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Pericyclic Reactions in Nature: Synthesis and Cope Rearrangement of Thermolabile Bis-alkenylcyclopropanes from Female Gametes of Marine Brown Algae (Phaeophyceae)

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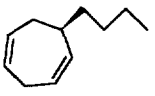
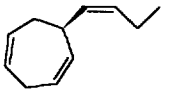
Abstract: The biosyntheses of the 6-substituted cyclohepta-1,4-dienes dictyotene **(1)**, ectocarpene **(2)**, desmarestene **(3)**, vinylcycloheptadiene **(4)** and lamoxirene **(5)** involve a spontaneous Cope rearrangement of thermolabile bis-alkenylcyclopropane precursors like **16**, **10**, **26** and **30**. The unstable precursors and the rearranged cycloheptadienes were synthesised from the chiral 2-iodovinylcyclopropane **12** using Pd^0 or Cu^I catalysed approaches. Activation parameters of the Cope rearrangements were determined. Bioassays with pre-ectocarpene **10** established the thermolabile cyclopropane (1*R*,2*R*)-**10**, rather than the cyclohepta-1,4-diene (6*S*)-**2**, as the genuine pheromone of the brown alga *Ectocarpus siliculosus*. © 1997 Elsevier Science Ltd.

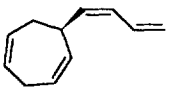
The sexual reproduction of marine brown algae (Phaeophyceae) is assisted by chemical signals which are released from the female gametes to attract their conspecific males and/or to induce spermatozoid mass release from male antheridia.[1,2,3,4] Most of these pheromones are simple acyclic or cyclic hydrocarbons with the molecular formulae $C_{11}H_{14}$, $C_{11}H_{14}O$, $C_{11}H_{16}$ and $C_{11}H_{18}$. Ectocarpene **(2)**, released from calling females of the cosmopolitan brown alga *Ectocarpus siliculosus*, was the first algal pheromone to be isolated and identified.[5] Later, desmarestene **(3)**, produced by fertile gynogametes of the North Atlantic brown alga *Desmarestia aculeata*, became known as the first example of a signal molecule endowed with the dual function of gamete-release and gamete-attraction.[6]



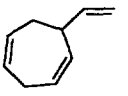
dictyotene **1**



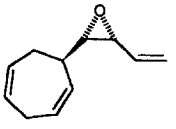
ectocarpene **2**



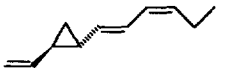
desmarestene **3**



4



lamoxirene **5**

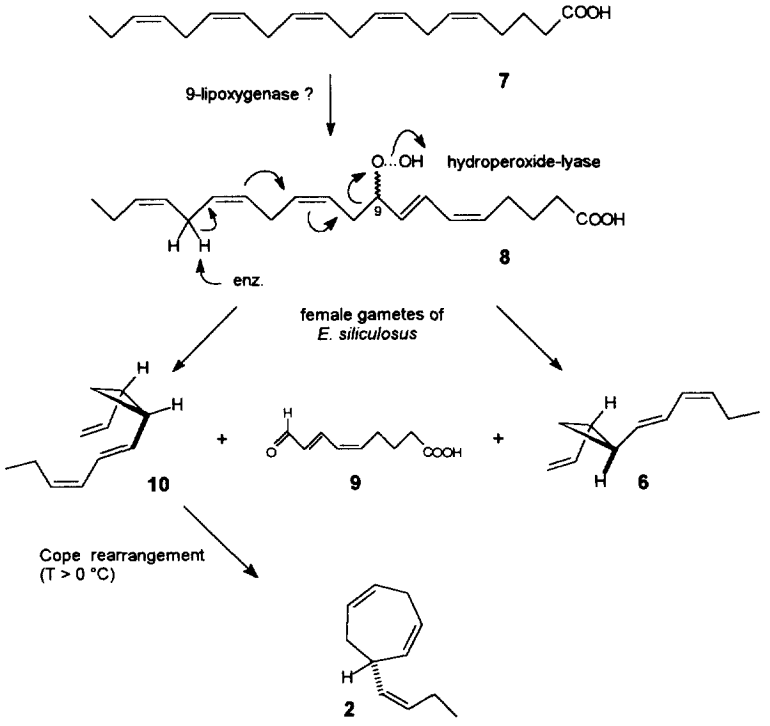


hormosirene **6**

In lower plants like the brown algae the whole family of C_{11} hydrocarbons is biosynthesised from highly unsaturated C_{20} fatty acids, e.g. arachidonic acid (20:4, ω-6), eicosapentaenoic acid (20:5, ω-3) **(7)** and eicosahexaenoic acid (20:6, ω-0).[7,8] In contrast, higher plants produce ectocarpene from linolenic acid by three consecutive ß-oxidations and a final oxidative decarboxylation of the resulting dodeca-3,6,9-trienoic acid.[9]

Exemplary studies with the fresh water diatom *Gomphonema parvulum* evidenced that eicosapentaenoic acid 7 is transformed into the unpolar C_{11} hydrocarbon hormosirene **(6)** and the highly water soluble C_9 frag-

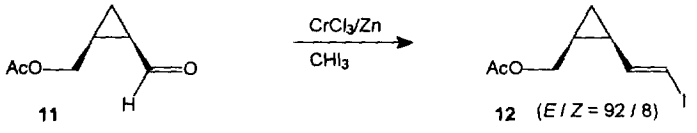
ment 9-oxo-nona-5,7-dienoic acid (**9**).[10] According to the current biogenetic concept (Scheme 1) a 9-lipoxygenase is believed to activate the eicosapentaenoic acid (**7**) as the 9-hydroperoxide **8** (9-HEPE). Subsequent cleavage of the hydroperoxide **8** by a novel type of a hydroperoxide-lyase may then generate the C_{11} hydrocarbon from the aliphatic segment and the 9-oxo-nonadienoic acid (**9**) from the polar head of the fatty acid. The same mechanistic implications in conjunction with a different conformation of the hydroperoxide **8** at the active centre of the hydroperoxide-lyase, could account for the formation of the thermolabile *cis*-disubstituted cyclopropane **10**, recently identified as the actual chemical signal of the *E. siliculosus* pheromone bouquet.[11,12] „Pre-ectocarpene" is thermolabile and rearranges at rt. to the inactive hydrocarbon ectocarpene (**2**) (Scheme 1).[11] The above enzymes can principally act on all types of naturally occurring eicosanoids and, thus, produce the whole variety of (functionalised) cyclohepta-1,4-dienes and cyclopropanes which are currently known as gamete releasing and/or gamete attracting pheromones of brown algae.[2,4]



Scheme 1.

To address the biological significance and the stability of the thermolabile progenitors of the cycloheptadienes **1** to **5** in more detail, effective syntheses of the unstable compounds had to be developed. We describe here the first stereo- and enantioselective low temperature syntheses of the *cis*-disubstituted C_{11} cyclopropanes **10**, **16** and **26** and the C_9-analogues **30** and **31**. The isolated, pure compounds allowed the determination of the kinetic parameters for the Cope rearrangements **16** → **1**, **10** → **2**, **26** → **3**, **30** → **4**, and **31** → **4** and matched previously published data of related compounds (cf. Table 1).[13] Bioassays established the thermolabile pre-ectocarpene (**10**) as the only relevant compound for the attraction of male gametes of *E. siliculosus*[11] and established the Cope rearrangement as a fast, but environmentally (temperature) controlled mechanism for the spontaneous deactivation of the pheromone.

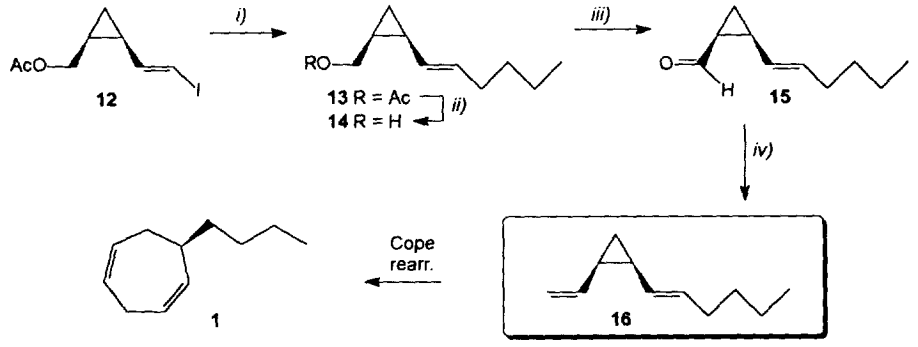
Low Temperature Syntheses of compounds 10, 16, 26, 30 and 31. As already documented, both enantiomers of the acetoxyaldehyde **11** (cf. scheme 2) are readily available in large quantities,[14,15] and both have served as versatile building blocks for the synthesis of several algal pheromones using phosphorous ylide methodology.[16] To adopt the previous route to the application of the especially mild an effective Pd^0- or Cu^I-catalysed carbon-carbon bond formations between vinylic halides and appropriate organometallic reagents, the aldehyde (1*R*,2*S*)-**11** (95% *e.e.*) was first converted into the 2-iodovinylcyclopropane **12** according to the protocol of *Takai et al.*[17]



Scheme 2.

Thus, treatment of **11** with triiodomethane in the presence of Cr(II), produced *in situ* by reduction of $CrCl_3$ with zinc dust, provided the vinylic iodide (1*S*,2*R*)-**12** (1'*E*/*Z* = 92/8) in 64% yield.[17,18] The vinyl iodide **12** served as a general precursor for the low temperature syntheses of the thermolabile cyclopropanes **16**, **10**, **26** and the corresponding valence isomers **1**, **2** and **3**, respectively.

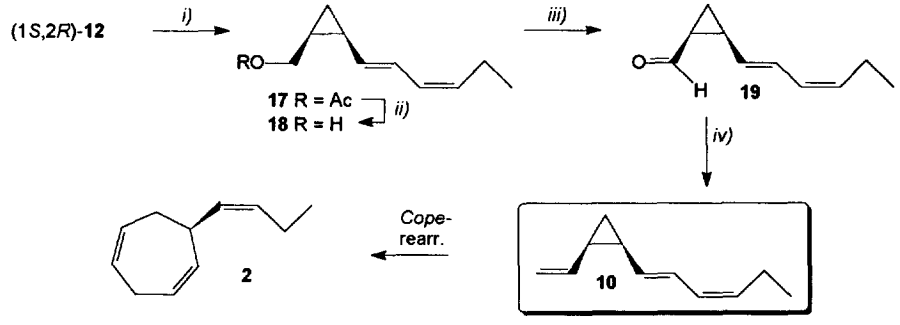
Pre-dictyotene: Dictyotene and its thermolabile progenitor „pre-dictyotene" ((1*R*,2*R*)-**16**) were obtained from (1*S*,2*R*)-**12** by alkylation with $(n\text{-Bu})_2CuLi$.[19] Reductive deacetylation with $LiAlH_4$ and Swern oxidation of the alcohol **14** gave the aldehyde **15**. A final Wittig olefination in DMSO (NaH/DMSO)[20] at 5 °C produced the thermolabile olefin (1*R*,2*R*)-**16** within only 3 min and 90% yield after isolation at low-temperature (cf. Experimental). The short reaction time and a rapid work-up (at ≈ 0 °C) were essential to minimise the thermal rearrangement of pre-dictyotene (**16**). As expected, the Cope rearrangement of **16** proceeded spontaneously at rt.[20,21] and transformed the cyclopropane quantitatively and with complete transfer of chirality into dictyotene (86% *e.e.* according to chiral GLC, cf. Experimental). Due to the presence of (*E*)- and (*Z*)-isomers (92:8) in the vinyl iodide **12**, the optical purity of the product was lower than that of the acetoxyaldehyde **11**. No attempts were made to separate the isomers. The kinetics of the Cope rearrangement were followed by ^1H NMR spectroscopy in $CDCl_3$ (*vide infra*).



Reagents: *i)* *n*-BuLi/CuI. *ii)* $LiAlH_4$/THF. *iii)* Swern oxidation. *iv)* NaH/DMSO, methyltriphenylphosphonium iodide, 5 °C, 3 min.

Scheme 3.

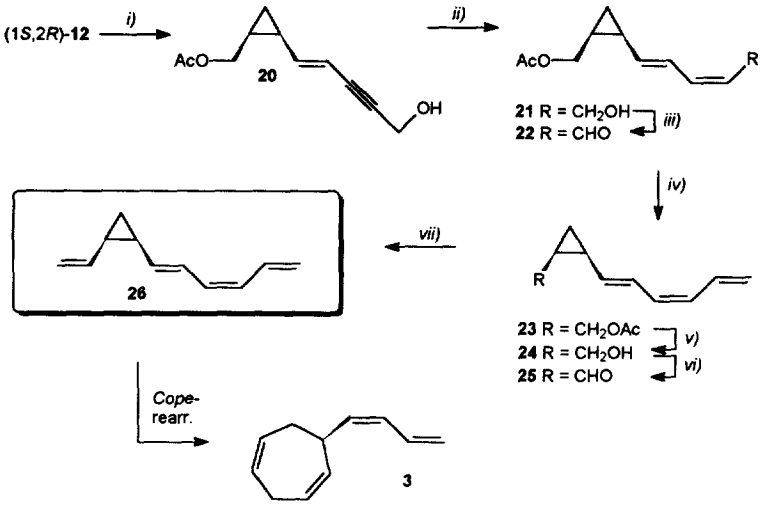
Pre-ectocarpene: Ectocarpene and its thermolabile precursor pre-ectocarpene were obtained from **12** by alkylation with 1-(*Z*)-butenylzincate, generated *in situ* (Scheme 4) according to the protocol of *Normant*.[22] Thus, addition of diethyl copper to acetylene yielded 1-(*Z*)-butenylcuprate, which, after transmetallation with Zn(II), could be coupled in a „one pot" operation with the vinyl iodide **12** using $Pd(PPh_3)_4$ (5 mol %) as the catalyst. If the alkylation of **12** was carried out in a solvent mixture containing pyrrolidine as a cosolvent as described by Linstrumelle et al.,[23] a high stereoselectivity of the coupling reaction (2'*E*/*Z* ≥ 97:3) could be attained by simple kinetic control (GLC) due to the fact that the (*E*)-isomer of **12** reacted significantly faster than the (*Z*)-iodide. Moreover, since the carbocupration[22] of acetylene is a highly stereoselective process (*Z*/*E* ≥ 98:2), the correct 1'*E*,3'*Z*-configuration of the hexadienyl substituent was introduced in a single operation upon coupling of the 1-(*Z*)-butenylzincate with **12**. Deacetylation of **17** was achieved by stirring with K_2CO_3 in aqueous methanol. Oxidation, Wittig olefination and a work-up at low temperature as described for **16** allowed the isolation of the unstable pre-ectocarpene ((1*R*,2*R*)-**10**). GLC analysis (cf. Experimental) of the valence isomeric ectocarpene indicated the compound to be of ≥ 92% *e.e.* and, thus, proved the high efficiency of the kinetically controlled, preferred alkylation of (*E*)-**12**.



Reagents: *i)* EtMgBr, CuBr, C_2H_2, $ZnBr_2$, $Pd(PPh_3)_4$. *ii)* K_2CO_3/MeOH/H_2O. *iii)* Swern oxidation. *iv)* NaH/DMSO, methyltriphenylphosphonium iodide, 5 °C, 3 min.

Scheme 4.

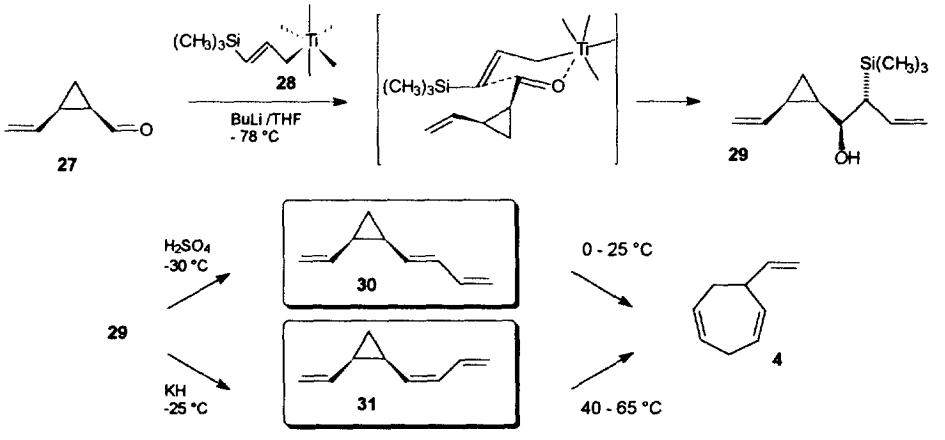
Pre-desmarestene: Desmarestene and its thermolabile progenitor pre-desmarestene ((1*R*,2*R*)-**26**) were produced from the vinyliodide **12** along the sequence depicted in Scheme 5. Alkylation of **12** with propynol was achieved in benzene/pyrrolidine in the presence of $Pd(PPh_3)_4$ (5.0 mol %).[23] Again, the choice of the solvent was essential to warrant a high stereoselectivity of the coupling reaction (1'*E*/*Z* ≥ 98:2). Reduction of the conjugated triple bond was accomplished with activated Zn(*Cu*/*Ag*)[24,25] in aqueous methanol and furnished the (3'*Z*)-isomer stereospecifically (3'*E*/*Z* < 2/98). Oxidation of **21** with activated MnO_2 was complete within 10 min at rt. (prolonged treatment led to significant isomerisation of the conjugated *Z*-double bond). The unstable aldehyde **22** was immediately converted into the hexatrienylcyclopropane **23** by reaction with methylidenetriphenylphosphorane in DMSO. Manipulation of the C_2-side chain and work-up of thermolabile product at low temperature followed, in all respects, the synthesis of pre-dictyotene (**16**) (*vide supra*). According to chiral GLC desmarestene was obtained with 93% *e.e.*



Reagents: *i)* 3-propyn-1-ol, $Pd(PPh_3)_4$, piperidine. *ii)* Zn(*Cu/Ag*), MeOH/H_2O. *iii)* MnO_2. *iv)* NaH/DMSO, methyltriphenylphosphonium iodide. *v)* K_2CO_3/MeOH/H_2O. *vi)* Swern oxidation. *vii)* NaH/-DMSO, methyltriphenylphosphonium iodide, 5 °C, 3 min.

Scheme 5.

6-Vinylcyclohepta-1,4-diene. Racemic 6-vinylcyclohepta-1,4-diene **(4)**, previously identified as a trace constituent of the pheromone bouquet of the Mediterranean phaeophyte *Cutleria multifida*[26] and its thermolabile biosynthetic precursors **30** or **31** were synthesised as outlined in Scheme 6. As the key step of the synthesis we employed a titanium mediated version[27] of the Peterson reaction. Alkylation of the racemic *cis*-aldehyde[28] **27** proceeded with high diastereoselectivity and yielded **29** (*threo:erythro* > 95:5) in accord with a chair-like transition state.



Scheme 6

The β-hydroxysilane **29** was stable at rt. and allowed purification on deactivated SiO_2. An acid induced for-

mation of the 1-(*E*)-butadiene could be achieved in high yield (88 %) by stirring with H_2SO_4 at -30 °C and afforded the configurationally pure *cis*-disubstituted cyclopropane **30**. The isomeric (*Z*)-alkene **31** was obtained at -25 °C by *syn* elimination of the hydroxysilane **29** upon treatment with potassium hydride. Low temperature work-up (cf. Experimental) gave **30** or **31** without significant thermal isomerisation.

Kinetics. The Cope rearrangements **10** → **2**, **26** → **3**, **30** → **4** and **31** → **4** were studied at different temperatures by UV spectroscopy. Owing to the irreversible formation of the cycloheptadienes **2**, **3** and **4**, the rearrangement was easily followed by the disappearance of the UV absorption of the conjugated dienes **10**, **30** and **31** at 245 nm. In the case of the rearrangement **26** → **3**, the disappearance of the triene absorption at the highest wavelength (279 nm, octane) could be used to monitor the reaction without interference by the increasing diene absorption. Each reaction was followed over 2 to 3 half lives at 5 different temperatures, and each run was typically repeated in triplicate. The data were analysed according to first-order kinetics following the method of Swinbourne[29] which allows the calculation of the rate constants without the need for exact concentrations of the unstable hydrocarbons at the beginning or the end of the reaction. Due to the absence of a useful UV absorption, the rearrangement of **16** → **1** was followed by ^{1}H NMR using the signal of the ring methylene protons at δ 2.95 and the resonance of the terminal vinyl protons at δ 4.99 for integration. Activation parameters and half lives (at 8 °C and 18 °C, two typical spring temperatures in arctic and mediterranean environments of marine brown algae) of the thermolabile cyclopropanes are compiled in Table 1.

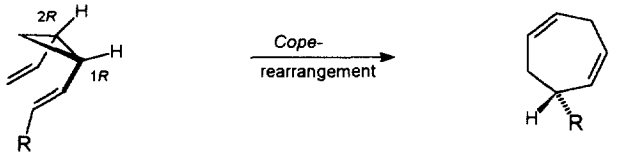


Table 1. First order rate constants and activation parameters of the Cope rearrangements

R	rearrangement	Ea [kJ mol^{-1}]	ln *A*	$t_{0.5}$ (8 °C) [min]	$t_{0.5}$ (18 °C) [min]
-CH=CH-CH=CH_2	**26** → **3**	62.6 ± 1.5	18.5 ± 0.5	45	18
-CH=CH-C_2H_5	**10** → **2**	63.8 ± 1.2	18.9 ± 0.4	56	21
-CH_2CH_2-C_2H_5	**16** → **1**	ca.74		136	58
-CH=CH_2 (1′*E*)	**30** → **4**	64.9 ± 1.2	19.0 ± 0.4	77	30
-CH=CH_2 (1′*Z*)	**31** → **4**	ca. 82.9	-	280 (43 °C)	41 (62 °C)

Spectroscopic Evidence for the Release of Pre-ectocarpene (10) from Female Gametes of *E. siliculosus*. Ca. 5 x 10^7 freshly released female gametes of *E. siliculosus* were kept for 4 hours at 4 °C in 10.0 ml of seawater. Then, the dense gamete suspension was extracted with CH_2Cl_2, and the extract was immediately submitted to HPLC separation (C18, MeOH:H_2O, 9:1, *v:v* for elution). The retention data and the UV spectrum (λ_{max} = 245 nm, MeOH/H_2O = 9/1) of the natural product proved to be identical with those of a synthetic reference of pre-ectocarpene **(10)** (Fig. 1). Moreover, the slowly fading UV absorption of the natural compound (cf. Fig. 2) showed identical half life as the synthetic reference under the same conditions.

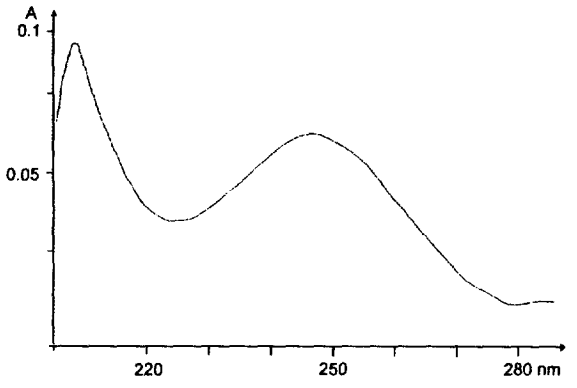


Fig. 1. UV-spectrum of (1*R*,2*R*)-**10** from an extract of female gametes of *Ectocarpus siliculosus*.

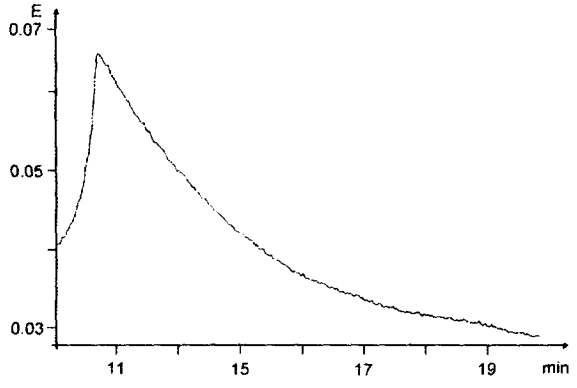


Fig. 2. The half life of the fading signal was determined in the HPLC UV-detector flow cell, by stopping the flow at the peak maximum of the eluting compound, and corresponded to 110 s at 45 °C (flow cell temp.). Identical data were obtained with the synthetic reference.

Bioassays and Biological Significance of the Cope Rearrangement. Comparative bioassays with (1*R*,2*R*)-**10** and (6*S*)-**2** were performed with male gametes of *E. siliculosus* (clone P.ar. 27a) as described.[11,30,31] While (6*S*)-**2** proved to be virtually inactive, the thermolabile cyclopropane (1*R*,2*R*)-**10** caused a very strong accumulation of male gametes down to a threshold concentration of ca. 5.0 pmol. Maximum accumulation of male gametes was observed at 50.0 nmol, followed by a steep decrease at higher pheromone concentrations. Such a dose-response behaviour is probably due to saturation effects and appears to be typical for most algal communication systems.[32,33] In consequence of these findings the thermolabile, *cis*-disubstituted cyclopropane (1*R*,2*R*)-**10** rather than the thermostable ectocarpene has to be considered as the true male-attracting signal. Obviously, the Cope rearrangement has a function as a fast and reliable mechanism for the spontaneous deactivation of the pheromone. Since the rate of the above rearrangements (Table 1) depends only on the temperature of the environment, the life time of the thermolabile precursors is determined by the natural habitat (e.g. tropic or arctic environments) of the alga. This may have interesting consequences. It is, for example, conceivable that the male gametes of certain algae, which occur in cold and warm zones may respond to either of the two or to both valence isomers. In fact, the release of male gametes from gametangia of the North Atlantic species *Desmarestia aculeata*, can be triggered with pre-desmarestene and desmarestene at comparable threshold concentrations,[16] and represents the first known example of a pheromone blend composed of valence tautomers. Highly evolved receptor systems (e.g. those of the genus *Laminaria* and *Sporochnus*) may even use the ratio of the valence isomers to determine gradients, or, more conceivably, may utilise lamoxirene (**6**) and its thermolabile precursor to trigger gamete-release and gamete-attraction with different efficiencies.[34]

EXPERIMENTAL

General: Reactions were performed under Ar; solvents were dried according to standard methods. IR: Perkin-Elmer Series 1600 FTIR Spectrophotometer. UV: Perkin Elmer Lambda 2, equipped with a thermostatised cell holder, connected to a Haake Cryostat. ^{1}H- und ^{13}C NMR: Bruker AC 250 or Bruker AC 400 Spectrometer; $CDCl_3$ as solvent. Chemical shifts of ^{1}H- and ^{13}C NMR are given in ppm (δ) downfield relative to TMS. GC-MS (70eV): Finnigan MAT 90 or Finnigan ITD 800 coupled with a Carlo Erba GC 6000, Model Vega. HR-MS: Kratos MS 20. Optical rotations: Perkin-Elmer 241 (CH_2Cl_2). GLC: Carlo Erba, Series 4100, equipped with fused silica capillaries coated with SE30 (10m x 0.31 mm) or 6-methyl-2,3-di-*O*-pentyl-γ-cyclodextrin (50m x 0.31mm) from Macherey & Nagel (Düren, Germany). HPLC: Barspec Chrom-A-Scope scanning photometer, combined with a Kontron 420 HPLC pump. The separation was achieved on reversed phase, Merck LiChrospher 100 RP-18 (25 x 0.4 cm). Silica gel, Si 60 (0.200-0.063 mm, E. Merck, Darmstadt, Germany) was used for chromatography. Thin layer chromatography was performed with silica gel plates Polygram Sil G_{F254}, from Merck.

(1*S*,2*S*)-1-Acetic acid 2-(hex-1′*E*-enyl)cyclopropylmethyl ester ((1*S*,2*S*)-13)

n-BuLi (32 ml of a 15% solution in *n*-hexane, 75.2 mmol) was slowly added to a well stirred suspension of CuI (7.2 g, 37.6 mmol) in ether (70.0 ml) at -20 °C. The resulting brown suspension was cooled to -78 °C, and a soln. of **12** (1.58 g, 5.94 mmol) in ether (40.0 ml) was added dropwise. After 30 min at -78 °C the alkylation was complete with respect to the *E*-iodide **12**, and the mixture was poured into a sat. soln. of NH_4Cl. The solids were filtered off and washed with ether. Following extraction of the aqueous phase, drying (Na_2SO_4) and removal of solvents, the resulting ester was purified by chromatography on SiO_2 (pentane:ether, 90:10). Yield: 0.85 g (73%, *E*:*Z* > 92:8). $[\alpha]_{578}^{22}$ = 20.7° (c = 13.2, CH_2Cl_2). IR (KBr, film, cm^{-1}): 3074, 3004, 2958, 2928, 2873, 2858, 1741, 1457, 1370, 1237, 1027, 970, 899. ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 5.62-5.45 (m, 1H-C(2′)); 5.26-4.97 (m, 1H-C(1′)); 4.2-4.03 (m, 1H-C$\underline{H}_2$OAc); 3.98-3.84 (m, 1H-C$\underline{H}_2$OAc); 2.04 (s, 3H-COC$\underline{H}_3$); 2.05-1.91 (m, 2H-C(3′)); 1.72-1.51 (m, 1H-C(2)); 1.44-1.15 (m, 2H-C(4′), 2H-C(5′), 1H-C(cyclopr.)); 1.02-0.81 (m, 1H-C(cyclopr.), 3H-C(6′)); 0.52-0.36 (m, 1H-C(cyclopr.)). ^{13}C NMR ($CDCl_3$, 65 MHz) δ: 171.32; 132.41; 127.35; 65.31; 32.35; 31.78; 22.41; 18.48; 16.62; 14.00; 10.45. MS (70 eV): 196($M^{+\cdot}$; 26); 136(28); 93(55); 91(24); 81(91); 80(98); 67(43); 55(18); 43(100); 41(23). HR-MS: *m/z* calcd. for $C_{12}H_{20}O_2$ 196.1463, found: 196.1466.

(1*S*,2*S*)-2-(Hex-1′*E*-enyl-cyclopropyl)-methanol ((1*S*,2*S*)-14)

A soln. of **13** (0.85 g, 4.33 mmol) in THF (30.0 ml) was added slowly to a cooled (0 °C) suspension of $LiAlH_4$ dry THF (40.0 ml). The mixture was allowed to come to rt. and stirring was continued for 30 min. After complete reduction, the mixture was poured into a chilled soln. of sat. NH_4Cl. Extractive work-up with Et_2O (5 x 30.0 ml) and chromatography on SiO_2 (pentane:ether, 60:40) afforded (1*S*,2*S*)-**14** as a colourless liquid. Yield: 0.62 g (93%). $[\alpha]_{578}^{22}$ = 11° (c = 13.2, CH_2Cl_2). IR (KBr, film, cm^{-1}): 3439(br), 2999, 2924, 2856, 1727, 1626, 1462, 1107, 1005, 974, 898. ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 5.68-5.5 (m, 1H-(2′)); 5.3-5.15 (m, 1H-C(1′)); 3.72 (t, 1H-C$\underline{H}_2$OH); 3.44 (t, 1H-C$\underline{H}_2$OH); 1.99 (m, 2H-C(3′)); 1.65-1.48 (m, 1H-C(2)); 1.46 (s(br), 1H-O$\underline{H}$); 1.4-1.16 (m, 2H-C(4′), 2H-C(5′), 1H-C(cyclopr.)); 0.95-0.82 (m, 1H-C(cyclopr.), 3H-C(6′)); 0.43-0.32 (quart., 1H-C(cyclopr.)). ^{13}C NMR ($CDCl_3$, 65 MHz) δ: 132.45; 127.71; 63.5; 32.43; 31.82; 22.27; 20.53; 18.16; 14; 10.68. MS (70 eV): 154($M^{+\cdot}$; 1); 136(18); 123(8); 93(23); 91(19); 79(91); 67(100); 57(24); 54(76); 41(40). HR-MS: *m/z* calcd. for $C_{10}H_{18}O$ 154.1359, found: 154.1356.

(1*S*,2*S*)-2-Hex-1′*E*-enyl-cyclopropanecarbaldehyde ((1*S*,2*S*)-15)

A soln. of DMSO (65.5 mg, 0.84 mmol) in CH_2Cl_2 (2.0 ml) was added to a well stirred, cold (-60 °C) soln. of oxalyl chloride (53.3 mg, 0.42 mmol) in CH_2Cl_2 (1.0 ml). After 5 min., a soln. of alcohol **14** (43.0 mg, 0.28 mmol) in CH_2Cl_2 (2.0 ml) was slowly added and stirring was continued for 25 min at - 60 °C prior to the addition of triethylamine (0.19 g, 1.9 mmol). The reaction mixture was allowed to come to rt. and, following hydrolysis with H_2O (20.0 ml), the organic phase was successively washed with dil. HCl (5%), sat. aq. soln. of $NaHCO_3$ and brine. After removal of solvents the product was purified by flash chromatography on SiO_2 (pentane:ether, 80:20). Yield: 38.0 mg (89%). $[\alpha]_{578}^{22} = 9.68°$ (c = 1.33, CH_2Cl_2). IR (KBr, film, cm^{-1}): 3009, 2959, 2930, 2860, 2729, 1707, 1466, 1167, 1007, 914, 864, 737. ^1H NMR ($CDCl_3$, 250 MHz) δ: 9.24 (d, 1H-CHO); 5.72-5.6 (1H-C(2′)); 5.42-5.31 (1H-C(1′)); 2.1 (quart., 1H-C(2)); 2.12-1.92 (2H-C(3′), 1H-C(cyclopr.)); 1.47 (1H-C(cyclopr.)); 1.42-1.24 (m, 1H-C(cyclopr.), 2H-C(4′), 2H-C(5′)); 0.85 (t, 3H-C(6′)). ^{13}C NMR ($CDCl_3$, 65 MHz) δ: 201.38; 134.14; 125.64; 32.23; 31.56; 29.96; 27.03; 26.15; 14.38; 14.02. MS (70 eV): 152($M^{+\cdot}$; 11); 123(8); 109(15); 95(31); 81(61); 79(46); 67(100); 55(26); 41(39). HR-MS: *m/z* calcd. for $C_{10}H_{16}O$ 152.1201, found: 152.1198.

(1*R*,2*R*)-1-Hex-1′*E*-enyl-2-vinyl-cyclopropane ((1*R*,2*R*)-16)

Sodium hydride (0.10 g, 2.5 mmol, 60% dispersion in mineral oil) was suspended in pentane (5.0 ml). After brief stirring the supernatant solvent was removed and DMSO (7.0 g, 89.7 mmol) was added. Formation of the dimsyl anion was forced by heating to 75 °C for 40 min. The soln. was allowed to come to rt. and methyltriphenylphosphonium iodide (1.67 g, 4.1 mmol) was added with stirring. The yellow soln. was cooled to 5 °C, the aldehyde **15** (30.0 mg, 0.20 mmol) was added, and after 3 minutes the mixture was poured into ice water. Extractive work-up and chromatography at -10 °C on SiO_2 with cold pentane (-10 °C) afforded **16** as an intense smelling colourless oil. Yield: 27.8 mg (94%). IR (KBr, film, cm^{-1}): 3015, 2959, 2926, 2858, 1636, 1466, 908, 735. ^1H NMR ($CDCl_3$, 250 MHz) δ: 5.60-5.49 (m, 1H-C(2′)); 5.22-5.18 (m 1H-C(1′), 1H-C(1′′)); 4.99 (m, 2H-C(2′′)); 2.01 (m, 1H-C(3′)); 1.84 (quart., 1H-C(cyclopr.)); 1.5-1.24 (m, 1H-C(cyclopr.), 2H-C(4′), 2H-C(5′)); 0.87 (t, 3H-C(6′)); 1.08 (m, 1H-C(cyclopr.)); 0.58 (quart., 1H-C(cyclopr.).

(6*R*)-Butylcyclohepta-1,4-diene (1)

The hydrocarbon **16** was thermolabile and rearranged at rt. quantitatively to dictyotene (**1**) (86% *e.e.* according to GLC).

(1*S*,2*S*)-1-Acetic acid 2-(hexa-1′*E*,3′*Z*-dienyl)cyclopropylmethyl ester ((1*S*,2*S*)-17)

A soln. of ethylmagnesium bromide (8.9 g, 67.0 mmol) in ether (15.0 ml) was slowly added to a cold (-40 °C) and well stirred suspension of $CuBr{\bullet}S(CH_3)_2$ (12.0 g, 58.3 mmol) in ether (70.0 ml). The resulting brown mixture was stirred for 30 min and allowed to come to -25 °C. Dry acetylene (1.16 g, 44.6 mmol) was slowly passed into the reaction vessel while the temperature was maintained below -15 °C. The resulting dark greenish suspension was cooled to -25 °C and $ZnBr_2$ (4.6 g, 20.0 mmol) and THF (30.0 ml) were added. Transmetallation was finished after 20 min. $Pd(PPh_3)_4$ (1.0 g, 0.86 mmol) was added as the catalyst, followed by a soln. of the vinyl iodide **12** (3.6 g, 13.5 mmol) in a solvent mixture of ether (70.0 ml) THF (30.0 ml) and pyrrolidine (15.0 ml) were added. Within 2 h the temperature was allowed to come to -5 °C. The reaction mixture was poured into a soln. of sat. aq. NH_4Cl, the solids were removed and washed with ether. After extractive work-up of the aq. phase with ether the combined organic phases were successively washed with sat. aq. $NaHCO_3$ and brine. Removal of solvents and chromatography on SiO_2 (pentane:ether, 90:10) afforded the es-

ter (1*S*,2*S*)-**17** as a colourless liquid. Yield: 1.87 g (71%, 1*E*/*Z* > 97/3, 3*E*/*Z* < 2/98). $[\alpha]_{578}^{22}$ = 8.61° (c = 3.23, CH_2Cl_2). IR (KBr, film, cm^{-1}): 2964, 2931, 1734, 1654, 1458, 1370, 1236, 1027, 978, 945, 738. ^1H NMR (250 MHz, $CDCl_3$) δ: 6.52-6.36 (dd, 1H-C(2′)); 5.95-5.81 (t, 1H-C(3′)); 5.43-5.21 (m, 1H-C(1′), 1H-C(4′)); 4.19-4.07 (m, 1H-C$\underline{H}_2$OAc); 3.96-3.88 (m, 1H-C$\underline{H}_2$OAc); 2.15 (quint., 2H-C(5′)); 2.04 (s, 3H-COC$\underline{H}_3$); 1.75-1.59 (m, 1H-C(cyclopr.)); 1.46-1.26 (m, 1H-C(cyclopr.)); 0.99-0.94 (m, 1H-C(cyclopr.)); 0.97 (t, 3H-C(6′)); 0.52-0.43 (quart., 1H-C(cyclopr.)). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.26; 131.93; 131.6; 127.59; 126.91; 115.64; 65.09; 21.07; 19.19; 17.38; 14.34; 11.6. MS (70 eV): 194($M^{+\cdot}$; 43); 137(47); 119(52); 105(97); 91(71); 79(82); 69(57); 55(20); 43(100). HR-MS: *m/z* calcd. for $C_{12}H_{18}O_2$ 194.1307, found 194.1308.

(1*S*,2*S*)-2-(Hexa-1′*E*,3′*Z*-dienylcyclopropyl)-methanol ((1*S*,2*S*)-18)

A soln. of the acetate **17** (65.0 mg, 0.34 mmol) in methanol/water (5.0 ml, 9:1, v:v) was stirred at rt. with K_2CO_3 (0.15 g, 1.1 mmol). After 3 h the suspension was poured into dil. HCl (pH ≈ 4). Extractive work up with ether and chromatography on SiO_2 (pentane:ether, 80:20) afforded (1*S*,2*S*)-**18** as a colourless liquid. Yield: 50.3 mg (99%). $[\alpha]_{578}^{22}$ = 32.6° (c = 9.4, CH_2Cl_2). IR (KBr, film, cm^{-1}): 3371(br), 3004, 2964, 2933, 2875, 1683, 1647, 1463, 1415, 1375, 1039, 982, 739. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.55-6.42 (dd, 1H-C(2′)); 5.98-5.81 (t, 1H-C(3′)); 5.58-5.18 (m, 1H-C(1′), 1H-C(4′)); 3.85-3.66 (m, 1H-C$\underline{H}_2$OH); 3.53-3.37 (m, 1H-C$\underline{H}_2$OH); 2.24-2.09 (quint., 2H-C(5′)); 1.77-1.61 (m, 1H-C(cyclopr.)); 1.59 (s, 1H-O$\underline{H}$); 1.51-1.19 (m, 1H-C(cyclopr.)); 1.04-0.92 (t, 3H-C(6′)); 0.52-0.41 (quart., 1H-C(cyclopr.)). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.09; 132.02; 127.62; 126.96; 63.46; 21.72; 21.15; 19.03; 14.39; 11.82. MS (70 eV): 152($M^{+\cdot}$; 38); 135(17); 121(18); 107(36); 93(93); 79(100); 67(32); 55(25). HR-MS: *m/z* calcd. for $C_{10}H_{16}O$ 152.1201; found 152.1206.

(1*S*,2*S*)-2-(Hexa-1′*E*,3′*Z*-dienyl-cyclopropanecarbaldehyde ((1*S*,2*S*)-19)

Prepared from **18** (50.0 mg, 0.33 mmol) as described for **15**. Yield: 45.0 mg (91%). $[\alpha]_{578}^{22}$ = 117.81° (c = 0.73, CH_2Cl_2). IR (KBr, film, cm^{-1}): 3023, 3006, 2965, 2933, 2873, 2851, 2758, 2731, 1701, 1456, 1366, 1171, 1059, 912, 733. ^1H NMR (HH-COSY 250 MHz, $CDCl_3$) δ: 9.29 (d, 1H-C$\underline{H}$O); 6.52-6.44 (dd, 1H-C(2′)); 5.88-5.79 (t, 1H-C(3′)); 5.56-5.49 (dd, 1H-C(1′)); 5.33-5.26 (dt, 1H-C(4′)); 2.2-2.04 (m, 2H-C(5′), 2H-C(cyclopr.)); 1.5-1.43 (m, 1H-C(cyclopr.)); 0.96-0.88 (t, 3H-C(6′)); 0.83-0.72 (m, 1H-C(cyclopr.)). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 200.62; 133.37; 129.11; 128.12; 127.04; 30.5; 26.81; 21.07; 15.07; 14.24. MS (70 eV): 150($M^{+\cdot}$; 27); 133(18); 121(16); 105(14); 103(13); 93(50); 91(58); 79(100); 77(56); 67(51); 55(47). HR-MS: *m/z* calcd. for $C_{10}H_{14}O$ 150.1045, found 150.1045.

(1*R*,2*R*)-1-Hexa-1′*E*,3′*Z*-dienyl-2-vinyl-cyclopropane ((1*R*,2*R*)-10)

Prepared from **19** (45.0 mg, 0.3 mmol) as described for **16**. Yield: 38.5 mg (88%). ^1H NMR (250 MHz, $CDCl_3$) δ 6.51-6.4 (dd, 1H-C(2′)); 5.95-5.84 (t, 1H-C(3′)); 5.6-5.49 (m, 1H-C(1′), 1H-C(4′)); 5.21-5.18 (m, 1H-C(1″)); 5.04-4.97 (dd, 2H-C(2″)); 2.24-2.01 (m, 2H-C(5′), 1H-C(cyclopr.)); 1.8-1.71 (m, 1H-C(cyclopr.)); 1.01-0.92 (t, 3H-C(6′)); 0.91-0.82 (m, 1H-C(cyclopr.)); 0.72-0.65 (m, 1H-C(cyclopr.)).

(6*S*)-But-(1*Z*)-enyl-cyclohepta-1,4-diene ((6*S*)-2)

(1*R*,2*R*)-**10** was unstable at rt. and rearranged quantitatively to ectocarpene (6*S*)-**2** (92% *e.e.* according to GLC).

(1*S*,2*S*)-1-Acetic acid 2-(5′-hydroxy-pent-1′*E*-en-3′-ynyl)-cyclopropylmethyl ester ((1*S*,2*S*)-20)
A soln. of the iodide **12** (1.0 g, 3.76 mmol) and $Pd(PPh_3)_4$ (220.0 mg, 0.19 mmol) in benzene (2.0 ml) was treated after five min stirring at rt. with piperidine (0.74 ml, 7.52 mmol), propynol (0.44 ml, 7.52 mmol) and CuI (70.0 mg, 0.38 mmol). The progress of the reaction was monitored by GLC. After stirring for 10 h at rt. the stereoselectivity decreased (increasing alkylation of the Z-iodoalkene), and the mixture was poured into a chilled soln. of sat. aq. NH_4Cl. Extractive work up and column chromatography on SiO_2 (pentane:ether, 50:50) yielded the acetate (1*S*,2*S*)-**20** as a colourless oil. Yield: 0.46 g (63%, *E*:*Z* > 98:2). $[\alpha]_{578}^{22}$ = -9.53° (c = 1.72, CH_2Cl_2). IR (KBr, film, cm^{-1}): 3414(br), 3004, 2956, 2925, 2856, 2212, 2175, 1734, 1626, 1455, 1370, 1259, 1159, 1097, 1026, 957, 800. ^1H NMR ($CDCl_3$, 250 MHz) δ: 5.93-5.81 (dd, 1H-C(2′)); 5.66-5.54 (m, 1H-C(1′)); 4.35 (d, 2H-C(5′)); 4.22-4.13 (dd, 1H-C$\underline{H}_2$OAc); 3.94-3.84 (dd, 1H-C$\underline{H}_2$OAc); 2.05 (s, 3H-COC$\underline{H}_3$); 1.74 (s, 1H-O$\underline{H}$); 1.7 (m, 1H-C(cyclopr.)); 1.47 (m, 1H-C(cyclopr.)); 1.05 (m, 1H-C(cyclopr.)); 0.55 (m, 1H-C(cyclopr.)). ^{13}C NMR ($CDCl_3$, 65 MHz) δ: 171.27; 143.33; 109.59; 86.58; 84.40; 64.73; 51.74; 21.12; 19.56; 18.17; 12.11. MS (70 eV): 194($M^{+\cdot}$; 3); 177(5); 133(7); 105(15); 91(29); 79(25); 65(7); 55(6); 43(100). HR-MS: *m/z* calcd. for $C_{11}H_{14}O_3$ 194.0943, found 194.0949.

(1*S*,2*S*)-1-Acetic acid 2-(5′-hydroxy-penta-1′*E*,3′*Z*-dienyl)-cylclopropylmethyl ester ((1*S*,2*S*)-21)
A soln. of (1*S*,2*S*)-**20** (1.3 g, 6.7 mmol) in methanol:water (40.0 ml, 1:1, *v/v*) was stirred at 30 °C with activated Zn(*Cu/Ag*)[22,23] (12.0 g). The progress of the reduction was followed by GLC. After complete conversion (ca. 40 h) the metal was removed by filtration, and the solids were carefully washed with methanol (2 x 20.0 ml) and ether (4 x 20.0 ml). Ca. 2/3 of the solvents were removed *i.v.*, and the remaining aq. soln. was extracted with ether (4 x 50.0 ml). Removal of the solvent followed by chromatography on SiO_2 (pentane:ether, 30:70) afforded the configurationally pure acetate (1*S*,2*S*)-**21**. Yield: 0.87 g (67%, 3′*E*:*Z* < 1:99). $[\alpha]_{578}^{22}$ = 56.4° (c = 2.12, CH_2Cl_2). IR (KBr, film, cm^{-1}): 3410, 3074, 3023, 2954, 2893, 1736, 1648, 1371, 1241, 1028, 739. ^1H NMR (250 MHz, $CDCl_3$) δ: 6.46 (t, 1H-C(2′)); 6.11-5.96 (t, 1H-C(3′)); 5.53-5.4 (m, 1H-C(1′), 1H-C(4′)); 4.3 (d, 2H-(C5′)); 4.2-4.09 (m, 1H-C$\underline{H}_2$OAc); 4.01-3.87 (m, 1H-C$\underline{H}_2$OAc); 2.04 (s, 3H-COC$\underline{H}_3$); 1.79-1.63 (m, 1H-C(cyclopr.), 1H-O$\underline{H}$); 1.49-1.34 (m, 1H-C(cyclopr.)); 1.12-0.98 (m, 1H-C(cyclopr.)); 0.57-0.46 (m, 1H-C(cyclopr.)). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 171.32; 134.54; 130.63; 127.35; 126.05; 64.92; 58.76; 21.07; 19.21; 17.69, 11.81. MS (70 eV): 196 ($M^{+\cdot}$; 27); 136(16); 117(39); 105(44); 91(61); 79(86); 67(32); 55(11); 54(11); 43(100). HR-MS: *m/z* calcd. for $C_{11}H_{16}O_3$ 196.1110, found 196.1100.

(1*S*,2*S*)-1-Acetic acid 2-(5′-oxo-penta-1′*E*,3′*E*-dienyl)-cylclopropylmethyl ester ((1*S*,2*S*)-22)
A soln. of the alcohol **21** (0.10 g, 0.51 mmol) in dichloromethane (20.0 ml) was vigorously stirred with activated MnO_2 (2.2 g). After complete conversion (GLC, 10 min) the MnO_2 was immediately filtered off and washed with ether (4 x 25.0 ml). The combined ethereal solutions were evaporated, and the crude product was used without purification for the subsequent Wittig-reaction.

(1*S*,2*S*)-1-Acetic acid 2-hexa-1′*E*,3′*Z*,5′-trienyl-cylclopropylmethyl ester ((1*S*,2*S*)-23)
(1*S*,2*S*)-**22** (60.0 mg, 2.5 mmol) was converted into the olefin as described for **16**. Chromatography on SiO_2 (pentane:ether, 70:30) afforded **23** as a pale yellow oil. Yield: 67.0 mg (69% from **21**). $[\alpha]_{578}^{22}$ = 73.73° (c = 1.07, CH_2Cl_2). IR (KBr, film, cm^{-1}): 3085, 3008, 2957, 2898, 1738, 1632, 1619, 1452, 1439, 1370, 1237, 1027, 974, 940, 904, 845. ^1H NMR (HH-COSY 500 MHz, $CDCl_3$) δ: 6.85-6.73 (dt, 1H-C(5′)); 6.68-6.57 (dd, 1H-C(2′)); 5.98-5.82 (m, 1H-C(3′), 1H-C(4′)); 5.5-5.42 (dd, 1H-C(1′)); 5.23-5.08 (m, 2H-C(6′)); 4.2-

4.09 (quart, -C$\underline{H}_2$OAc); 3.98-3.88 (quart, -C$\underline{H}_2$OAc); 2.02 (s, -COC$\underline{H}_3$); 1.78-1.64 (m, 1H-C(cyclopr.)); 1.5-1.39 (m, 1H-C(cyclopr.)); 1.12-1.01 (m, 1H-C(cyclopr.)); 0.53 (quart., 1H-C(cyclopr.)). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.24; 133.95; 132.17; 129.75; 127.88; 126.76; 117.52; 63.26; 21.07; 19.43; 17.81; 12.01. MS (70 eV): 192($M^{+\cdot}$; 46); 132(29); 117(100); 104(25); 91(89); 78(42); 67(25); 54(18); 43(87). HR-MS: *m/z* calcd. for $C_{12}H_{16}O_2$ 192.1150, found 192.1154.

(1*S*,2*S*)-2-(Hexa-1′*E*,3′*Z*,5′-trienyl-cyclopropyl)-methanol ((1*S*,2*S*)-24)

Prepared from **23** (64.5 mg, 0.33 mmol) as described for **18**. Yield: 42.3 mg (86%). $[\alpha]_{578}^{22}$ = 63.64° (c = 0.47, CH_2Cl_2). IR (KBr, film, cm^{-1}): 3375(br), 3072, 3004, 2924, 2881, 1722, 1680, 1625, 1414, 1367, 1334, 1300, 1018, 989, 905, 733. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 6.89-6.59 (m, 1H-C(5′), 1H-C(2′)); 6.01-5.8 (dt, 1H-C(3′), 1H-C(4′)); 5.57-5.42 (dd, 1H-C(1′)); 5.28-5.01 (m, 2H-C(6′)); 3.82-3.70 (m, -C$\underline{H}_2$OH); 3.55-3.3 (m, -C$\underline{H}_2$OH); 1.78-1.61 (m, 1H-C(cyclopr.)); 1.51 (s, 1H-O$\underline{H}$); 1.5-1.33 (m, 1H-C(cyclopr.)); 1.12-0.98 (m, 1H-C(cyclopr.)); 0.55-0.41(m, 1H-C(cyclopr.)). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 134.42; 132.16; 129.70; 127.82; 126.68; 117.57; 63.28; 22.01; 19.23; 12.08. MS (70 eV): 150($M^{+\cdot}$; 43); 131(24); 119(79); 117(98); 105(65); 91(100); 81(20); 79(29); 67(35); 41(22). HR-MS: *m/z* calcd. for $C_{10}H_{14}O$ 150.1045, found 150.1054.

(1*S*,2*S*)-2-(Hexa-1′*E*,3′*Z*,5′-trienyl)cyclopropanecarbaldehyde ((1*S*,2*S*)-25)

Prepared from **24** (0.15 g, 1.0 mmol) as described for **15**. Yield: 0.13 g (89%). $[\alpha]_{578}^{22}$ = 17.8° (c = 0.75, CH_2Cl_2). IR (KBr, film, cm^{-1}): 3086, 3035, 3008, 2977, 2928, 2839, 2731, 1701, 1632, 1618, 1440, 1399, 1365, 1267, 1171, 1062, 997, 975, 934, 907, 737. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.33 (d, 1H-C$\underline{H}$O); 6.8-6.61 (m, 1H-C(5′), 1H-C(2′)); 5.92-5.84 (m, 1H-C(3′), 1H-C(4′)); 5.66-5.56 (dd, 2H-C(1′)); 5.21-5.05 (m, 2H-C(6′)); 2.21-2.09 (m, 2H-C(cyclopr.)); 1.5 (quart., 1H-C(cyclopr.)); 1.41 (m, 1H-C(cyclopr.)). ^{13}C-NMR (65 MHz, $CDCl_3$) δ: 200.46; 131.98; 131.26; 129.2; 129.12; 127.96; 118.24; 30.70; 27.1; 15.43. MS (70 eV): 148($M^{+\cdot}$; 23); 130(17); 117(23); 104(37); 91(100); 84(51); 81(67); 79(68); 69(64); 40(43). HR-MS: *m/z* calcd. for $C_{10}H_{12}O$ 148.0888, found 148.0886.

(1*R*,2*R*)-Hexa-1′*E*,3′*Z*,5′-trienyl-2-vinyl-cyclopropane ((1*R*,2*R*)-26)

Prepared from **25** (36.0 mg, 0.24 mmol) as described for **16**. Yield: 27.9 mg (78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88-6.58 (m, 1H-C(5), 1H-C(2)); 5.95-5.81 (m, 1H-C(3), 1H-C(4′)); 5.66-5.41 (m, 1H-C(1), 1H-C(1′)); 5.26-5.05 (m, 2H-C(6), 2H-C(2′)); 1.85-1.74 (m, 1H-C(cyclopr.), 1.62-1.4 (m, 1H-C(cyclopr.)); 1.16-1.03 (m, 1H-C(cyclopr.)); 0.78-0.67 (m, 1H-C(cyclopr.)).

(6*R*) -Buta-(1*Z*,3)-dienyl-cyclohepta-1,4-diene ((6*R*)-3)

The hydrocarbon (1*R*,2*R*)-**26** was unstable at rt. and rearranged quantitatively to desmarestene ((6*R*)-**3**) (93% *e.e.* according to GLC).

2-(Trimethylsilanyl)-1-(*cis*-2-vinyl-cyclopropyl)-but-3-en-1-ol (29)

A soln of *t*-BuLi (1.0 ml of 1.7 M solution in *n*-hexane, 1.8 mmol) was added to a cold (-78 °C) and well stirred solution of allyltrimethylsilane (0.22 g, 2.0 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (0.21 g, 1.8 mmol) in dry THF (10.0 ml). Stirring was continued for 2 h at -30 °C, and, after recooling to -78 °C, Ti(*O*-*i*Pr)$_4$ (0.56 g, 2.0 mmol) was added. After 1 h at -78 °C, the aldehyde[27] **27** (0.84 g, 0.87 mmol) was added. The reaction was complete after 2 h at -78 °C. The mixture was poured into a chilled, sat. aq. solution of

NH_4Cl. Extractive work up with ether and removal of the solvents afforded **29** which was further purified on deactivated SiO_2 (10% water, pentane:ether, 90:10) to yield **29** as a colourless liquid. Yield: 0.99 g (54%). IR (KBr, film, cm^{-1}): 3452(br), 3073, 3000, 2955, 2899, 1937, 1805, 1708, 1634, 1625, 1452, 1416, 1367, 1287, 1247, 1170, 1127, 1086, 1049, 1005, 984, 962, 934, 903, 867, 841, 780, 755, 733. ^1H NMR (400 MHz, $CDCl_3$) δ: 5.94 (dt, 1 H-C(3)); 5.74-5.6 (dt, 1 H-C(1′)); 5.22-4.89 (m, 2H-C(4), 2H-C(2′)); 3.43 (m, 1H-C(1)); 1.71-1.52 (m, 1H-C(cyclopr.), 1H-C(2)); 1.62 (s, 1H-OH); 1.36-1.16 (m, H-C(cyclopr.)); 1.02-0.76 (m, H-C(cyclopr.)); 0.48 (quart, 1 H-C(cyclopr.)); 0.01 (s, 9H-$SiMe_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.27; 135.47; 115.16; 114.85; 72.35; 42.42; 25.06; 20.3; 11.14; -2.28. MS (70 eV): 210($M^{+\cdot}$; 2); 195(6); 171(17); 156(37); 105(14); 91(11); 79(46); 75(66); 73(100); 66(38); 45(16); 41(12). HR-MS: *m/z* calcd. for $C_{12}H_{22}OSi$ 210.1440, found 210.1428.

cis-1-Buta-1′*E*,3′-dienyl-2-vinyl-cyclopropane (30)

A soln. of the hydroxysilane **29** (86.0 mg, 0.41 mmol) was cooled to -78 °C and H_2SO_4 (0.2 ml) in THF (2.0 ml) was added. The reaction was slowly warmed to -30 °C and stirring was maintained for 15 min at this temperature. The mixture was poured into cold aq. $NaHCO_3$, and the aq. layer was extracted with cold (0 °C) ether. The combined organic layers were concentrated in vacuo at -10 °C. Chromatography at -10 °C on SiO_2 (pentane) yielded the unstable hydrocarbon **30** as a colourless liquid. Yield: 43.3 mg (88%). ^1H NMR (400 MHz, $CDCl_3$) δ: 6.32-6.12 (m, 1H-C(2′), 1H-C(3′)); 5.6-5.42 (m, 1H-C(1′), 1H-C(1′′)); 5.12-4.88 (m, 2H-C(2′′), 2H-C(4′)); 1.81-1.56 (m, 1H-C(cyclopr.)); 1.23-1.11 (m, 1H-C(cyclopr.)); 0.98-0.8 (m, 1H-C(cyclopr.)); 0.71 (quart., 1 H-C(cyclopr.)).

cis-1-Buta-1′*Z*,3′-dienyl-2-vinyl-cyclopropane (31)

A slurry of potassium hydride in mineral oil (0.10 g of a 35% slurry in oil, ~0.78 mmol) was briefly stirred with pentane (5.0 ml). The supernatant solvent was removed and replaced by dry THF (10.0 ml). Then, the suspension was cooled to -78 °C, and a solution of **29** (64.0 mg, 0.31 mmol) in dry THF (2.0 ml) was added. The mixture was allowed to come slowly to -25 °C and, after stirring for 15 min at this temperature, the solution was poured into a cold, sat. aq. solution of NH_4Cl. Extractive work-up (ether), removal of solvents, followed by chromatography on SiO_2 (pentane for elution) afforded **4** as a colourless liquid. Yield: 33.0 mg (72%). ^1H NMR (250 MHz, $CDCl_3$) δ: 6.82-6.65 (m, 1H-C(3′)); 6.04 (t, 1H-C(2′)); 5.59 (m, 1H-C(1′′)), 5.23-5.1 (m, 1H-C(1′); 5.09-4.96 (m, 2H-C(4′), 2H-C(2′′)); 2.1-1.96 (m, 1H-C(cyclopr.)); 1.88-1.77 (m, 1H-C(cyclopr.)); 1.29-1.2 (m, 1H-C(cyclopr.)); 0.66 (quart., 1 H-C(cyclopr.)).

6-Vinyl-cyclohepta-1,4-diene (4)

The hydrocarbon **30** was unstable at rt. and rearranged quantitatively to **4.** Higher temperatures (40 to 65 °C) were necessary for the rearrangement of **31** to **4**.

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