96. Stereospecific Syntheses and Spectroscopic Properties of Isomeric 2,4,6,8-Undecatetraenes. New Hydrocarbons from the Marine Brown Alga *Giffordia mitchellae*

Part IV[1])

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Giffordene (= (2Z,4Z,6E,8Z)-2,4,6,8-undecatetraene; **9f**) and five stereoisomers are new $C_{11}H_{16}$ hydrocarbons from the marine brown alga *Giffordia mitchellae*. Their synthesis is based on non-stereoselective *Wittig* reactions of (E)-2-alkenals with appropriate acetylenic phosphoranes and subsequent chromatographic separation of the resulting (E/Z)-pairs. The uniform enynes (> 98% purity) are then stereospecifically reduced to (Z)-alkenes with Zn(Cu/Ag) in aq. MeOH at r.t. ^{13}C- and ^{1}H-NMR data of the new tetraenes are presented. Biosynthetically, giffordene (**9f**) originates from dodeca-3,6,9-trienoic acid *via* an unstable (3Z,5Z,8Z)-1,3,5,8-undecatetraene followed by a thermally allowed antarafacial 1,7-sigmatropic hydrogen shift to the (2Z,4Z,6E,8Z)-isomer **9f**.

Introduction. – Alicyclic and linear $C_{11}H_{14}$ to $C_{11}H_{18}$ hydrocarbons are formed by many plants. Some of them have shown to be mating pheromones and/or release factors for male gametes of several marine brown algae [1] [2]. Due to their intense smell, such compounds are sometimes easily to detect in maturing laboratory cultures. This is particularly true for sporo- and gametophytes of *Giffordia mitchellae*. The species is monoecious and exhibits pronounced chemotactic activities [3].

To collect these odoriferous volatiles from *G. mitchellae*, we used air circulation in a modified 'closed-loop' system for continuous enrichment of these compounds from living cultures [4] [5]. After desorption from the carbon filters (30 µl CH_2Cl_2), the eluates were analyzed by gas chromatography (GC) and mass spectroscopy (MS). Nine compounds were resolved and identified as six isomeric 2,4,6,8-undecatetraenes and three 1,3,5-undecatrienes on the basis of GC/FT-IR, GC/MS, UV, and microhydrogenation [3] (*cf.* below, *Fig. 3*). The exact configuration, however, had to remain open and required unequivocal syntheses of configurationally uniform references.

While conjugated (E/Z)-dienes and trienes are accessible with a plethora of organophosphorus [6], organoboron [7], or transition-metal reagents [8], there is still a need for versatile and efficient approaches to higher unsaturated (E/Z)-polyolefines with controllable and, above all, uniform configuration.

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[1])   *Part III:* [28].

The synthesis and identification of the isomeric 2,4,6,8-undecatetraenes from *G. mit-chellae* and their spectroscopic properties, with particular emphasis on ¹H- and ¹³C-NMR data, are presented.

Synthesis of Acetylenic Intermediates. – *Trienynes.* Based on the experience, that (*E,Z*)-isomers of conjugated enynes may be conveniently separated by chromatography on silica gel, we planned to synthesize in the first instance (*E,Z*)-pairs of acetylenic trienes and dienes. Subsequent reduction of the separated, uniform acetylenes by appropriate methods should then result in a highly flexible, simple, but nonetheless specific route to conjugated tetraenes with complete control of the configuration.

(*E,Z*)-pairs of the acetylenic trienes **3a–d** are obtained by *Wittig* reaction of (2*E*,4*E*)-2,4-hexadienal (**1**) or (2*E*,4*E*)-2,4-heptadienal (**2**) with (2-pentynylidene)- and (2-butynyl-idene)triphenylphosphorane according to *Scheme 1* (BuLi as base). The resulting (*E,Z*)-pairs ((*E*)/(*Z*) *ca.* 1:1) **3a/b** and **3c/d** are readily separated by column chromatography on silica gel using pentane (base-line separation; *cf. Exper. Part*).
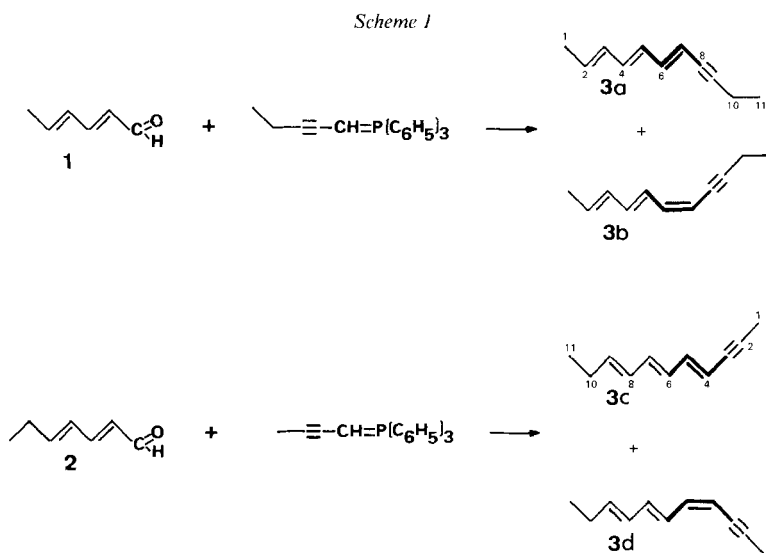

Scheme 1

Dienediynes. The bisacetylenic intermediates **6a–c**, serving as precursors for the synthesis of terminal (*Z*)-olefines, were synthesized from the readily available (*E*)-pent-2-en-4-yn-1-ol [9] as depicted in *Scheme 2* by alkylation of the protected alcohol with RBr(I) [10], deacetalization with MeOH/pyridinium *p*-toluenesulfonate (PPTS), oxidation of the alcohols **4a–c** with MnO₂, and *Wittig* reaction of **5a** or **5b** with (2-butynylidene)- or (2-pentynylidene)triphenylphosphorane. The separation of the resulting (*E/Z*)-pairs was achieved as described for **3a/b** or **3c/d**, but was incomplete in the case of **6a/c** (*ca.* 90% purity for each isomer).

The same sequence also provided a very convenient access to the acetylenes **7** and **8** *(Scheme 3)*, serving as intermediates for a stereospecific synthesis of the two algal pheromones fucoserratene (**10**) [11] and cystophorene (**11**) [12] [27].

Scheme 2

a R = CH$_3$ **b** R = C$_2$H$_5$ **c** R = C$_5$H$_{11}$
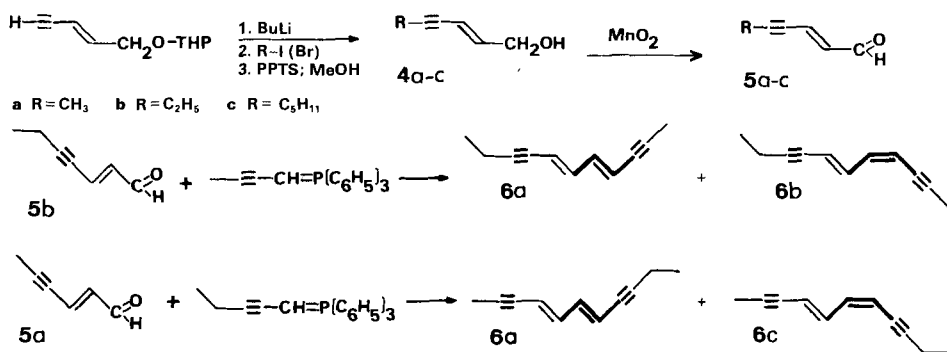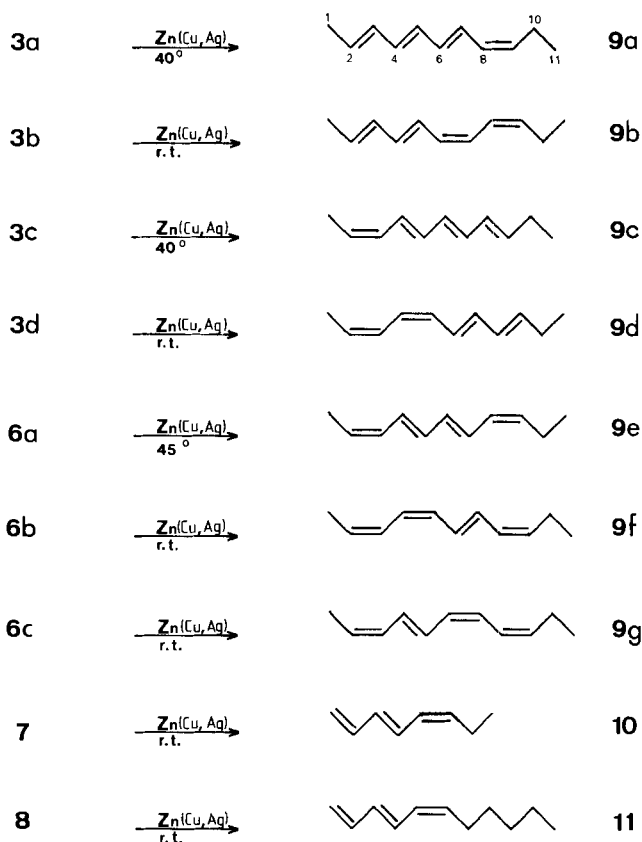
Scheme 3
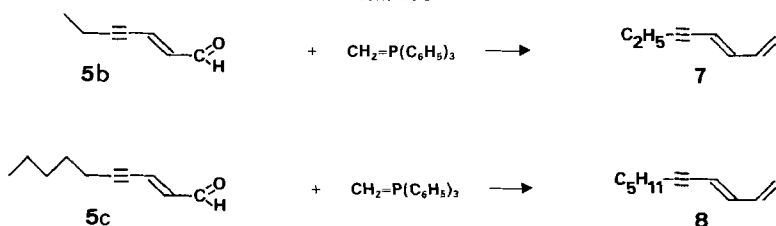
Stereospecific Reduction of Conjugated Alkynes to (Z)-Alkenes. – Due to the high degree of unsaturation and sensitivity of the acetylenes **3a–d** and **6a–c** or the products **9a–g** in particular, the common hydrogenation procedures with *Lindlar*'s catalyst or dicycloalkylboranes failed. Better results were obtained with activated Zn prepared according to recommended procedures [13] [14]. However, reproducible and complete reductions could be achieved at elevated temperatures only (*ca.* 60–80°) which caused extensive isomerization and polymerization of the products. We, therefore, tried various activation procedures and found a successive treatment of the metal with Cu(OAc)$_2$ (10%) and AgNO$_3$ (10%) to be most effective. Using this highly activated metal, the trienynes **3a–d** and the diendiynes **6a–c** were smoothly converted at r.t. into the pure (Z)-tetraenes **9a–g** (maximal temp.: 40°; *Scheme 4*). The same procedure was used for the reduction of **7** and **8** to fucoserratene (**10**) and cystophorene (**11**), respectively.

The (all-*E*)-2,4,6,8-undecatetraene (**9h**) was simply obtained from (*E*)-2-pentenal by *Wittig* reaction with [(2*E*,4*E*)-2,4-hexadienylidene]triphenylphosphorane, which afforded **9h** and **9i** in a ratio of 3:2 (*Scheme 5*).

The olefines **9h/9i** could not be separated by column chromatography, but two recrystallizations of the isomeric mixture from Et$_2$O at $-80°$ yielded **9h** in $>99\%$ configurational purity.

In contrast to *Lindlar*'s catalyst, the system Zn(*Cu/Ag*) does not reduce simple, nonactivated acetylenes. Also α-branched enynes are reduced with difficulties only. On the other hand, common hydrogenation procedures usually fail with such highly unsatu-

Scheme 4

3a	$\xrightarrow[40°]{Zn(Cu,Ag)}$		9a
3b	$\xrightarrow[r.t.]{Zn(Cu,Ag)}$		9b
3c	$\xrightarrow[40°]{Zn(Cu,Ag)}$		9c
3d	$\xrightarrow[r.t.]{Zn(Cu,Ag)}$		9d
6a	$\xrightarrow[45°]{Zn(Cu,Ag)}$		9e
6b	$\xrightarrow[r.t.]{Zn(Cu,Ag)}$		9f
6c	$\xrightarrow[r.t.]{Zn(Cu,Ag)}$		9g
7	$\xrightarrow[r.t.]{Zn(Cu,Ag)}$		10
8	$\xrightarrow[r.t.]{Zn(Cu,Ag)}$		11

Scheme 5

$$\text{(aldehyde)} + \text{(ylide =P(C}_6\text{H}_5)_3) \longrightarrow \textbf{9h} + \textbf{9i}$$

9i $\xrightarrow[\text{–80°}]{\text{crystallization,}}$ > 99% **9h**
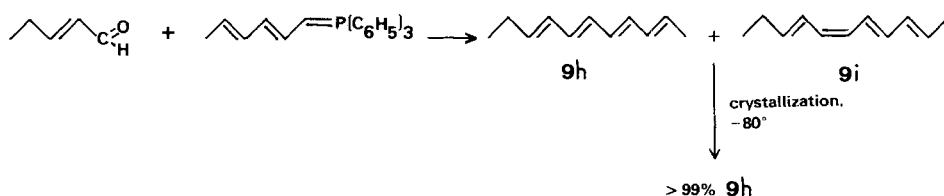
rated substrates where $Zn(Cu/Ag)$ works best. Thus, the newly developed reduction of enynes with $Zn(Cu/Ag)$ extends the widely used catalytic reduction of triple bonds to medium and highly unsaturated polyolefines. Various functional groups like alcohols, ethers, esters, or ketones remain unaffected under the assigned conditions [13].

^{13}C- and ^{1}H-NMR Spectroscopy of the Tetraenes 9a–h and Acetylenic Intermediates 3a–d and 6a–c. – a) *Assignments.* The 400-MHz ^{1}H-NMR spectra of the tetraenes and (bis)acetylenic olefines provide sufficient resolution for the assignment of the H-atoms in
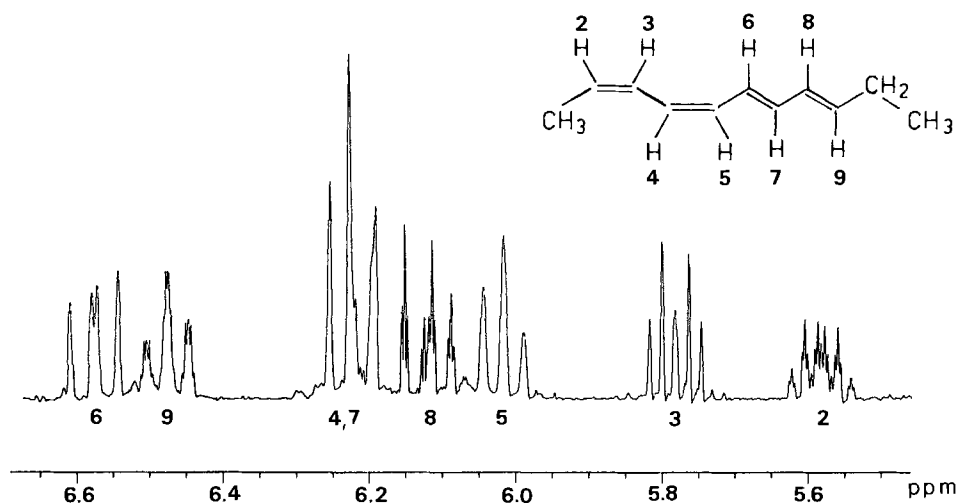
Fig. 1. *Olefinic part of the 400-MHz ^{1}H-NMR spectrum of* (CDCl$_3$) *of* (*2 Z,4 Z,6 E,8 E)-2,4,6,8-undecatetraene* **(9d**; 0.2M)
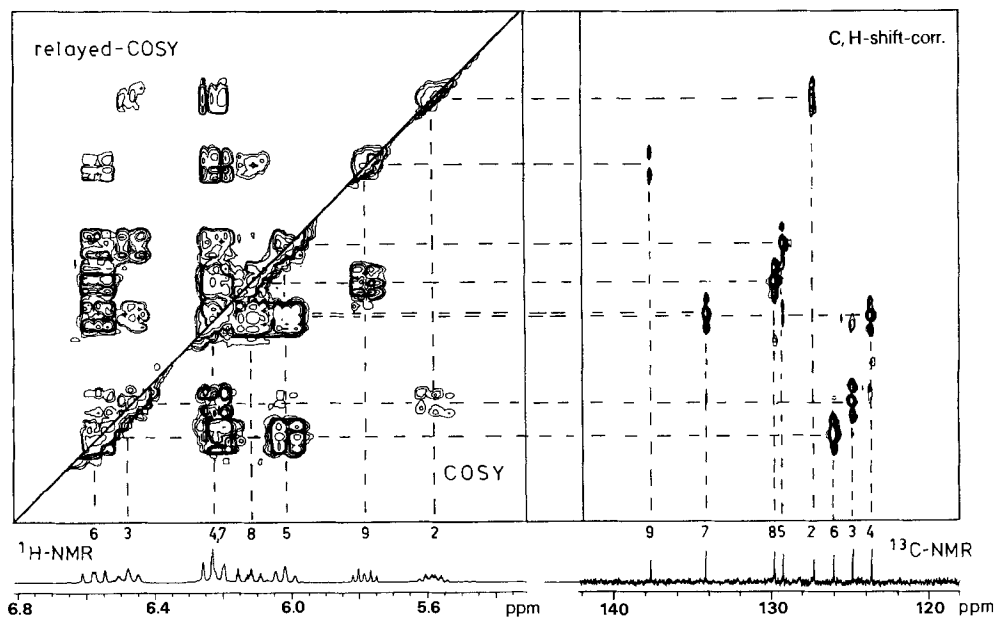

Fig. 2. *2D-NMR spectra* (CDCl$_3$) *of* (*2 Z,4 Z,6 E,8 E)-2,4,6,8-undecatetraene* (**9d**; 0.2M). The COSY and relayed COSY spectra (left part) give the assignment of the protons; the C,H-shift correlation (right part) identifies then the C-atoms.

the olefinic region (see *Fig. 1* for **9d**). Further correlation is evident from the COSY and relayed COSY [15] spectra as well as from C,H correlations [16] (see *Fig. 2* for **9d**). The results are compiled in *Tables 1* and *2*.

Table 1. ^{13}C-NMR Chemical Shifts (ppm; TMS, CDCl$_3$) of the Tetraenes **9a–h** and their Acetylenic Precursors **3a–d** and **6a/b**[a])

Compound[b])[c])	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)
9h (E,E,E,E)	18.33	129.41	131.95	130.63[d])	(132.31)	(132.48)	130.83[d])	129.63	136.54	25.86	13.56
9a (E,E,E,Z)	18.29	129.82	131.83	(130.54)	(132.67)	(132.91)	127.42	128.10	134.03	21.13	14.20
9c (Z,E,E,E)	13.52	126.35	129.67	127.26	(133.08)	(132.66)	(130.89)	129.59	136.98	25.90	13.52
3a (E,E,E,T)	18.40	131.49	131.58	134.35	129.57	140.76	110.74	79.70	94.70	13.30	13.80
3c (T,E,E,E)	4.56	88.85	79.43	110.65	140.82	129.74	134.57	129.19	138.56	25.90	13.41
9b (E,E,Z,Z)[e])	18.40	130.42	132.01	133.99	125.60	129.24	123.70	123.14	134.81	20.90	14.20
9d (Z,Z,E,E)	13.21	127.08	124.67	123.50	129.08	125.86	134.06	129.63	137.51	25.88	13.47
3b (E,E,Z,T)	18.48	131.54	131.89	135.16	127.56	138.90	108.73	77.41	98.50	13.02	14.04
3d (T,Z,E,E)	4.66	92.56	77.23	108.66	139.06	127.74	135.39	129.48	138.71	25.90	13.38
9e (Z,E,E,Z)	13.52	126.76	129.68	127.90[d])	(132.67)	(132.83)	(128.10)[d])	128.16	134.49	21.25	14.24
6b (T,Z,E,T)	4.65	93.63[d])	76.82[d])	111.10	137.88	137.49	114.03	79.36[d])	96.39[d])	13.41	13.81
9f (Z,Z,E,Z)	13.22	127.46	124.64	124.11	129.04	127.68	128.96	128.16	135.03	21.25	14.23

[a]) Values in brackets are not clearly assigned.
[b]) T = triple bond; E = (E)-alkene; Z = (Z)-alkene.
[c]) Compounds **6c** and **9g** were not measured because of insufficient purity.
[d]) These chemical shifts may be reversed.
[e]) Assignment of the chemical shifts for the unstable (E,E,Z,Z)-compound **9b** was made by analogy to **9d** (Z,Z,E,E).

Table 2. ^1H-NMR Chemical Shifts (ppm; TMS, CDCl$_3$) of the Tetraenes **9a–h** and their Acetylenic Precursors **3a–d** and **6a/b**[a])

Compound [b])[c])	H-Atom at										
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)
9h (E,E,E,E)	1.765	5.685	(6.08)	(6.12)	(6.15)	(6.15)	(6.12)	(6.06)	5.725	2.109	0.999
9a (E,E,E,Z)	1.773	5.707	(6.09)	(6.17)	(6.17)	(6.17)	6.449	5.984	5.416	2.200	0.955
9c (Z,E,E,E)	1.769	5.490	6.046	6.475	(6.20)	(6.20)	(6.20)	(6.09)	5.751	2.122	1.009
3a (E,E,E,T)	1.765	5.742	(6.05)	(6.20)	(6.13)	6.483	5.496	–	–	2.326	1.145
3c (T,E,E,E)	1.970	–	–	5.511	6.498	(6.12)	(6.21)	(6.04)	5.799	2.119	1.002
9b (E,E,Z,Z)	1.776	5.741	(6.12)	(6.19)	6.548	6.021	(6.19)	6.404	5.493	2.199	0.994
9d (Z,Z,E,E)	1.769	5.581	6.476	(6.23)	6.017	6.576	(6.23)	6.115	5.783	2.128	1.013
3b (E,E,Z,T)	1.783	5.763	(6.15)	(6.25)	6.582	(6.29)	5.347	–	–	2.388	1.190
3d (T,Z,E,E)	2.030	–	–	5.336	(6.31)	6.626	(6.29)	6.146	5.826	2.116	1.015
9e (Z,E,E,Z)	1.775	5.513	6.059	(6.50)	(6.26)	(6.26)	(6.50)	6.005	5.448	2.211	0.983
6b (T,Z,E,T)	2.018	–	–	5.396	6.299	6.996	5.693	–	–	2.358	1.170
9f (Z,Z,E,Z)	1.775	5.601	6.471	6.266	6.073	6.650	6.521	6.013	5.475	2.224	1.006

[a]) Values in brackets are approximations because of signal overlap.
[b]) T = triple bond; E = (E)-alkene; Z = (Z)-alkene.
[c]) Compounds **6c** and **9g** were not measured because of insufficient purity.

The protons at C(2), C(3), C(8), and C(9) of e.g. **9d** (Fig. 1) are readily identified by their multiplicity due to coupling with the terminal Me or Et group, respectively. Only the protons at C(4) and C(7) are not conclusively assigned by COSY and relayed COSY, since even at 400 MHz, there is still substantial overlap of these signals. This is particularly true for π-systems with small structural differentiation like the (2E,4E,6E,8E)-undecatetraene **9h**, where only the H-atoms at C(2), C(3), C(8), and C(9) could be localized.

Using the C,H correlation (Fig. 2), all ^{13}C-NMR signals of the (2Z,4Z,6E,8E)-undecatetraene **9d**, except C(4) and C(7), could be immediately identified. However, since C(4) as part of a (Z)-olefinic moiety should appear at higher field than C(7), its assignment is likewise possible.
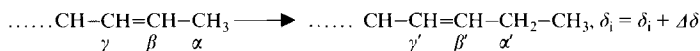
b) *Chemical Shifts*. Many of the tetraenes **9a–h** and their acetylenic precursors **3a–d**, **6a–c** exhibit *retro*-sequences like (E,E,E,T) *vs.* (T,E,E,E) $(T =$ triple bond). In this case, pairs of identical signals for C- and H-atoms of the inner double bonds, *e.g.* C(4) (E,E,E,T) and C(7) (T,E,E,E) or C(5) (E,E,E,T) and C(6) (T,E,E,E) can be expected. This is confirmed by the data of *Table 1*. The same correlation holds for the other *retro*-sequences $(T,Z,E,E)/(E,E,Z,T)$, $(Z,E,E,E)/(E,E,E,Z)$, $(E,E,Z,Z)/(Z,Z,E,E)$ as well as for the symmetrical olefinic moieties in (E,E,E,E) and (Z,E,E,Z). The deviations are generally less than 0.3 ppm for the ^{13}C-, and less than 0.04 ppm for the ^{1}H-NMR. Thus, a significant influence of the terminal Me or Et group on the conformation of the inner π-electron system is excluded.

The chemical shifts of the C- and H-atoms at the two terminal double bonds may be calculated considering the influence of an additional Me group – C(11) – on the chemical shifts of a basic α,ω-dimethyltetraene. In the case of a terminal (E)-olefine, a set of five combinations (for a terminal (Z)-olefine the *retro*-pairs $(E,E,E,Z)/(Z,E,E,E)$, $(E,E,Z,Z)/(Z,Z,E,E)$, and (Z,E,E,Z)) can be used for such a calculation. The results are summarized in the increment system of *Table 3*.

Table 3. *Increments ($\Delta\delta$) for the Chemical Shift of the ^{13}C- and ^{1}H-Atoms in the Positions α, β, and γ of the Tetraenes* **9a–h** *on Replacement of an H-Atom of a Terminal Me Group by a Me Group*[a]

Nucleus	Geometry	$\Delta\delta$ [ppm] (max. deviation)		
		α	β	γ
^{13}C	(E)	+ 7.46 (0.08)	+ 7.12 (0.05)	– 2.33 (0.09)
^{13}C	(Z)	+ 7.61 (0.02)	+ 7.71 (0.03)	– 1.54 (0.03)
^{1}H	(E)	+ 0.346 (0.013)	+ 0.049 (0.01)	– 0.01 (0.01)
^{1}H	(Z)	+ 0.432 (0.004)	– 0.077 (0.012)	– 0.063 (0.01)

[a] The data were calculated by averaging the shift differences of *Table 1* and *Table 2* (*cf.* text). Values for an (E)-alkene result from five, those for (Z)-alkenes from three examples. The ^{13}C-values may be compared to known ^{13}C-increments [17] [18] which do not differentiate between (E)- and (Z)-double bonds.

$$......CH-CH=CH-CH_3 \longrightarrow ...... CH-CH=CH-CH_2-CH_3, \quad \delta_i = \delta_i + \Delta\delta$$
$$\quad\quad\quad\gamma\quad\ \beta\quad\ \alpha \qquad\qquad\qquad\quad \gamma'\quad\ \beta'\quad\ \alpha'$$

The homogeneity of the mean values of *Table 3* clearly underlines, that the conformation of the alkyl group at the first olefinic bond is not affected by the $(E)/(Z)/(T)$ composition of the residual parts of the molecule. However, the significant differences in the γ-increments going from (Z) to (E) at the alkyl-substituted double bond (^{13}C and ^{1}H) may point to a different sterical situation for an Et group at the (Z)-bond compared to the (E)-bond. Similar indications are also reflected in the coupling constants.

Summarizing the above results, it should be possible to calculate increments for inner double bonds useful for identification of unknown polyolefines. The experimental data set is sufficient to do this for central (E)-double bonds; a central (Z)-double bond is not regarded, since no (E,Z,E) sequence is present among **9a–h**.

Based on a ^{1}H-NMR shift of 6.15 ppm for a proton on an inner (E)-double bond with (all-E)-neighbours, *e.g.* **9h**, we observe an increase of *ca.* 0.4 ppm for H–C(α), if the one neighboured double bond has (Z)-geometry. H–C(β) keeps unchanged. The chemical shifts in α-parinaric acid which has a (Z,E,E,Z)-geometry [19] were reproduced well with

these data. Increments for substitution by a triple bond are: for $H-C(\alpha)$, -0.6 ppm; for $H-C(\beta) + 0.4$ ppm. Analogous differences hold for the ^{13}C-NMR signals. Starting with the standard value of *ca.* 132 ppm for C(5) or C(6) of **9h**, a shift of -5.3 ppm for $C(\alpha)$ and $+0.1$ ppm for $C(\beta)$ is observed, if an (E)-double bond is replaced by a (Z)-bond. Replacement by a triple bond shifts $C(\alpha)$ by -22 ppm and $C(\beta)$ by $+8.5$ ppm.

c) *Vicinal Proton Coupling Constants.* Three different types of vicinal coupling constants have to be regarded: the coupling between $-CH=CH-$ (Z), the one between $-CH=CH-$ (E), and the s-*cis* and s-*trans* coupling *via* single bonds. According to *Table 4*, (E)-double bonds exhibit $^3J(H,H)$ couplings in the range of 14.5–15.5 Hz, independent of the geometry of neighboured double bonds. Similarly, (Z)-double bonds elaborate ^3J-values between 10.5 and 11 Hz only. Since the ^3J-values of the single bonds also show very minute alterations between 10.0 and 11.6 Hz, while s-*cis* bonds should give values around 5 Hz [20], a predominant s-*trans* conformation has to be assumed for all stereo-isomers.

Table 4. *Virtual $^3J(H,H)$ Coupling Constants (Hz; 400 MHz, $CDCl_3$) of the Tetraenes **9a–h** and their Acetylenic Precursors **3a–d** and **6a/b**[a])*

Compound[b][c])	$J(1,2)$	$J(2,3)$	$J(3,4)$	$J(4,5)$	$J(5,6)$	$J(6,7)$	$J(7,8)$	$J(8,9)$	$J(9,10)$	$J(10,11)$
9h (E,E,E,E)	6.8	14.9	/	/	/	/	/	14.8	6.8	7.4
9a (E,E,E,Z)	6.9	14.5	(10)	/	/	/	11.2	10.6	7.8	7.6
9c (Z,E,E,E)	7.3	10.5	10.9	(15)	/	/	/	14.8	6.8	7.4
3a (E,E,E,T)	6.8	14.8	10.2	14.5	10.4	15.5	–	...	–	7.5
3c (T,E,E,E)		–	–	15.5	10.6	14.8	10.6	14.7	6.6	7.4
9b (E,E,Z,Z)	7.3	15.3	(11)	(14)	(11)	(11)	10.5	10.8	7.5	7.5
9d (Z,Z,E,E)	7.2	10.9	(11)	(11)	11.3	14.3	10.5	15.0	6.6	7.4
3b (E,E,Z,T)	7.0	14.5	10.6	14.6	(10)	10.7	–	...	–	7.6
3d (T,Z,E,E)	–	–	–	10.6	11.4	14.5	10.6	15.0	6.8	7.4
9e (Z,E,E,Z)	7.3	10.6	(11)	/	/	/	(11)	10.9	7.6	7.6
6b (T,Z,E,T)	...	–	–	10.6	10.6	15.6	–	–	–	7.6
9f (Z,Z,E,Z)	7.2	10.9	(11)	(11)	11.5	14.8	(11)	11.1	7.6	7.5

[a]) In some compounds, a detailed analysis of the coupling constants is impossible without spin simulation. Values in brackets are approximations because of overlapping signals.

[b]) T = triple bond; E = (E)-alkene; Z = (Z)-alkene.

[c]) Compounds **6c** and **9g** were not measured because of insufficient purity.

A larger band-width is observed for $^3J(9,10)$. (E)-Configuration of the neighboured double bond leads to $^3J(9,10) = 6.7$ Hz, while (Z)-geometry causes enlargement to 7.5–7.8 Hz. On the other hand, significantly lower variations are observed for the *same couplings* between $H-C(1)$ and $H-C(2)$ (*cf. Table 4*), $^3J(1,2) = 6.8$–7.3 Hz. In consequence, we assume that in terminal (Z)-olefines, an adjacent Et group more frequently populates those conformations which are outwarded of the plane of the π-electron system.

In general, the ^1H- and ^{13}C-NMR data of the tetraenes **9a–h** are consistent with freely rotating molecules having s-*trans* configuration around all single bonds.

Identification of the Hydrocarbons from *G. mitchellae*. – Sporophyte and predominantly unisexual gametophyte cultures of *G. mitchellae* were grown in enriched natural
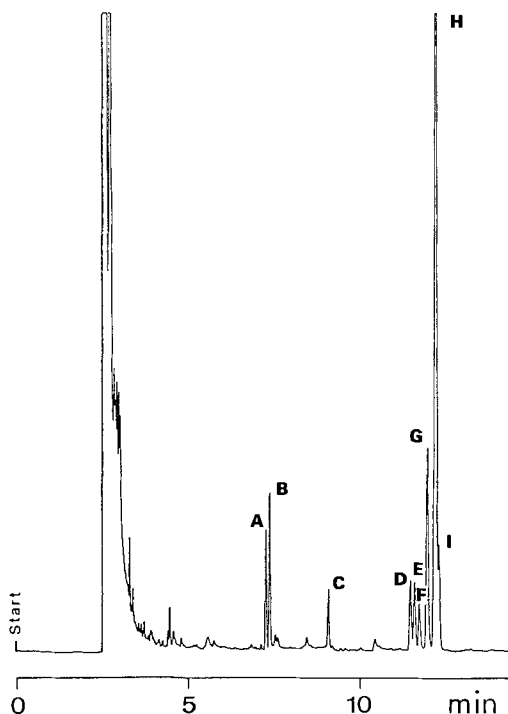
Fig. 3. *GC Analyses of the* Giffordia *hydrocarbons*. Column: fused silica, 50 m × 0.31 mm coated with *SE 30*. Conditions: 110° isotherm; H_2 = 1.2 bar; flame ionization detector (FID) 1 × 32, 220°; sample size 1 µl. Compounds are indexed according to their elution order. For their structural assignment, see *Table 5*.

seawater (*Provasoli-ES;* [21]). Volatiles containing compounds **A–M** were collected from these cultures over a two-week period by the 'closed-loop-stripping' technique [4] [5] and analyzed by GC and GC/MS. A typical GC with at least nine well resolved compounds is shown in *Fig. 3*.

While **A–C** were readily identified as the previously known (3*E*,5*E*)-1,3,5-undecatriene, (3*E*,5*Z*)-1,3,5-undecatriene, and (3*Z*,5*Z*)-1,3,5-undecatriene [14] [22], respectively, none of the other compounds could be attributed to the known $C_{11}H_{16}$ hydrocarbons from marine brown algae [1]. However, on the basis of GC/FT-IR, microhydrogenation experiments (exclusive product: undecane), and the UV absorption of the major product (λ_{max} = 289, 302, and 316 nm), the compounds **E–M** of *Fig. 3* had to be stereoisomeric 2,4,6,8-undecatetraenes.

Using the synthetic references **9a–h**, unambiguous assignment of the geometrical isomers of the *Giffordia* hydrocarbons was possible by determination of their gas-chromatographic retention indices [3] on two columns of different polarity (*Table 5*).

Of particular importance is the occurrence of (3*Z*,5*Z*)-1,3,5-undecatriene (**C**) [14] which, at low temperature, elutes from the polar column (*OV 17;* 90°) largely in its non-rearranged (3*Z*,5*Z*)-form (*cf. Table 5, Footnote d*). This compound has hitherto not been isolated from natural sources and gives valuable hints on the biosynthesis of giffordene (**9f**).

Table 5. *Identification by GC of Isomeric 2,4,6,8-Undecatetraenes and 1,3,5-Undecatrienes from Giffordia mitchellae*

Compound[a])		Occurence in *Giffordia*	Retention indices[b])	
			SE 30 110°	*OV 17*[c]) 90°
A	(3*E*,5*Z*)-1,3,5-triene	+	1164.2 ± 0.1	1224.2 ± 0.5
			(1164.3 ± 0.1)	n.r.
B	(3*E*,5*E*)-1,3,5-triene	+	1173.5 ± 0.1	1215.9 ± 0.3
			(1173.6 ± 0.1)	(1215.5 ± 0.5)
C[d])	(3*Z*,5*Z*)-1,3,5-triene	+	1217.9 ± 0.10	1275.8 ± 0.3
			(1217.9 ± 0.10)	(1275.5 ± 0.1)
D	(2*E*,4*E*,6*E*,8*E*)	–	1270.2 ± 0.1	1347.3 ± 0.4
			(1270.2 ± 0.1)	
E	(2*E*,4*E*,6*E*,8*Z*)	+	1270.2 ± 0.1	1345.0 ± 0.2
			(1270.2 ± 0.1)	(1345.3 ± 0.2)
F[e])	(2*E*,4*Z*,6*E*,8*Z*)	+	1272.4 ± 0.1	1353.3 ± 0.3
			(1272.4 ± 0.1)	n.r.
G	(2*E*,4*E*,6*Z*,8*Z*)	–	1274.7 ± 0.1	1351.4 ± 0.4
H	(2*E*,4*Z*,6*E*,8*E*)	+	1275.0 ± 0.1	1353.0 ± 0.2
			(1275.1 ± 0.1)	(1352.6 ± 0.4)
I	(2*Z*,4*E*,6*E*,8*Z*)	+	1279.2 ± 0.1	1355.9 ± 0.1
			(1279.2 ± 0.1)	(1355.8 ± 0.2)
J	(2*Z*,4*E*,6*E*,8*E*)	–	1282.8 ± 0.1	1358.4 ± 0.1
K	(2*Z*,4*Z*,6*E*,8*Z*)	+ + +	1283.2 ± 0.1	1362.9 ± 0.2
	(Giffordene)		(1283.2 ± 0.1)	(1362.7 ± 0.3)
L	(2*Z*,4*E*,6*Z*,8*Z*)	–	1284.6 ± 0.1	1363.0 ± 0.3
M	(2*Z*,4*Z*,6*E*,8*E*)	+	1285.1 ± 0.1	1362.9 ± 0.2
			(1285.1 ± 0.1)	(1362.7 ± 0.3)

[a])   Compounds are indexed according to their elution order on *SE 30* (*cf. Fig. 5*).

[b])   *Kováts* indices were determined at properly adjusted isothermal temperature levels as indicated. Values in brackets refer to the natural products.

[c])   The separation on the more polar *OV 17* column is incomplete for the isomeric 2,4,6,8-undecatetraenes. Poorly resolved compounds are indicated as n.r. = not resolved.

[d])   *Kováts* index corresponding to the rearranged (2*Z*,4*Z*,6*E*)-isomer.

[e])   (2*E*,4*Z*,6*E*,8*Z*)-2,4,6,8-undecatetraene (**F**) was prepared by non-stereoselective *Wittig* reaction of **5b** with [(*E*)-but-2-enylidene]triphenylphosphorane.

Biosynthetic Considerations. – Model experiments with the composite *Senecio isatideus*, which produces larger quantities of such algal pheromones [23], evidenced (3*Z*,6*Z*,9*Z*)-3,6,9-dodecatrienoic acid as the immediate precursor to the $C_{11}H_{16}$ hydrocarbons. In the case of linear hydrocarbons, *e.g.* (3*E*,5*Z*,8*Z*)-1,3,5,8-undecatetraene (**14**), a single H-atom from C(5) of the precursor acid is split off (*Scheme 6*), and the activated intermediate stabilizes itself by fragmentation into the conjugated (3*E*,5*Z*,8*Z*)-1,3,5,8-undecatetraene (**14**) and CO_2 [23]. Since giffordene (**9f**) does not posess a vinyl group, this hydrocarbon either is not formed from the same precursor, or, more likely, requires an additional isomerization of a still unknown intermediate not present in the original hydrocarbon blend. In fact, the same basic mechanism would apply for the biosynthesis of giffordene (**9f**), if the newly formed double bond adopts (*Z*)-geometry as depicted in *Scheme 6*. The resulting (3*Z*,5*Z*,8*Z*)-1,3,5,8-undecatetraene (**15**) is unstable (*vide infra*)

Scheme 6

9f Giffordene
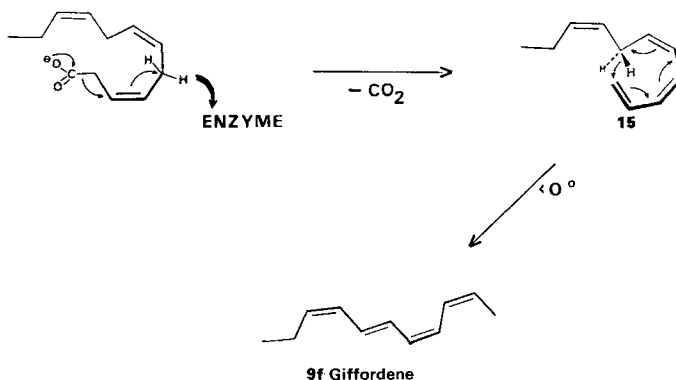
and spontaneously rearranges by a thermally allowed antarafacial 1,7-sigmatropic H-shift [14] to the (2*Z*,4*Z*,6*E*,8*Z*)-2,4,6,8-undecatetraene (**9f**).

This assumption could be confirmed as follows: 1) The structurally related (3*Z*,5*Z*)-1,3,5-undecatriene (**C**) is present among the *Giffordia* hydrocarbons (see *Fig. 3*; precursor: (3*Z*,6*Z*)-dodecadienoic acid). Its limited, but still sufficient thermal stability allows for unambiguous structural assignment by GC. 2) Independent synthesis of the hypothetical intermediate (3*Z*,5*Z*,8*Z*)-1,3,5,8-undecatetraene (**15**) clearly indicates the very pronounced thermal lability of this hydrocarbon. If (2*Z*,5*Z*)-2,5-octadienal is condensed with (2-propenylidene)triphenylphosphorane, only giffordene (**9f**) and (3*E*,5*Z*,8*Z*)-1,3,5,8-undecatetraene (**14**), together with some minor by-products are obtained in roughly equal amounts (*cf. Scheme 7*). Even if the *Wittig* reaction is conducted at 0°, an immediate formation of **9f** is observed (HPLC; UV detection to avoid thermal stress of the compounds). Thus, the assumption of an (3*Z*,5*Z*,8*Z*)-1,3,5,8-undecatetraene intermediate in the biosynthesis of giffordene (**9f**) is justified.

Scheme 7
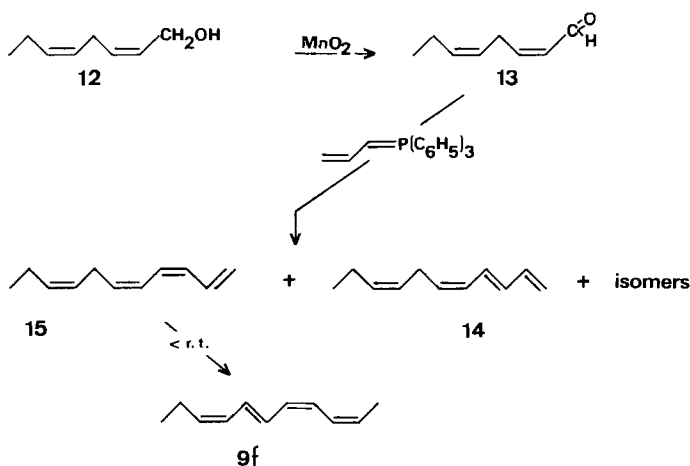
The other isomeric tetraenes of *Fig. 3* probably derive from **9f** by simple isomerization, caused by illumination of the cultures, since pure samples of **9f** show a similar isomer distribution after brief exposure to sunlight.

Biological Activity of the Isomeric 2,4,6,8-Undecatetraenes. – All compounds of *Table 5* were assayed with male gametes of *G. mitchellae* according to the previously described droplet test [24] [29]. In no case, however, biological activity could be recognized. The same observation was made with conventional solvent extracts of the culture medium. Since, on the other hand, male gametes of *G. mitchellae* exhibit very pronounced chemotactic activity in the presence of their conspecific females [3], the chemical nature of the involved pheromone is still open.

Experimental Part

1. *General.* Solvents and reagents were purified prior to use. Anh. MgSO$_4$ was used for drying operations. Solns. were generally concentrated by flash evaporation under reduced pressure. CC = Column chromatography. Anal. GC: *Carlo-Erba* gas chromatograph, series *4200,* equipped with fused-silica capillaries, *SE 30* (50 m × 0.31 mm), *OV 17* (25 m × 0.31 mm). M.p.: *Kofler* block; like b.p., not corrected. UV (nm): *Cary 14.* IR (cm^{-1}): *Pye-Unicam-SP3-200* spectrophotometer. ^{1}H-NMR: *Bruker AC 80* and *Bruker AM 300,* if not noted otherwise. MS (*m/z*): *Finnigan 4510* GC/MS system.

2. *NMR Measurements.* The NMR of **9a–h, 3a–d,** and **6a–c** were obtained with a *JEOL JNM-GX400* FT instrument (400 MHz (^{1}H), 100.4 MHz (^{13}C)). Some 1D ^{13}C-NMR were measured at a *Bruker AM 300* instrument. Solns. (0.2M) in CDCl$_3$ were used at 23°. Chemical shifts are measured relative to the CDCl$_3$ signal and converted to the TMS scale using δ(CHCl$_3$) = 7.25 ppm or δ(CDCl$_3$) = 70.0 ppm for ^{1}H and ^{13}C, resp. In the COSY and relayed COSY [15] experiments, 1K × 1K data matrices were accumulated with a frequency width of 2700 Hz. The matrix of the C,H-shift correlation [16] consists of 2K × 512 data points in f_2 (16000 Hz) and f_1 (2700 Hz). Sine bell apodiazation was applied to FID's in both dimensions in case of COSY-type experiments, but only in f_1 (proton) in case of C,H-correlated spectra.

3. *Non-stereoselective Olefinations; General Procedure.* To a chilled suspension of a phosphonium bromide (0.03 mmol) in 50 ml of dry THF were added with stirring 12 ml of BuLi (2.5M in hexane). The resulting deeply colored ylide was gradually treated with a soln. of an aldehyde (20 mmol) in 5 ml of dry THF. The mixture slightly decolorized, and stirring was continued for 1 h at 0°. Pentane (100 ml) was added and the precipitate removed by suction. The org. layer was successively washed with 2N HCl (20 ml), sat. Na$_2$CO$_3$ soln. (20 ml), and H$_2$O (2 × 20 ml). The soln. was concentrated and the residue purified by CC on silica gel with pentane.

4. *Separation of* (*E/Z*)-*Pairs; General Procedure.* Ca. 1.5–2.0 g of the crude (*E/Z*)-pairs **3a/b, 3c/d, 6a/b,** or **6a/c** were loaded on a large column (5 × 80 cm) filled with 400–600 g of silica gel, and the hydrocarbons were eluted with pentane. Elution order and purity of the emerging substances was monitored by GC (*SE 30*). In all cases, the (*Z*)-isomer eluted first and was well separated from the (*E*)-olefine. Except for **6a/c,** a configurational purity > 98% was obtained.

5. *(2 E,4 E,6 E)-2,4,6-Undecatrien-8-yne* (**3a**). From 1 (10.4 mmol) and (2-pentynyl)triphenylphosphonium bromide (13.5 mmol), **3a/3b** ((*E*)/(*Z*) 55:45), was obtained in 79% yield. Separation (see *4*) gave 0.25 g (16.4%) **3a** as a colorless solid. M.p. not det. UV (MeOH): 281.5 (40330), 293 (62420), 306.6 (60180). IR (CCl$_4$): 3010, 2970, 2920, 2860, 2840, 2200, 1630, 1605, 1440, 1310, 1255, 990, 920, 800. MS (70 eV): 146 (52, M^+), 131 (45), 117 (45), 118 (37), 115 (51), 105 (10), 103 (12), 91 (100), 79 (13), 77 (33), 65 (21), 63 (18), 55 (21), 51 (28), 41 (20), 39 (53). HR-MS: 146.10996 (C$_{11}$H$_{14}$, calc. 146.10955).

6. *(2E,4E,6Z)-2,4,6-Undecatrien-8-yne* (**3b**). Separation of **3a/3b** (see *4* and *5*), gave **3b** (19.7%) as a colorless liquid. UV (MeOH): 281.5 (sh, 29150), 293 (41750), 306.1 (37800). IR (neat): 3020, 2980, 2940, 2920, 2880, 2210, 1640, 1605, 1430, 1400, 1320, 995, 960, 930, 750. MS (70 eV): 146 (37, $M^{+\cdot}$), 131 (40), 117 (43), 116 (35), 115 (50), 105 (11), 103 (13), 91 (100), 89 (7), 79 (18), 78 (15), 77 (37), 65 (24), 63 (22), 53 (28), 51 (35), 41 (25), 39 (63). HR-MS: 146.10967 ($C_{11}H_{14}$, calc. 146.10955).

7. *(4E,6E,8E)-Undecatrien-2-yne* (**3c**). From **2** (18.2 mmol) and (2-butynyl)triphenylphosphonium bromide (23.6 mmol), **3c/3d** ((*E*)/(*Z*) 1:1) was obtained in 56.3% yield. Separation (see *4*) gave 0.31 g (11.8%) of **3c** as a colorless solid. M.p. 33.5°. UV (MeOH): 282.3 (sh, 41200), 292 (63100), 306.6 (60050). IR (CCl₄): 3025, 2980, 2940, 2915, 2880, 2850, 2210, 1640, 1610, 1450, 1320, 995, 925. MS (70 eV): identical with **3d**. HR-MS: 146.10924 ($C_{11}H_{14}$, calc. 146.10955).

8. *(4Z,6E,8E)-4,6,8-Undecatrien-2-yne* (**3d**). Separation of **3c/3d** (see *4* and *7*) gave **3d** in 16.8% yield. UV (MeOH): 275.4 (sh, 26600), 286.3 (47500), 299.8 (68000), 313.4 (58200). IR (neat): 3050, 2970, 2920, 2880, 2860, 2010, 1640, 1620, 1460, 1440, 1410, 1380, 1155, 998, 960, 755. MS (70 eV): 146 (42, $M^{+\cdot}$), 131 (49), 129 (12), 117 (45), 116 (35), 115 (59), 105 (8), 103 (13), 91 (100), 79 (16), 78 (15), 77 (40), 65 (25), 63 (22), 53 (32), 51 (41), 41 (21), 39 (68). HR-MS: 146.10996 ($C_{11}H_{14}$, calc. 146.10955).

9. *(4E,6E)-4,6-Undecadiene-2,8-diyne* (**6a**). From **5b** (11.1 mmol) and (2-butynyl)triphenylphosphonium bromide (14.4 mmol), **6a/6b** ((*E*)/(*Z*) 1:1) was obtained in 61.3% yield. Separation (see *4*) afforded 0.43 g (26.9%) of **6a** as a colorless liquid. UV (MeOH): 277.6 (sh, 39500), 290.0 (54400), 303.5 (52200). IR (neat): 3040, 2980, 2940, 2920, 2880, 2860, 2220, 1835, 1730, 1665, 1580, 1455, 1435, 1380, 1320, 1300, 1165, 1065, 980*vs*. MS (70 eV): 144 (38, $M^{+\cdot}$), 129 (57), 128 (100), 127 (32), 115 (26), 103 (8), 101 (8), 91 (9), 89 (7), 77 (21), 65 (11), 63 (23), 51 (32), 39 (31). HR-MS: 144.09391 ($C_{11}H_{12}$, calc. 144.0939).

10. *(4Z,6E)-4,6-Undecadiene-2,8-diyne* (**6b**). Separation of **6a/6b** (see *4* and *9*) gave **6b** in 19% yield as a colorless liquid. UV (MeOH): 280.0 (sh, 26200), 291.2 (37240), 304.7 (32370). IR (neat): 3030, 2980, 2940, 2920, 2880, 2850, 2210, 1815, 1690, 1600, 1455, 1435, 1405, 1375, 1318, 975, 940, 850, 780, 755. MS (70 eV): 148 (22, $M^{+\cdot}$), 133 (7), 119 (31), 105 (27), 91 (100), 80 (11), 79 (25), 77 (29), 65 (12), 55 (24), 53 (13), 51 (11), 41 (58), 39 (50). HR-MS: 144.09348 ($C_{11}H_{12}$, calc. 144.0939).

11. *(4E,6Z)-4,6-Undecadiene-2,8-diyne* (**6c**). From **5a** (19.2 mmol) and (2-pentynyl)triphenylphosphonium bromide (23.0 mmol), **6a/6c** ((*E*)/(*Z*) 48:52) was obtained in 48% yield. Separation (see *4*) was incomplete (purity: *ca.* 90%) and afforded only 0.2 g (7.9%) of **6c** as a colorless liquid. Because of the insufficient purity, no ¹H-NMR and UV were recorded. IR (neat): 3030, 2980, 2940, 2920, 2880, 2850, 2210, 1815, 1690, 1600, 1455, 1435, 1405, 1375, 1318, 975, 940, 850, 780, 755. MS (70 eV): 148 (20, $M^{+\cdot}$), 133 (8), 119 (33), 105 (27), 91 (100), 80 (10), 79 (24), 77 (29), 65 (12), 55 (21), 53 (13), 51 (11), 41 (60), 39 (50). HR-MS: 144.09327 ($C_{11}H_{12}$, calc. 144.0939).

12. *Stereospecific Reductions of Conjugated Alkynes to (Z)-Alkenes; General Procedure. 12.1. Preparation of Activated Zn.* Ar was passed through a suspension of 5.0 g of Zn dust (*Anker zinc, Ultra 25; Metallchemische Produkte GmbH & Co. Kg,* Köln, FRG) in 30 ml of H_2O for *ca.* 15 min, and 0.5 g of Cu(OAc)₂ · H_2O were added. Stirring was continued for 15 min, before 0.5 g of AgNO₃ were introduced (exothermic reaction). The suspension was stirred for further 30 min. The metal was collected by suction and carefully washed with H_2O (2 × 30 ml), MeOH (2 × 30 ml), acetone (2 × 30 ml), and Et₂O (2 × 30 ml), resp. The Et₂O-moist Zn dust was immediately transferred into 20 ml of MeOH/H_2O 1:1 (*v*/*v*) and was ready for use.

12.2. Reduction of Triple Bonds. A soln. of 0.4 g of alkyne in 3 ml of MeOH was added to the suspension of activated Zn (see *12.1*) and stirred at r.t. until complete conversion of the alkyne (GC control; *ca.* 6–12 h). While (*Z*)-enynes were smoothly converted at r.t., the corresponding (*E*)-isomers required gentle heating to 40–45°. For isolation of the tetraenes, the metal was removed by filtration, washed with MeOH (5–10 ml), and the combined soln. were concentrated to *ca.* 1/3 of the original volume. Pentane (50 ml) was added, and the org. layer carefully washed with H_2O (3 × 20 ml). After drying and evaporation of the solvent, the crude tetraenes were purified by CC on silica gel using pentane.

13. *(2E,4E,6E,8Z)-2,4,6,8-Undecatetraene* (**9a**). Reduction of 0.3 g (2.05 mmol) of **3a** (see *12.2*) yielded, after purification, 0.17 g (55.9%) of a colorless solid. M.p. 25.5°. UV (MeOH): 275 (sh, 38250), 286.8 (64430), 299.3 (95000), 313.4 (87500). IR (CCl₄): 3020, 2970, 2930, 2880, 2850, 1625, 1460, 1440, 1380, 1305, 1070, 1000, 935, 875, 800, 770, 735. MS (70 eV): 148 (28, $M^{+\cdot}$), 133 (5), 119 (27), 105 (26), 91 (100), 79 (22), 77 (29), 69 (3), 67 (5), 65 (14), 63 (5), 55 (21), 53 (11), 51 (13), 41 (48), 39 (32). HR-MS: 148.12557 ($C_{11}H_{16}$, calc. 148.1252).

14. *(2E,4E,6Z,8Z)-2,4,6,8-Undecatetraene* (**9b**). Reduction of 0.2 g (1.4 mmol) of **3b** (see *12.2*) yielded, after chromatography, 0.105 g (50.7%) of a colorless liquid. UV (MeOH): 274.6 (sh, 21000), 286.2 (41900), 298.3 (67800), 312.6 (53020). IR (neat): 3030, 3020, 2980, 2940, 2920, 2880, 2860, 1645, 1605, 1460, 1440, 1380, 1300, 995, 975, 930, 870, 735. MS (70 eV): 148 (20, M^+), 133 (4), 119 (24), 105 (23), 91 (100), 79 (21), 77 (25), 67 (5), 65 (13), 63 (4), 55 (21), 53 (9), 51 (13), 41 (57), 39 (43). HR-MS: 148.12543 ($C_{11}H_{16}$, calc. 148.1252).

15. *(2Z,4E,6E,8E)-2,4,6,8-Undecatetraene* (**9c**). Reduction of 0.4 g (2.7 mmol) of **3c** (see *12.2*) yielded, after chromatography, 0.26 g (65.1%) of a colorless liquid. UV (MeOH): 174.5 (sh, 23700), 187.1 (46630), 199.6 (71800), 241.1 (64400). IR (neat): 3010, 2955, 2920, 2860, 2840, 1630, 1600, 1450, 1430, 1405, 1365, 1295, 990, 915, 800, 710, 630. HR-MS: 148.12586 ($C_{11}H_{16}$, calc. 148.1252).

16. *(2Z,4Z,6E,8E)-2,4,6,8-Undecatetraene* (**9d**). Reduction of 0.4 g (2.7 mmol) of **3d** (see *12.2*) yielded, after chromatography, 0.18 g (45%) of a colorless liquid. UV (MeOH): 264.2 (sh, 23300), 275.9 (42700), 298.2 (60150), 311.8 (50450). IR (neat): 3040, 3020, 2970, 2940, 2920, 2880, 1645, 1610, 1460, 1445, 995, 975, 925, 715. MS (70 eV): 148 (19, M^+), 133 (4), 119 (24), 105 (19), 91 (100), 79 (23), 77 (25), 67 (4), 65 (13), 63 (5), 55 (20), 53 (11), 51 (10), 41 (53), 39 (41). HR-MS: 148.12586 ($C_{11}H_{16}$, calc. 148.1252).

17. *(2Z,4E,6E,8Z)-2,4,6,8-Undecatetraene* (**9e**). Reduction of 0.4 g (2.8 mmol) of **6a** (see *12.2*) yielded, after chromatography, 0.26 g (62.7%) of a colorless liquid. UV (MeOH): 278.2 (sh, 25350), 289.7 (48100), 302.3 (73000), 316.9 (66600). IR (neat): 3025, 2970, 2940, 2880, 1635, 1465, 1440, 1400, 1370, 1315, 995, 955, 925, 875, 840, 720, 630. MS (70 eV): 148 (25, M^+), 133 (4), 119 (28), 105 (23), 91 (100), 79 (24), 77 (28), 67 (4), 65 (14), 55 (22), 53 (11), 51 (13), 61 (61), 39 (42). HR-MS: 148.12571 ($C_{11}H_{16}$, calc. 148.1252).

18. *(2Z,4Z,6E,8Z)-2,4,6,8-Undecatetraene* (= *Giffordene;* **9f**). Reduction of 0.4 g (2.8 mmol) of **6b** (see *12.2*) yielded, after chromatography, 0.11 g (26.5%) of a colorless liquid. UV (MeOH): 277.1 (sh, 22100), 289.4 (41400), 301.9 (60000), 316.2 (51400). IR (neat): 3020, 2970, 2940, 2920, 2880, 2840, 1630, 1465, 1455, 1400, 1385, 1370, 1315, 1070, 990, 935, 875, 800, 750, 720, 615. MS (70 eV): 148 (36, M^+), 133 (9), 119 (47), 117 (9), 105 (32), 91 (100), 80 (17), 79 (28), 77 (28), 69 (5), 67 (9), 65 (14), 63 (5), 55 (25), 53 (13), 51 (12), 41 (57), 39 (34). HR-MS: 148.12614 ($C_{11}H_{16}$, calc. 148.1252).

19. *(2Z,4E,6Z,8Z)-2,4,6,8-Undecatetraene* (**9g**). Reduction of **6c** (*ca.* 90% pure; see *12.2*) gave *ca.* 75% pure **9g** (facile isomerization). No UV and ¹H-NMR were recorded. MS (70 eV): 148 (23, M^+), 133 (5), 119 (31), 105 (27), 91 (100), 79 (27), 77 (32), 67 (6), 65 (15), 55 (23), 53 (12), 51 (11), 41 (58), 39 (49). HR-MS: 148.12604 ($C_{11}H_{16}$, calc. 148.1252).

20. *(2E,4E,6E,8E)-2,4,6,8-Undecatetraene* (**9h**). From (*E*)-2-pentenal (23.8 mmol) and [(*E*)-2,4-hexadienyl-idene]triphenylphosphorane (28.5 mmol), **9h/9i** ((*E*)/(*Z*) 3:2) was obtained in 55% yield. Two recrystallizations from Et₂O at − 80° afforded 440 mg (12.5%) of **9h** as a colorless solid (purity: > 99%). M.p. 115°. IR (CCl₄): 3020, 2970, 2940, 2920, 2880, 2850, 1645, 1450, 1380, 1000. UV (MeOH): 273.1 (35450), 284.1 (62550), 296.6 (93800), 310.5 (86160). MS (70 eV): 148 (30, M^+), 133 (5), 119 (32), 105 (23), 91 (100), 80 (11), 79 (21), 77 (23), 74 (4), 67 (4), 65 (15), 63 (4), 55 (22), 53 (12), 51 (9), 41 (51), 39 (39). HR-MS: 148.12629 ($C_{11}H_{16}$, calc. 148.1252).

21. *(E)-Hex-2-en-4-yn-1-ol* (**4a**). According to [10], 10.0 g (122 mmol) of (*E*)-pent-2-en-4-yn-1-ol [9] were protected and alkylated with CH₃I. After deblocking with pyridinium *p*-toluenesulfonate (PPTS) in MeOH, usual workup, and CC on silica gel, 6.8 g (58.1%) of **4a** were obtained. IR (neat): 3320, 3020, 2940, 2905, 2220, 1625, 1430, 1360, 1090, 1010, 950, 910. ¹H-NMR (CDCl₃, 80 MHz): 1.4 (*d, J* = 1.7, 3H); 2.27 (br. *s*, 1H); 4.05 (*d, J* = 4.9, 2H); 5.55 (*dm, J* = 13.3, 1H); 6.08 (*td, J* = 13.3, 6.7, 1H). MS (70 eV): 96 (8, M^+), 95 (19), 81 (100), 77 (16), 67 (32), 65 (20), 63 (15), 55 (10), 53 (41), 52 (18), 51 (29), 50 (20), 41 (69), 39 (75).

22. *(E)-Hept-2-en-4-yn-1-ol* (**4b**). From (*E*)-pent-2-en-4-yn-1-ol and EtBr as described in *21* in 62% yield. IR (neat): 3310, 3020, 2970, 2930, 2910, 2870, 2220, 1630, 1450, 1430, 1370, 1315, 1165, 1090, 1010, 955, 910. ¹H-NMR (CDCl₃, 80 MHz): 1.15 (*t*, 3H); 2.27 (*q*, 2H); 2.75 (*s*, 1H); 4.97 (*d, J* = 5.5, 2H); 5.58 (*md, J* = 15, 1H); 6.08 (*td, J* = 15, 5, 1H). MS (70 eV): 110 (7, M^+), 109 (3), 95 (100), 91 (11), 81 (43), 79 (21), 77 (29), 67 (59), 65 (31), 63 (19), 55 (15), 53 (61), 51 (38), 41 (72), 39 (81).

23. *(E)-Dec-2-en-4-yn-1-ol* (**4c**). From (*E*)-pent-2-en-4-yn-1-ol and C₅H₁₁Br as described in *21* in 42.6% yield. IR (neat): 3320, 3020, 2950, 2920, 2850, 2210, 1625, 1450, 1370, 1325, 1090, 1010, 950, 900, 720. ¹H-NMR (CDCl₃, 80 MHz): 0.95 (*t, J* = 5.5, 3H); 1.00–1.70 (*m*, 6H); 1.88 (br. *s*, 1H); 2.27 (br. *t, J* = 7.5, 2H); 4.12 (*d, J* = 5.5, 2H); 5.65 (*md, J* = 15.5, 1H); 6.10 (*dt, J* = 15.5, 5.3, 1H). MS (70 eV): 152 (9, M^+), 123 (13), 95 (100), 81 (28), 79 (18), 77 (16), 67 (75), 55 (21), 53 (16), 51 (21), 41 (88), 39 (57).

24. *(E)-Hex-2-en-4-ynal* (**5a**). A mixture of 3.0 g (31.3 mmol) of **4a** and 30.0 g of MnO_2 in 70 ml of CH_2Cl_2 was stirred until GC indicated complete conversion (*ca.* 90 min). MnO_2 was filtered off and washed with CH_2Cl_2 (2 × 20 ml) and the combined org. layer evaporated. The crude residue was distilled: 1.8 g (61.2%) of pure **5a**. B.p. 56°/14 Torr. IR (neat): 3020, 2990, 2920, 2830, 2740, 2360, 2220, 1685, 1605, 1580, 1440, 1400, 1300, 1185, 1125, 965, 835, 805, 770. ^1H-NMR (CCl_4, 90 MHz): 2.1 (*d, J* = 3, 3 H); 6.28 (*dd, J* = 16.5, 7.5, 1 H); 6.55 (*md, J* = 16.5, 1 H); 9.55 (*d, J* = 7.5, 1 H). MS (70 eV): 94 (42, $M^{+\cdot}$), 66 (51), 65 (50), 63 (38), 62 (22), 61 (16), 51 (17), 50 (13), 40 (32), 39 (100).

25. *(E)-Hept-2-en-4-ynal* (**5b**). From **4b** as described in *24* in 91 % yield after CC on silica gel. IR (neat): 3050, 3020, 2850, 2810, 2720, 2200, 1680, 1600, 1460, 1420, 1385, 1320, 1290, 1165, 1115, 955, 720. ^1H-NMR (CCl_4, 90 MHz): 1.25 (*t, J* = 7.5, 3 H); 2.44 (*q, J* = 7.5, 2 H); 5.30 (*dd, J* = 16.5, 6.6, 1 H); 5.58 (*md, J* = 16.5, 1 H); 9.55 (*d, J* = 6.6, 1 H). MS (70 eV): 62 (62, $M^{+\cdot}$), 107 (20), 79 (100), 77 (85), 74 (8), 65 (35), 63 (30), 53 (31), 52 (32), 51 (53), 50 (32), 39 (87).

26. *(E)-Dec-2-en-4-ynal* (**5c**). From 0.7 g (4.6 mmol) **4c** as described in *24* in 74.4 % yield after CC on silica gel. IR (neat): 3040, 2970, 2930, 2905, 2870, 2810, 2729, 2330, 2200, 1660, 1600, 1580, 1450, 1310, 1290, 1170, 1120, 950, 825, 775, 655. ^1H-NMR ($CDCl_3$, 80 MHz): 0.92 (*t, J* = 6, 3 H); 1.10–1.80 (*m*, 6 H); 2.36 (*dt, J* = 6, 1.5, 2 H); 6.254 (*dd, J* = 15, 7, 1 H); 6.55 (*md, J* = 15, 1 H); 9.50 (*dd, J* = 8, 1, 1 H). MS (70 eV): 149 (18, $M^{+\cdot} - 1$), 135 (11), 121 (13), 107 (33), 94 (27), 91 (16), 79 (51), 77 (45), 66 (32), 65 (40), 63 (21), 55 (18), 51 (21), 41 (52), 39 (100). HR-MS: 152.12072 (calc. 152.1201).

27. *(E)-1,3-Octadien-5-yne* (**7**). See [11]. According to *3*, 0.75 g (6.0 mmol) of **5b** were treated with (methylidene)triphenylphosphorane yielding after CC on silica gel (pentane), 0.25 g (33%) of **8** (low yield due to severe losses on evaporation of the solvent). IR (neat): 3080, 3020, 2970, 2930, 2905, 2870, 2830, 2200, 1620, 1405, 1310, 1160, 995, 950, 900, 840, 760, 640. ^1H-NMR ($CDCl_3$, 300 MHz): 1.14 (*t*, 3 H); 2.31 (*dq, J* = 8, 1, 2 H); 5.10 (*md, J* = 10.5, 1 H); 5.23 (*md, J* = 16.5, 1 H); 5.59 (*md, J* = 16, 1 H); 6.32 (*ddd, J* = 16, 10.5, 9.8, 1 H); 6.48 (*ddquint., J* = 16, 11.3, 0.8, 1 H). ^{13}C-NMR ($CDCl_3$): 118.57 (C(1)); 136.31 (C(2)); 140.92 (C(3)); 112.54 (C(4)); 78.83 (C(5)); 94.75 (C(6)); 13.24 (C(7)); 13.83 (C(8)). MS (70 eV): 108 (83, $M^{+\cdot}$), 105 (32), 103 (19), 91 (100), 79 (51), 78 (49), 77 (51), 74 (8), 66 (15), 65 (63), 63 (29), 53 (13), 52 (22), 51 (50), 50 (21), 41 (23), 39 (57).

28. *(E)-1,3-Decadien-5-yne* (**8**). According to *3*, 0.45 g (3.0 mmol) of **5c** were treated with (methylidene)triphenylphosphorane yielding 0.20 g (46.7%) of **8**, after CC on silica gel. IR (neat): 3080, 3020, 2985, 2950, 2920, 2850, 2200, 1620, 1580, 1455, 995, 935, 895, 840, 720, 640. ^1H-NMR ($CDCl_3$, 300 MHz): 0.88 (*t, J* = 7, 3 H); 1.20–1.43 (*m*, 4 H); 1.52 (*mquint., J* = 7, 2 H); 2.30 (*dt, J* = 7, 2.5, 2 H); 5.10 (br. *d, J* = 10, 1 H); 5.23 (br. *d, J* = 17, 1 H); 5.60 (*td, J* = 16, 2, 1 H); 6.32 (*td, J* = 17, 10.2, 1 H); 6.48 (*dd, J* = 15, 15, 1 H). ^{13}C-NMR ($CDCl_3$): 118.52 (C(1)); 136.26 (C(2)); 140.88 (C(3)); 112.66 (C(4)); 79.49 (C(5)); 93.63 (C(6)); 19.58 (C(7)); 28.44 (C(8)); 31.09 (C(9)); 22.22 (C(10)); 13.98 (C(11)). MS (70 eV): 148 (17, $M^{+\cdot}$), 133(3), 119 (5), 105 (27), 91 (100), 79 (29), 78 (22), 77 (25), 55 (7), 51 (18), 41 (41), 39 (47). HR-MS: 150.14133 (calc. 150.1409).

29. *(3E,5Z)-1,3,5-Octatriene* (= *Fucoserratene;* **10**). Reduction of 0.25 g (2.4 mmol) of **7** (see *12.2*) gave 0.02 g (10%) of configurationally pure **10** (low yield due to severe losses on evaporation of the solvent). For a detailed spectroscopic study, see [11].

30. *(3E,5Z)-1,3,5-Undecatriene* (= *Cystophorene;* **11**). Reduction of 0.18 g (1.2 mmol) of **8** (see *12.2*) gave 0.08 g (44.4%) of configurationally pure **11**. For detailed spectroscopic analysis, see [14] [27].

31. *'Biomimetic' Synthesis of* **9f**. Ar was passed for *ca.* 15 min through a well stirred suspension of 20 g of MnO_2 in 50 ml of Et_2O, followed by addition of 2.0 g (15.8 mmol) of freshly distilled (2Z,5Z)-2,5-octadienol [26]. Oxidation proceeded instantaneously and was followed by GC. Stirring was continued for 90 min and MnO_2 filtered off. The soln. was evaporated to *ca.* ¼ of the original volume, and the very sensitive aldehyde was added without further purification to a chilled soln. of (2-propenylidene)triphenylphosphorane (18 mmol; BuLi as base) in 50 ml of dry THF. After usual workup and CC on silica gel, **9f**/**14** was obtained as the major products. Removal of **14** with 4-phenyl-1,2,4-triazolin-3,5-dione (PTAD) according to [25] left 0.46 (19.7%) of a moderately pure **9f** (purity: 64%), after CC on Ag^+-impregnated silica gel (10% $AgNO_3$). During the reaction, aliquots were analyzed by HPLC (*RP 18;* $MeOH/H_2O$ 9:1 (*v/v*) at 1 ml/min; UV (310 nm)) and confirmed the immediate formation of **9f** by its characteristic UV.

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