56. Unusual and Novel $C_{11}H_{16}$ Hydrocarbons from the Southern Australian Brown Alga *Dictyopteris acrostichoides* (Phaeophyceae)

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Unusual and novel $C_{11}H_{16}$ olefins with (*E*)- or (*E,E*)-configuration instead of the previously known (*Z*)- or (*E,Z*)-configuration at the double bond(s) within the longer side chain are the main products of the Australian phaeophyte *Dictyopteris acrostichoides*. This configuration anomaly refers to all four series of alicyclic $C_{11}H_{16}$ hydrocarbons, namely the disubstituted cyclopentenes and cyclopropanes, as well as the monosubstituted cycloheptadienes and cyclopentenes. Chiral compounds within the above series have the same absolute configuration. The two (cyclopent-3-enyl)hexa-1,3-dienes **11** and **13** are found for the first time. The absolute configuration and optical purity of the hydrocarbons are determined by gas chromatography on modified cyclodextrins as chiral stationary phases. The synthesis of chiral references *via* lipase-catalyzed resolutions is described.

Introduction. – The class of marine brown algae has evolved a unique pheromone system which to our present knowledge is almost exclusively based on a few series of simple acyclic, alicyclic, or aliheterocyclic $C_{11}H_{14}$, $C_{11}H_{14}O$, $C_{11}H_{16}$, $C_{11}H_{16}O$, and $C_{11}H_{18}$ olefins (*cf.* also *Table*) [1] [2]. Freshly released male gametes of many phaeophytes respond chemotactically to the genuine pheromones at the lower nmol→pmol level. The signal molecules are biosynthesized from unsaturated fatty acids as was previously shown by *in vivo* feeding studies with the flowering plant *Senecio isatideus* as a model system [3]. In this terrestrial plant, (3*Z*,6*Z*,9*Z*)-dodeca-3,6,9-trienoic acid serves as the immediate precursor for several $C_{11}H_{16}$ hydrocarbons among which ectocarpene (**8**) is by far the most abundant (94% of the total $C_{11}H_{16}$ hydrocarbons). However, recent advances with female gametes of the two phaeophytes *Ectocarpus siliculosus* and *Sphacelaria divaricata* indicate that in the marine plants, the group of unsaturated C_{12} acids is replaced by the family of C_{20} polyenoic fatty acids like, *e.g.*, icosatetraenoic, icosapentaenoic, and icosahexaenoic acid [4]. However, in contrast to the rather well understood biosynthesis of the C_{11} hydrocarbons in higher plants [3], nothing is known about the sequence of events of the algal metabolism leading from unsaturated C_{20} precursors to the C_{11} hydrocarbons. Since terrestrial plants lack the family of C_{20} polyenoic acids, at least for the present, the terrestrial model systems are no longer considered as being representative of the biosynthetic capacity of the enzymes from marine plants. To learn more about the various oxidation and degradation sites of, *e.g.*, arachidonic acid in marine brown algae, we directed our attention further onto the search for new C_{11} structures. The large, cosmopolitan genus of *Dictyopteris* spp. is a well known and rich source of such hydrocarbons [5]. Another major advantage is the fact that in some *Dictyopteris* spp., the production of

the C_{11} hydrocarbons does not depend on sexual events. Fairly large amounts of these compounds are produced and stored in the thallus from where they are slowly released into the seawater[1]), probably as a means of chemical defense [6].

We now report on the isolation, structure elucidation, and determination of the absolute configuration and enantiomeric purity of several unusual and novel hydrocarbons from the Australian brown alga *Dictyopteris acrostichoides*. The configuration and enantiomeric composition of the individual compounds shed further light onto possible biosynthetic interrelations within the class of algal pheromones.

I. C_{11} Hydrocarbons from *Dictyopteris acrostichoides*: Isolation and Characterization. – Gametophytes and sporophytes of *D. acrostichoides* were collected during February 1987 and 1990 at Point Lonsdale and Sorrento (Victoria, Australia). The whole plants were suspended in seawater and placed in a closed-loop extraction vessel as described previously [1] [2]. The volatiles were collected by air circulation and adsorbed to a bed of 1.5 mg of activated carbon. After desorption of the carbon traps with CH_2Cl_2 (30 µl), the eluates, containing *ca.* 10–20 µg of a complex hydrocarbon mixture, were subjected to GLC/MS analysis. Known substances were identified with references. In all other cases, the suspected structures had to be synthesized (*vide infra*) prior to final identification. The *Figure* shows the gas-chromatographic separation of the volatiles from *D. acrostichoides*. Besides of the major components **1**, **3**, **5**, **7**–**9**, **13**, **16**, and **17** (see *Table*), several trace constituents are present (**2**, **4**, **6**, **10**–**12**, **14**, and **15**).

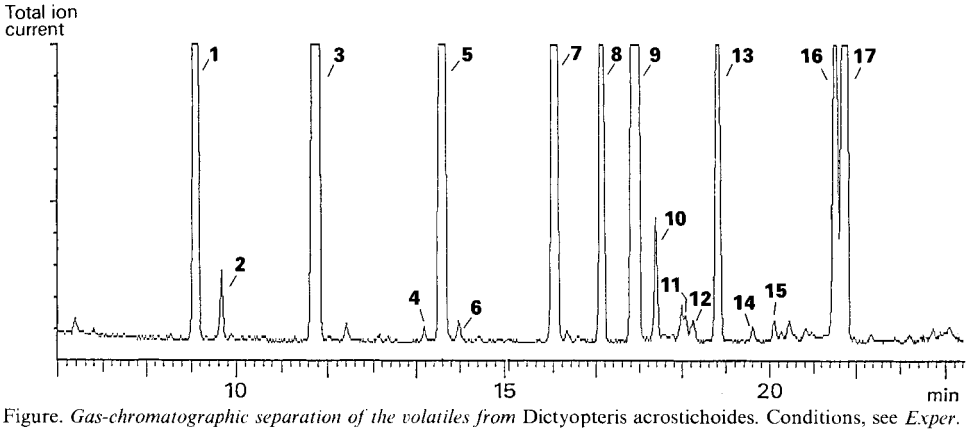


Figure. *Gas-chromatographic separation of the volatiles from* Dictyopteris acrostichoides. Conditions, see *Exper. Part.* For the structures of the major components, see *Table.* The minor constituents are identified as follows: **4**, $C_{10}H_{16}$ (unknown); **6**, $C_{11}H_{16}$ (unknown); **10**; (3*E*,5*Z*)-undeca-1,3,5-triene; **12**, (3*E*,5*E*)-undeca-1,3,5-triene; **14**, $C_{11}H_{14}$ (unknown); **15**, (3*E*,5*Z*,8*Z*)-undeca-1,3,5,8-tetraene.

Only the dienes **1**, **3**, **5**, and **7** and the trienes **8**, **9**, and **16** are identical with previously known pheromones or volatiles of brown algae. These are *cis*-3-butyl-4-vinylcyclopentene (**1**) [7], (1*E*)-1-(cyclopent-3-enyl)hex-1-ene (**3**) [8], *trans*-1-[(1*E*)-hex-1-enyl]-2-vinylcyclopropane (= dictyopterene A; **5**) [5], 6-butylcyclohepta-1,4-diene (= dictyotene; **7**)

[1]) *E.g.*, thallus (1 kg, wet weight) of the Mediterranean phaeophyte *Dictyopteris membranaceae* release within 24 h *ca.* 10–50 mg of C_{11} hydrocarbons into the surrounding seawater (*K. Dettmer* and *W. Boland*, unpublished results).

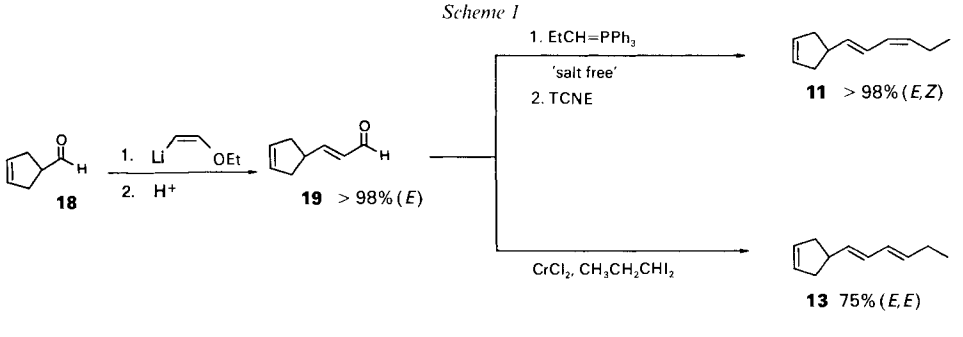
[5] [9], 6-[(1*Z*)-but-1-enyl]cyclohepta-1,4-diene (= ectocarpene; **8**) [1] [2] [5], 6-[(1*E*)-but-1-enyl]cyclohepta-1,4-diene (**9**) [8], and *trans*-1-[(1*E*,3*Z*)-hexa-1,3-dienyl]-2-vinylcyclopropane (= hormosirene; **16**) [5] [10]. To determine the C-framework of the unknown trienoic compounds **11**, **13**, and **17** (M^+ 148; $C_{11}H_{16}$), a sample is microhydrogenated (PtO_2, H_2). Surprisingly, no other (cyclo)alkanes than the ones expected from compound classes represented by **1**, **3**, **5**, and **7** are formed. Thus, the new substances **11**, **13**, and **17** have to be configurational isomers of the previously known structures. This is confirmed by synthesis of the suspected isomers and subsequent comparative GLC and GLC/MS analysis (*vide infra*).

The absolute configuration and enantiomeric composition of the volatiles are determined by GLC using modified β- or γ-cyclodextrins as chiral stationary phases. Chiral references (*vide infra*) of known absolute configuration and optical purity are used to determine the elution order of the corresponding enantiomers. With the exception of ectocarpene (**8**) and dictyotene (**7**), each chiral compound displays baseline separation for its enantiomers. The enantiomers of the three cyclopropanes **5**, **16**, and **17**, as well as of the cyclopentenes **1** and **2**, are separated on heptakis(3-*O*-methyl-2,6-di-*O*-pentyl)-β-cyclodextrin (column *I*), in the case of **9**, octakis(6-*O*-methyl-2,3-di-*O*-pentyl)-γ-cyclodextrin (column *II*) is used [11] (see *Table*).

II. Synthesis of Reference Compounds. – *Cyclopentenes.* The two novel 1-(cyclopent-3-enyl)hexa-1,3-dienes **11** and **13** are readily available from aldehyde **18** as outlined in *Scheme 1* [8]. Alkylation of **18** with *cis*-2-ethoxyvinyllithium [12] followed by acidic workup yields the configurationally pure (*E*)-aldehyde **19**. Subsequent *Wittig* reaction with triphenyl(propylidene)phosphorane under 'salt free' conditions introduces the new double bond in a highly (*Z*)-selective manner and provides **11** (92% (*E*,*Z*), 8% (*E*,*E*)). The small admixture of the (*E*,*E*)-isomer **13** is conveniently removed by *Diels-Alder* reaction with tetracyanoethene (= ethenetetracarbonitrile; TCNE) under controlled conditions. The (*E*,*E*)-isomer **13** can be stereoselectively prepared from the same aldehyde **19** using a geminal bimetallic organochromium reagent which is generated *in situ* from 1,1-diiodopropane and Cr^{II} [13]. The resulting olefin consists to 75% of the required (*E*,*E*)-isomer **13** and to 25% of the two possible (*E*,*Z*)-combinations which can not be removed by chromatography.

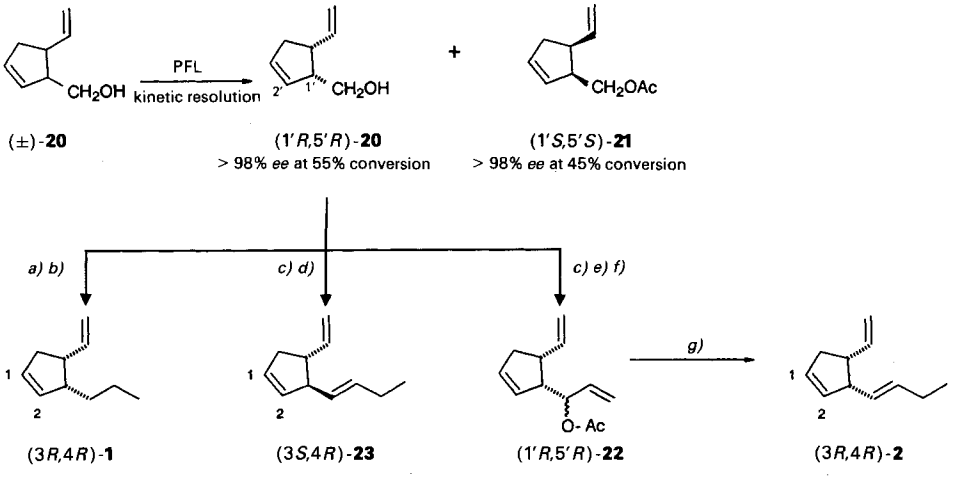
The synthesis of the two chiral cyclopentenes **1** and **2** is achieved according to our previous protocol for cyclopentenoid algal pheromones [14]. As the key step for the resolution of the enantiomers, the alcohol (±)-**20** is subjected to an enzyme-catalyzed

Scheme 1



acylation using a lipase from *Pseudomonas fluorescens* (PFL) under kinetically controlled conditions. Both enantiomers are obtained in very high purity provided that the acylation is stopped at an either low (45%) or at a high conversion rate (55%). In the first case, acetate (1′*S*,5′*S*)-**21** is obtained with > 98% *ee*, while at 55% conversion, the unreacted alcohol (1′*R*,5′*R*)-**20** is obtained as a highly enantiomerically pure (> 98% *ee*) compound (*Scheme 2*). For the synthesis of (3*R*,4*R*)-**1**, a less pure sample of alcohol (1′*R*,5′*R*)-**20** (89% *ee*) is first converted into the corresponding 4-toluenesulfonate. Subsequent alkylation with propylmagnesium bromide is readily achieved in the presence of a catalytical amount of Li_2CuCl_4 and introduces the C_4-side chain of (−)-(3*R*,4*R*)-**1** (90.2% *ee*; GLC) without difficulty [14]. The nonnatural (*E*)-'multifidene' (3*R*,4*R*)-**2** is likewise available from alcohol (1′*R*,5′*R*)-**20**. Following oxidation with pyridinium chlorochromate (PCC) and alkylation with vinylmagnesium bromide, the resulting secondary alcohol is treated with AcCl and provides the acetate (1′*R*,5′*R*)-**22**. Displacement

Scheme 2

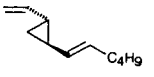
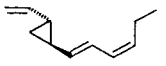
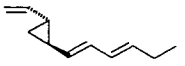
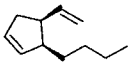
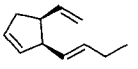
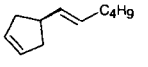
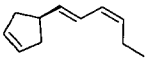
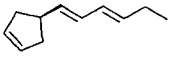
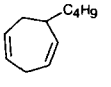
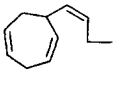
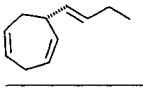


a) TosCl, C_5H_5N. *b*) PrMgBr, Li_2CuCl_4. *c*) PCC. *d*) $CrCl_2$, $CH_3CH_2CHI_2$. *e*) CH_2=CHMgBr. *f*) AcCl, C_5H_5N. *g*) $LiCuMe_2$.

of the acetate proceedes smoothly upon addition of lithium dimethylcuprate and yields the nonnatural (−)-(3*R*,4*R*)-**2** with complete allylic rearrangement of the double bond (*ca.* 90% of (*E*)- and 10% of (*Z*)-isomer (= multifidene)). An attempt, to prepare **2** from the intermediary aldehyde (product of PCC oxidation) with the above bimetallic organochromium reagent derived from 1,1-diiodopropane failed. Instead of the expected *cis*-disubstituted olefin **2**, mainly *trans*-isomer **23** was obtained. Since the intermediary aldehyde is extremely prone to enolization, the epimerization to the more stable *trans*-aldehyde is obviously faster than the addition of the polar, *Lewis*-acidic organometallic reagent.

Cyclopropanes and Cycloheptadienes. The most promising approach towards **9** and other cycloheptadienes is the [3,3]-sigmatropic rearrangement of a correspondingly functionalized cyclopropane, like *e.g.* (1*S*,2*R*)-**28**, in a 'biomimetic' fashion [3] [5]. Since this

Table. *Hydrocarbons from* Dictyopteris acrostichoides

Component		Composition [%]	Absolute configuration	*ee* [%][a])
	**5**	6.4	(+)-(1*R*,2*R*)	94.0 (*I*)
	**16**	2.5	(−)-(1*R*,2*R*)	*ca.*75 (*I*)[b])
	**17**	13.7	(+)-(1*R*,2*R*)	74.2 (*I*)
	**1**	6.4	(+)-(3*S*,4*S*)	96.6 (*I*)
	**2**	0.2	(−)-(3*S*,4*S*)	> 95 (*I*)[b])
	**3**	18.6	–	
	**11**	< 0.1	–	
	**13**	3.1	–	
	**7**	10.7	–	
	**8**	3.0	–	
	**9**	24.8	(−)-(6*R*)	25.8 (*II*)

[a]) *I* and *II* refer to GLC column *I* (heptakis(3-*O*-2,6-di-*O*-pentyl)-β-cyclodextrin) and *II* (octakis(6-*O*-methyl-2,3-di-*O*-pentyl)-γ-cyclodextrin); see text.

[b]) Peak areas of these compounds are only estimated due to too small signals for correct integration.

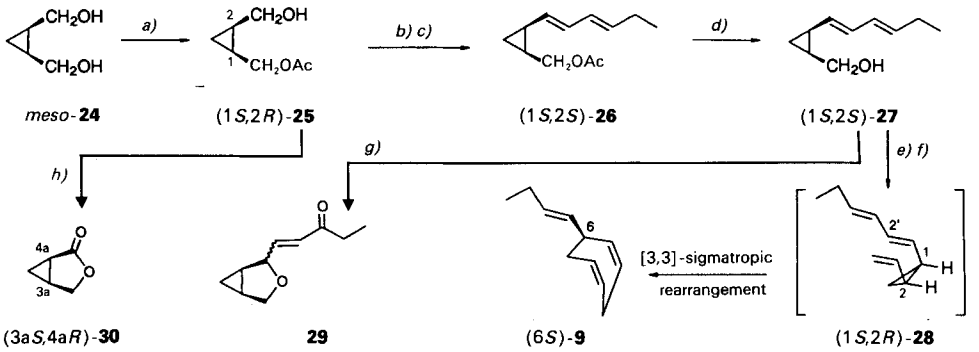
rearrangement proceeds exclusively *via* the *cis-endo* transition state as outlined in *Scheme 3*, a complete chirality transfer from the bis(alkenyl)cyclopropane into the cycloheptadiene **9** is expected [15]. Moreover, enzymatic routes to the highly enantiomerically pure monoacetate (1*S*,2*R*)-**25** using the *meso*-diol *meso*-**24** are known [16].

Particularly, a lipase from *Pseudomonas fluorescens* (SAM-II) was recommended for this purpose [17]. Unfortunately, we were unable to reproduce the high *ee* reported for this enzyme, but the lipase from porcine pancreas (PPL) provided (1*S*,2*R*)-**25** with *ee* values (78%) close to the literature data [16] for the hydrolytic mode.

Since biocatalytical resolutions depend on solvent and temperature conditions, we optimized the enantioselectivity of PPL by running the acyl transfer at lower temperatures, the limit for an acceptable conversion rate being 10°. Under these conditions, the *ee* of (1*S*,2*R*)-**25** was reproducibly raised to 91–96%. Several other lipases from microbial sources were scrutinized, but most of them failed to give acceptable results (*cf. Exper. Part*). On completition of this work, a superior approach towards chiral cyclopropanes of type **25** was published using PPL in the hydrolytic mode [18].

The optical purity of (1*S*,2*R*)-**25** is determined after oxidation (Ru^{VIII}, $NaIO_4$) [19] and cyclization of the resulting acetoxy acid (*Scheme 3*) by GLC analysis of the resulting lactone (3a*S*,4a*R*)-**30** using hexakis(3-*O*-acetyl-2,6-di-*O*-pentyl)-α-cyclodextrin [20] as the chiral stationary phase (separation factor: $\alpha = 1.3$). Control experiments confirm that this route proceeds without racemization (transacylation). *Swern* oxidation of

Scheme 3

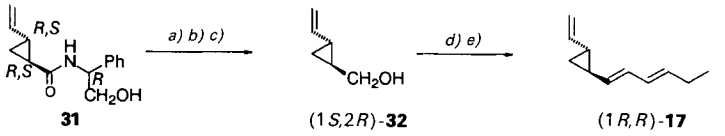


a) Porcine pancreas lipase (PPL). *b*) *Swern* oxidation. *c*) (*E*)-EtCH=CH–CH=$P(C_6H_{11})_3$. *d*) $LiAlH_4$. *e*) PDC. *f*) CH_2=PPh_3. *g*) PCC. *h*) Ru^{VII}, $NaIO_4$; H^+.

(1*S*,2*R*)-**25** yields an aldehyde which is converted to (1*S*,2*S*)-**26** (> 97% (*E*,*E*)) in a highly stereoselective fashion using tri(cyclohexyl)[(2*E*)-pent-2-enylidene]phosphorane for *Wittig* olefination [21]. Other methods, *e.g.* with titanium-moderated (alkenyl)-diphenylphosphines [22] or (alkenyl)diphenylphosphine oxides [23], are less satisfactory. The high (*E*)-selectivity in the formation of (1*S*,2*S*)-**26** is of great importance, since the configuration at C(2') of the hexadienyl side chain (see (1*S*,2*R*)-**28**) determines the configuration at C(6) of the cycloheptadiene **9** [15] [18]. Thus, following reductive deacylation to alcohol (1*S*,2*S*)-**27** and oxidation with pyridinium dichromate (PDC), to the corresponding aldehyde, the final *Wittig* reaction with (methylidene)triphenylphosphorane in affords nonnatural (6*S*)-**9** 96% *ee* (GLC). If the acidic PCC is used instead of the PDC oxidant, the yield of aldehyde is much lower, and the bicyclic furanylpentenone **29** is isolated as a by-product in 12% yield. Similar oxidative functionalizations of suitably oriented double bonds were reported by *Corey* and *Suggs* [24].

An optically pure sample of the hormosirene analogue (+)-(1*R*,2*R*)-**17** is readily available from amides **31** (*Scheme 4*). The latter, obtained from (–)-(*R*)-2-phenylglycinol and *rac-trans*-2-vinylcyclopropane-1-carboxylic acid [25], can be separated on a large scale by simple crystallization from heptane. Two crystallizations raise the optical purity of the less soluble amide to > 99% *de* (evidenced by HPLC separation on SiO_2). Follow-

Scheme 4



31 (1*S*,2*R*)-**32** (1*R*,*R*)-**17**

a) Crystallization. *b*) H^+. *c*) $LiAlH_4$. *d*) PCC. *e*) (*E*)-EtCH=CH–CH=P(C_6H_{11})$_3$.

ing acidic hydrolysis, reduction of the liberated acid, and oxidation (PCC) of the resulting alcohol (1*S*,2*R*)-**32**, *Wittig* reaction with tri(cyclohexyl)[(2*E*)-pent-2-enylidene]-phosphorane as described above gave (+)-(1*R*,2*R*)-**17**, again with $\geq$ 97% (*E*,*E*)-selectivity, and with $\gg$ 99% *ee* (GLC, column *I*).

III. Biosynthetic Aspects. – As shown above, the Australian brown alga *D. acrostichoides* produces a number of unusual or novel $C_{11}H_{16}$ olefins which possess (*E*)- or (*E*,*E*)-configuration instead of the previously known (*Z*)- or (*E*,*Z*)-combinations in the longer side chain. The two (cyclopent-3-enyl)hexa-1,3-dienes **11** and **13** are found for the first time. It is interesting to note that all compounds within the series of alicyclic hydrocarbons of the *Table* elaborate the same absolute configuration.

A special feature of $C_{11}H_{16}$ cyclopropanes is their generally low to moderate optical purity (*ca.* 52–90%, species-dependent [26]). The (1*R*,2*R*)-configuration is most often found, but the North-Atlantic species *Haplospora globosa* produces (1*S*,2*S*)-**16** as the major product (83% *ee*) [26]. The *ee* of the $C_{11}H_{18}$ cyclopropane (1*R*,2*R*)-**5** is much higher (94% *ee*; see *Table*). Whether or not this difference in the optical purity between the hexenyl- and hexadienylcyclopropanes is a general phenomenon is unknown and has to await further investigations.

In agreement with our previous work, both cyclopentenes **1** and **2** are of high *ee* [27]; their absolute configuration corresponds to multifidene (= *cis*-**2**) [28]. Until now, the series of cycloheptadienes can not be fully characterized, since **7** and **8** fail to separate on all of the hitherto employed chiral stationary phases. (*E*)-Isomer **9**, however, is of very low optical purity (*Table*). Furthermore, the *ee* of (*Z*)-isomer **8** which was previously isolated in larger quantities from the two Hawaiian phaeophytes *D. plagiogramma* and *D. australis* does not exceed 70% (based on optical rotations [5]).

The co-occurrence of the novel (*E*)- and (*E*,*E*)-isomers with the well known (*Z*)- and (*Z*,*E*)-combinations among the volatiles of *D. acrostichoides* might be interesting from the biogenetic point of view. The mixture of configurational isomers and enantiomers may be indicative of a reactive intermediate which escapes the control of the active center of the transforming enzyme(s) [3] [5] [27]. Another rationale for this finding could be seen in the formation of enantiomeric mixtures of still unknown intermediates between the fatty acid precursor(s) and the hydrocarbon products (*e.g.* hydroperoxides). Recent advances with female gametes of marine brown algae clearly indicate, that (3*Z*,6*Z*,9*Z*,12*Z*,15*Z*,18*Z*)-icosa-3,6,9,12,15,18-pentaenoic acid is the source for the $C_{11}H_{16}$ hydrocarbons, while the $C_{11}H_{18}$ compounds derive from arachidonic acid. However, further work on the activation of the C_{20} acids and the identification of intermediates are urgently necessary prior the outline of valid biosynthetic pathways or detailed mechanisms covering configurations and enantiomeric mixtures.

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Experimental Part

General. See [29]. In addition: Microbial enzymes were purchased from *Fluka* (Switzerland) and *Sigma* (USA). GLC: chiral stationary phases *I* and *II* were prepared as described in [11]; *Pyrex* glass capillaries (25 m × 0.25 mm i.d.).

Gas-Chromatographic Separation of the Volatiles from Dictyopteris acrostichoides. Compounds are collected from the headspace of living plants on a bed of activated carbon (1.5 mg) as described previously [1] [2]. The carbon traps are eluted with CH_2Cl_2 (30 µl), and the mixture is separated on a *Supelcowax* column (30 m × 0.32 mm, 0.25 μ layer thickness). Temp. program: 40° for 5 min, then at 10°/min to 220°. Detection: *Finnigan* ion trap, *ITD 800*. Transfer line: 270°; scan range: 35–249 Da/s. All compounds are identified by their retention indices and MS using synthetic references (see *Table* and *Fig.*).

(2E)-3-(Cyclopent-3-enyl)prop-2-enal (**19**). Into a cold. soln. (−78°) of *cis*-1-bromo-2-ethoxyethene (1.01 g, 6.72 mmol) in dry Et_2O (30 ml) is injected with stirring 1.5M *t*-BuLi in hexane (4.5 ml, 6.73 mmol). After 30 min, a soln. of aldehyde **18** (0.32 g, 2.62 mmol) in Et_2O (5 ml) is gradually added, and stirring is continued for 10 min at −78°. Then, the mixture is allowed to come to r.t. and hydrolyzed with 2N HCl (30 ml). Extractive workup with Et_2O (2 × 40 ml) and CC (silica gel, pentane/Et_2O 98:2) give **19** (0.16 g, 39%). Colorless liquid. IR (film): 3061*m*, 2931*m*, 2850*m*, 2747*w*, 1680*s*, 1633*m*, 1613*m*, 1441*w*, 1337*w*, 1179*m*, 1119*s*, 1008*m*, 978*s*, 691*m*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 9.51 (*d*, *J* = 7.8, CHO); 6.89 (*dd*, *J* = 15.6, 8.2, H–C(3)); 6.10 (*ddd*, *J* = 15.6, 8.0, 1.0, H–C(2)); 5.72 (*s*, H–C(3′), H–C(4′)); 3.26–3.11 (*m*, H–C(1′)); 2.73–2.60 (*m*, 2 H, H–C(2′ or 5′)); 2.34–2.23 (*m*, 2 H, H–C(2′ or 5′)). MS (70 eV): 122 (5, $M^{+\cdot}$), 104 (6), 93 (20), 91 (54), 81 (30), 80 (24), 79 (27), 78 (25), 77 (50), 68 (26), 67 (25), 66 (86), 65 (32), 57 (54), 53 (23), 51 (22), 41 (62), 39 (100), 38 (20). HR-MS: 122.0702 (C_8H_8O, $M^{+\cdot}$, calc. 122.07316).

(1E,3Z)-1-(Cyclopent-3-enyl)hexa-1,3-diene (**11**). Triphenyl(propylidene)phosphorane (10 ml, *ca.* 0.2M in benzene; $NaNH_2$ as base) is added at −78° to a well stirred soln. of **19** (110 mg, 0.9 mmol) in Et_2O (15 ml). The orange soln. is allowed to come to r.t., and 2N HCl (15 ml) is added. Extractive workup with pentane (2 × 25 ml) and CC (silica gel) afford **11** (64 mg, 48%; (*E,Z*)/(*E,E*) 92:8). The (*E,E*)-isomer is selectively titrated with tetracyanoethene in CH_2Cl_2 until GLC indicates its removal. CC as above yields pure **11** (53 mg, 40% overall; > 98% (*E,Z*)). Colorless liquid. IR (film): 3058*m*, 3023*m*, 2967*s*, 2934*s*, 2877*m*, 2846*s*, 1648*w*, 1611*m*, 1459*m*, 1440*m*, 1411*w*, 1066*m*, 981*s*, 947*s*, 735*m*, 698*s*. ^{1}H-NMR ($CDCl_3$): 6.32 (*ddt*, *J* = 15.0, 11.0, 0.9, H–C(2)); 5.92 (*t*, *J* = 10.9, H–C(3)); 5.74 (*dd*, *J* = 15.0, 7.2, H–C(1)); 5.74 (*s*, H–C(3′), H–C(4′)); 5.32 (*sext.*, *J* = 7.4, H–C(1′)); 2.62–2.47 (*m*, 2 H–C(5)); 2.25–2.10 (*m*, 2 H–C(2′), 2 H–C(5′)); 1.0 (*t*, *J* = 7.5, 3 H–C(6)). ^{13}C-NMR ($CDCl_3$): 139.0 (C(1)); 132.1 (C(4)); 129.8 (C(3′), C(4′)); 127.9 (C(3)); 124.0 (C(2)); 41.4 (C(1′)); 39.4 (C(2′), C(5′)); 21.0 (C(5)); 14.3 (C(6)). MS (70 eV): 149 (5, $[M + 1]^+$), 148 (17), 133 (4), 119 (18), 117 (9), 105 (25), 92 (17), 91 (81), 82 (26), 79 (100), 78 (24), 77 (45), 67 (73), 66 (64), 65 (34), 53 (18), 51 (26), 41 (56), 39 (93). HR-MS: 148.1255 ($C_{11}H_{16}$, $M^{+\cdot}$, calc. 148.12520).

(1E,3E)-1-(Cyclopent-3-enyl)hexa-1,3-diene (**13**). To a well stirred suspension of anh. $CrCl_2$ (201 mg, 1.6 mmol) in dry CH_2Cl_2 (15 ml) and DMF (0.14 ml, 1.8 mmol) is added 1,1-diiodopropane (239 mg, 0.8 mmol) and **19** (50 mg, 0.4 mmol). Stirring is maintained for 7 d. The dark, heterogeneous mixture is diluted with Et_2O (50 ml) and H_2O (20 ml). The org. layer is separated and the aq. phase extracted with Et_2O (50 ml). Then, the combined org. layers are stirred vigorously with 10% aq. $AgNO_3$ soln. (20 ml) to remove the excess of diiodopropane. CC (silica gel, pentane) yields **13** (18 mg, 30%; 75% (*E,E*)). IR ($CDCl_3$): 3058*w*, 3020*w*, 2969*s*, 2934*s*, 2877*m*, 2848*m*, 2249*m*, 1611*w*, 1458*w*, 1441*w*, 1092*w*, 990*s*, 888*m*, 700*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.02–5.81 (*m*, 2 H); 5.70–5.50 (*m*, 4 H); 2.93–2.77 (*m*, H–C(1′)); 2.55–2.39 (*m*, 2 H–C(5)); 2.14–1.95 (*m*, 2 H–C(2′), 2 H–C(5′)); 0.93 (*t*, *J* = 7.5, 3 H–C(6)). ^{13}C-NMR ($CDCl_3$): 136.9; 134.4; 129.9 (C(3′), C(4′)); 129.3; 128.8; 41.2 (C(1′)); 39.4 (C(2′), C(5′)); 25.7 (C(5)); 13.7 (C(6)). MS (70 eV): 148 (13, $M^{+\cdot}$), 133 (2), 119 (19), 105 (27), 91 (87), 82 (23), 79 (100), 78 (24), 77 (47), 67 (74), 66 (68), 65 (29), 51 (23), 41 (58), 39 (97). HR-MS: 148.1258 ($C_{11}H_{16}$, $M^{+\cdot}$, calc. 148.12520).

(1′R,5′R)-(5′-Vinylcyclopent-2′-enyl)methanol ((1′*R*,5′*R*)-**20**). A suspension of (±)-**20** (3.8 g, 30.6 mmol) and PFL (*Pseudomonas fluorescens*, lipase; 31 mg, *Fluka*) in freshly distilled vinyl acetate (50 ml) is gently stirred at r.t. until GLC indicates a conversion rate of 45% (29 h). The enzyme is filtered off and the solvent evaporated. CC (silica gel, pentane/Et_2O 95:5→80:20) affords acetate (1′*S*,5′*S*)-**21** (2.18 g; 86%; $[\alpha]_{578}^{20} = +217.7$ (*c* = 4.08, CH_2Cl_2)) and (1′*R*,5′*R*)-**20** (1.73 g; 92%; $[\alpha]_{578}^{20} = -165.6$ (*c* = 1.65, CH_2Cl_2)). For spectroscopic data, optical rotation, and absolute configuration of (−)-(1′*R*,5′*R*)-**20**, see [30].

Data of (1'S,5'S)-**21**: IR (neat): 3061*m*, 2983*m*, 2929*m*, 2849*m*, 1743*vs*, 1639*w*, 1614*w*, 1464*w*, 1444*w*, 1422*w*, 1384*s*, 1364*s*, 1246*vs*, 1033*vs*, 1002*m*, 975*w*, 913*s*, 716*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.90–5.87 (*m*, CH_2=C*H*,H–C(2'), H–C(3')); 5.06 (*dt*, *J* = 16.7, 0.7, 1 H, CH_2=CH); 5.00 (*dd*, *J* = 10.2, 1.9, 1 H, CH_2=CH); 4.13 (*dd*, *J* = 11.9, 5.6, 1 H–C(1)); 3.86 (*dd*, *J* = 10.9, 6.4, 1 H–C(1)); 3.04–2.95 (*m*, H–C(1'), H–C(5')); 2.49–2.43 (*m*, 1 H–C(4')); 2.29–2.21 (*m*, 1 H–C(4')); 2.01 (*s*, Me). ^{13}C-NMR ($CDCl_3$): 171.0 (C=O); 138.5 (CH_2=*C*H); 131.9 (C(2' or 3')); 131.0 (C(2' or 3')); 115.1 (*C*H_2=CH); 64.7 (C(1)); 47.7 (C(1')); 44.7 (C(5')); 37.7 (C(4')); 21.0 (Me). MS (70 eV): 107 (3, $[M - 59]^+$), 106 (22), 105 (8), 91 (75), 79 (13), 78 (37), 77 (23), 65 (12), 51 (8), 44 (20), 43 (100), 42 (11), 39 (31). HR-MS: 106.0784 ($C_{10}H_{14}O_2$, $[M - AcOH]^{+\cdot}$, calc. 106.07825).

*(3*R*,4*R*)-3-Butyl-4-vinylcyclopent-1-ene* ((3*R*,4*R*)-**1**) is prepared from a less pure sample of (1'*R*,5'*R*)-**20** (89.3% *ee*) as described previously [14]. $[\alpha]_{578}^{25} = -170.9$ (*c* = 5.27, CH_2Cl_2), corresponding to 90.2% *ee* (GLC, column *I*).

*(1*RS,*1'*R,*5'*R*)-1-(5'-Vinylcyclopent-2'-enyl)prop-2-en-1-yl Acetate* ((1'*R*,5'*R*)-**22**). A suspension of pyridinium chlorochromate (5.0 g, 23.2 mmol) in CH_2Cl_2 (70 ml) is stirred with (1'*R*,5'*R*)-**20** (1.15 g, 9.3 mmol; $[\alpha]_{578}^{20} = -137.6$ (*c* = 5.02, CH_2Cl_2); 74.2% *ee*) for 7 h at 0°. Then, the dark mixture is diluted with pentane (100 ml), and anh. $MgSO_4$ is added. The precipitated and adsorbed chromium salts are removed by filtration, and the soln. is evaporated. Another portion of pentane (70 ml) and $MgSO_4$ removes last admixtures of the inorg. salts. After evaporation, the crude aldehyde is dissolved in THF (70 ml) and cooled (–78°). Vinylmagnesium bromide (13 ml, 3.0M in THF) is injected within 10 min. The mixture is allowed to come to r.t., treated with AcCl (2 ml, 28 mmol), and after 15 min, 2N HCl (50 ml) is added. Extractive workup (3 × 50 ml Et_2O) and purification by CC (silica gel, pentane/Et_2O 98:2) yields (1'*R*,5'*R*)-**22** (diastereoisomer mixture 75:15; 501 mg, 28% overall). Colorless, viscous oil. Spectroscopic data refer to the main diastereoisomer. IR (neat): 3069*m*, 2983*m*, 2929*s*, 2849*s*, 1736*vs*, 1639*m*, 1616*w*, 1441*m*, 1421*s*, 1371*vs*, 1234*vs*, 1101*m*, 1020*vs*, 995*s*, 964*s*, 917*vs*, 736*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.90–5.87 (*m*, H–C(2' or 3')); 5.86–5.76 (*m*, CH=C*H*, H–C(2)); 5.69–5.66 (*m*, H–C(2' or 3')); 5.25 (*tt*, *J* = 5.2, 1.2, H–C(1)); 5.18–4.99 (*m*, CH_2=CH, 2 H–C(3)); 3.00–2.87 (*m*, H–C(1), H–C(5')); 2.48–2.41 (*m*, 1 H–C(4')); 2.29–2.21 (*m*, 1 H–C(4')); 2.02 (*s*, Me). ^{13}C-NMR ($CDCl_3$): 170.0 (C=O); 138.6, 135.5 (CH_2=*C*H, C(2)); 132.4, 129.3 (C(2'), C(3')); 116.0, 115.6 (*C*H_2=CH, C(3)); 74.4 (C(1)); 52.4 (C(5')); 44.9 (C(1')); 38.3 (C(4')); 21.3 (Me). MS ((70 eV): 150 (0.5), 132 (3), 117 (5), 105 (2), 93 (17), 92 (7), 91 (32), 77 (16), 65 (8), 43 (100), 41 (5), 39 (18). HR-MS: 192.1164 ($C_{12}H_{16}O_2$, $M^{+\cdot}$, calc. 192.11503).

*(3*R*,4*R*)-3-[(1*E*)-But-1-enyl]-4-vinylcyclopent-1-ene* ((3*R*,4*R*)-**2**). To a chilled suspension of CuCN (33.5 mg, 0.375 mmol) and (1'*R*,5'*R*)-**22** (323 mg, 1.68 mmol) in Et_2O (20 ml) is gradually added with stirring MeMgBr (1 ml, 3M in Et_2O). After 15 min, the mixture turns yellow, and stirring is continued for 16 h. The mixture is diluted with Et_2O (100 ml) and hydrolyzed with H_2O (30 ml). Usual workup and CC (silica gel, pentane) afford (–)-(3*R*,4*R*)-**2** (173 mg, 70%; (*E*)/(*Z*) 90:10). Final purification is achieved by prep. GLC (*Fractonitril III*, 20% on *Chromosorb P*). $[\alpha]_{578}^{20} = -246.5$ (*c* = 1.76, $CHCl_3$); 76.2% *ee*. For spectroscopic data of (±)-**2**, see [31].

*(1*S*,2*R*)-2-(Hydroxymethyl)cyclopropane-1-methyl Acetate* ((1*S*,2*R*)-**25**). A suspension of PPL (porcine pancreas lipase; 1.0 g) and *meso*-**24** (8.6 g, 0.085 mol) in freshly distilled vinyl acetate (40 ml) is stirred at 10° until most *meso*-**24** (*ca.* 90%, according to GLC) is converted (*ca.* 24–48 h). The enzyme is removed by suction and washed with Et_2O. The combined filtrate is evaporated and the oily residue (GLC: 15% diacetate, 75% monoacetate, < 10% *meso*-**24**) separated by FC (SiO_2, hexane/Et_2O): 8.35 g (68.2%) of (1*S*,2*R*)-**25**. $[\alpha]_D^{22} = -15.95$ (*c* = 9.612, CH_2Cl_2); *ca.* 91% *ee*.

Less satisfactory results were obtained with certain lipases from microbial origin; all reactions were conducted at r.t.: *Pseudomonas fluorescens*: 78% *ee* at 100% conversion (24 h); *Aspergillus niger*: 78% *ee* at 100% conversion (36 h); *Aspergillus niveus*: 7% *ee* at 100% conversion (2 h); *Mucor javanicus*: 72% *ee* at 74% conversion (216 h): *Penicillium roquefortii*: 56% *ee* at 39% conversion (216 h).

Determination of the enantiomeric purity (1*S*,2*R*)-**25**: $RuCl_3$ monohydrate (5 mg, 0.024 mmol) is added to a well stirred, heterogeneous mixture of (1*S*,2*R*)-**25** (0.15 g, 1 mmol) and $NaIO_4$ (0.89 g, 4.16 mmol) in MeCN/CCl_4/H_2O 2:2:3 (7 ml). When the originally dark color brightens (*ca.* 30 min), conc. HCl soln. (*ca.* 1 ml) is added and stirring continued for 15 min. Extractive workup (Et_2O) and CC (silica gel, hexane/Et_2O) yield *(3a*S*,4a*R*)-1*H*-3,3a,4,4a-tetrahydrocyclopropa[c]furan-1-one* ((3a*S*,4a*R*)-**30**). The *ee* of **30** is determined by GLC according to [20] (separation factor: $\alpha = 1.3$).

*(1*S*,2*S*)-2-[(1*E*,3*E*)-Hexa-1,3-dienyl]cyclopropane-1-methyl Acetate* ((1*S*,2*S*)-**26**). To a cold (–50°) soln. of $(COCl)_2$ (1 ml, 11 mmol) in CH_2Cl_2 (25 ml) is added with stirring DMSO (1.7 ml, 22 mmol). After 2 min, a soln. of (1*S*,2*R*)-**25** (1.44 g, 10 mmol) in CH_2Cl_2 (10 ml) is added with 5 min. Stirring is continued for 15 min, and Et_3N (7 ml, 50 mmol) is added dropwise. The mixture is allowed to come to r.t., H_2O (50 ml) is added, and the product extracted with several portions of Et_2O. The combined layers are successively washed with 1% aq. HCl soln., 5% aq. $NaHCO_3$ soln., and brine, dried, and evaporated. The crude aldehyde (1.29 g, 90.1%) is directly used for the

olefination. BuLi (1.88 ml, 4.7 mmol, 2.5M in hexane) is slowly added with stirring to a chilled suspension of tri(cyclohexyl)[(2*E*)-pent-2-enyl]phosphonium bromide [21] (2.0 g, 4.7 mmol) in THF (20 ml). After 30 min, the above aldehyde (0.66 g, 4.7 mmol) in THF (18 ml) is added to the yellow soln., and the mixture is allowed to react for 2 h. Then, the soln. is poured onto ice/HCl and the product/extracted with Et_2O. After CC (silica gel, hexane/Et_2O) pure (1*S*,2*S*)-**26** (0.49 g, 54%; > 98% (*E*,*E*), GLC) is obtained. Colorless liquid. $[\alpha]_D^{22} = +31.36$ (*c* = 2.08, CH_2Cl_2). IR (film): 3077, 3022, 2968*s*, 2937, 2877, 2850, 1742*s*, 1654, 1622, 1458, 1406, 1368, 1343, 1324, 1234*s*, 1163, 1024*s*, 986*s*, 898, 829, 788, 733, 635. ^{1}H-NMR ($CDCl_3$, 400 MHz): 6.18–6.11 (*dd*, *J* = 10.4, 4.5, H–C(2′)); 6.03–5.96 (*dd*, *J* = 10.4, 4.6, H–C(3′)); 5.66–5.59 (*dt*, *J* = 6.6, 2.3, H–C(4′)); 5.37–5.31 (*dd*, *J* = 8.3, 6.6, H–C(1′)); 4.11–3.92 (*AB* of *ABX*, CH_2OAc); 2.05 (*s*, Ac); 2.14–2.01 (*m*, 2 H–C(5′)); 1.73–1.61 (*m*, H–C(2)); 1.41–1.32 (*m*, H–C(1)); 1.0 (*t*, 3 H–C(6′)); 1.10–0.93 (*m*, 1 H–C(3)); 0.49–0.45 (*q*, 1 H–C(3)). ^{13}C-NMR ($CDCl_3$): 171.18, 134.25, 131.79, 129.10, 128.94, 65.05, 25.56, 21.01, 18.82, 17.11, 13.56, 11.16. MS (70 eV): 194 (5, M^+), 151 (3), 134 (13), 119 (16), 107 (7), 106 (6), 105 (48), 93 (22), 92 (13), 91 (38), 83 (7), 81 (11), 79 (41), 78 (9), 77 (16), 69 (7), 67 (12), 65 (8), 57 (7), 55 (15), 53 (11), 43 (100), 41 (29). HR-MS: 194.1292 ($C_{12}H_{18}O_2$, M^+, calc. 194.13067).

(1S,2S)-2-[(1E,3E)-Hexa-1,3-dienyl]cyclopropane-1-methanol ((1*S*,2*S*)-**27**). A soln. of **26** (1.31 g, 6.75 mmol) in THF (40 ml) is added with stirring to a chilled suspension of $LiAlH_4$ (0.13 g, 3.38 mmol) in the same solvent (60 ml). The mixture is allowed to come to r.t. Usual workup CC (silica gel) provide (1*S*,2*S*)-**27** (0.83 g, 81%). $[\alpha]_D^{22} = +43.36$, $[\alpha]_{578}^{22} = +45.73$ (*c* = 1.084, CH_2Cl_2). IR (film). 3361 (br.), 3072, 3018*s*, 2965*s*, 2934*s*, 2876*s*, 1458, 1412, 1374, 1343, 1322, 1254, 1126, 1098, 1037*s*, 1018*s*, 987*s*, 944, 889, 825, 790, 732, 660. ^{1}H-NMR ($CDCl_3$): 6.24–6.14 (*dd*, *J* = 10.4, 4.5, H–C(2′)); 6.06–5.99 (*dd*, *J* = 10.8, 4.4, H–C(3′)); 5.69–5.57 (*dt*, *J* = 6.6, 1.7, H–C(4′)); 5.42–5.32 (*dd*, *J* = 8.7, 6.3, H–C(1′)); 3.79–3.50 (*AB* of *ABX*, CH_2OH); 2.14–2.02 (*quint.*, 2 H–C(5′)); 1.68–1.56 (*m*, H–C(1)); 1.45–1.32 (*m*, H–C(2)); 1.06–0.90 (*m*, 1 H–C(3)); 0.99 (*t*, 3 H–C(6′)); 0.48–0.41 (*q*, 1 H–C(3)). ^{13}C-NMR (200 MHz, $CDCl_3$): 134.32, 131.76, 129.75, 129.03, 63.39, 25.67, 21.44, 18.70, 13.66, 11.49. MS (70 eV): 152 (4, M^+), 121 (6), 119 (8), 110 (7), 105 (15), 103 (4), 95 (12), 93 (45), 92 (12), 91 (53), 81 (8), 80 (10), 79 (100), 78 (15), 77 (46), 67 (20), 65 (20), 55 (33), 53 (16), 51 (15), 50 (9), 43 (38), 41 (44), 39 (57). HR-MS: 152.1167 ($C_{10}H_{16}O$, M^+, calc. 152.1201).

(6S)-6-[(1E)-But-1-enyl]cyclohepta-1,4-diene ((6*S*)-**9**). A soln. of (1*S*,2*S*)-**27** (0.09 g, 0.59 mmol) in CH_2Cl_2 (10 ml) is oxidized with pyridinium dichromate (0.34 g, 0.89 mmol) as usual. The crude aldehyde (0.09 g, 0.6 mmol) is added at 0° to a soln. of (methylidene)triphenylphosphorane (0.9 mmol) in THF (4 ml). After 2 h, the mixture is poured onto ice/HCl and extracted with pentane. A pure sample of (6*S*)-**9** is obtained by CC (silica gel, pentane): 0.017 g (17% overall). $[\alpha]_D^{20} = +63.7$ (*c* = 1.26, CH_2Cl_2). IR (film): 3016, 2965, 2934, 2875, 2854, 1647, 1459, 1380, 967, 954, 898, 785, 714, 643. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.71–5.63 (*m*, H–C(1), H–C(2)); 5.58–5.56 (*m*, H–C(4), H–C(5)); 5.47–5.42 (*m*, H–C(1′), H–C(2′)); 3.05 (br. *s*, H–C(6)); 2.91–2.86 (*d*, *J* = 18, 1 H–C(3)); 2.74–2.68 (*dt*, *J* = 18, 4.5, 1 H–C(3)); 2.28–2.18 (*m*, 2 H–C(7)); 2.01–1.94 (*q*, 2 H–C(3′)); 0.93 (*t*, 3 H–C(4′)). ^{13}C-NMR ($CDCl_3$): 135.1 (C(5)), 133.0 (C(1′)), 131.3 (C(2′)), 129.8 (C(2)), 129.1 (C(1)), 127.3 (C(4)), 40.9 (C(6)), 33.6 (C(7)), 28.4 (C(3)), 25.8 (C(3′)), 13.9 (C(4′)). MS (70 eV): 148 (3, M^+), 133 (5), 120 (3), 119 (20), 117 (6), 115 (5), 107 (7), 106 (7), 105 (27), 103 (7), 92 (24), 91 (100), 82 (10), 80 (10), 79 (76), 78 (22), 77 (39), 67 (21), 66 (21), 65 (23), 55 (12), 53 (12), 51 (21), 43 (24), 41 (53), 39 (75). HR-MS: 148.1259 ($C_{11}H_{16}$, M^+, calc. 148.1252).

(1E)-1-[(3aS,4aR)-1H-3,3a,4,4a-Tetrahydrocyclopropa[c]furan-1-yl]pent-1-en-3-one (**29**). With pyridinium chlorochromate (2.95 g, 13.7 mmol), (1*S*,2*S*)-**27** (1.04 g, 6.84 mmol) in CH_2Cl_2 (100 ml) is oxidized as usual. After 12 h at 4°, the products are isolated as described for (6*S*)-**9**: aldehyde (0.5 g, 48.7%) and **29** (0.14 g, 12.3%). **29**: IR (neat): 3053, 2976, 2939, 2876, 2250, 1696, 1767, 1632, 1458, 1413, 1368, 1339, 1264, 1233, 1196, 1171, 1120, 1080, 1043, 985, 961, 939, 906, 867, 818, 766, 728. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.76–6.71 (*d*, *J* = 15.9, 4.9, CH=C*H*); 6.28–6.24 (*dd*, *J* = 15.9, 1.5, C*H*=CH); 4.53–4.49 (*dd*, *J* = 4.9, 1, H–C(1′)); 3.95–3.80 (*m*, 2 H–C(3′)); 2.63–2.56 (*q*, CH_3CH_2); 1.67–1.61 (*m*, H–C(3′a or 4′a)); 1.58–1.53 (*m*, H–C(3′a or 4′a)); 1.11 (*t*, CH_3CH_2); 0.71–0.65 (*m*, 1 H, CH_2(4′)); 0.49–0.41 (*m*, 1 H, CH_2(4′)). ^{13}C-NMR ($CDCl_3$): 200.98, 144.65, 127.91, 78.78, 68.68, 33.88, 20.95, 16.97, 8.18, 7.93. MS (70 eV): 167 (10, $M + 1]^+$), 149 (7), 131 (4), 126 (8), 125 (100), 119 (8), 112 (8), 109 (28), 97 (7), 93 (7), 91 (11), 83 (27), 81 (50), 79 (27), 77 (10), 57 (60), 55 (79), 54 (12), 53 (28), 51 (12), 43 (12), 41 (32), 39 (70).

Separation of the Diastereoisomeric Amides **31**. (*S*,*R*,*R*)-**31**/(*R*,*S*,*R*)-**31** is prepared from *rac*-2-vinylcyclopropane-1-carboxylic acid and (−)-(*R*)-2-phenylglycinol as described [25]. A suspension of (*S*,*R*,*R*)-**31**/(*R*,*S*,*R*)-**31** (10.0 g, 43.2 mmol) in heptane (200 ml) is heated with stirring until a clear soln. results. Then, the soln. is allowed to cool to r.t. at which the less soluble amide (*S*,*R*,*R*)-**31** crystallized spontaneously. Recrystallization of this material affords optically pure (*S*,*R*,*R*)-**31** as evidenced by HPLC (SiO_2, *Nucleosil 50-5*, 10 × 0.4 cm, isooctane/AcOEt 1:1): 3.5 g (70%). $[\alpha]_{578}^{22} = +11.4$ (*c* = 3.70, MeOH). (*S*,*R*,*R*)-**31** is further processed to (1*S*,2*R*)-**32** as described [25].

(1R,2R)-1-[(1E,3E)-Hexa-1,3-dienyl]-2-vinylcyclopropane ((1*R*,2*R*)-**17**). A soln. of optically pure (1*S*,2*R*)-**32** (0.68 g, 6.9 mmol) in CH_2Cl_2 is oxidized with pyridinium chlorochromate as described for (1′*R*,5′*R*)-**22**: 0.35 g (53%). The crude aldehyde (0.3 g, 3.1 mmol) is olefinated with the phosphorane derived from tricyclohexyl[(2*E*)-

pent-2-enyl]phosphonium bromide (BuLi as base) as described for (1*S*,2*S*)-**27**: 0.24 g (52%) of (1*R*,2*R*)-**17**. $[\alpha]_{578}^{23} = +58.1$ ($c = 3.495$, CH_2Cl_2). IR (neat): 3083*w*, 3018*s*, 2967*s*, 2934*s*, 2875*s*, 2850*m*, 1655*m*, 1634*s*, 1460*m*, 1073*m*, 1043*s*, 983*s*, 927*s*, 895*s*, 856*m*, 832*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.13–6.03 (*dd*, $J = 14.7, 10.3$, H–C(2′)); 6.20–5.91 (*ddt*, $J = 14.6, 10.4, 1.5$, CH_2=C*H*); 5.66–5.54 (*dt*, $J = 14.5, 6.5$, H–C(4′)); 5.48–5.33 (*m*, H–C(1′)); 5.22–5.12 (*dd*, $J = 14.8, 8.3$, H–C(3′)); 5.04 (*dd*, $J = 18.6, 1.6$, 1 H, C*H*$_2$=CH); 4.87 (*dd*, $J = 10.2, 1.6$, 1 H, C*H*$_2$=CH); 2.1 (*t*, 2 H–C(5′)); 1.44 (*m*, H–C(1), H–C(2)); 0.99 (*t*, 3 H–C(6′)); 1.08–0.93 (*m*, 1 H–C(3)); 0.92–0.81 (*m*, 1 H–C(3)). ^{13}C-NMR ($CDCl_3$): 140.3, 133.7, 133.5, 128.9, 128.8, 112.2, 25.6, 25.0, 23.9, 15.3, 13.6. MS (70 eV): 148 (3, $M^{+\cdot}$), 133 (4), 120 (5), 119 (19), 117 (7), 115 (5), 107 (6), 105 (25), 94 (5), 93 (7), 92 (21), 91 (100), 82 (10), 80 (8), 79 (75), 78 (22), 77 (33), 67 (20), 66 (19), 53 (13), 51 (21), 41 (41), 39 (69). HR-MS: 148.1237 ($C_{11}H_{16}$, $M^{+\cdot}$, calc. 148.1252).

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