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AMIDES AND OTHER CONSTITUENTS FROM *ACMELLA CILIATA*

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Key Word Index—*Acmella ciliata*; Compositae; amides; unbranched olefinic hydrocarbons; sesquiterpenes.

Abstract—Fourteen highly unsaturated amides were isolated from *Acmella ciliata*. Their structures were determined by means of high field ^{1}H NMR including 2D-NMR, high resolution mass spectrometry and GC-MS. Some considerations on the biosynthesis of the amides are made.

INTRODUCTION

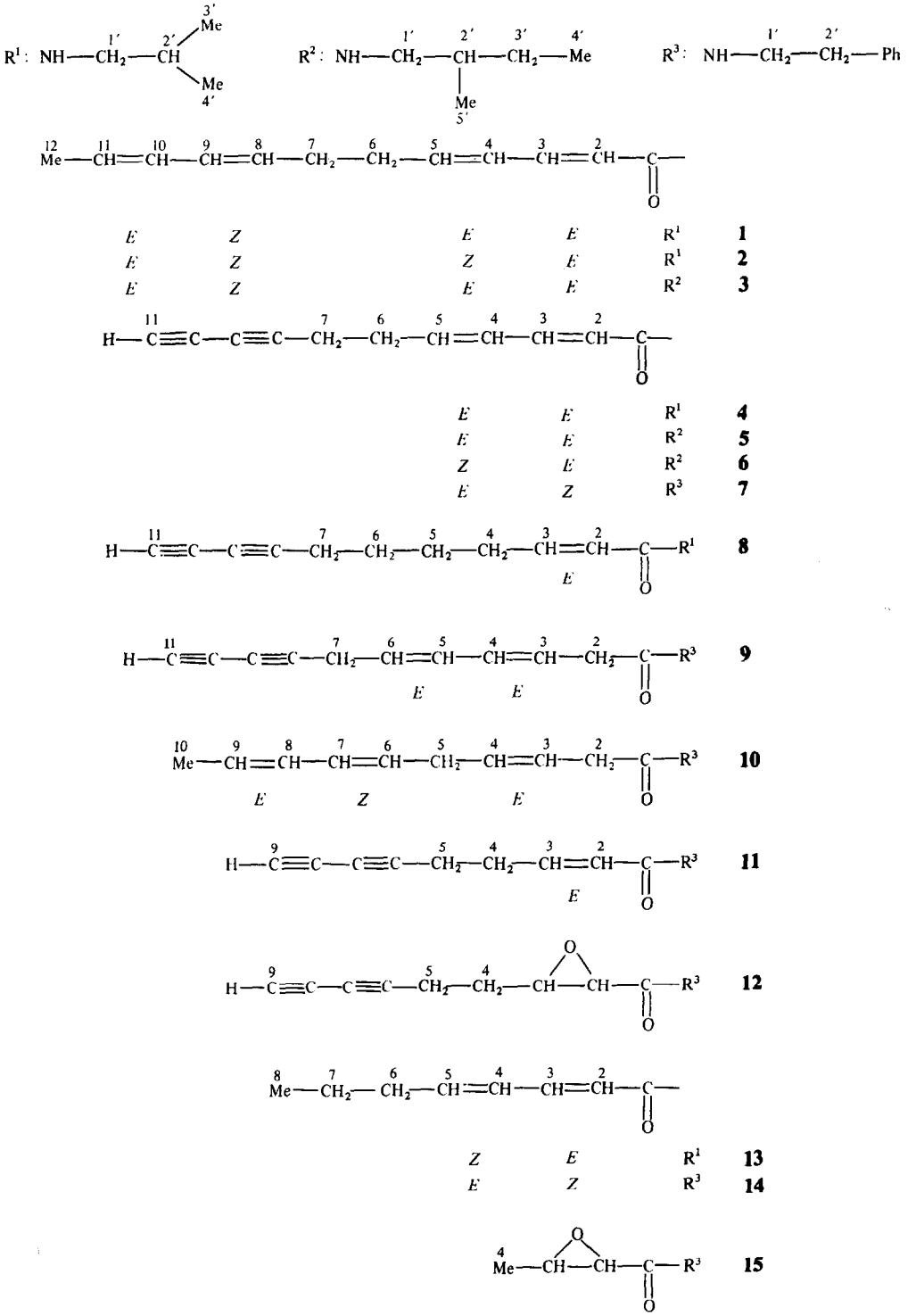
In a previous paper [1] we reported the occurrence of spilanthol and closely related amides in the flower heads of *Acmella ciliata* (H.B.K) Cass. From the same source we isolated 14 more amides, most of them with new structures. Additionally we investigated the essential oil of the total aerial parts by GC-MS. From the roots scopoletin was isolated.

RESULTS AND DISCUSSION

Isolation of pure compounds from the amide fraction extracted from the flower heads was difficult but could be achieved by combination of low and high pressure LC [1, 2]. This method revealed, in addition to amides reported previously [1], compounds **1** through **14**. Structure **1**, already known from different plants (*vide infra*), was deduced by comparing its ^{1}H NMR spectrum with literature data [3] and confirmed by a proton–proton correlated COSY experiment. The latter method is very helpful for the structure elucidation of such compounds since it makes difficult spin decoupling experiments unnecessary and requires considerably less amounts of compound than ^{13}C NMR [4, 5]. The mass spectra of **1** and **2** were nearly identical and exhibited the characteristic fragment with *m/z* 81 accompanied by *m/z* 167 due to cleavage between C-7 and C-8. This resembles the analogue behaviour of the spilanthic acid amides [1]. The high intensity of both peaks is explainable by the fact that the C-6/C-7 bond is in an allylic position to both double bonds C-4/C-5 and C-8/C-9. Since *m/z* 161 represents the fragment containing the amine moiety and an additionally transferred hydrogen, it is replaced by the homologue fragment with *m/z* 181 in the spectrum of **3**.

While structures **4** through **7** were easily deduced from both ^{1}H NMR and mass spectra, the determination of **8** made it necessary to irradiate the signals of H-4 and H-7 which always simplified the multiplet at δ1.58. The structure was also supported by fragments with *m/z* 91 and *m/z* 63 in the mass spectrum. While *m/z* 91 most probably represents the part of the molecule C-5 to C-11 due to cleavage in an allylic position to the α-double bond, *m/z* 63 is caused by cleavage in the 'allylic' position to the diyn-system. This could be proven by high resolution of *m/z* 63 in the spectra of **11** and **12** which gave the molecular formula C_5H_3. Since this fragment can be observed in the mass spectra of all diynamides presented here, it appears to be of general significance for these structures. In **9**, the formation of this fragment may be preceded by isomerization of the acid part to that of **4**. The ^{1}H NMR spectrum of **9** was characterized by two broad doublets of methylene groups at δ2.98 and δ3.10. Clear assignments were possible after irradiation of both which always caused the appropriate olefinic signals to change to doublets. The disappearence of the triplet sub-structure at δ2.05 (H-11) upon irradiation at δ3.10 allowed the distinction of both methylene groups. The acid moiety of **9** thus represents a positional isomer to that of **4**. Similarly, compound **10** is a positional isomer of the already reported spilanthic acid 2-phenylethylamide [1]. This structure could only be elucidated by careful comparison of the ^{1}H NMR spectra of the two isomers, for which the signals of H-6 through H-10 and H-1′ through H-3′/4′ were nearly identical. A special difficulty was caused by the partial overlapping of the signals of H-2/H-5 and H-3/H-4 which made a normal spin decoupling impossible. This problem was overcome by irradiation at δ2.89 which affected both methylene groups together and simplified the signals of H-3/H-4 to an AB-system showing a coupling constant of 15 Hz. Based on this information, an interpretation according to first order of all involved signals was possible (Table 1). A further support for this unusual structure is lent by the mass spectrum that exhibited a peak at *m/z* 163 which is not present in the corresponding spectrum of the isomeric spilanthic acid 2-phenylethylamide. This fragment may be formed by McLafferty rearrangement and is similar to a fragmentation pathway already proposed for an amide from the Piperaceae [6].

Although structure **11** easily resulted from the ^{1}H NMR and mass spectrum, structure elucidation of the related epoxide **12** caused difficulties because its ^{1}H NMR mainly displayed signals not known from the other amides. High resolution of the molecular peak in the mass spectrum indicated the presence of two oxygens while in the ^{1}H NMR no olefinic signals were visible. This led, together with the calculation of the double bond equivalents, to the conclusion of an epoxide-structure. The signals in the ^{1}H NMR could only be assigned after nearly



complete spin decoupling. Because C-2 and C-3 represent chiral centres, the protons at C-4 were not magnetically equivalent. However, the most striking fact was the non-equivalence of both protons at C-1′. Their signals could be assigned after irradiation of the N–H proton. This non-equivalence might be an effect of the chirality of C-2 and C-3, the magnetic anisotropy of the epoxy ring, a hindered rotation of the amide bond or the existence of H-bridges between protons of the amine part with the epoxy oxygen. To confirm the structure and make it more easy to determine the reason for this behaviour, the partial structure **15** was synthesized by epoxidation of crotonic acid phenylethylamide (*E*-configuration checked by ^{1}H NMR) with *m*-chloroperbenzoic acid. The protons at

Table 1. ^{1}H NMR spectral data of compounds **1–15** (250 MHz; $CDCl_3$; TMS int. stand.)

H No.	1	2	3
2	5.77 *d* (15)	5.83 *d* (15)	5.75 *d* (15)
3	7.19 *dd* (15; 9.5)	7.54 *dd* (15; 11.5)	7.19 *dd* (15; 9.5)
4	6.17 *dd* (9.5; 15)	6.11 *dd* (11.5; 11.5)	6.17 *dd* (9.5; 15)
5	6.07 *dt* (15; 6)	5.78 *dt* (11.5; 7)	6.07 *dt* (15; 6)
6	} 2.27 *m*	2.41 *br dt* (7; 7)	} 2.27 *m*
7		2.29 *br dt* (7; 7)	
8	5.26 *dt* (11; 7)	5.26 *dt* (11; 7)	5.26 *dt* (11; 7)
9	5.97 *dd* (11; 10)	5.98 *dd* (11; 10)	5.97 *dd* (11; 10)
10	6.3 *br dd* (10; 15)	6.3 *br dd* (10; 15)	6.3 *br dd* (10; 15)
11	5.7 *dq* (15; 6.5)	5.7 *dq* (15; 6.5)	5.7 *dq* (15; 6.5)
12	1.79 *d* (6.5)	1.78 *d* (6.5)	1.78 *d* (6.5)
1′	3.17 *dd* (6.5; 6.5)	3.18 *dd* (6.5; 6.5)	3.22 *m*
2′	1.8 *tqq* (6.5; 7; 7)	1.78 *tqq* (6.5; 7; 7)	*
3′	} 0.93 *d* (7)	} 0.93 *d* (7)	1.18/1.4 *m*
4′			0.91 *t* (7)
5′	—	—	0.91 *d* (6.5)

H No.	4	5	6
2	5.81 *d* (15)	5.8 *d* (15)	5.87 *d* (15)
3	7.19 *dd* (15; 10)	7.2 *dd* (15; 10)	7.5 *dd* (15; 11)
4	6.21 *dd* (10; 15)	6.21 *dd* (10; 15)	6.18 *dd* (11; 11)
5	6.05 *dt* (15; 6.5)	6.05 *dt* (15; 6.5)	5.82 *dt* (11; 7)
6	} 2.4 *m* (2 lines)	} 2.4 *m* (2 lines)	2.56 *br dt* (7; 7)
7			2.38 *dt* (7; 1)
8	—	—	—
9	—	—	—
10	—	—	—
11	1.99 *br s*	1.98 *br s*	1.98 *t* (1)
12	—	—	—
1′	3.17 *dd* (7; 6.5)	3.23 *m*	3.24 *m*
2′	1.81 *tqq* (6.5; 7; 7)	*	*
3′	} 0.93 *d* (7)	*	*
4′		0.91 *t* (7)	0.92 *t* (7)
5′	—	0.91 *d* (6.5)	0.92 *d* (7)

H No.	7	8	9
2	5.45 *d* (11.5)	5.78 *dt* (15; 1.5)	2.98 *br d* (7)
3	6.37 *dd* (11.5; 11.5)	6.81 *dt* (15; 7)	5.67 *dt* (15; 7)
4	7.48 *dd* (11.5; 15.5)	2.2 *ddt* (1.5; 7; 7)	6.10 *br dd* (15; 10)
5	5.98 *dt* (15.5; 6.5)	} 1.58 *m*	6.26 *ddt* (10; 15; 1.5)
6	} 2.4 *m*		5.58 *dt* (15; 6)
7		2.28 *dt* (1; 6.5)	3.10 *br d* (6)
8	—	—	—
9	—	—	—
10	—	—	—
11	1.99 *br s*	1.98 *t* (1)	2.05 *t* (1)
12	—	—	—
1′	3.58 *dt* (6.5; 7)	3.16 *dd* (7; 6.5)	3.51 *dt* (6.5; 7)
2′	2.86 *t* (7)	1.78 *tqq* (6.5; 7; 7)	2.8 *t* (7)
3′	†	} 0.93 *d* (7)	†
4′	—		—
5′	—	—	—

H No.	10	11	12
2	2.91 *d* (6)	5.78 *d* (15)	3.51 *d* (5)
3	5.48 *dt* (15; 6)	6.81 *dt* (15; 7)	3.25 *ddd* (5; 5; 7.5)
4	5.58 *dt* (15; 5.5)	} 2.41 *m*	1.43/1.65 *m*
5	2.88 *dd* (5.5; 7.5)		2.34 *ddd* (7; 7; 1)

Table 1. (*Continued*)

H No.	10	11	12
6	5.22 *dt* (10.5; 7.5)	—	—
7	6.01 *dd* (10.5; 10.5)	—	—
8	6.28 *br dd* (10.5; 15)	—	—
9	5.73 *dq* (15; 7)	1.99 *br s*	2.02 *t* (1)
10	1.79 *br d* (7)	—	—
11	—	—	—
12	—	—	—
1′	3.51 *dt* (7; 7)	3.6 *dt* (6.5; 7)	3.69/3.51 *m*
2′	2.8 *t* (7)	2.86 *t* (7)	2.85 *m*
3′	†	†	†
4′	—	—	—
5′	—	—	—

H No.	13	14	15
2	5.82 *d* (15)	5.39 *d* (11.5)	3.16 *d* (2)
3	7.57 *dd* (15; 11.5)	6.36 *dd* (11.5; 11.5)	2.89 *dq* (2; 5)
4	6.1 *br dd* (11.5; 10.5)	7.43 *dd* (11.5; 15)	1.36 *d* (5)
5	5.79 *dt* (10.5; 8)	5.96 *dt* (15; 7)	—
6	2.29 *br dt* (8; 7.5)	2.16 *br dt* (7; 7.5)	—
7	1.44 *tq* (7.5; 7.5)	1.46 *tq* (7.5; 7.5)	—
8	0.89 *t* (7.5)	0.89 *t* (7.5)	—
9	—	—	—
10	—	—	—
11	—	—	—
12	—	—	—
1′	3.18 *dd* (6.5; 7)	3.58 *dt* (6.5; 7)	3.5 *m*
2′	1.8 *tqq* (7; 7; 7)	2.86 *t* (7)	2.8 *br dd* (7; 7)
3′	} 0.93 *d* (7)	†	†
4′	}	—	—
5′	—	—	—

Chemical shifts in δ-values (ppm); numbers in parentheses are coupling constants in Hz; NH always between $\delta 5$ and $\delta 6.5$, caused one coupling constant given for H-1′; the signals are interpreted according to first order.

*Not assigned.

†Phe: 7.25 *m*.

C-1′ of this compound were obviously also non-equivalent. The ^{1}H NMR in deuteriotoluene at 100° clearly showed no remarkable influence of temperature on the appearence of the multiplet of both protons which nearly excludes the above mentioned hindered rotation or H-bridges as the reason for the effect. So this problem remains unsolved. However, comparing the coupling constants of the epoxy-protons in **12** and **15** allows the determination of the relative configuration of C-2 and C-3 in **12**. $J_{2,3}$ in **15** was only 2 Hz, the respective coupling constant in **12** was 5 Hz. Since **15** was of the *trans*-configuration due to synthesis from the *E*-olefin, **12** must therefore be *cis*-configurated. Thus it represents the α-epoxide corresponding to the 2*Z*-isomer of **11**.

Compounds **13** and **14** posess acid parts with only eight carbons. Since this chain length has only been found in amides from fungi [7], at the present time they represent the most chain-shortened derivatives of oleic acid with amide structures in higher plants.

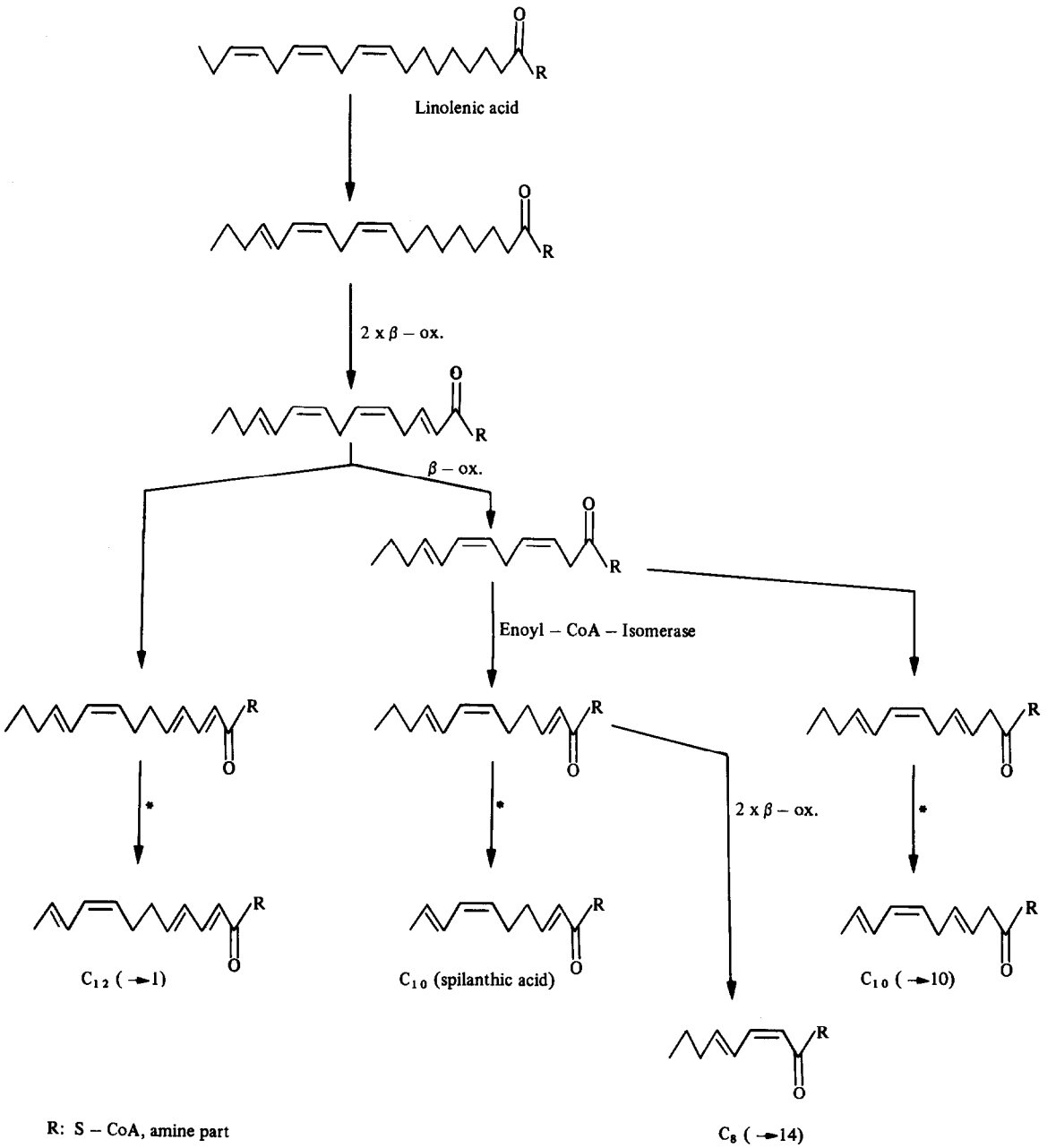
The steam distillate of the aerial parts was separated into hydrocarbons and oxygenated compounds by CC using silica gel and *n*-hexane followed by dichloromethane as eluents. Both fractions were submitted to GC-MS analysis. Humulene and caryophyllene were identified by their mass spectra which were identical with literature data [8] and by comparing their GC R_ts with those of authentic samples. Four peaks of the gas chromatogram gave mass spectra with molecular peaks at *m/z* 208, *m/z* 210, *m/z* 236 and *m/z* 238 with fragmentation patterns which proved them to be straight chain olefins. However, because of double bond migration, both the position and the *Z/E* isomerism of such olefins normally cannot be deduced from standard mass spectra using EI. Thus we tentatively identified them as pentadeca-1,8*Z*-diene, pentadeca-1-ene, heptadeca-1,8*Z*-diene and heptadeca-1-ene, respectively. They may well be derived from palmitoleic, palmitic, oleic and stearic acid by decarboxylation and dehydrogenation [9]. The structure of heptadeca-1,8*Z*-diene could be corroborated by its identical GC R_t with an authentic sample synthesized from oleic acid [10], which was not identical to the 8*E*-isomer synthesized from elaidic acid. Pentadeca-1-ene, that makes up *ca* 50% of the hydrocarbon fraction as shown by GC, is also reported to occur in *Spilanthes alba* [3]. In *Spilanthes oleracea* a hydrocarbon with M_r 210 has been reported and named 'spilanthen' [11]. This spilanthen might be identical with

pentadeca-1-ene, since the genus *Spilanthes* is very closely related to *Acmella* [12, 13]. Additionally, several spectra of sesquiterpenes which could not be identified, were obtained. The presence of considerable amounts of caryophyllene epoxide in the oxygenated fraction was proven by comparing the mass spectrum and the R_t with that of a synthesized sample.

Scopoletin from the roots was identified after separation from an extract by comparing the ^1H NMR with that of an authentic sample and by the fact that the UV spectra were identical both before and after addition of NaOMe. This excluded isoscopoletin as a possible structure.

It should be mentioned that all parts of *A. ciliata* obviously contain amides as can be shown by the tongue numbing effect which they produce when chewed [14]. However, this effect is much stronger with the flower heads.

The collection of 20 amides which we investigated in *A. ciliata* enables us to draw some conclusions as to their chemotaxonomy and biosynthesis. The acetylenic amides indicate a clear relationship to the amides from *Spilanthes alba* [3], *Echinacea angustifolia* and *E. purpurea* [15, 16]. However, the diyn-amides with terminal Me groups which correspond biogenetically to those with terminal hydrogen [17], seem to be present only there and could not be found in *A. ciliata*. Also the co-occurrence of **1** in the above mentioned plants is a clear indication for their



Scheme 1. Proposed biosynthetic pathway for polyenic amides from *Acmella ciliata*. *See ref. [17].

taxonomical relationship although it is worth mentioning, that the same compound has also been found in *Asiasarum heterotropoides* Maek. var. heterotropoides Maek., a member of the Araliaceae [5]. The co-existence of the isomeric acid parts in compounds **1** through **3** and **4** through **7** in the same plant shows, that isomerization of double bonds can take place very easily. Nevertheless, the presence of a *Z*-configurated double bond always at the same distance from the end of the acid chain in compounds **1**, **2**, **3**, **10** and spilanthic acid deserves special interest. In our opinion, this can be explained by a biosynthesis starting with linolenic acid according to Scheme 1. With the exception of the isomerization of linolenic acid to the olefin with conjugated double bonds which is known as a partial step in the formation of olefinic hydroperoxides [18], this scheme mainly requires enzymes of the primary metabolism. The terminal chain shortening has already been proven for analogous diynamides [13]. Since amide **10** most probably contains the 9Z-double bond of linoleic acid in the isomerized *E*-configuration, this structure gives support for the proposed pathway.

EXPERIMENTAL

For identification of the plant and isolation of the amides see ref. [1]. Yields were 10 mg for **1** and between 1 and 3 mg for **2** through **14**, starting from 180 g of fresh flower heads.

*GC of heptadeca-*1,9*Z-diene and heptadeca-*1,9*E-diene.* Column OV 101 fused silica 25 m; carrier gas N_2 0.8 bar; injector 230°; detector FID 250°; initial temp. 170°/5 min then programmed at 2°/min., R_ts: 15.17 min. (9*Z*-isomer), 15.37 min. (9*E*-isomer).

The following mass spectra were by EI at 100 eV, direct inlet and are given in the form *m/z* (rel. int). *Dodeca-*2E,4E,8Z,10E*-tetraenoic acid isobutylamide* (**1**). Mass spectrum nearly identical with that of (**2**). *Dodeca-*2E,4Z,8Z,10E*-tetraenoic acid isobutylamide* (**2**). 247.1940 $[M]^+$ (11) ($C_{16}H_{25}NO$, requires: 247.1936), 175 (3) $[M-R^1]^+$, 167.1308 (96) ($C_{16}H_{17}NO$, requires: 167.1310), 128.1078 (17), ($C_7H_{14}NO$, requires: 128.1075), 81 (100), 57 $[i\text{Bu}]^+$ (73). *Dodeca-*2E,4E,8Z,10E*-tetraenoic acid 2-methylbutylamide* (**3**). 261.2108 $[M]^+$ (6) ($C_{17}H_{27}NO$, requires: 261.2093), 232 $[M-Et]^+$ (1), 181 (67), 142 (10), 81 (100), 71 [2 − MeBu]$^+$ (30). *Undeca-*2E,4E*-dien-*8,10*-diynoic acid isobutylamide* (**4**). 229 $[M]^+$ (28), 214 $[M-Me]^+$ (5), 157 $[M-R^1]^+$ (100), 128 (56), 63 (17), 57 $[i\text{Bu}]^+$ (30). *Undeca-*2E,4E*-dien-*8,10*-diynoic acid 2-methylbutylamide* (**5**). 243 $[M]^+$ (36), 228 $[M-Me]^+$ (4), 214 $[M-Et]^+$ (4), 157 $[M-R^2]^+$ (100), 128 $[M-R^2-CO-H]^+$ (39), 71 [2 − MeBu]$^+$ (54), 63 (11), 57 (73). *Undeca-*2E,4Z*-dien-*8,10*-diynoic acid 2-methylbutylamide* (**6**). 243 $[M]^+$ (47), 242 (58), 228 (14), 214 (8), 157 (63), 128 (100), 71 (17), 63 (23), 57 (23). *Undeca-*2Z,4E*-dien-*8,10*-diynoic acid 2-phenylethylamide* (**7**). 277.1472 $[M]^+$ (25) ($C_{19}H_{19}NO$, requires: 277.1467), 214 (41), 200 (58), 157 $[M-R^3]^+$ (70), 129 $[M-R^3-CO]^+$ (73), 128 (100), 105 (90), 104 $[R^3-H]^+$ (72) (McLafferty), 63 (34). *Undeca-*2E*-en-*8,10*-diynoic acid isobutylamide* (**8**). 231 $[M]^+$ (17), 216 $[M-Me]^+$ (10), 159 $[M-R^1]^+$ (18), 131 $[M-R^1-CO]^+$ (58), 91 (100), 63 (35), 57 $[i\text{Bu}]^+$ (45). *Undeca-*3E,5E*-dien-*8,10*-diynoic acid 2-phenylethylamide* (**9**). 277 $[M]^+$ (2), 105 $[R^3]^+$ (100), 91 (29), 63 (12). *Deca-*3E,6Z,8E*-trienoic acid 2-phenylethylamide* (**10**). 269 $[M]^+$ (67), 202 (12), 187 (21), 163 (13) (McLafferty), 105 $[R^3]^+$ (100), 104 (52), 91 (38), 77 (27). *Nona-*2E*-en-*6,8*-diynoic acid 2-phenylethylamide* (**11**). 251.1317 $[M]^+$ (25) ($C_{17}H_{17}NO$, requires: 251.1310), 131 $[M-R^3]^+$ (100), 104 (66), 91 (18), 77 (29), 63.0228 $[C_5H_3]^+$ (22) (requires: 63.0235) 2,3(c) *Epoxy-nona-*6,8*-diynoic acid 2-phenylethylamide* (**12**). 267.1256 $[M]^+$ (8) ($C_{17}H_{17}NO_2$, requires 267.1259), 238 (13) consisting of 238.0993 $[M-MeN]^+$ ($C_{16}H_{14}O_2$, requires: 238.0994) and 238.1231 $[M-CHO]^+$ ($C_{16}H_{16}NO$, requires: 238.1232), 104 (100), 91 (66), 77 (31), 63.0228 $[C_5H_3]^+$ (53). *Octa-*2E,4Z*-dienoic acid isobutylamide* (**13**). 195.1630 $[M]^+$ (31) ($C_{12}H_{21}NO$, requires: 195.1623), 180 $[M-Me]^+$ (5), 166 $[M-Et]^+$ (3), 139 $[M-i\text{Bu}+H]^+$ (McLafferty) (5), 123.0812 $[M-R^1]^+$ (100) ($C_8H_{11}O$, requires: 123.081), 57 $[i\text{Bu}]^+$ (14). *Octa-*2Z,4E*-dienoic acid 2-phenylethylamide* (**14**). 243.1628 $[M]^+$ (50) ($C_{16}H_{21}NO$, requires: 243.1623), 200.1070 $[M-C_3H_7]^+$ (97) ($C_{13}H_{14}NO$, requires: 200.1075), 123.0815 $[M-R^3]^+$ (100) ($C_8H_{11}O$, requires: 123.081), 105 (26), 104 (26), 91 (15). 2,3(t)-*Epoxy-butyric acid 2-phenylethylamide* (**15**). 205.1103 $[M]^+$ (56) ($C_{12}H_{15}NO_2$, requires: 205.1103), 190 $[M-Me]^+$ (1), 104 (100), 91 (91), 77 (34).

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