HIGHLY UNSATURATED ISOPENTYL AMIDES FROM
ACHILLEA WILHELMSII

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ABSTRACT.—The petroleum ether/Et$_2$O extract of the underground parts of *Achillea wilhelmsii* afforded 13 novel alkamides. Their structures and stereochemistries were determined by spectroscopic methods. The general pattern is characterized by derivatives with highly unsaturated acid moieties with different carbon chain lengths. The C$_{10}$ amides predominate, and smaller amounts of C$_{14}$ derivatives are observed. This species is particularly characterized by the accumulation of isopentyl amides that represent a new type of alkamide.

The genus *Achillea* is characterized chemically by the frequent accumulation of olefinic and acetylenic alkamides, a biogenetic capacity that it shares with some other genera of the Compositae-Anthemideae as well as with members of the Compositae-Heliantheae. Besides the more widespread isobutyl and phenethyl amides, the occurrence of compounds with cyclic amide moieties is confined to the tribe Anthemideae (1). As shown in preceding articles, *Achillea* species are especially rich in piperidides, pyrrolidides, and the corresponding dehydro derivatives (piperideides, pyrrolideides) (1-4). More recently, a series of hitherto unknown pyrrolides has been isolated from *Achillea ageratifolia* (Sibth. & Smith) Boiss. (5). Apart from the different amine parts, trends towards different carbon chain lengths and stereochemistries as well as different levels of unsaturation within the acid residues have been shown to serve as additional chemotaxonomic criteria within *Achillea* (1,4,5).

As part of a continuing comparative analysis on alkamides within that genus, we have now investigated *Achillea wilhelmsii* C. Koch (syn: *Achillea santolina* auct. mult., non L.), originating from Turkey. This is a Irano-Turanian element that is particularly characterized by strongly developed root suckers. In Egypt and in some Mediterranean countries the plant is used for stomach ailments and digestive disorders (6). Previous papers on this species have been concerned with sesquiterpene lactones (7-10) and polyacetylenes (11), whereas a more recent article has described the different essential oil compositions of a Turkish and of an Egyptian provenance (6). The present study on the underground parts reveals a series of 13 new alkamides whose structures were elucidated by spectroscopic methods.

RESULTS AND DISCUSSION

The polar column fractions (Si gel) of the petroleum ether/Et$_2$O extract afforded alkamides that fall into two groups on the basis of different carbon chain lengths of the acid residues. The C$_{10}$ amides predominated, and smaller amounts of C$_{14}$ derivatives were observed.

The structure elucidation of the new alkamides was mainly based on ^{1}H nmr (Tables 1 and 2) and mass spectra (see Experimental section). However, apart from the characteristic uv spectra of the highly unsaturated acid residues, special attention was also paid to the very informative ir data (4,18).

C$_{10}$ ALKAMIDES **1-7**.—Due to the highly unsaturated C$_{10}$ fatty acid moieties of the acetylenic derivatives, the ^{1}H-nmr spectra were relatively simple and, thus, allowed a straightforward interpretation. In the uv spectra the 2,4-dienamide

TABLE 1.   [1]H-nmr Data for Compounds 1–7[a]

Proton No.	Compound						
	1	2	3	4	5	6	7
2-H	6.33 d	6.35 d	6.33 d	6.25 d	5.74 d	6.29 d	5.68 d
3-H	6.80 d	6.72 d	6.82 d	6.80 d	7.20 dd	6.73 d	c
4-H	—	—	—	—	6.14 dd	—	6.10 m
5-H	—	—	—	—	6.08 dt	—	6.10 m
6-H	—	—	—	—	2.15 dt	—	2.14 dt
7-H	—	—	—	—	1.45 m	—	1.44 m
8-H	5.59 dq[b]	—	5.60 dq[b]	5.59 dq[b]	1.30 m	—	1.29 m
9-H	6.24 dq	—	6.24 dq	6.23 dq	1.30 m	—	1.29 m
10-H	1.95 dd	2.02 s	1.95 dd	1.95 dd	0.88 t	2.02 s	0.89 t
NH	5.69 br t	5.48 br t	5.55 br t	5.55 br t	5.38 br t	5.52 br t	5.45 br t
1'-H	3.37 dt	3.37 dt	3.19 dt	3.61 dt	3.36 dt	3.61 dt	3.60 dt
2'-H	1.44 dt	1.44 dt	1.84 m	2.88 t	1.45 dt	2.85 t	2.85 t
3'-H	1.63 m	1.61 m	0.93 d	—	1.64 m	—	—
4'-H	0.92 d	0.92 d	—	—	0.92 d	—	—
Aryl H	—	—	—	7.17-7.36 m	—	7.18-7.37 m	7.17-7.37 m

[a]250 MHz, δ/ppm, CDCl$_3$/TMS.
[b]br pseudo d.
[c]Obscured by the aromatic resonances.
Coupling constants (Hz): Acid moieties: **1,3,4**: 2,3=15; 8,9=11; 8,10=1.8; 9,10=7. **2,6**: 2,3=15. **5,7**: 2,3=4,5=15; 5,6=6,7=9,10=7. Amine moieties: **1,2,5**: NH,1'=1',2'=2',3'=3',4'=7. **3**: NH,1'=1',2'=2',3'=7. **4,6,7**: NH,1'=1',2'=7.

chromophore of **5** and **7** was indicated by a sharp maximum at 251 nm; the en-diyn-enamide and triyn-enamide chromophores of the remaining compounds **1-4** and **6** were clearly distinguished by a series of typical maxima (see Experimental). The ir spectra with the >N-H stretching at 3440 cm^{-1} and a strong band at 1500 cm^{-1} (>N-H/C-H bend) were indicative for secondary amides. Phenethyl moieties were characterized

TABLE 2.   [1]H-nmr Data for Compounds 8–13[a]

| Proton No.	Compound					
	8	9	10	11	12	13
2-H	5.93 d	5.91 d	5.77 d	5.95 d	5.93 d	5.78 d
3-H	7.32 dd	7.26 dd	7.19 dd	7.31 dd	7.25 dd	7.20 dd
4-H	6.48 dd	6.40 dd	6.18 dd	6.47 dd	6.39 dd	6.21 dd
5-H	7.05 dd	6.56 dd	6.06 dt	7.05 dd	6.56 dd	6.08 dt
6-H	6.58 dd	6.77 dd	2.39 m	6.58 dd	6.76 dd	c
7-H	5.66 d	5.83 d	2.39 m	5.66 d	5.83 d	c
12-H	5.61 dq[b]	5.60 dq[b]	2.24 t	5.60 dq[b]	5.60 dq[b]	5.50 dq[b]
13-H	6.21 dq	6.19 dq	d	6.20 dq	6.18 dq	6.14 dq
14-H	1.97 dd	1.95 dd	0.99 t	1.98 dd	1.95 dd	1.93 dd
NH	5.46 br t	5.45 br t	5.39 br t	5.52 br t	5.52 br t	5.43 br t
1'-H	3.36 dt	3.37 dt	3.37 dt	3.18 dd	3.18 dd	3.37 dt
2'-H	1.44 dt	1.44 dt	1.43 dt	1.81 m	1.81 m	1.45 dt
3'-H	1.63 m	1.63 m	d	0.94 d	0.94 d	1.65 m
4'-H	0.93 d	0.92 d	0.93 d	—	—	0.93 d

[a]250 MHz, δ/ppm, CDCl$_3$/TMS.
[b]br pseudo d.
[c]2.38-2.50 ppm.
[d]1.50-1.70 ppm.
Coupling constants (Hz): Acid moieties: **8,11**: 2,3=4,5=15; 3,4=5,6=6,7=12,13=11; 12,14=1.8; 14,15=7. **9,12**: 2,3=4,5=6,7=15; 3,4=5,6=12,13=11; 12,14=1.8; 14,15=7. **10**: 2,3=4,5=15; 3,4=11; 5,6=13,14=7. **13**: 2,3=4,5=15; 3,4=12,13=11; 5,6=13,14=7; 12,14=1.8. Amine moieties: **8,9,10,13**: NH,1'=1',2'=2',3'=3',4'=7. **11,12**: NH, 1'=1',2'=2',3'=7.
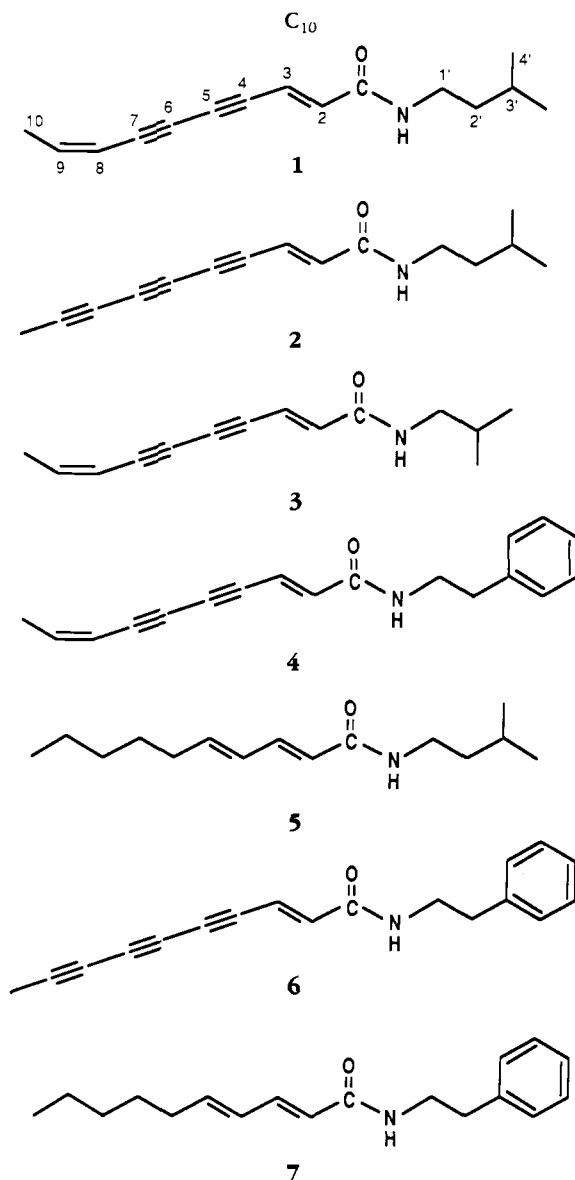
by weak or medium-sized bands at 3055 and 3020 cm^{-1} (aryl-H stretching) as well as at 699 cm^{-1}; acetylenic stretching vibrations were reflected in the resonances at 2200 cm^{-1}. A weak to medium-sized band at 1362 cm^{-1} was typical for a terminal methyl group attached to a double bond (compare **1**, **3**, **4**, **8**, **9**, and **11-13**). Moreover, the number of E-oriented double bonds conjugated with the carbonyl of the amide group may be deduced from two or three bands in the $>$N-C=O/(C=C)$_n$ stretching region (at 1672 and 1605 cm^{-1} or 1670, 1633, and 1611 cm^{-1}) and from a sharp band in the =C-H out-of-plane region (at 995 or 950 cm^{-1}; compare also compounds **8-13** and Experimental).

The major component **1** showed four olefinic protons: an AB system at 6.33 and 6.80 ppm for a *trans*-orientated -CH=CH- element (J= 15 Hz) with no further vicinal couplings ($\equiv$C-CH=CH-CO-) and a *cis*-orientated -CH=CH- element (J=11 Hz) with an additional vicinal coupling of 7 Hz for the proton at 6.24 ppm and a long range

C_{14}

8

9

10

11

12

13
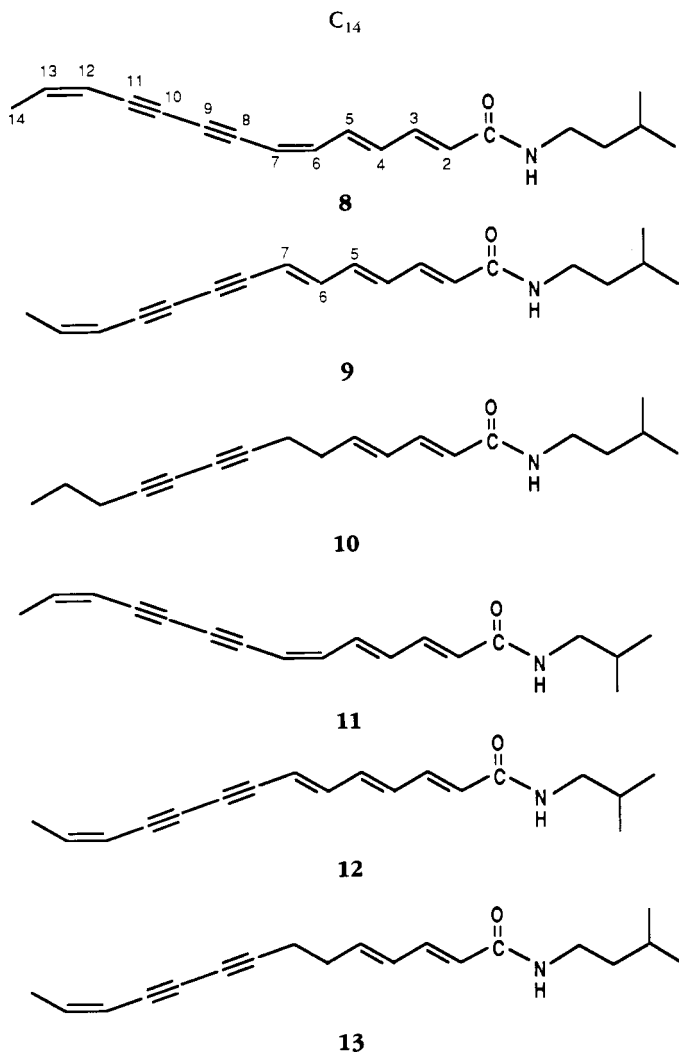
coupling of 1.8 Hz for the proton at 5.59 ppm. The latter coupling showed up very clearly in the resonance signal of the terminal methyl group at 1.95 ppm (dd, $J=7$ and 1.8 Hz). The separation of the two olefinic systems by four acetylenic carbon atoms followed clearly from the mass fragments m/z 143 (100%, CH_3-CH=CH-C≡C-C≡C-CH=CH-CO$^+$, equivalent to M$^+$-NHC$_5$H$_{11}$) and m/z 115 (79%, 143-CO). The isopentyl amide structure for the NHC$_5$H$_{11}$ moiety followed from the ^{1}H-nmr spectrum: a dt (appearing as a somewhat broadened pseudo q) at 3.37 ppm (-NH-CH$_2$-CH$_2$-), a dt (pseudo q) at 1.44 ppm (-CH$_2$-CH$_2$-CH<), a multiplet for 1H at 1.63 ppm {-CH$_2$-CH(CH$_3$)$_2$}, and a d for 6H at 0.92 ppm {-CH$_2$-CH(CH$_3$)$_2$}. The ^{13}C-nmr spectrum was in full agreement with the proposed structure {Experimental, compare Hofer *et al.* (3)}. The acid moiety of **1** is already well known from *cis,trans*-matricaria ester (11).

Comparing the triacetylenic compound **2** with **1**, it lacked the terminal CH_3-CH=CH- unit; all other ^{1}H-nmr resonances were very similar. The prominent ms fragments m/z 141 (100%) and m/z 113 (71%) presented additional evidence for structure **2**.

The isobutyl amide **3** is characterized by the same acid moiety as **1**, attached to the

most common isobutyl amide unit. This was reflected in the practically identical ^{1}H-nmr pattern for the acid portion and the characteristic fragments m/z 143 (100%) and 115 (81%).

The phenethyl amide **4** showed again all typical ^{1}H-nmr resonances and ms fragments for a (2E,8Z)-deca-2,8-dien-4,6-diynoic acid unit. The phenethyl amine moiety is fairly common in alkamides [for characteristic ^{1}H-nmr resonances compare Table 1 and Jente et al. (19) and Bohlmann et al. (20)]. In addition to the M^+-amine and M^+-amine-CO fragments typical for the ms spectra of highly unsaturated C_{10}-alkamides, the fragment m/z 104 (25%, $[CH_2=CH_2-Ph]^+$, product of McLafferty rearrangement) was of interest (19).

Compound **5** is the isopentyl amide of the rather common (2E,4E)-deca-2,4-dienoic acid (1,21). Phenethyl amides **6** and **7** possess the same acid moieties as **2** and **5**, respectively. Following the arguments outlined above, ^{1}H-nmr and ms evidence indicated the proposed structures.

C_{14}-ALKAMIDES **8-13**.—The isopentyl amides **8** and **9** differ only by the 6Z- [**8**] or 6E-double bond [**9**] in the completely conjugated acid moiety. Highly unsaturated, polyacetylenic compounds are very sensitive to light-induced polymerization leading to blue insoluble products [Bohlmann et al. (12), compare also compounds **2** and **6** in the Experimental]. In addition, olefinic bonds in conjugation to a diyne-unit [**8-9**, **11-12**] tend to isomerize easily. Nevertheless, pure samples of **8** and **9** could be isolated by careful tlc. The two isomers may already be distinguished by different uv spectra; the 6E-isomer [**9**] shows a distinct maximum at 368 nm whereas the 6Z-isomer [**8**] deviates by a shoulder at 365 nm. Although there was not enough pure material available from the corresponding isomers **11** and **12** for ir and ms analysis, traces of pure **11** and **12** exhibited nearly identical uv spectra as obtained from **8** and **9**. The ir spectra of **8** and **9** showed only minor differences in the fingerprint region (compare Experimental).

The eight olefinic protons (see Table 2) can be assigned unambiguously by systematic decoupling experiments (see Experimental), and the configurations were deduced from the coupling constants. The most interesting difference in the ^{1}H-nmr spectra of the isomers **8** and **9** is shown by the proton at C-5. In **8** the resonance for 5-H (γ-position to the triple bond) is found at 7.05 ppm (dd, J= 15 and 11 Hz), the corresponding chemical shift for 5-H of **9** is 6.56 ppm (also dd, J= 15 and 11 Hz). In **8** the proton 5-H is close (syn) to the anisotropic 8,9-triple bond resulting in a strong downfield shift; in **9** 5-H is relatively unaffected (anti to $C^8 \equiv C^9$). Further characteristic differences are shown by 6-H and 7-H; **8**: 6-H at 6.58 ppm (dd, appearing as a pseudo t with J= 11 and 11 Hz, β-position to the triple bond), 7-H at 5.66 ppm (d, J= 11 Hz); **9**: 6-H at 6.77 ppm (dd, J= 15 and 11 Hz), 7-H at 5.83 (d, J= 15 Hz). A similar influence of the $C \equiv C$ anisotropy on the chemical shifts of the olefinic protons of an yn-diene partial structure [relatively large downfield shift for the proton γ to $C \equiv C$ in the (Z,E)-isomer and for β in the (E,E)-isomer] was also observed for other alkamides (21,22). The isopentyl amide resonances are the usual ones (see **1**). The chain length is confirmed by the mass spectrum (M^+ and the characteristic fragment M^+-CONHC$_5$H$_{11}$).

In compound **10** the 6,7- and 12,13-carbon bonds are saturated. The ^{1}H-nmr pattern in the olefinic region is the usual one for the (2E,4E)-diene unit in conjugation to the amide carbonyl. The CH_2-triplet at 2.24 ppm (-CH_2-CH_2-C $\equiv$) together with two CH_2-multiplets at 2.39 ppm and the CH_3-triplet at 0.99 ppm allow only the proposed structure for the acid moiety. Additional evidence was furnished by the ms data.

The isobutyl amides **11** and **12** are characterized by the same (6Z)/(6E) isomerization of the acid component as already discussed for the pair **8** and **9**. In the case of **11/12** the isomers were not obtained in pure state. The spectral data were recorded for a mixture **11-12**=30:70%. However, using the results obtained for **8** and **9**, the ^{1}H-nmr as-

signments of the mixture presented no problem. For ms no significant differences in the spectral behavior of **11** and **12** are expected.

In the isopentyl amide **13** the conjugation within the acid moiety is interrupted by a 6,7-dimethylene unit. The characteristic ^{1}H-nmr resonances for CH_3-CH=CH-C $\equiv$ (compare compounds **1**, **3**, **4**, **8**, **9**, **11**, **12**), $(CH_2)_2$-CH=CH-CH=CH-CO- (compare **10**) and the isopentyl amide unit, together with the mass spectrum (m/z 103, 33%, CH_3-CH=CH-C$\equiv$C-C$\equiv$C-CH$_2$$^+$), allowed a clear structural assignment for **13**.

Generally, C_{10} and C_{14} derivatives show a common trend in accumulating highly unsaturated amides. Besides the two olefinic derivatives **5** and **7** that contain the widespread 2E,4E-decadienoic acid, all the other amides possess two or three acetylenic linkages. Of special systematic interest is the occurrence of matricaria acid (deca-2E,8Z-dien-4,6-diynoic acid) as part of the major amides **1** and **4** as well as of the amide **3**. Although esters and lactones of this acetylenic acid are widely distributed, especially in the tribe Astereae, their occurrence within the Anthemideae is as yet only known from the genus *Tripleurospermum* (11). Moreover, the closely related dehydromatricaria acid derived amides **2** and **6** were also isolated here for the first time. However, the corresponding isobutyl amide has already been reported for *Achillea ptarmica* L. (11) and *Achillea spinulifolia* Fenzl ex Boiss. (13) as well as for two other genera of the Anthemideae [see Greger (1)]. Similarly, the tetradeca-2E,4E-dien-8,10-diynoic acid residue of amide **10** is also known from the corresponding isobutyl amide anacyclin which was the first alkamide to be shown to possess acetylenic linkages (14). Due to a rapid photoisomerization, the fully unsaturated C_{14} amides form a pair of stereoisomers on tlc. Inasmuch as the isomerizations **8**⇌**9** and **11**⇌**12** approach an approximately 1:1 ratio from both sides, no decision concerning the original configuration(s) in the plant was possible. In the case of the isopentyl amides **8** and **9** careful chromatography led to the isolation of pure samples, but the corresponding pair of isobutyl amides **11** and **12** could only be analyzed as a mixture.

Apart from smaller quantities of phenethyl and isobutyl amides, *A. wilhelmsii* is particularly characterized by a preponderance of isopentyl amides. With regard to the amide formation, isopentyl amines are only known so far as parts of cinnamic and piperic [=5-(3,4-methylenedioxyphenyl)-2,4-pentadienoic] acid amides from the Piperaceae (15). Thus, the present series of isopentyl amides belongs to a new type of alkamide.

Considering the allelopathic properties of C_{10} polyacetylenes (16) and the larvicidal activity of decadienamides (1,17) on the one hand and the extensive propagation of *A. wilhelmsii* by root suckers on the other hand, it is tempting to suppose that at least the dominating C_{10} amides play an important ecological role in the underground parts.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points (uncorrected) were measured on a Kofler micro hotstage. Uv spectra were obtained with a Perkin-Elmer "Lambda 5" and ir spectra with a Perkin-Elmer 398, both linked with a Perkin-Elmer 3600 data station. Mass spectra were recorded on a Varian MAT CH-7 and ^{1}H-nmr spectra on a Bruker WM-250 equipped with an 80K ASPECT-2000 computer.

PLANT MATERIAL AND ISOLATION PROCEDURE.—Plant material was grown from achenes received from wild collections (Turkey, E. Anatolia, near Van; coll. F. Sorger). The plants were cultivated under field conditions in the Botanical Garden of the University of Vienna. Voucher specimens (A-1688) are deposited at the herbarium of the Institute of Botany, University of Vienna (WU).

Fresh, air-dried, underground parts (170 g) of *A. wilhelmsii* were cut into small pieces and extracted at room temperature with petroleum ether (bp 60-80°)-Et$_2$O (2:1) for several days. The concentrated extract was roughly fractionated on a Si gel column eluted with petroleum ether/Et$_2$O mixtures, with Et$_2$O increasing from 0 to 100% and, finally, with 3-10% (v/v) MeOH in Et$_2$O. The polar fractions obtained with

Et_2O-petroleum ether (1:1) and Et_2O were separated by repeated tlc (Si gel) using Et_2O/petroleum ether mixtures and CH_2Cl_2-Et_2O (19:1) as solvents.

The tlc fractions yielded 35 mg **1**, 5 mg **2**, 2 mg **3**, 8 mg **4**, 4 mg **5**, 2 mg **6**, 1.5 mg **7**, 1 mg **8**, 1.5 mg **9**, 2 mg **10**, 1.5 mg **11** and **12**, and 2 mg **13**.

(2E,8Z)-Deca-2,8-dien-4,6-diynoic acid isopentyl amide [**1**] were colorless crystals, mp 88-91°; uv λ max (Et_2O) nm 328, 307, 288, 254, 243; ir ν max (CCl_4) cm^{-1} 3438m, 3314m, 2954s, 2928w, 2865w, 2200m, 1671s, 1605s, 1501s, 1464, 1432w, 1398w, 1382w, 1363m, 1318m, 1246m, 1187m, 950s, 850w, 712w; ms (80°, 70 eV, m/z, rel. int. %) 229.147 (20%, M$^+$, $C_{15}H_{19}NO$ requires 229.1467), 173 (39), 172 (22), 149 (24), 146 (22), 145 (31), 144 (47), 143 (100, M$^+$-NHC$_5$H$_{11}$), 132 (14), 131 (14), 130 (33), 117 (19), 116 (39), 115 (79, M$^+$-CONHC$_5$H$_{11}$), 114 (16), 95 (34), 91 (30); ^{13}C nmr ($CDCl_3$, δ/ppm) 164.3 s (C1), 143.9 d (C3), 135.1 d (C9), 120.2 d (C2), 108.9 d (C8); 81.5 s, 80.7 s, 79.1 s, 77.8 s (acetylenic C); 38.4 t, 38.3 t (C1', C2'); 25.9 d (C3'), 22.4 q (Me10), 22.4 q (Me4').

(2E)-Dec-2-en-4,6,8-triynoic acid isopentyl amide [**2**] were colorless crystals (decomposition to blue polymers during heating on the micro hotstage); uv λ max (Et_2O) nm 340, 317, 298, 280, 252, 242; ir ν max (CCl_4) cm^{-1} 3437m, 3323m, 2953s, 2924w, 2866w, 2221m, 1673s, 1604s, 1502s, 1463m, 1431w, 1382w, 1365w, 1349w, 1308m, 1259m, 1187m, 1101w, 949s, 850w; ms (70°, 70 eV, m/z, rel. int. %) 227.131 (18%, M$^+$, $C_{15}H_{17}NO$ requires 227.1310), 172 (13), 144 (21), 142 (39), 141 (100, M$^+$-NHC$_5$H$_{11}$), 130 (17), 114 (32), 113 (71, M$^+$-CONHC$_5$H$_{11}$), 95 (28), 91 (26).

(2E,8Z)-Deca-2,8-dien-4,6-diynoic acid isobutyl amide [**3**] were colorless crystals, mp 85-89°; uv λ max (Et_2O) nm 328, 307, 288, 254, 244; ir ν max (CCl_4) cm^{-1} 3442m, 3323m, 2955s, 2923w, 2865w, 2199m, 1673s, 1606s, 1500s, 1462m, 1431w, 1398w, 1384w, 1362m, 1317m, 1243m, 1187m, 950s, 849w, 711w; ms (80°, 70 eV, m/z, rel. int. %) 215.131 (21%, M$^+$, $C_{14}H_{17}NO$ requires 215.1310), 173 (21), 172 (18), 145 (31), 144 (47), 143 (100, M$^+$-NHC$_4$H$_9$), 132 (12), 131 (11), 130 (22), 117 (17), 116 (41), 115 (81, M$^+$-CONHC$_4$H$_9$), 95 (27), 91 (49).

(2E,8Z)-Deca-2,8-dien-4,6-diynoic acid 2-phenylethyl amide [**4**] were colorless crystals, mp 108-111°; uv λ max (Et_2O) nm 329, 307, 288, 254, 243; ir ν max (CCl_4) cm^{-1} 3439m, 3325w, 3058w, 3022m, 2921m, 2851w, 2201m, 1672s, 1606s, 1499s, 1450w, 1433w, 1398w, 1362w, 1318m, 1246m, 1182m, 1028w, 950s, 850w, 712w, 699m; ms (80°, 70 eV, m/z rel. int. %) 263.131 (8%, M$^+$, $C_{18}H_{17}NO$ requires 263.1310), 159 (24), 149 (20), 145 (19), 144 (14), 143 (100, M$^+$-NHC$_2$H$_4$C$_6$H$_5$), 130 (22), 115 (35, M$^+$-CONHC$_2$H$_4$C$_6$H$_5$), 104 (25), 91 (51).

(2E,4E)-Deca-2,4-dienoic acid isopentyl amide [**5**] were colorless crystals, mp 63-65°; uv λ max (Et_2O) nm 251; ir ν max (CCl_4) cm^{-1} 3442m, 3310m, 2952s, 2923s, 2865m, 2852w, 1669s, 1633s, 1611m, 1498s, 1463m, 1432w, 1364w, 1339w, 1315w, 1244m, 1152m, 995s; ms (80°, 70 eV, m/z rel. int. %) 237.209 (9%, M$^+$, $C_{15}H_{27}NO$ requires 237.2092), 152 (32), 151 (100, M$^+$-NHC$_5$H$_{11}$), 130 (33), 124 (29), 123 (63, M$^+$-CONHC$_5$H$_{11}$), 91 (22).

(2E)-Dec-2-en-4,6,8-triynoic acid 2-phenylethyl amide [**6**] were colorless crystals (decomposition); uv λ max (Et_2O) nm 340, 318, 298, 280, 253, 242; ir ν max (CCl_4) cm$^+$ 3441m, 3328w, 3057w, 3020w, 2953m, 2921m, 2866w, 2222m, 1672s, 1604s, 1500s, 1460m, 1450w, 1431w, 1373w, 1330w, 1260m, 1181m, 1117w, 1035w, 949s, 850w, 699m; ms (80°, 70 eV, m/z, rel. int. %) 261.115 (11%, M$^+$, $C_{18}H_{15}NO$ requires 261.1154), 149 (18), 142 (33), 141 (100, M$^+$-NHC$_2$H$_4$C$_6$H$_5$), 129 (17), 113 (81, M$^+$-CONHC$_2$H$_4$C$_6$H$_5$), 104 (33), 91 (47).

(2E,4E)-Deca-2,4-dienoic acid 2-phenylethyl amide [**7**] were colorless crystals, mp 96-98°; uv λ max (Et_2O) nm 250; ir ν max (CCl_4) cm^{-1} 3441m, 3333w, 3053w, 3018w, 2950s, 2920s, 2850m, 1671s, 1634s, 1611m, 1496s, 1461w, 1449w, 1431w, 1361w, 1331w, 1314w, 1241m, 1145m, 1028w, 994s, 699s; ms (80°, 70 eV, m/z, rel. int. %) 271.194 (25%, M$^+$, $C_{18}H_{25}NO$ requires 271.1936), 160 (26), 152 (12), 151 (100, M$^+$-NHC$_2$H$_4$C$_6$H$_5$), 105 (21), 104 (37), 96 (25), 95 (16), 91 (18).

(2E,4E,6Z,12Z)-Tetradeca-2,4,6,12-tetraen-8,10-diynoic acid isopentyl amide [**8**] were colorless oil; uv λ max (Et_2O) nm 365sh, 347, 332sh, 277, 265; ir ν max (CCl_4) cm^{-1} 3440m, 3321w, 2951s, 2922s, 2862w, 2190w, 1669s, 1613s, 1497s, 1461m, 1431w, 1381w, 1361w, 1316m, 1265w, 1238m, 1176w, 1149m, 996s, 950w, 880w, 700w, 663w; ms (100°, 70 eV, m/z, rel. int. %) 281.178 (11%, M$^+$, $C_{19}H_{23}NO$ requires 281.1779), 168 (19), 167 (36, M$^+$-CONHC$_5$H$_{11}$), 166 (18), 165 (37), 153 (41), 152 (33), 141 (13), 115 (17), 97 (10), 43 (100).

(2E,4E,6E,12Z)-Tetradeca-2,4,6,12-tetraen-8,10-diynoic acid isopentyl amide [**9**] were colorless crystals, mp 136-139°; uv λ max (Et_2O) nm 368, 347, 333sh, 279, 217; ir ν max (CCl_4) cm^{-1} 3439m, 3322w, 2951s, 2920s, 2863w, 2848w, 2190w, 1667s, 1615s, 1496s, 1461m, 1432w, 1398w, 1376w, 1362m, 1345w, 1309w, 1271w, 1248w, 1179m, 1136w, 1117w, 996s, 959w, 881w, 712w; ms (100°, 70 eV, m/z, rel. int. %) 281.178 (13%, M$^+$, $C_{19}H_{23}NO$ requires 281.1779), 168 (12), 167 (28, M$^+$-CONHC$_5$H$_{11}$), 166 (16), 165 (31), 153 (36), 152 (30), 141 (10), 115 (12), 97 (9), 43 (100).

(2E,4E)-Tetradeca-2,4-dien-8,10-diynoic acid isopentyl amide [**10**] were colorless crystals, mp 95-97°; uv λ max (Et_2O) nm 250; ir ν max (CCl_4) cm^{-1} 3441m, 3333w, 2954s, 2924s, 2864m, 1671s, 1637s, 1613m, 1497s, 1458m, 1424w, 1381w, 1363w, 1335w, 1314w, 1248m, 1164m, 1124m,

993s, 947w, 861w; ms (100°, 70 eV, m/z, rel. int. %) 285.21 (9%, M^+, $C_{19}H_{27}NO$ requires 285.2093), 270 (3), 199 (4, M^+-NHC_5H_{11}), 181 (7), 171 (5, M^+-$CONHC_5H_{11}$), 143 (13), 129 (17), 97 (12), 43 (100).

(2E,4E,6Z,12Z)-Tetradeca-2,4,6,12-tetraen-8,10-diynoic acid isobutyl amide [11] were colorless oil; uv λ max (Et$_2$O) nm 366sh, 348, 335sh, 277, 264; ir ν max (CCl$_4$) cm^{-1} (11+12) 3444m, 3317w, 2952s, 2919s, 2865m, 1669s, 1615s, 1497s, 1462m, 1431w, 1382w, 1362m, 1335w, 1315w, 1267m, 1179m, 1136m, 996s, 958w, 880w, 710w; ms see data for 12.

(2E,4E,6E,12Z)-Tetradeca-2,4,6,12-tetraen-8,10-diynoic acid isobutyl amide [12] were colorless oil; uv λ max (Et$_2$O) nm 368, 348, 333sh, 279, 264; ir see data for 11; ms (containing 30% of the 6Z-isomer 11, 100°, 70 eV, m/z, rel. int. %) 267.162 (16%, M^+, $C_{18}H_{21}NO$ requires 267.1623), 210 (6), 195 (8, M^+-NHC_4H_9), 168 (9), 167 (38, M^+-$CONHC_4H_9$), 165 (31), 153 (33), 152 (30), 149 (19), 141 (17), 139 (14), 115 (19), 43 (100).

(2E,4E,12Z)-Tetradeca-2,4,12-trien-8,10-diynoic acid isopentyl amide [13] were colorless crystals, mp 83-85°; uv λ max (Et$_2$O) nm 282, 266, 252; ir ν max (CCl$_4$) cm^{-1} 3441m, 3303m, 2952s, 2922s, 2864m, 2230w, 1670s, 1636s, 1612m, 1498s, 1463w, 1432w, 1398w, 1382w, 1362m, 1317m, 1246m, 1163w, 1136w, 993s, 946w, 920w, 861w, 713w; ms (100°, 70 eV, m/z, rel. int. %) 283.194 (15%, M^+, $C_{19}H_{25}NO$ requires 283.1936), 141 (12), 129 (13), 103 (33, $C_8H_7^+$), 77 (53), 43 (100).

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