Tetrahedron Vol. 47, No. 18/19, pp. 3037-3044, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00
Pergamon Press plc

PHOTOCHEMICAL REACTIONS OF P-MENTHA-1,3,8-TRIENE AND STRUCTURAL RELATED P-MENTHADIENES

Martin H. Spraul, Siegfried Nitz and Friedrich Drawert*

Institut für Lebensmitteltechnologie und analytische Chemie der T.U.München-Weihenstephan, 8050 Freising-Weihenstephan, FRG

(*Received in Germany* 22 *June* 1990)

Abstract - The photochemical and thermal behaviour of cyclic olefins like p-mentha-1,3,8-triene **(2)** and structural related p-mentha-1,3- and -1,4-dienes under the influence of oxygen have been investigated. Dehydration, ring opening, (4+2)-cycloaddition of singlet oxygen[1] and dimerization were observed as concurring mechanisms. The photochemical and thermal dehydrogenation of α-terpinene **(1)**, α-phellandrene **(3)**, γ-terpinene **(4)** and p-mentha-1,3,8-triene **(2)** leads to p-cymene **(5)** and p-cymenene **(6)**, respectively. The mechanism of this aromatization reaction will be discussed in this paper.

INTRODUCTION

The deterioration of certain essential oils containing the widespread terpenic hydrocarbons α-terpinene (1-methyl-4-(1-methylethyl)-1,3-cyclohexadiene) **(1)**, α-phellandrene (2-methyl-5-(1-methylethyl)-1,3-cyclohexadiene) **(3)** and γ-terpinene (1-methyl-4-(1-methylethyl)-1,4-cyclohexadiene) **(4)** as well as p-mentha-1,3,8-triene (1-methyl-4-(1-methylethenyl)-1,3-cyclohexadiene) **(2)**, which is believed to be essential for the typical fresh parsley flavour, [2] is characterized by the formation of the aromatic system p-cymene (1-methyl-4-(1-methylethyl)-benzene) **(5)** or p-cymenene (1-methyl-4-(1-methylethenyl)-benzene) **(6)** and the development of a so-called "cymey" odour. In the case of lemon oil for example, the deterioration is parallel to the appearance of p-cymene **(5)** and the dissapearance of γ-terpinene **(4)**. [3] In order to elucidate the chemical reactions involved, model studies about the stability of p-menthadiene hydrocarbons in solution and in the gas phase against light, temperature and oxygen were performed.

RESULTS AND DISCUSSION

Light induced dehydrogenation, ring opening, dimerization and photooxygenation are observed during

UV irradiation of p-mentha-1,3,8-triene (2) [1] or related p-menthadienes under different experimental conditions (see fig. 1). Thermal treatment leads to the aromatization product in high yield. (see fig. 3). In the case of limonene (1-methyl-4-(1-methylethenyl)-1-cyclohexene) (7) and terpinolene (2-methyl-5-(1-methylethyliden)-cyclohexene) (8) no aromatization but only reaction with singlet oxygen is observed.[4-6] The conversion of γ-terpinene (4) or α-terpinene (1) via p-cymene (5) to thymol (5-methyl-2-(1-methylethyl)-phenol) (7) and / or carvacrol (6-methyl-3-(1-methylethyl)-phenol) (8) as discussed in literature [7, 8] could not be confirmed under the described nonenzymatic reaction conditions.

The kinetics of the involved reactions could be pursued directly by GC because of the insolubility of the functionalized rose bengal sensitizer in the used organic solvent.

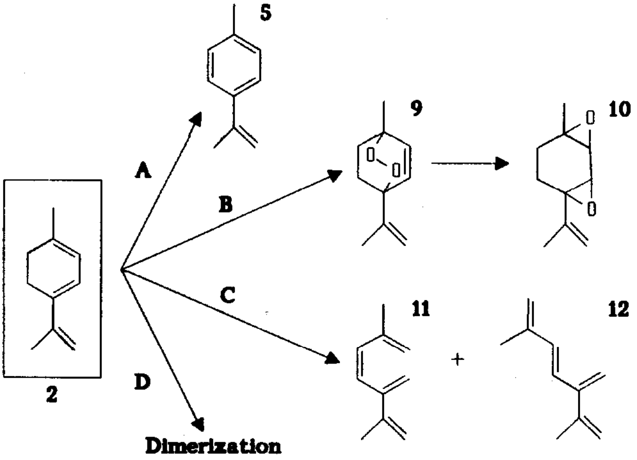

Fig. 1. Reaction products of the irradiation of 2, representing the discussed 1,3-dienic systems.

A) Dehydrogenation. The reactions observed in liquid and gaseous phase, especially the reaction in presence of the radical scavenger BHT (fig. 2, column III) and the AIBN-induced radical reaction without irradiation (fig. 2, column VI), the nonsensitized irradiation in gaseous phase (fig. 3, column II, III) and the thermal treatment under nitrogen (fig. 3, column IV) can be interpreted as follows: The elimination of hydrogen of the investigated 1,3- and 1,4-cyclohexadienic skeletons proceeds by means of at least two aromatization mechanisms. A temperature-independent but oxygen-dependent radical photodehydration is superimposed by a temperature- dependent but oxygen-independent dehydrogenation.

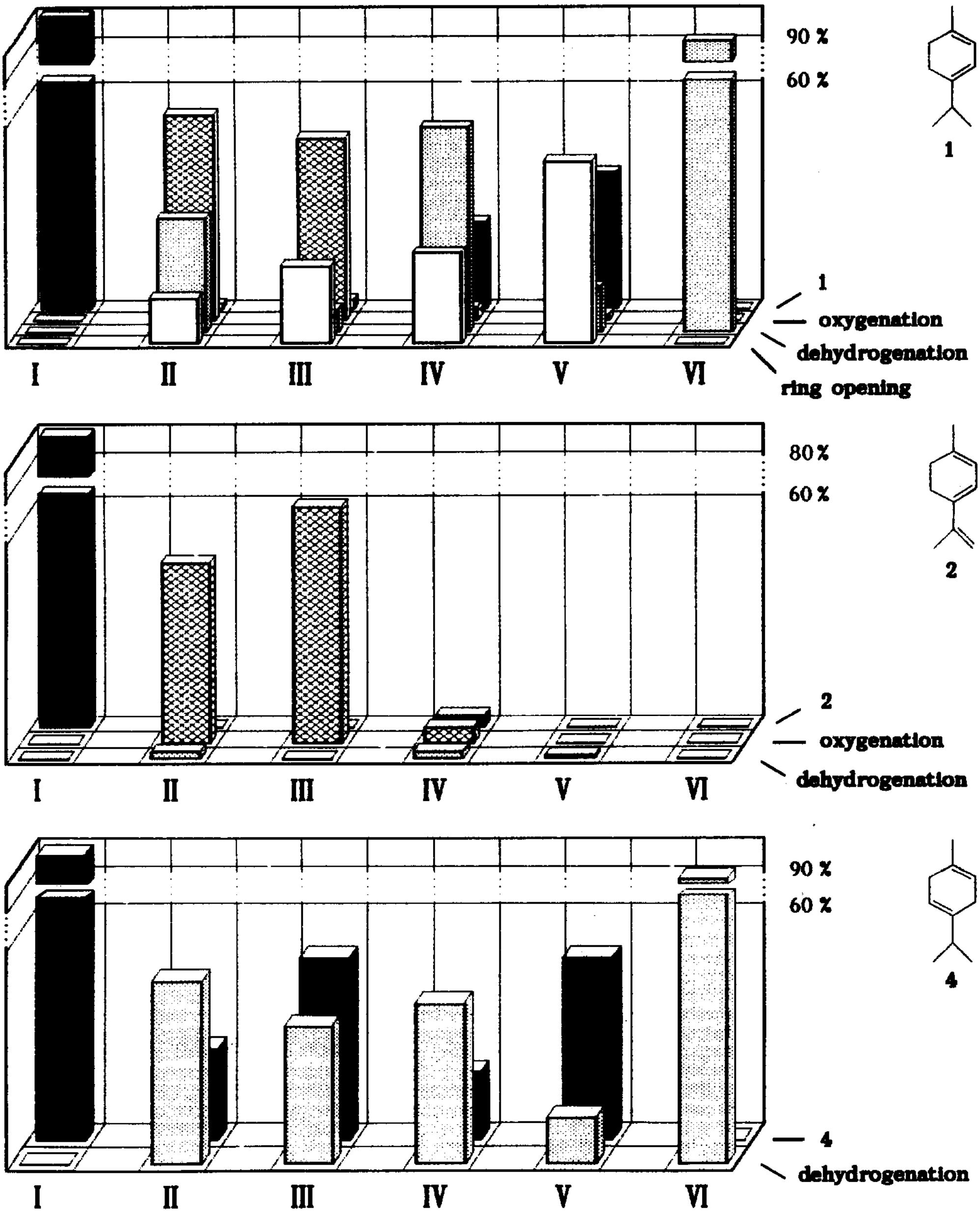

Fig. 2. Irradiation of **1** and **4** in pentane and **2** in acetone (repressed ring opening) over 4h under different reaction conditions at 10°C. . The distribution of the reaction products of **1** and α-phellandrene **3** is comparable.

I zero level

II sensitized irradiation, O_2

III sensitized irradiation, O_2, BHT

IV sensitized irradiation, O_2, DABCO

V sensitized irradiation, --

VI --- --- , --, AIBN

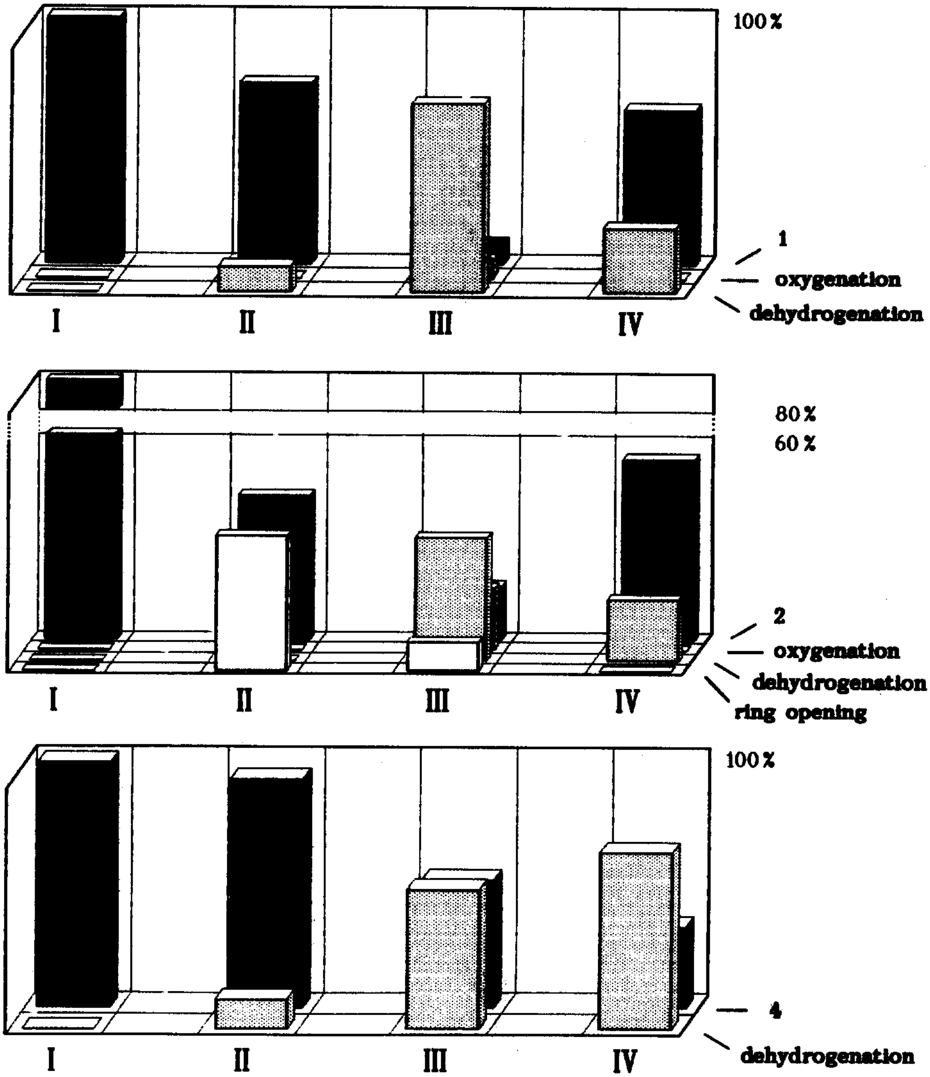

Fig. 3. Irradiation of **1**, **2** and **4** in gaseous phase under different reaction conditions. The distribution of the reaction products of **1** and α-phellandrene **3** is comparable.

I zero level
II irradiation, N_2, -10°C.
III irradiation, O_2, -10°C.
IV --- , N_2, 100°C.

The formation of phenanthrenes and related polynuclear aromatic molecules by ultraviolet irradiation of stilbenes or stilbene derivatives in solutions containing an oxidant like iodine or oxygen has been extensively studied.[9-12] As an intermediate the reaction involves a dihydrophenanthrene system with two tertiary and doubly allylic hydrogen atoms which are susceptible to abstraction by a suitable oxidant. It is believed that the radical formed by hydrogen abstraction is stabilized by the phenyl groups. As can be seen from our results, the reaction can also proceed with systems possessing a p-menthadiene skeleton. Based on literature data and own experiments (see fig. 2 and 3), a propagation mechanism as shown in figure 4 can be proposed for the discussed radical reaction.

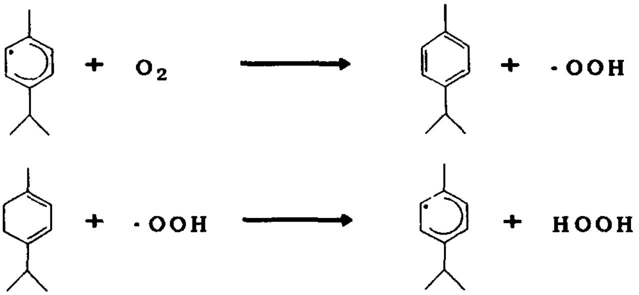

Fig. 4. Propagation mechanism of the radical aromatization of the discussed dienic systems.

The particularity of this radical reaction is the propagation step. Since formation of hydroperoxides is not observed,[13] the hydrogen abstraction mechanism prevails over the addition of a peroxy radical to the double bound.[14, 15] This effect is apparently related to the presence of secondary doubly activated allylic hydrogen atoms in the ring system. An influence of rose bengal on the radical reaction cannot be excluded, as it is capable of forming a stable radical cation.[16] In the gas phase oxidation (fig. 3), a marked difference in the reactivity of 1,3- and 1,4-p-menthadienes is observed. From these experiments it can be concluded, that in addition to the photooxidation a thermal aromatization occurs. The results obtained are in accordance with the Woodward-Hoffmann rules, which state that a synchronous thermal elimination of hydrogen for 1,4-cyclohexadienes can be expected. A higher activation energy is required for the aromatization of 1,3-cyclohexadienes which takes place via a complex radical reaction.[17, 18]

Depending on the temperature and alignment of the transfer line with the E.I. ion source a marked increase in typical aromatic fragments m/e 91, 119 and 134 is observed.

B) Photochemical reaction with singlet oxygen (photooxidation). The reaction mechanism of the investigated p-mentha-1,3-dienes with singlet oxygen [1, 4, 6, 13, 19-22] and the rearrangements of the oxygenated derivatives has been already described in literature. Based on the results presented in figure 2 and 3, especially those obtained with DABCO, it is concluded that the reaction of p-mentha-1,3,8-triene (**2**) with singlet oxygen ($O_2(^1\Delta g)$) represents a (4+2)-cycloaddition. The reaction products 1-methyl-4-(1-methylethenyl)-2,3-dioxabicyclo[2.2.2]oct-5-ene (**9**) and 4-methyl-7-(1-methylethenyl)-3,8-dioxatricyclo[5.1.0^{2-4}]octane (**10**), their structure elucidation and their sensorical properties were discussed in a separate paper. [1]

C) Photochemical ring opening. The yield of products due to the ring opening reaction under different experimental conditions is shown in figure 2 and 3. Irradiation of a solution of α-phellandrene (**3**) can result in the formation of a mixture of the four possible geometrical isomers of 3,7-dimethylocta-1,3,5-triene (**13**). [23-26] These findings are in accordance with our results obtained with α-terpinene (**1**) and p-mentha-1,3,8-triene (**2**), which are converted upon ring opening to cis- and trans- 2,6-dimethyl-5-methenyl-hepta-1,3-diene (**14, 15**), and cis- and trans-2,6-dimethyl-5-methenyl-hepta-1,3,6-triene (**11, 12**) , respectively. Hydrogenation of each isomer leads to 2,3,6-trimethylheptane (**16**). The conrotatoric electrocyclic ring opening is preferentially exhibited by the p-menthatriene system, but cannot take place with limonene (**7**), terpinolene (**8**) and γ-terpinene (**4**), as they do not possess the 1,3-cyclohexadienic moiety. In the case of p-mentha-1,3,8-triene (**2**) the solvent dependence of the ring opening reaction is noticeable. In pentane this mechanism predominates and upon prolonged irradiation other concurring reactions except polymerization are neglectable.

D) Dimerization (polymerization). Dimerization and polymerization were only observed in the case of p-mentha-1,3,8-triene (**2**). Dimerization products as described for 1,3-cyclohexadiene [27, 28] could not be found in the case of the investigated dienes. A low amount of a dimer of **2** was observed during irradiation in solution and in fresh parsley extracts as already reported in literature. [29] Prolonged irradiation as well as the radical reaction induced by AIBN results in the case of **2** and **6** in the disappearance of substances detectable by means of gas chromatography. This is a strong evidence for the formation of polymeric compounds derived from α-p-dimethylstyrene (**6**). In the presence of oxygen photooxygenation predominates. (see fig. 2 and 3).

EXPERIMENTAL

Isolation of p-mentha-1,3,8-triene (2). It was isolated from a commercial oil (Melchers & Co, Bremen, No. 4/2176/7670) by means of "flash-chromatography". [1, 30]

Irradiation in liquid phase. The photoreactions were carried out in an irradiation vessel as described [31] at 10°C., while a slight stream of oxygen or nitrogen was bubbled through the stirred solution. The sensitizer was prepared as follows: A solution of 10mg Rose Bengal (3,4,5,6-tetrachloro-2-(2,4,5,7-tetraiodo-6-hydroxy-3-oxo-3H-xanthen-9-yl)benzoic acid disodium salt, SIGMA) in 50ml distilled water and 10g Dowex 1x8 (100-200 mesh, anionic exchange resin, SERVA) was stored for 12 h, filtered and washed exhaustively with water and acetone. The fixed sensitizer (3g) and a solution of 100 mg of **2** in organic solvent (90ml) was irradiated (Phillips HPK 125, high-pressure Hg-lamp) through Pyrex ($\lambda > 290$nm). The irradiations were performed with solvents of different polarity (methanol, acetone, ether and pentane) and/or treatment with 0.1 g of the quencher DABCO (1,4-diazabicyclo[2.2.2]octane), the radical scavenger BHT (2,6-di-tert.-butyl-p-cresol) or by replacement of oxygen by iodine. Commercially available α-terpinene, γ-terpinene, α-phellandrene, limonene and terpinolene (Roth) were treated in the same way.

Initiation of a radical reaction with AIBN. Same configuration as described above, but without irradiation and streaming of oxygen or nitrogen. 0.1 g of the initiator AIBN (α,α-azaisobutyronitrile) and each of the investigated molecules including p-cymenene were dissolved in methanol as well as in heptane and stirred over 17 h at a temperature of 60°C.

Reaction in gaseous phase. The reactions were performed without solvent and sensitizer in a 10ml headspace vessel, closed with a septum. 5µl of the pure investigated substance were injected with a Hamilton syringe into the thermostated vessel, previously purged with oxygen or nitrogen. For GC-injection a thermostated 250µl gas tight syringe was used. Irradiation time 4 h, for **2** only 2h.

Hydrogenation of the ring opening products. Hydrogenation of the two pairs of ring opening products of α-terpinene and p-mentha-1,3,8-triene were performed with H_2 over Pd/C in ethanol for 4 h at 20° C. .

GC. Siemens Sichromat I equipped with a 26m x 0.25mm i.d. fused silica capillary column coated with 0.3µm cross-linked SE 54. Carrier gas, 1.7ml/min H_2; temp. programme, 60° (5min)-2°/min-250°; injectorand detector temperature, 250°C..

GC/MS. Finnigan 1020 (quadrupole) linked on-line to an Incos data processing system; directly coupled to a Sigma III (Perkin Elmer) GC. J&W 30m x 0.25mm i.d. fused silica capillary column coated with 0.25µm bonded DB 5; carrier gas, 1.2ml/min He; temp. programm, 60° (5min)-2°/min-250°; injector and transfer-line temperature, 200°C.; ionization energy, 70 eV.

Acknowledgement - We thank DECHEMA for financial support.

REFERENCES

1. **Nitz, S., Kollmannsberger, H., Spraul, M.H., Drawert, F.,** Phytochem. (1989), 11, 3051.
2. **MacLeod, A., Snyder, C., Subramanian, A.,** Phytochem. (1985), 24, 2623.
3. **Ikeda, R., Stanley, W., Vannier, S., Rolle, L.,** Food Technol. (1961), 15, 379.
4. **Schenk, G.O.,** Angew. Chem. (1952), 64, 12.

5. **Monroe, B.M.**, J. Am. Chem. Soc. (1981), 103, 7253.
6. **Foote, C.S.**, ACS Symp. Ser. (1987), 339, 22.
7. **Croteau, R.**, in Biosynthesis of Isoprenoid Compounds, John Wiley, New York (1981), 225.
8. **Banthorpe, D., Charlwood, B., Francis, J.**, Chem. Rev. (1971), 72, 115.
9. **Mallory, F.B., Mallory, C.W.**, J. Am. Chem. Soc. (1972), 94, 6041.
10. **Blackburn, E.V., Loader, C.E., Timmons, C.J.**, J. Chem. Soc. (C) (1970), 163.
11. **Knittel-Wismonsky, T., Fischer, G., Fischer, E.**, Tetrahedron Lett. (1972), 28, 2853.
12. **Muszkat, K.A., Fischer, E.**, J. Chem. Soc. (B) (1967), 662.
13. **Wasserman, H.H., Murray, R.M.**, in Singlet Oxygen; Academic Press (1979), 200, 307.
14. **Howard, J.A., Ingold, K.U.**, Canad. J. Chem. (1967), 45, 785.
15. **Nonhebel, D., Tedder, J., Walton, J.**, in Radicals; Cambridge University Press (1979), 158.
16. **Jefford, C.W., Boschung, A.F.**, Helv. Chim. Acta (1977), 60, 2673.
17. **Benson, S.W., Shaw, R.**, Trans Faraday Soc. (1967), 63, 985.
18. **Woodward, R., Hoffmann, R.**, Angew. Chem. (1969), 81, 797; Angew. Chem. Int. Ed. Engl. (1969), 8, 781.
19. **Foote, C.S.**, Acc. Chem. Res. (1968), 1, 104.
20. **Pfoertner, K.**, Spec. Publ.- R. Soc. Chem. (1986), 57, 189.
21. **Jefford, C.W., Rimbault, C.G.**, Tetrahedron Lett. (1981), 22, 91.
22. **Maheshwari, K., DeMayo, P., Wiegand, D.**, Can. J. Chem. (1970), 48, 3265.
23. **Crowley, K., Erickson, K., Eckell, A., Meinwald, J.**, Perk.Transaction I (1973), 2671.
24. **Kaupp, G.**, Angew. Chem. (1978), 90, 161; Angew. Chem. Int. Ed. Engl. (1978), 17, 150.
25. **Baldwin, J.E., Krueger, S.M.**, J. Am. Chem. Soc. (1969), 91, 6444.
26. **Datta, P., Goldfarb, T.D., Boikess, R.S.**, J. Am. Chem. Soc. (1971), 93, 5189.
27. **Jones, C., Allman, B., Mooring, A., Spahic, B.**, J. Am. Chem. Soc. (1983), 105, 652.
28. **Bahurel, Y., MacGregor, D., Penner, T., Hammond, G.**, J. Am. Chem. Soc. (1972), 94, 637.
29. **Simon, J.E., Quinn, J.**, J. Agric. Food Chem. (1988), 36, 467.
30. **Matissek, R., Häussler, M.**, Deutsche Lebensm. Rundschau (1985), 81, 50.
31. **Hohler, A., Nitz, S., Drawert, F.**, Chem. Mikrobiol. Technol. Lebensm. (1988), 11, 115.