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ON THE ODOR OF THE MEDITERRANEAN SEAWEED DICTYOPTERIS MEMBRANACEA; NEW C_{11} HYDROCARBONS FROM MARINE BROWN ALGAE - III.

Wilhelm Boland[a,*] and Dieter G. Müller[b]

a) Institut für Biochemie, An der Bottmühle 2, D-5000 Köln 1, BRD

b) Fakultät für Biologie der Universität, D-7750 Konstanz, BRD

Summary: The complete analysis of the odoriferous C_{11} polyenes of the Mediterranean seaweed Dictyopteris membranacea is described. Besides seven known hydrocarbons, 3-undecanone **11** and dictyoprolene **12**, the 4-((1E)-1-hexenyl)-cyclopentene **3** and 6-((1E)-1-butenyl)-cyclohepta-2,5-diene **5** were isolated for the first time and their structures confirmed by synthesis.

Members of the genus Dictyopteris are known for their characteristic odor which is, inter alia, due to a number of volatile $C_{11}H_{14\ to\ 18}$ hydrocarbons. For example, D. plagiogramma and D. australis collected around Hawaii by Moore and coworkers produce 0.1-0.2% of essential oil composed mainly (99%) of the same nine C_{11} hydrocarbons[1]. Similar results were reported by Kajiwara et al.[2a] for D. prolifera and D. undulata from Japan.

Since the simultaneous occurrence of various C_{11} polyenes within the same plant provides valuable information on their biosynthesis, we examined the European member of this genus, Dictyopteris membranacea (Stackh.) Batt. Whole plants were collected in May 1986 in the harbour of Beaulieu and at the pier of the Station Zoologique at Villefranche-sur-mer (near Nice, French Mediterranean coast). Freshly harvested plants were suspended in seawater and their volatiles collected by the 'Closed-Loop-Stripping' technique[3,4]. Extracts from both habitats were analyzed by gaschromatography (GC) and showed a remarkable difference (**Figure 1A/B**). It is at present unknown, whether this is due to genetical factors of the populations or to different conditions of the habitats. On average, a total of 0,1-0,2 mg hydrocarbons was obtained in single extracts.

Compounds were identified by GC/MS (Finnigan 4510 instrument; 70 eV) and GC comparison with authentic references[5] (coinjection and Kovàts-indices) on two columns of different polarity (**SE 30**, 50m x 0,31mm; **OV 17**, 25m x 0.31mm), as well as by microhydrogenation.

This is part III of a series; for part I and II see references 12 and 13.

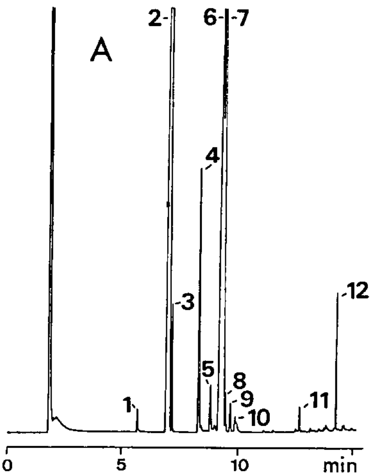
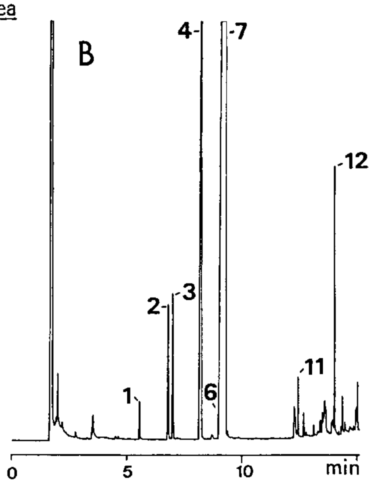
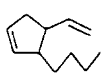


Fig. 1 Hydrocarbons from D. membranacea

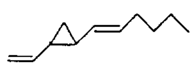
Habitat: A : Villefranche
B : Beaulieu

Conditions:
Column: 50m x 0.32mm, SE 30
Temperature: 90 °C(10 min) - 200 °C at 10 °C/min
Carrier gas: 1.6 bar H_2
Detection: FID

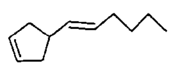




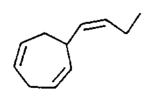
1 0.3 (0.5) %



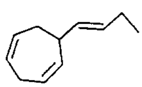
2 53.3 (2.2) %



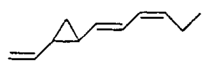
3 1.8 (2.3) %



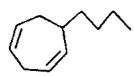
4 5.3 (13.4) %



5 1.1 %



6 19.2 (5.0) %

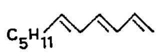


7 15.8 (74.1) %

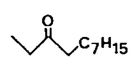
8 0.7 %

$C_{11}H_{16}$

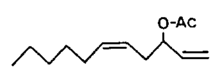
9 0.6%



10 0.2 %



11 0.3 (0.6) %



12 1.2 (1.9) %

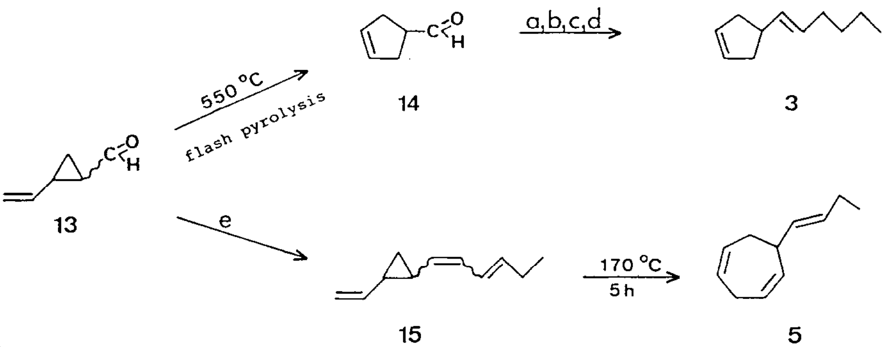
Scheme 1
The listed compounds are standardized to 100%. Values in brackets refer to Fig. 1B

2, 4, 6, 7, 8, 10, 11, 12[2b)] are known hydrocarbons of seaweed volatiles. The two cyclopentenes 1[5,12)], 3 and the cycloheptadiene 5 were isolated for the first time from this genus. Ring size and chain length of 5 followed from the presence of hexylcyclopentane among the hydrogenation products (10% Pt/C); its stereochemistry was predicted from biogenetic considerations[6)] (see below) and confirmed by stereospecific synthesis as follows:

Rearrangement[7)] of the readily available vinylcyclopropylaldehyde 13 (1:1 mixture of isomers)[8)] by flash vacuum thermolysis at 550 °C gives 14 in 78%

yield. Reaction of 14 with CBr_4 and $(Ph)_3P$[9] and dehydrohalogenation of the resulting dibromide with 2.2 eq. n-BuLi in THF/HMPA (90/10, v/v; -78 °C; 30 min), followed by alkylation with 1.1 eq. C_4H_9Br (-78 °C to r.t., then reflux, 1h) produces an alkyne (21% from 13); final reduction with Na in lq. NH_3 gives 3[10] in 50% yield (>99% E).

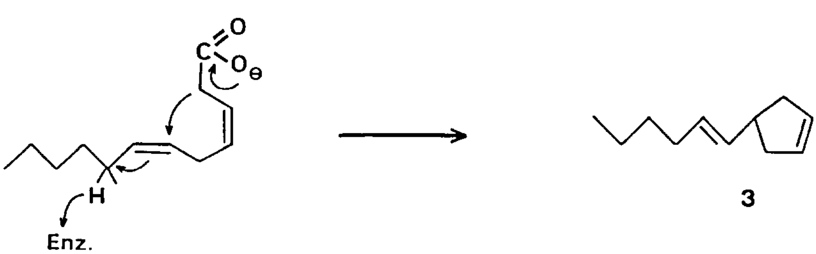
The trans isomer of ectocarpene[5] 5[11] is also obtained from 13 by Wittig reaction with 1.2 eq. Ph_3P=CH-CH=(E)CH-CH_2-CH_3 (n-BuLi; THF, -50 °C) and subsequent thermal rearrangement (170 °C, 5h) of the products 15 to 6-((1E)-1-butenyl-cyclohepta-2,5-diene 5 (E:Z = 97:3; 29% overall yield).



Scheme 2

a) CBr_4, $(C_6H_5)_3P$ according to ref. 9. b) 2.2 eq. n-BuLi in THF/HMPA, 90/10 v,v at -78 °C for 30 min. c) addition of 1.1 eq. n-BuBr and warm up to r.t., then reflux for 1h. d) 1.2 eq. Na in lq. NH_3 at -78 °C. e) 1.2 eq. $(C_6H_5)_3P$=CH-CH=(E)CH-CH_2-CH_3, n-BuLi, THF, -50 °C, 30 min, then work up.

The new hydrocarbon 3 is biosynthetically clearly related to the cyclopropane- and cycloheptadiene families. The latter originate from dodeca-3,6,9-trienoic acid[6] by enzymatic abstraction of a hydrogen from C(8) accompanied by appropriate ring closure[1,6] and loss of CO_2. The new hydrocarbon may be formed by analogy, if the cyclopentene is formed between C(2) and C(6) of the starting fatty acid as depicted in Scheme 3.



Scheme 3

The hydrocarbon 3 represents the first <u>unequivocal</u> case of a ring closure between C(2) and the enzymatically attacked allyl segment of the fatty acid and may be an important clue for further biosynthetic considerations.

1 and 3 probably also occur in *D. undulata* and *D. prolifera* since their MS data are in agreement with the fragmentation pattern of two unspecified $C_{11}H_{18}$ compounds reported by Kajiwara et al[2].

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10. Spectroscopic data of new compounds: ^{1}H NMR (300 MHz, $CDCl_3$). 3: 0.89 (t, 3H,$C\underline{H}_3$); 1.25-1.40 (m,4H,$CH_2C\underline{H}_2C\underline{H}_2CH_3$); 1.97 (q,2H,$C\underline{H}_2(CH_2)_2CH_3$); 2.11 and 2.48 (m,4H,$C\underline{H}_2$-ring); 5.40 and 5.47 (m,2H,$C\underline{H}$=$C\underline{H}(CH_2)_3CH_3$), 5.66 (s, broad,2H, $C\underline{H}$=$C\underline{H}$ ring). - 5: 0.97 (t,3H,$C\underline{H}_3$), 2.01 (m,2H,$C\underline{H}_2CH_3$), 2.27 (m, $C\underline{H}_2$-ring), 2.90 and 2.75 (m,2H,$C\underline{H}_2$-ring,allylic), 5.35-5.85 (m,6H,$C\underline{H}$=$C\underline{H}$). **MS** (70 eV): 3: 150 M^+(14), 135(1), 122(3), 107(6), 93(32), 91(27), 80(49), 79(100), 77(31), 67(28), 66(51), 55(13), 53(12), 51(8), 41(56), 39(37). - 5: 148 M^+(16), 133(3), 119(28), 92(28), 91(100), 82(16), 79(87), 78(27), 77(40), 70(8), 67(23), 66(24), 65(21), 55(14), 53(18), 51(18), 41(68), 39 (50). - 9: 148 M^+(19), 133(2), 119(24), 107(8), 105(25), 92(22), 91(77), 82(21), 79(100), 77(41), 67(29), 66(31), 65(19), 55(13), 53(15), 51(12), 41(63), 39(41). All compounds gave satisfactory high resolution mass spectra.
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