be verified by transformation to hydrocarbons.

On the basis of the described concept 27 1-methoxyalkanes could be identified in the natural extract of silk from *L. triangularis* (see Tab. 2). The ethers identified belong to several types of compounds exhibiting different branching patterns: 1-methoxy-(ω–3)-methylalkanes with an odd number of carbons and 1-methoxy-(ω–2)-methylalkanes with an even number of carbons in the chain together with their respective 1-methoxy-2,(ω–3)-dimethylalkanes represent the largest part of the ethers. A single main component could be identified to be 1-methoxy-2,14,18-trimethylpentacosane (mass spec-



Scheme 1.

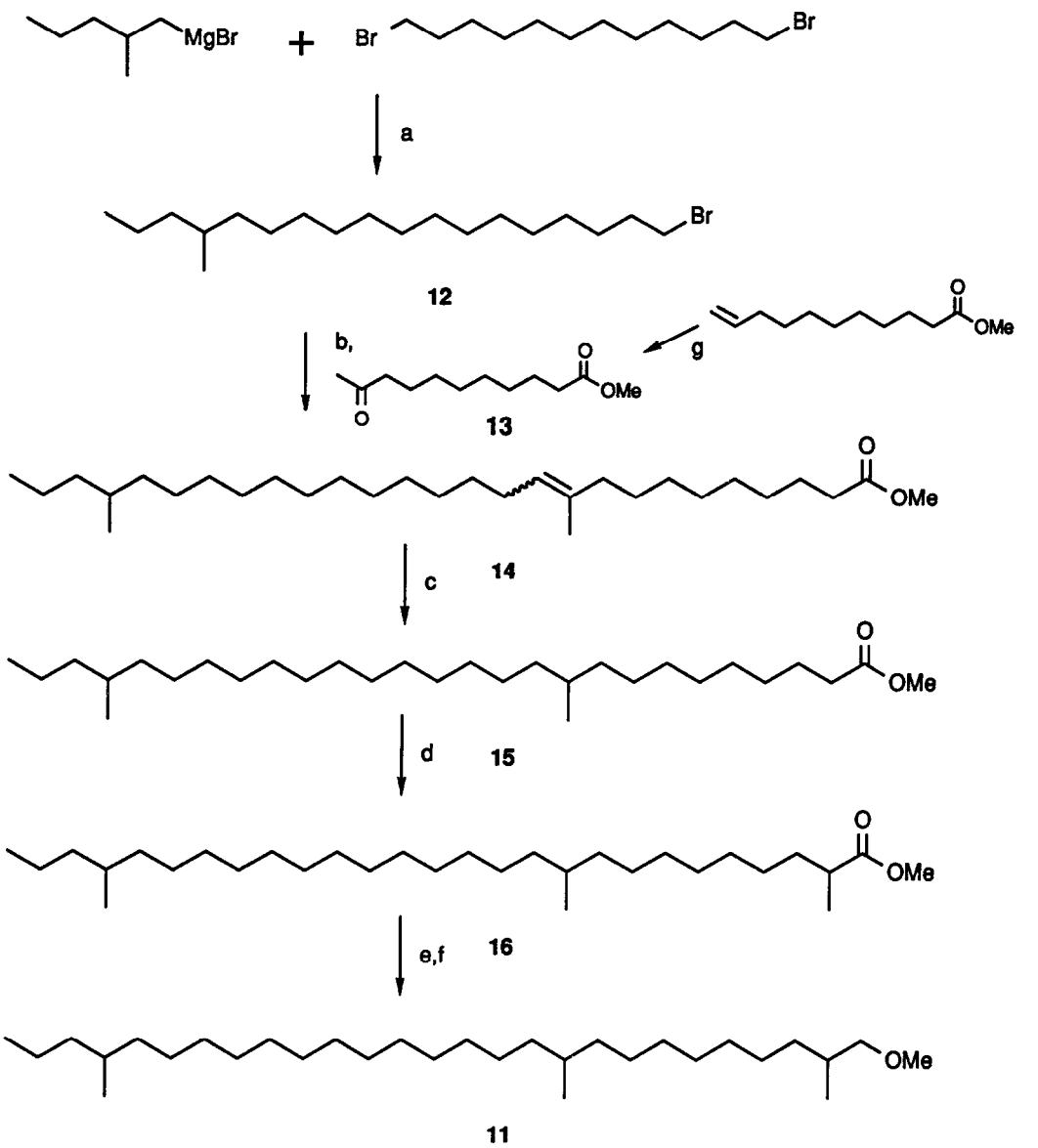
1: R^2=CH_3, $R^{1,3-5}$=H
2: R^1=CH_3, R^{2-5}=H
3: $R^{1,5}$=CH_3, R^{2-4}=H
4: $R^{1,4}$=CH_3, $R^{2,3,5}$=H
5: $R^{1,3}$=CH_3, $R^{2,4,5}$=H
6: $R^{1,2}$=CH_3, R^{3-5}=H
7: $R^{1,4,5}$=CH_3, $R^{2,3}$=H
8: $R^{1,3,5}$=CH_3, $R^{2,4}$=H
9: $R^{1,2,5}$=CH_3, $R^{3,4}$=H
10: $R^{1,2,4}$=CH_3, $R^{3,5}$=H
11: $R^{1,2,4,5}$=CH_3, R^3=H

trum see Fig. 1c) by the indicative fragments C, which occur at m/z = 255 and 325 in the mass spectrum of the natural product, its I value, and the presence of 2,14,18-trimethylpentacosane in extracts derivatized with trimethylsilyl iodide and lithium aluminum hydride. This hydrocarbon is not present in underivatized extracts and must therefore be formed during the derivatization procedure. In addition to these compounds, minor amounts of internally branched monomethyl 1-methoxyalkanes and the respective 1-methoxy-2,X-dimethylalkanes could be identified.

Several representative 1-methoxyalkanes, shown in Scheme 1, and the respective methyl esters were synthesized for comparison of mass spectra and determination of I values. A representative procedure is outlined in Scheme 2, which depicts the synthesis of 1-methoxy-2,10,24-trimethylheptacosane (**11**). Reaction of the Grignard derivative of 1-bromo-2-methylpentane with 1,12-dibromododecane in the presence of Li_2CuCl_4[14] furnished 1-bromo-14-methylheptadecane (**12**), which was converted into its phosphonium salt by reaction with triphenylphosphine. Wittig reaction with methyl 10-oxoundecanoate (**13**) (obtained by $Hg(OAc)_2/Na_2Cr_2O_7$ oxidation of methyl 10-undecenoate[15]) furnished a 1:1 *E/Z*-mixture of methyl 10,24-methylheptacos-10-enoate (**14**) in moderate yield. The saturated ester **15**, obtained by hydrogenation over Pd/C, was alkylated at C-2 by use of LDA and methyl iodide, or directly transformed into **10** by the procedure described below. The alkylation did not proceed to completion, even with excess of reagents, and furnished only mixtures of the 2-methylalkanoate **16** and the starting material **15**, the compositions of which varied between 5:1 and 1:1 in favor of the alkylated product in different experiments. These mixtures could be partly separated by column chromatography. The methyl esters were reduced to the corresponding alcohol, and converted to **11** by reaction with methyl iodide and silver oxide.[5]

The 1-methoxyalkanes **1-9** were prepared by identical methods using the appropriate starting materials methyl 10-oxodecanoate, methyl 12-oxotridecanoate, as well as 1-bromoheptadecane and 1-bromo-14-methylhexadecane. All 1-methoxyalkanes and methyl esters synthesized exhibited identical mass spectra and retention indices I as compared to the corresponding compounds occurring in natural or derivatized extracts.

In addition to the 1-methoxyalkanes, several other classes of compounds could be identified in the silk extracts by their mass spectra: saturated and unsaturated unbranched as well as saturated methyl-branched straight chain hydrocarbons, of which 2-methylhexacosane and 2-methyloctacosane are major components, and a stereotypic row of bishomologue saturated and some unsaturated straight



Scheme 2: a) Li_2CuCl_4, THF; b) PPh_3, 170 °C then *n*-BuLi, **13**, DME, −70 °C to RT; c) H_2, Pd/C; d) LDA, −78 °C to −20 °C, again to −78 °C MeI, to RT; e) $LiAlH_4$, THF; f) Ag_2O, MeI, 40 °C; g) $Hg(OAc)_2$, $Na_2Cr_2O_7$, H^+.

chain fatty acids from C_{12} to C_{26}. Among these are minor amounts of 12-methyltetradecanoic acid and 14-methylhexadecanoic acid, for which anti microbial activity has been shown,[19] as well as 4-methylhexadecanoic acid. Squalene is also a major component, while minor amounts of wax type esters, aldehydes, and amides are present, too.

About 30% of the whole extract consists of the 27 different 1-methoxyalkanes identified (see Tab. 2). We found similar or identical 1-methoxyalkanes also in silk from other linyphiids closely related to *L. triangularis*. Interestingly, they show species specific patterns, while the other classes of compounds identified are present in similar proportions in all investigated species.[3]

It has been shown in another linyphiid that webs of this species contain different chemicals which mediate several different types of information.[16] These findings suggest that the ethers might play a role in the chemical communication system of the spiders, most probably for species identification.[3] Nevertheless these compounds could also fulfill other roles crucial for web existence: regulation of the water content of the web which is essential for the proper function of spider webs,[17] or protection against microorganisms, which may attack the protein rich silk. The lipids may also act as solvents for the pheromones deposited on the silk of female spiders.[3]

The methoxyalkanes are also present on the cuticle of the spiders, but in smaller amounts as compared to the hydrocarbons which make up the largest parts of the cuticle lipids. Webs collected in the field were heavily contaminated with chemicals from the surrounding vegetation, but, nevertheless, also contained 1-methoxyalkanes, thus proving the production of these compounds under natural conditions. Interestingly, similar 1-methoxyalkanes occur also in webs of *Nephila*, an orb weaving spider belonging to another family.[18] This may indicate a more general occurrence of these compounds in lipids from spiders.

To our knowledge, 1-methoxyalkanes have not previously been reported from nature and thus represent a new class of natural products. Aliphatic ethers are seldomly found in nature. Polymethoxyalkanes have been reported from blue-green algae.[20] Dialkyl ethers with long chains at both sides of the oxygen atom have been found in the cuticles of the locust *Locusta migratoria cinerascens*[21] and the beetle *Monolepta australis*.[22]

EXPERIMENTAL

General Methods

High and low resolution EI mass spectra (70 eV) were recorded with a VG 70/250 S mass spectrometer coupled to a Hewlett-Packard HP 5890 A gas chromatograph. ^{1}H-NMR and ^{13}C-NMR spectra were obtained with Bruker WM 400 and AC 250P instruments in $CDCl_3$ and TMS as internal standard. Analytical GLC analyses were carried out with a Carlo-Erba Fractovap 2101 gas chromatograph with a flame-ionization detector and on-column injection. Separations were performed using a 30m Rt_x-5 (id = 0.32 mm, d_f = 0.25 μm) fused-silica column with hydrogen as the carrier gas, programmed from 60 °C to 150 °C with 50 °C/min, then with 3 °C/min to 300 °C.

Sample preparation

Individual spiders were kept in boxes and allowed to build clean webs between plastic or glass frames (10 cm x 10 cm x 10 cm). About 20 webs were collected with a glass rod after two days, without feeding the spider in the meantime to avoid contamination by food residues. Collected webs were directly put into vials containing 200 μl of CH_2Cl_2 (Merck, pro analysi). The samples were concentrated at room temperature to a volume suitable for analyses by GC or GC/MS or for derivatization.

Derivatization of natural extracts

Oxidation with RuO_4.[6] A 2 ml vial, equipped with a stirring bar, was filled with a mixture of 50 μl CCl_4, 50 μl acetonitrile, 75 μl water, and 10 mg sodium metaperiodate. The natural dichloromethane extract (10 μl) was added, followed by 1 mg ruthenium trichloride hydrate. The mixture was stirred vigorously and after 2 h at room temp. 250 μl CH_2Cl_2 were added. The phases were separated using a pipette, and the water phase (the most part of it sticks to the wall of the pipette) extracted again with 250 μl CH_2Cl_2. The combined organic phases were diluted with 500 μl diethyl ether and filtered over prewashed sodium sulfate. Then the modified extract was concentrated to a volume suitable for GC or GC/MS analyses by evaporation of the solvents at 40 °C.

Reaction with trimethylsilyl iodide. To 50 μl of a dichloromethane extract in a 2 ml vial filled with nitrogen was added 25 μl of trimethylsilyl iodide with a syringe. The vial was closed and the dark mixture heated to 50 °C for 2 h in a dark place. Then 50 μl water, followed by 50 μl saturated sodium thiosulfate were added. The mixture was thoroughly shaken, and the phases separated using a Pasteur pipette. The water phase, the reaction vial, and the pipette were washed with two additional portions of dichloromethane. The organic phases were combined and dried by filtration over a small amount of prewashed sodium sulfate. The resulting solution could be used directly for GC/MS analyses or for reduction with lithium aluminum hydride.

Reaction with lithium aluminum hydride or deuteride. The solution containing the iodides was evaporated to dryness and taken up with 200 μl of dry diethyl ether, 5 mg $LiAlH_4$ ($LiAlD_4$), prewashed with hexane, was added, and the mixture stirred for 5 h at room temperature. Small pieces of ice and additional diethyl ether, to compensate for evaporation during hydrolysis of excess hydride, was added. The phases were separated using a Pasteur pipette, and the water phase, the reaction vial and the pipette washed twice with diethyl ether. The combined organic phases were dried by filtration over prewashed sodium sulfate, and the volume reduced to about 20 μl by evaporation of the solvent at room temperature.

Syntheses of 1-methoxyalkanes **1–11** *and of the corresponding methyl esters*

The synthesis of **11** will be described in detail in the following paragraphs. The synthesis of compounds **1–10** used similar reactions starting from methyl 10-oxodecanoate (prepared by ozonolysis of methyl 10-undecenoate), or methyl 12-oxotridecanoate (prepared by alkylation of ethyl acetoacetate with methyl 10-bromodecanoate, followed by Krapcho decarbethoxylation). These compounds were chain elongated by Wittig reaction with the triphenylphosphonium salts of 1-bromopentadecane, 1-bromoheptadecane, and 1-bromo-14-methylhexadecane (prepared from 1-bromo-2-methylbutane and

1,12-dibromododecane as described for **12**), respectively. 1-Bromo-2-methylbutane and 1-bromo-2-methylpentane were prepared from the respective alcohols by reaction with HBr. The similar ^{1}H-NMR spectra of **1–11** and the respective esters exhibited the following absorptions depending on the actual structure of the compound: δ 0.84 (d, 3H, J = 6.2 Hz, C-10-, C-12, and C-24-CH_3 as well as C-2-CH_3 in **3**, **7**, **8**, **9**, and **11**), 0.88 (t, 3H, J = 7.0 Hz, H-27 (H-26 in case of **1**)), 1.04-1.12 (m, two of the four protons in α-position to a methyl substituent, e. g. H-9 and H-11 for **4**), 1.14 (d, 3H, -CH(CH_3)-COOCH$_3$), 1.22-1.45 (m, alkyl-H), 1.56 (quin., 2H, -CH_2-CH$_2$-OCH$_3$), 1.64 (quin., 2H, -CH_2-CH$_2$-COOCH$_3$), 1.68–1.77 (m, 1H, -HC*H*-CH(CH$_3$)-COOCH$_3$), 1.82–1.91 (m, 1H, -HC*H*-CH(CH$_3$)-COOCH$_3$), 2.30 (t, 2H, J = 7.2 Hz, -CH_2-COOCH$_3$), 2.37–2.42 (m, 1H, -C*H*(CH$_3$)-COOCH$_3$), 3.14 (q, 1H, J = 9.0 Hz, J = 6.8 Hz, -CH(CH$_3$)-HC*H*-OCH$_3$), 3.23 (q, 1H, J = 9.0 Hz, J = 6.0 Hz, -CH(CH$_3$)-HC*H*-OCH$_3$), 3.33 (s, 3H, -CH$_2$-OCH_3), 3.37 (t, 2H, J = 6.6 Hz, -CH$_2$-CH_2-OCH$_3$), 3.67 (s, 3H, -CH$_2$-COOCH_3), 3.71 (s, 3H, -CH(CH$_3$)-COOCH_3).

***1-Bromo-14-methylheptadecane* (12).**[14] To a stirred solution of 11 g (33.6 mmol) 1,12-dibromododecane in 50 ml abs. THF was added 15 ml 0.1 M Li_2CuCl_4 solution in THF at 0 °C. Then a freshly prepared Grignard solution of 8.2 g (50 mmol) 1-bromo-2-methylpentane in 50 ml THF was added dropwise. The cooling bath was removed and the mixture stirred for 2 h. Saturated NH_4Cl solution was added, and the mixture extracted three times with diethyl ether. After drying with $MgSO_4$, filtration and removal of the solvent the product was distilled to afford 9 g (27 mmol, 80%, b. p. 118-123 °C, 17 Torr) **12**, containing about 15% 1,12-dibromododecane. The product can be purified further by freezing out the dibromide at –20 °C. ^{1}H-NMR (400 MHz) δ 0.83 (d, 3H, J = 6.8 Hz, -CH-CH_3), 0.88 (t, 3H, J = 7.0 Hz, H-17), 1.04–1.12 (m, 2H, H-13 and H-15[24]), 1.20–1.50 (m, 24H, CH$_2$), 1.86 (quin, 2H, J = 7.2 Hz, H-2), 3.41 (t, 2H, J = 7.0 Hz, H-1); ^{13}C-NMR (100 MHz) σ 14.4 (C-17), 19.7 (C-14-*C*H$_3$), 20.1 (C-16), 27.1 (C-12), 28.2 (C-3), 28.8 and 29.4–29.7 and 30.0 (C-4–C-11), 32.5 (C-14), 32.9 (C-2), 34.0 (C-1), 37.1 (C-13), 39.4 (C-15).

***Methyl 10-oxoundecanote* (13).**[15] This compound was prepared according to method B of the literature.[15] ^{1}H-NMR (250 MHz) δ 1.2–1.4 (m, 8H), 1.5–1.7 (m, 4H, H-3 and H-8), 2.13 (s, 3H, H-11), 2.26 (t, 2H, H-2), 2.38 (t, H-9), 3.67 (s, 3H, OCH_3).

***Methyl 10,24-dimethylheptacos-10-enoate* (14).** According to the procedure of Naoshima and Mukaidani,[23] a mixture of 2 g (6 mmol) **12** and 1.57 g (6 mmol) triphenylphosphane was heated for 8 h at 170 °C. After cooling, the oily mixture was dissolved in $CHCl_3$ and poured into abs. diethyl ether. The solvent was removed by evaporation and the semi-solid residue formed three times thoroughly shaken with abs. diethyl ether, which was decanted each time from the residue. The resulting colorless, glasslike triphenylphosphonium salt (2.9 g, 81% yield) was dried *in vacuo* for 1h and suspended in 25 ml abs. dimethoxyethane (DME). Under a nitrogen atmosphere 3.6 ml of a 1.6 M *n*-butyl lithium solution in hexane was added dropwise and the solution stirred for 2 h. After cooling to –50 °C, a solution of 0.9 g **13** in 2 ml abs. DME was added, the cooling bath removed, and the reaction mixture allowed to warm to room temperature. After additional stirring at 40 °C for 4 h, the reaction mixture was poured on sat. NH_4Cl and extracted three times with diethyl ether. The combined organic phases were washed with brine, dried with $MgSO_4$, and the solvent removed. The resulting solid residue was taken up with hexane and stored at 4 °C overnight. The solvent was removed

after filtration and the residue subjected to flash chromatography (SiO_2, hexane/diethyl ether 95:5) to afford 920 mg (50% yield) of a 1:1 mixture of (*E*/*Z*)-**14**. ^{1}H-NMR (400 MHz) δ 0.84 (d, 3H, J = 6.2 Hz, C-24-CH_3), 0.88 (t, 3H, J = 7.0 Hz, H-27), 1.04-1.12 (m, 2H, H-23 and H-25), 1.18–1.40 (m, 26H), 1.57 (s, 3H, C-10-CH_3), 1.58–1.64 (m, 2H, H-3), 1.66 (s, 3H, C-10-CH_3), 1.92–2.01 (m, 4H, H-9 and H-12), 2.29 (t, 2H, J = 7.2 Hz, H-2), 3.66 (s, 3H, O-CH_3), 5.10 (bt, 1H, J = 6.6 Hz, H-10); ^{13}C-NMR (100 MHz) σ 14.4 (C-27), 15.8 (*E*-C-10-*C*H$_3$), 19.7 (C-24-*C*H$_3$), 20.1 (C-26), 23.4 (*Z*-C-10-*C*H$_3$), 25.0 (C-3), 27.1 (C-22), 27.9–28.0 (C-12), 29.1–30.2 (C-4–C-8, *Z*-C-9, and C-13–21), 32.5 (C-24), 34.1 (C-2), 37.1 (C-23), 39.5 (C-25), 39.7 (*E*-C-9), 51.4 (OCH$_3$), 174.3 (C-1);
exact mass, m/z 450.4443 and 450.4441 (calcd for $C_{30}H_{58}O_2$, m/z 450.4437).

***Methyl 10,24-dimethylheptacosanoate* (15).** A mixture of 400 mg **14**, 5 ml abs. methanol, 50 mg Pd/C and 0.2 ml acetic acid was hydrogenated until no more hydrogen was consumed. Filtration and evaporation of the solvent furnished 360 mg (90% yield) of **15**. ^{13}C-NMR (100 MHz) σ 14.4 (C-27), 19.7 (C-10- and C-24-*C*H$_3$), 20.1 (C-26), 25.0 (C-3), 27.1–27.3 (C-8, C-12, and C-22), 29.1–30.1 (C-4–C-7, C-13–C-21), 32.5 (C-24), 32.8 (C-10), 34.1 (C-2), 37.1 (C-9, C-11, and C-23), 39.5 (C-25), 51.4 (OCH$_3$), 174.3 (C-1); exact mass, m/z 452.4591 (calcd for $C_{30}H_{60}O_2$, m/z 452.4593);
I = 3026 (I_c = 3025).

***Methyl 2,10,24-trimethylheptacosanoate* (16).** A solution of 200 mg **15** (0.44 mmol) in 5 ml abs. THF was cooled to –78 °C and 4 ml of a 0.4 M solution of LDA in THF added under a nitrogen atmosphere. After addition of 0.2 ml DMPU, the solution was allowed to warm to –20 °C and held a this temp. for 1h. The solution was cooled again to –78 °C, 1 ml methyl iodide added, and allowed to warm to room temperature. Finally the mixture was poured onto sat. NH_4Cl and extracted three times with diethyl ether. The combined organic phases were washed successively with 1 N HCl, sat. $NaHCO_3$, and brine. After drying with $MgSO_4$, the solvent was removed and the resulting oil subjected to flash chromatography (SiO_2, hexane/diethyl ether 1.5:100) affording 150 mg (73% yield) of a 5:1 mixture of product **16** and educt **15**. ^{13}C-NMR (100 MHz) σ 14.4 (C-27), 17.0 (C-2-*C*H$_3$), 19.7 (C-10- and C-24-*C*H$_3$), 20.1 (C-26), 27.1–27.3 (C-8, C-12, and C-22), 29.1–30.1 (C-4–C-7 and C-13–C-21), 32.5 (C-24), 32.8 (C-10), 33.9 (C-3), 37.1 (C-9, C-11, and C-23), 39.5 (C-25), 39.6 (C-2), 51.4 (OCH$_3$), 177.0 (C-1); MS m/z 88 (100), 101 (46), 143 (9), 144 (4), 157 (15), 181 (3), 185 (3), 186 (2), 213 (6), 409 (6), 423 (3), 466 (61, M$^+$); exact mass, m/z 466.4765 (calcd for $C_{31}H_{62}O_2$, m/z 466.4750).

***1-Methoxy-2,10,24-trimethylheptacosane* (11).** To a suspension of 50 mg $LiAlH_4$ in 4 ml abs. diethyl ether was added 100 mg of a 5:1 mixture of **16** and **15**, and the mixture stirred for 6 h at room temperature. Ice was added, followed by sodium chloride, and the mixture extracted three times with diethyl ether. After drying of the combined organic phases with $MgSO_4$ the solvent was removed and the residue dissolved in 2 ml methyl iodide. After addition of 200 mg Ag_2O, the mixture was heated to reflux for 6 h. Filtration and washing of the Ag_2O with diethyl ether, followed by evaporation of the solvent afforded 60 mg of a pale yellow oil consisting of a 5:1 mixture of **11** and **10** (62% yield). ^{13}C-NMR (100 MHz) σ 14.4 (C-27), 17.0 (C-2-*C*H$_3$), 19.7 (C-10- and C-24-*C*H$_3$), 20.1 (C-26), 27.1–27.3 (C-8, C-12, and C-22), 27.0 (C-4) 29.1–30.1 (C-5–C-7 and C-13–C-21), 32.5 (C-24), 32.8 (C-10), 33.3 (C-2), 33.6 (C-3), 37.1 (C-9, C-11, and C-23), 39.5 (C-25), 58.8 (OCH$_3$), 78.7 (C-1); MS m/z 43 (85), 45 (40), 55 (63), 56 (55), 57 (100), 69 (64), 70 (35), 71 (68), 83 (54), 84 (44), 85 (56),

97 (64), 111 (38), 125 (16), 139 (11), 166 (7), 167 (19), 168 (5), 169 (3), 181 (3), 182 (10), 183 (5), 195 (2), 199 (1), 278 (3), 279 (4), 280 (3), 281 (3), 294 (3), 377 (2), 420 (7), 451 (0.5), 452 (0.2, M^+);
exact mass, m/z 452.4949 (calcd for $C_{31}H_{64}O_1$, m/z 452.4957); $I = 3061$ ($I_c = 3064$).

Methyl 24-methylhexacosanoate. ^{13}C-NMR (100 MHz) σ 11.4 (C-26), 19.2 (C-24-CH_3), 25.0 (C-3), 27.1 (C-22), 29.1–30.1 (C-4–C-21 and C-25), 34.1 (C-2), 34.4 (C-24), 36.6 (C-23), 51.3 (OCH_3), 174.4 (C-1); MS (70 eV) 74 (78), 87 (82), 143 (37), 185 (8), 199 (12), 325 (10), 363 (4), 367 (4), 381 (18), 393 (3), 395 (5), 424 (57, M^+);
exact mass, m/z 424.4283 (calcd for $C_{28}H_{56}O_2$, m/z 424.4280); $I = 3011$.

Methyl 2-methylheptacosanoate. ^{13}C-NMR (100 MHz) σ 14.1 (C-27), 17.0 (C-2-CH_3), 22.8 (C-26), 29.1–30.0 (C-4–C-24), 32.0 (C-25), 33.9 (C-3), 39.6 (C-2), 51.4 (OCH_3), 177.0 (C-1); MS m/z 88 (100), 101 (56), 143 (12), 157 (18), 381 (11), 395 (4), 407 (2), 438 (88, M^+);
exact mass, m/z 438.4440 (calcd for $C_{29}H_{58}O_2$, m/z 438.4437); $I = 3066$.

Methyl 10-methylheptacosanoate. ^{13}C-NMR (100 MHz) σ 14.1 (C-27), 19.7 (C-10-CH_3), 22.8 (C-26), 25.0 (C-3), 27.1 (C-8 and C-12), 29.1–30.1 (C-4–C-7 and C-13–C-24), 32.0 (C-25), 32.8 (C-10), 34.1 (C-2), 37.2 (C-9 and C-11), 51.4 (OCH_3), 174.4 (C-1); MS m/z 74 (100), 75 (44), 87 (74), 129 (12), 143 (37), 167 (8), 168 (2), 199 (12), 395 (8), 407 (2), 409 (2), 438 (54, M^+);
exact mass, m/z 438.4438 (calcd for $C_{29}H_{58}O_2$, m/z 438.4437); $I = 3068$.

Methyl 12-methylheptacosanoate. ^{13}C-NMR (100 MHz) σ 14.1 (C-27), 19.7 (C-12-CH_3), 22.8 (C-26), 25.0 (C-3), 27.1 (C-10 and C-14), 29.1–30.1 (C-4–C-9 and C-15–C-24), 32.0 (C-25), 32.8 (C-12), 34.1 (C-2), 37.2 (C-11 and C-13), 51.4 (OCH_3), 174.4 (C-1); MS m/z 74 (100), 75 (42), 87 (75), 129 (14), 130 (13), 143 (40), 195 (4), 196 (2), 227 (8), 395 (7), 407 (2), 409 (2), 438 (49, M^+);
exact mass, m/z 438.4436 (calcd for $C_{29}H_{58}O_2$, m/z 438.4437); $I = 3068$.

Methyl 24-methylheptacosanoate. ^{13}C-NMR (100 MHz) σ 14.4 (C-27), 19.7 (C-24-CH_3), 20.1 (C-26), 25.0 (C-3), 27.1 (C-22), 29.1–30.1 (C-4–C-21), 32.5 (C-24), 34.1 (C-2), 37.1 (C-23), 39.5 (C-25), 51.3 (OCH_3), 174.4 (C-1); MS (70 eV) 74 (78), 87 (63), 143 (22), 185 (8), 199 (12), 339 (11), 353 (6), 395 (18), 438 (M^+, 100); exact mass, m/z 438.4444 (calcd for $C_{29}H_{58}O_2$, m/z 438.4437); $I = 3094$.

Methyl 2,10-dimethylheptacosanoate. ^{13}C-NMR (100 MHz) σ 14.1 (C-27), 17.0 (C-2-CH_3), 19.7 (C-10-CH_3), 22.8 (C-26), 27.1 (C-8 and C-12), 29.1–30.1 (C-4–C-7 and C-13–C-24), 32.0 (C-25), 32.8 (C-10), 33.9 (C-3), 37.2 (C-9 and C-11), 39.6 (C-2), 51.4 (OCH_3), 177.0 (C-1); MS m/z 88 (100), 101 (44), 143 (10), 157 (17), 181 (4), 185 (4), 213 (9), 395 (10), 409 (4), 421 (2), 452 (86, M^+);
exact mass, m/z 452.4588 (calcd for $C_{30}H_{60}O_2$, m/z 452.4593); $I = 3099$ ($I_c = 3097$).

Methyl 2,12-dimethylheptacosanoate. ^{13}C-NMR (100 MHz) σ 14.1 (C-27), 17.0 (C-2-CH_3), 19.7 (C-12-CH_3), 22.8 (C-26), 27.1 (C-10 and C-14), 29.1–30.1 (C-4–C-9 and C-15–C-24), 32.0 (C-25), 32.8 (C-12), 33.9 (C-3), 37.2 (C-11 and C-13), 39.6 (C-2), 51.4 (OCH_3), 177.0 (C-1); MS m/z 88 (100), 101 (41), 143 (11), 157 (21), 185 (5), 209 (4), 241 (7), 395 (9), 409 (4), 421 (2), 452 (81, M^+);
exact mass, m/z 452.4586 (calcd for $C_{30}H_{60}O_2$, m/z 452.4593); $I = 3099$ ($I_c = 3097$).

Methyl 2,24-dimethylheptacosanoate. ^{13}C-NMR (100 MHz) σ 14.4 (C-27), 17.0 (C-2-CH_3), 19.7 (C-24-CH_3), 20.1 (C-26), 27.1 (C-22), 29.1–30.1 (C-4–C21), 32.5 (C-24), 33.9 (C-3), 37.1 (C-23), 39.5 (C-25), 39.6 (C-2), 51.4 (OCH_3), 177.0 (C-1); MS m/z 88 (100), 101 (42), 143 (12), 157 (15), 213 (4), 339 (3), 395 (11), 409 (5), 452 (83, M^+);

exact mass, m/z 452.4588 (calcd for $C_{30}H_{60}O_2$, m/z 452.4593); $I = 3124$ ($I_c = 3124$).

1-Methoxy-24-methylhexacosane (**1**). ^{13}C-NMR (100 MHz) σ 11.4 (C-26), 19.2 (C-24-CH_3), 26.1 (C-3), 27.1 (C-22), 29.1–30.1 (C-2, C-4–C-21, and C-25), 34.4 (C-24), 36.6 (C-23), 58.5 (OCH_3), 73.0 (C-1); MS m/z 43 (61), 45 (48), 55 (65), 56 (39), 57 (100), 69 (59), 70 (92), 71 (78), 82 (32), 83 (77), 84 (18), 85 (28), 97 (72), 111 (37), 125 (19), 139 (12), 153 (8), 167 (6), 181 (5), 195 (3), 321 (4), 348 (6), 349 (9), 378 (4), 410 (0.4, M^+); exact mass, m/z 410.4479 (calcd for $C_{28}H_{58}O$, m/z 410.4488); $I = 2907$.

1-Methoxy-heptacosane (**2**). ^{13}C-NMR (100 MHz) σ 14.1 (C-27), 22.8 (C-26), 26.1 (C-3), 29.1–30.0 (C-2 and C-4–C-24), 32.0 (C-25), 58.5 (OCH_3), 73.0 (C-1); MS m/z 43 (87), 45 (66), 55 (67), 56 (33), 57 (100), 68 (46), 69 (69), 70 (30), 71 (56), 82 (58), 83 (91), 84 (22), 85 (35), 97 (78), 111 (43), 125 (25), 139 (15), 153 (9), 167 (7), 350 (8), 378 (25), 410 (0.6, M^+);
exact mass, m/z 410.4491 (calcd for $C_{28}H_{58}O$, m/z 410.4488); $I = 2932$.

1-Methoxy-2-methylheptacosane (**3**). ^{13}C-NMR (100 MHz) σ 14.1 (C-27), 17.0 (C-2-CH_3), 22.8 (C-26), 27.0 (C-4), 29.1–30.0 (C-5–C-24), 32.0 (C-25), 33.3 (C-2), 33.6 (C-3), 58.8 (OCH_3), 78.7 (C-1); MS m/z 43 (78), 45 (53), 55 (59), 56 (43), 57 (100), 69 (55), 70 (32), 71 (54), 82 (40), 83 (70), 84 (20), 85 (38), 97 (74), 111 (40), 125 (20), 139 (12), 153 (9), 167 (7), 181 (5), 195 (5), 350 (3), 364 (8), 392 (36), 424 (0.1, M^+); exact mass, m/z 424.4650 (calcd for $C_{29}H_{60}O$, m/z 424.4644); $I = 2971$.

1-Methoxy-10-methylheptacosane (**4**). ^{13}C-NMR (100 MHz) σ 14.1 (C-27), 19.7 (C-10-CH_3), 22.8 (C-26), 26.1 (C-3), 27.1 (C-8 and C-12), 29.1–30.1 (C-2, C-4–C-7, and C-13–C-24), 32.0 (C-25), 32.8 (C-10), 37.2 (C-9 and C-11), 58.5 (OCH_3), 73.0 (C-1); MS m/z 43 (61), 45 (33), 55 (52), 56 (31), 57 (100), 69 (56), 70 (21), 71 (53), 83 (63), 84 (12), 85 (35), 97 (62), 111 (37), 125 (22), 139 (12), 152 (17), 153 (19), 154 (5), 155 (3), 168 (10), 264 (3), 265 (6), 266 (10), 267 (9), 280 (4), 281 (2), 392 (4), 423 (0.2), 424 (0.1, M^+); exact mass, m/z 424.4647 (calcd for $C_{29}H_{60}O$, m/z 424.4644);
$I = 2963$.

1-Methoxy-12-methylheptacosane (**5**). ^{13}C-NMR (100 MHz) σ 14.1 (C-27), 19.7 (C-12-CH_3), 22.8 (C-26), 26.1 (C-3), 27.1 (C-10 and C-14), 29.1–30.1 (C-2, C-4–C-9, and C-15–C-24), 32.0 (C-25), 32.8 (C-12), 37.2 (C-11 and C-13), 58.5 (OCH_3), 73.0 (C-1); MS m/z 43 (64), 45 (33), 55 (54), 56 (38), 57 (100), 69 (56), 70 (22), 71 (57), 83 (60), 84 (13), 85 (37), 97 (66), 111 (40), 125 (20), 139 (8), 153 (9), 180 (16), 181 (21), 182 (6), 183 (3), 196 (11), 197 (5), 236 (4), 237 (7), 238 (14), 239 (11), 252 (9), 253 (3), 364 (2), 392 (5), 423 (0.2), 424 (0.1, M^+);
exact mass, m/z 424.4640 (calcd for $C_{29}H_{60}O$, m/z 424.4644); $I = 2963$.

1-Methoxy-24-methylheptacosane (**6**). ^{13}C-NMR (100 MHz) σ 14.4 (C-27), 19.7 (C-24-CH_3), 20.1 (C-26), 26.1 (C-3), 27.1 (C-22), 29.1–30.1 (C-2 and C-4–C-21), 32.5 (C-24), 37.1 (C-23), 39.5 (C-25), 58.5 (OCH_3), 73.0 (C-1); MS: see Fig. 1a;
exact mass, m/z 424.4638 (calcd for $C_{29}H_{60}O$, m/z 424.4644); $I = 2991$.

1-Methoxy-2,10-dimethylheptacosane (**7**). ^{13}C-NMR (100 MHz) σ 14.1 (C-27), 17.0 (C-2-CH_3), 19.7 (C-10-CH_3), 22.8 (C-26), 27.0 (C-4), 27.1 (C-8 and C-12), 29.1–30.1 (C-5–C-7 and C-13–C-24), 32.0 (C-25), 32.8 (C-10), 33.3 (C-2), 33.6 (C-3), 37.2 (C-9 and C-11), 58.8 (OCH_3), 78.7 (C-1); MS m/z 43 (59), 45 (30), 55 (48), 56 (42), 57 (100), 69 (52), 70 (22), 71 (52), 83 (45), 84 (13), 85 (36), 97 (56), 111 (36), 125 (16), 139 (13), 153 (5), 166 (10), 167 (24), 168 (7), 182 (15), 183 (7),

264 (5), 265 (10), 266 (9), 267 (5), 280 (11), 281 (4), 378 (2), 406 (9), 438 (0.1, M^+);
exact mass, *m/z* 438.4779 (calcd for $C_{29}H_{60}O$, *m/z* 438.4801); $I = 3002$ ($I_c = 3002$).

1-Methoxy-2,12-dimethylheptacosane **(8)**. ^{13}C-NMR (100 MHz) σ 14.1 (C-27), 17.0 (C-2-CH_3), 19.7 (C-12-CH_3), 22.8 (C-26), 27.0 (C-4), 27.1 (C-10 and C-14), 29.1–30.1 (C-5–C-9 and C-15–C-24), 32.0 (C-25), 32.8 (C-12), 33.3 (C-2), 33.6 (C-3), 37.2 (C-11 and C-13), 58.8 (OCH_3), 78.7 (C-1); MS *m/z* 43 (62), 45 (32), 55 (50), 56 (39), 57 (100), 69 (53), 70 (22), 71 (53), 83 (51), 84 (12), 85 (34), 97 (62), 111 (39), 125 (14), 139 (11), 153 (4), 194 (12), 195 (22), 196 (6), 197 (2), 210 (12), 211 (7), 236 (5), 237 (8), 238 (12), 239 (10), 252 (8), 253 (3), 378 (2), 406 (8), 438 (0.1, M^+);
exact mass, *m/z* 438.4812 (calcd for $C_{29}H_{60}O$, *m/z* 438.4801); $I = 3002$ ($I_c = 3002$).

1-Methoxy-2,24-dimethylheptacosane **(9)**. ^{13}C-NMR (100 MHz) σ 14.4 (C-27), 17.0 (C-2-CH_3), 19.7 (C-24-CH_3), 20.1 (C-26), 27.0 (C-4), 27.1 (C-22), 29.1–30.1 (C-5–C21), 32.5 (C-24), 33.3 (C-2), 33.6 (C-3), 37.1 (C-23), 39.5 (C-25), 58.8 (OCH_3), 78.7 (C-1); MS see Fig. 1b;
exact mass, *m/z* 438.4771 (calcd for $C_{29}H_{60}O$, *m/z* 438.4801); $I = 3032$ ($I_c = 3030$).

1-Methoxy-10,24-dimethylheptacosane **(10)**. ^{13}C-NMR (100 MHz) σ 14.4 (C-27), 19.7 (C-10- and C-24-CH_3), 20.1 (C-26), 26.1 (C-3), 27.1–27.3 (C-8, C-12, and C-22), 29.1–30.1 (C-2, C-4–C-7, and C-13–C-21), 32.5 (C-24), 32.8 (C-10), 37.1 (C-9, C-11, and C-23), 39.5 (C-25), 58.5 (OCH_3), 73.0 (C-1); MS *m/z* 43 (95), 45 (30), 55 (62), 56 (35), 57 (100), 69 (50), 70 (31), 71 (71), 83 (49), 84 (28), 85 (42), 97 (46), 111 (23), 125 (12), 152 (6), 153 (11), 154 (2), 155 (2), 167 (3), 168 (4), 169 (2), 278 (1), 279 (1), 280 (2), 281 (4), 294 (2), 406 (2), 438 (0.1, M^+);
exact mass, *m/z* 438.4777 (calcd for $C_{29}H_{60}O$, *m/z* 438.4801); $I = 3022$ ($I_c = 3022$).

Acknowledgements: We thank Prof. W. Francke, Universität Hamburg, for helpful discussions and his critical review of the manuscript. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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