STROBILURINS F, G AND H, THREE NEW ANTIFUNGAL METABOLITES FROM *BOLINEA LUTEA*

II. STRUCTURE DETERMINATION

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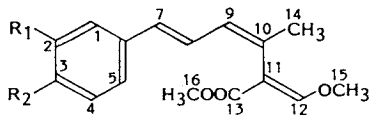
The structures of the new antibiotics strobilurins F, G and H and of compound **8** were determined by spectroscopic methods, mainly ^{1}H and ^{13}C NMR and confirmed by degradation reactions.

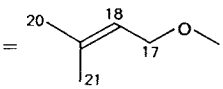
To date six antifungal antibiotics of the strobilurin-type are known (Scheme 1): Strobilurin A (**1**)[1,2] which is identical with mucidin[3], strobilurin B (**2**)[1,2], strobilurin C (**3**)[4], methoxymucidin (**4**)[5], hydroxystrobilurin D[6] and strobilurin E[7]. They contain an unsaturated side chain with a terminal (*E*)-β-methoxyacrylate moiety and differ usually in their aromatic substitution. In the preceding paper[8] we described the fermentation, isolation and biological properties of three new strobilurins F, G and H

Scheme 1. Chemical structure of some strobilurins and compound **8**.

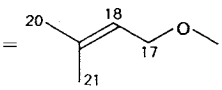


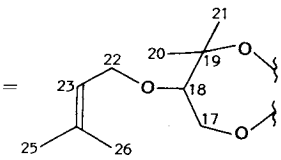
Strobilurin A (**1**) $R_1=R_2=H$ $R_1=R_2=H$

Strobilurin B (**2**) $R_1=OCH_3$ (17) $R_2=Cl$

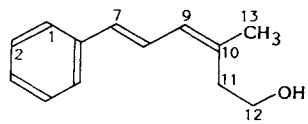
Strobilurin C (**3**) $R_1=$  $R_2=H$

Methoxymucidin (**4**) $R_1=H$ $R_2=OCH_3$

Strobilurin F (**5**) $R_1=OH$ $R_2=$ 

Strobilurin G (**6**) $R_1=R_2=$ 

Strobilurin H (**7**) $R_1=OCH_3$ (17) $R_2=H$



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(**5**~**7**) as well as the related compound **8**. The latter substance is produced in the early stage of the fermentation and might be formed as a side-product during the biosynthesis of strobilurin A or as a precursor for the latter. In this paper we will present the structure elucidation and physico-chemical properties of these compounds.

All ^{13}C NMR signals were assigned by a ^{1}H-^{13}C COSY and a fully coupled ^{13}C NMR spectrum

Table 1. ^{1}H NMR chemical shifts of **2**, **5**, **6**, **7**, **8**, **10** and **11**.

Proton	**2**	**5**	**6**	**7**	**8**	**10**[a]	**11**
1	6.84 d	6.99 br s	6.94 br s	6.87 br t	7.39 br d	7.54 m	7.71 d
2					7.30 br t		
3				6.75 ddd	7.19 br t		
4	7.25 d	6.78 m	6.85* dd	7.20 t	7.30 br t	6.90 d	7.08 d
5	6.90 d	6.78 m	6.93* dd	6.95 br b	7.39 br d	7.51 m	7.75 m
7	6.43 d	6.40 d	6.37 d	6.46 d	6.48 d		
8	6.56 dd	6.48 dd	6.48 dd	6.61 dd	7.02 dd		
9	6.25 qd	6.23 qd	6.22 qd	6.26 qd	6.18 br d		
11					2.57 t		
12	7.44 s	7.42 s	7.43 s	7.42 s	3.76 t		
14	1.98 br s	1.96 br s	1.96 br s	1.97 br s	1.88 br s		
15	3.85 s	3.84 s	3.84 s	3.84 s			
16	3.74 s	3.73 s	3.73 s	3.73 s			
17(a)	3.90 s	4.55 s	4.23 dd	3.80 s		4.54 dd	4.18 dd
17b			3.95 dd			4.02 dd	4.27 dd
18		5.47 m	3.50 dd			3.88 dd	3.67 dd
20		1.79 br s	1.21 s			1.31 s	1.25 s
21		1.73 br s	1.47 s			1.32 s	1.53 s
22a			4.15 br dd				
22b			4.06 br dd				
23			5.34 t, m				
25			1.76 br s				
26			1.69 br s				

	Coupling constants (Hz)						
	2	**5**	**6**	**7**	**8**	**10**[a]	**11**
1,5	2	1		2			
1,3				2			
3,4				8	7.5		
3,5				1			
4,5	8		8.5	8	7.5	8	8
7,8	15.5	15.5	15.5	15.5	15.5		
8,9	10.5	10	10.5	10.5	11		
11,12					6.5		
17a,17b			12.5			11.5	12.5
17a,18		7	3			2	1.2
17b,18			8			9	4
18,20		1.5					
18,21		1.5					
22a,22b			11.5				
22a,23			6.5				
22b,23			7				
23,25			1.5				
23,26			1.5				

Chemical shifts given in ppm. Solvent: $CDCl_3$ except for **10**. Assignments with asteriks may be interchanged.
[a] Solvent: CD_3OD.

Table 2. ^{13}C NMR chemical shifts of **2**, **5**, **6**, **7**, **8**, **10** and **11**.

Carbon	2	5	6	7	8	10[a]	11[a]
1	110.1	111.4	121.6	111.9	126.2	124.5	127.0
2	155.0	145.9*	146.8	159.7	128.6	144.9	147.4
3	121.1	145.4*	150.8	112.5	127.2	149.1	156.8
4	130.1	111.9	120.6	129.4	128.6	117.7	121.6
5	119.1	119.1	122.4	119.0	126.2	119.9	126.4
6	137.9	130.4	133.7	139.3	137.7*	124.9	125.5
7	130.3	130.8	130.4	131.1	131.1	169.5	171.0
8	127.3	125.1	125.7	126.9	124.9		
9	129.5	129.8	129.8	129.7	128.7		
10	132.2	131.6	130.8	131.6	135.9*		
11	110.7	110.8	110.8	110.7	35.8		
12	158.9	158.8	158.9	158.9	60.9		
13	167.7	167.8	167.9	167.7	24.1		
14	23.7	23.6	23.7	23.7			
15	61.9	61.9	61.9	61.9			
16	51.6	51.6	51.6	51.6			
17	56.1	65.8	68.7	55.2		66.5	71.1
18		119.2	81.9			80.4	75.3
19		138.9	80.6			71.2	80.8
20		25.8	27.7			25.1*	24.2*
21		18.2	20.8			26.5*	25.2*
22			67.3				
23			120.9				
24			137.5				
25			25.8				
26			16.1				

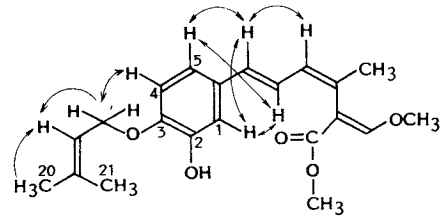
Chemical shifts given in ppm. Solvent for **2**, **5**~**8**: $CDCl_3$. Assignments with asterisks may be interchanged.
[a] Solvent: CD_3OD.

where appropriate. The ^1H NOE experiments were recorded as difference spectra.

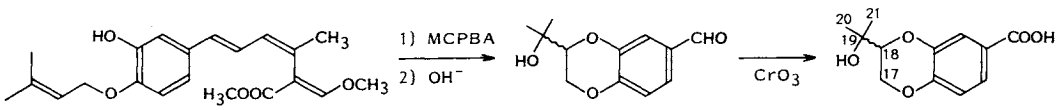
Fermentation of *Bolinea lutea* Sacc. gave strobilurin B (**2**) as the main product. For reference purposes the ^1H and ^{13}C NMR data of **2** were examined (Tables 1 and 2). Good correlation was found with the published data by SCHRAMM *et al.*[1] except that the signals for C-6 and C-10 as well as the ^1H NMR assignments for the methyl groups 15 and 16 should be interchanged. The same correction had to be made for the spectrum of strobilurin A, as shown by NEHRUD *et al.*[9].

Structure of Strobilurin F (**5**)

The IR spectrum of **5** shows in addition to signals typical for strobilurins a sharp band at 3530 cm^{-1} indicative of a hydroxy group. The HR-MS gives the elementary composition $C_{21}H_{26}O_5$ which is one oxygen atom more than strobilurin C (**3**). The ^1H NMR spectrum of **5** is very similar to **3** in that it displays all signals of the strobilurin side-chain and the coupling pattern of a 3,3-dimethylallyloxy residue. However an additional phenolic hydrogen signal at 5.7 ppm and the absence of one aromatic proton signal can be observed. The following NOE's were observed in a $CDCl_3$-C_6H_6 mixture in which all proton signals are well separated.



It revealed the protons in 1, 4 and 5 position. The ether linkage must be next to 4-H at C-3 leaving only C-2 for the hydroxy group. The ^{13}C NMR data corroborate the above findings. Epoxidation and cyclization of **5** under basic conditions leads to the



5 9 10

aldehyde **9**[10] which was oxidized with Jones reagent to the acid **10**.

The MS spectrum of **10** shows a large signal at *m/z* 180, corresponding to a loss of 58 (C_3H_6O) and supporting a dimethylcarbinol side chain and therefore a six membered ring. Analysis of the fully coupled ^{13}C NMR supports the position of the ether linkage as derived from structure **5**: Whereas the signal of the oxygenated C-2 (144.9 ppm) shows only couplings within the aromatic ring, C-3 (149.1 ppm) is characterized by two 2 *meta*-couplings shown by selective decoupling of 1-H and 5-H. Additionally it has a coupling of $J=6$ Hz to 17-Hb leading to an ether between those carbons and to structure **10**. The aldehyde **9** synthesized by BACKENS[10], exhibits the same coupling pattern. The rest of the ^{13}C NMR spectrum is consistent with the proposed structure.

Structure of Strobilurin G (6)

The molecular formula of compound **6** was determined to be $C_{26}H_{34}O_6$ from the HR-MS or one isoprene unit more than **5**. Though there are three more oxygens present than in simple strobilurins, there are no hydroxy- or additional carbonyl-functions present (IR and ^{13}C NMR) which suggests ether linkages. The mass spectrum (see Experimental section) further contained characteristic signals of the strobilurin side chain[1]: *m/z* 305 (M − 137) and *m/z* 75 as well as *m/z* 69 of a dimethylallyloxy moiety[4].

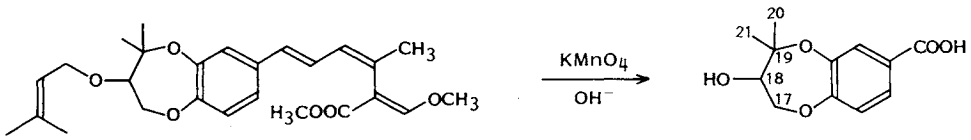
The ^1H NMR data document the following structural fragments: The strobilurin side chain, a 1,4,5-trisubstituted benzene ring (according to the splitting), a 3,3-dimethyl-allyloxy residue, two singlet methyl groups (1.2 and 1.5 ppm) and a methylene group with two geminal protons at 3.9 and 4.3 ppm further coupling to a methine resonance at 3.5 ppm. The latter spin-system has to be oxygenated at both carbons according to the observed chemical shifts.

Irradiation (in $CDCl_3$-C_6H_6) on the singlet methyl group at 1.5 ppm gives rise to a strong NOE on 18-H and irradiation on the 1.2 ppm methyl group to a 5% NOE at 17-Ha. The two methyl groups must share a quarternary carbon and are part of a triple oxygenated isoprene unit. Furthermore both methyl groups show a NOE on 1-H (3%) of the aromatic ring system upon irradiation, proving their spatial closeness.

The ^{13}C NMR data support an ether linkage at C-19, the only signal of a quarternary carbon atom in that part of the spectrum. In the fully coupled spectrum and long range selective decoupling experiments C-22 discloses a long-range coupling of $J=2.5$ Hz to 23-H and one of $J=6$ Hz to 18-H across the ether linkage. These NMR experiments clearly revealed the location of one of the three ether groups in this molecule. The two other must be part of a seven-membered dioxygenated ring fused to the aromatic ring system. As shown above the methyl groups 20 and 21 are close to hydrogen 1, which leads to structure **6**.

In order to confirm this structure, acid **11** was prepared by oxidation of **6** with $KMnO_4$ at 60°C.

The ether at C-18 was cleaved as revealed by HR-MS. Upon irradiations on the singlet methyl groups the same NOE effects were observed like with the mother compound, though stronger (3~7%) on 1-H. Analysis of the ^1H coupled ^{13}C NMR spectrum was much easier than of the mother compound **6**, as there were no long range couplings from the unsaturated side-chain. Spectrum and decoupling experiments were fully consistent with the proposed structure **11**.



6 11

While compounds **6** and **11** are optically active, the stereochemistry at C-18 was not determined.

Structure of Strobilurin H (**7**)

Mass spectroscopy of **7** gave the same elementary composition (HR-MS) and fragmentation pattern as methoxymucidin (**4**)[5]. A spectral comparison of the ^{1}H NMR clearly showed the two compounds to be different in their aromatic substitution. Whereas **4** showed the AA',BB' spin-system at 6.8 and 7.3 ppm characteristic for a *para* substitution, compound **7** has four clearly separated resonances and has to be *meta* substituted according to the coupling constants. Analysis of the ^{13}C NMR lines proves formula **7** to be correct.

Structure of **8**

The UV spectrum below 250 nm (see Experimental section) and the IR absorption bands indicate that **8** is not closely related to the strobilurins. An IR band at 3600 cm^{-1} reveals the presence of an alcohol function. The molecular formula was determined to be $C_{13}H_{16}O$ by HREI-MS. The ^{1}H NMR spectrum displays the following structural fragments: A monosubstituted phenyl ring, an A_2-B_2 system (2.6, 3.8 ppm) a methyl singlet at 1.9 ppm and a olefinic CH–CH–CH fragment. Irradiation at 2.6 ppm leads to a 16% NOE at the middle olefinic proton (8-H) suggesting a *Z* double bond with a quarternary carbon between them. Linked to this carbon is the methyl group which upon irradiation gives rise to a NOE ($\approx$20%) on 9-H. These findings define the middle part C-7 to C-12 of the molecule with hydroxy- and phenyl-groups at the end. The J=15.5 Hz coupling among 8-H and 9-H indicates an *E* configuration. The ^{13}C NMR lines were consistent with these findings.

Experimental

The following instruments were used in this study: Mass spectrometer CEC-121 B, VG 70-4SE (for HREI-MS): NMR spectrometer Bruker AM 360 and Varian VXR-400 S, UV/VIS spectrophotometer Perkin-Elmer Lamda 5, polarimeter Perkin-Elmer 241, IR spectrophotometer Perkin-Elmer 983G.

Preparation of **9**

To a solution of strobilurin F (**5**, 500 mg, 1.4 mmol) in CH_2Cl_2 (3 ml) *m*-chloroperbenzoic acid (1.4 g, 85%, 7 mmol) in 10 ml of CH_2Cl_2 was added. An exothermic reaction was observed and soon colorless crystals of *m*-chlorobenzoic acid started to precipitate. After cooling, the precipitate was filtered off and the filtrate was diluted with 50 ml of CH_2Cl_2 and washed three times with 5% $NaHCO_3$. The organic solvent was removed and the oily residue dissolved in 50 ml each of dioxane and of water. Cyclization was achieved by adding 5 ml of saturated Na_2CO_3 and stirring for 2 days. Removal of dioxane *in vacuo*, acidification with conc HCl and extraction with CH_2Cl_2 gave the crude product as a brown oil after evaporation of the solvent (500 mg). That crude material was used directly for the next step. A small sample (10 mg) was purified with HPLC on silica gel (Lichrosorb Si60, 5 μm; 4.6 × 250 mm; CH_2Cl_2 - ethyl acetate, 90 : 10; 2 ml/minute; 254 nm; 2 runs; Rt 6.6 minutes) to give 1.3 mg of **9** as a yellowish oil.

Preparation of **10**

A stirred solution of crude **9** (500 mg) in acetone (5 ml) was treated dropwise with Jones reagent (4 ml;

26.7 g CrO_3 in 23 ml of conc sulfuric acid diluted with water to a volume of 100 ml). The mixture was stirred for 2 hours and distributed between CH_2Cl_2 (100 ml) and saturated Na_2CO_3 (100 ml). The aqueous phase was acidified (conc HCl) and extracted twice with CH_2Cl_2 (100 ml), which was washed with water. Evaporation of the solvent gave yellowish crystals consisting of 50% product **10** and *m*-chlorobenzoic acid. The pure material was obtained by chromatography on a preparative reversed-phase column (Nucleosil 7-C18, 7 μm; 16 × 300 mm; gradient from acetonitrile - water - TFA, 84 : 16 : 0.1 to 68 : 32 : 0.09 in 30 minutes; 10 ml/minute; Rt 16 minutes; 220 nm; 2 runs) to give **10** as colorless crystals (51 mg, 14% overall yield).

Prepatation of **11**

A solution of $KMnO_4$ (2.57 g, 16 mmol) in water (40 ml), KOH (4% solution, 1.6 ml) and strobilurin G (**6**: 400 mg, 0.9 mmol) was stirred at 60°C until the pink color had disappeared (2 hours). The brown precipitate was filtered off and extracted with water (60 ml) at 70°C for 15 minutes and removed by filtration. The combined aqueous filtrates were extracted once with CH_2Cl_2 (120 ml), acidified with HCl (4 N; 20 ml, pH 1) and extracted twice with CH_2Cl_2 (100 ml). The organic phase was filtered to remove water, and the solvent evaporated *in vacuo* to give 48 mg of colorless crystals (22% yield).

Data of **5**

Colorless crystals from hexane - ether, mp 77.5 ~ 78°C.

Anal Calcd for $C_{21}H_{26}O_5$: C 70.37, H 7.31, O 22.32.
Found: C 70.10, H 7.24, O 22.30.

HREI-MS: *m/z* 358.1768 ($C_{21}H_{26}O_5$, δ_m 1.2 mmu); EI-MS: *m/z* 358 (92, M^+), 291 (29), 290 (100), 289 (38), 258 (30), 257 (45), 243 (22), 229 (49), 199 (30), 153 (82), 134 (29), 75 (41), 69 (55); UV λ_{max}^{EtOH} nm (ε) 230 (26,100), 299 (24,700), 322 (25,200); IR (CH_2Cl_2) cm^{-1} 3530, 3030, 2940, 2860, 1705, 1630, 1580, 1510, 1460, 1440, 1390, 1320, 1240, 1200, 1140, 1120, 1080, 990, 970; ^1H NMR (360 MHz, $CDCl_3$): See Table 1; ^{13}C NMR (90 MHz, $CDCl_3$): See Table 2.

Data of **6**

Yellowish oil. HREI-MS: *m/z* 442.2373 ($C_{26}H_{34}O_6$, δ_m 1.8 mmu); EI-MS: *m/z* 442 (66, M^+), 305 (33), 153 (27), 95 (20), 83 (22), 81 (28), 75 (36), 69 (100), 55 (32); UV λ_{max}^{EtOH} nm (ε) 229 (19,800), 301, (21,700); IR (CH_2Cl_2) cm^{-1} 2970, 2940, 2880, 2850, 1705, 1630, 1570, 1500, 1450, 1440, 1240, 1210, 1200, 1190, 1140, 1120, 1080, 1020, 1000, 990, 970; $[\alpha]_D^{20}$ +26.8° (*c* 0.75, EtOH); ^1H NMR (360 MHz, $CDCl_3$): See Table 1; ^{13}C NMR (90 MHz, $CDCl_3$): See Table 2.

Data of **7**

Yellowish oil. HREI-MS: *m/z* 288.1358 ($C_{17}H_{20}O_4$, δ_m 0.3 mmu); EI-MS: *m/z* 288 (75, M^+), 256 (43), 229 (47), 197 (53), 172 (61), 151 (80), 75 (100), 69 (55); UV λ_{max}^{EtOH} nm (ε) 232 (23,200), 298 (23,400); IR (CH_2Cl_2) cm^{-1} 2940, 2850, 2840, 1705, 1630, 1590, 1570, 1490, 1470, 1450, 1440, 1240, 1190, 1160, 1150, 1120, 1080, 1050, 1040, 1000, 990, 970; ^1H NMR (360 MHz, $CDCl_3$): See Table 1; ^{13}C NMR (90 MHz, $CDCl_3$): See Table 2.

Data of **8**

Yellowish oil. HREI-MS: *m/z* 188.1188 ($C_{13}H_{16}O$, δ_m 1.3 mmu); EI-MS: *m/z* 188 (87, M^+), 157 (100), 143 (29), 142 (48), 141 (30), 129 (77, $C_{10}H_9^+$), 128 (27), 115 (39), 91 (49), 79 (22), 77 (21); UV λ_{max}^{EtOH} nm (ε) 213 (11,000), 223 (10,300), 229 (10,300), 237 (7,600), 293 (24,600); IR (CH_2Cl_2) cm^{-1} 3600, 3450 (br), 3120, 2960, 2940, 2880, 1705, 1640, 1590, 1490, 1450, 1440, 1380, 1360, 1240, 1190, 1120, 1050, 1030, 1000, 980, 970, 880; ^1H NMR (360 MHz, $CDCl_3$): See Table 1; ^{13}C NMR (90 MHz, $CDCl_3$): See Table 2.

Data of **9**

Yellowish oil. HREI-MS: *m/z* 222.0893 ($C_{12}H_{14}O_4$, δ_m 0.1 mmu); EI-MS: *m/z* 222 (44, M^+), 164 (100), 163 (25), 149 (57), 135 (36), 107 (40), 106 (28), 59 (88), 43 (47); IR (CH_2Cl_2) cm^{-1} 3580 (br), 3040, 2960, 2940, 2910, 2880, 2860, 2740, 1690, 1600, 1580, 1510, 1440, 1390, 1370, 1340, 1310, 1230, 1210, 1170, 1120, 1080, 1020, 890, 870, 820; ^1H NMR (400 MHz, $CDCl_3$) δ 9.84 (1H, s, CHO), 7.48 (1H, d, J=2 Hz, 1-H), 7.41 (1H, dd, J=8 and 2 Hz,5-H), 7.00 (1H, d, J=8 Hz, 4-H), 4.52 (1H, dd, J=11 and 2 Hz, 17-Ha),

4.10 (1H, dd, $J=11$ and 9 Hz, 17-Hb), 3.94 (1H, dd, $J=9$ and 2 Hz, 18-H), 1.40 (3H, s, 20*-H_3), 1.33 (3H, s, 21*-H_3).

Data of **10**

Colorless crystals from toluene-hexane, mp 157~159°C. HREI-MS: *m/z* 238.0848 ($C_{12}H_{14}O_5$, δ_m 0.7 mmu); EI-MS: *m/z* 238 (34, M^+), 221 (11), 180 (96), 165 (78), 135 (50), 134 (24), 59 (100), 43 (26); IR (KBr) cm^{-1} 3530, 3420, 2980, 2940, 1680, 1610, 1590, 1510, 1450, 1410, 1390, 1380, 1320, 1310, 1280, 1230, 1200, 1170, 1130, 1100, 1090, 1080, 1030, 1010, 950, 900, 830, 770, 670, 630; ^1H NMR (400 MHz, $CDCl_3$): See Table 1; ^{13}C NMR (100 MHz, $CDCl_3$): See Table 2.

Data of **11**

Colorless crystals from MeOH, mp 255~260°C (dec). HREI-MS: *m/z* 238.0834 ($C_{12}H_{14}O_5$, δ_m 0.7 mmu); EI-MS: *m/z* 238 (44, M^+), 194 (25), 179 (75), 165 (25), 154 (100), 137 (30), 71 (20), 43 (30); IR (CH_2Cl_2) cm^{-1} 3600, 3560 (br), 3500 (br), 2980, 2940, 1730, 1690, 1600, 1580, 1500, 1430, 1300, 1250, 1160, 1090, 1060, 980, 970; $[\alpha]_D^{20}$ +18° (*c* 0.7, MeOH); ^1H NMR (400 MHz, $CDCl_3$): See Table 1; ^{13}C NMR (100 MHz, CD_3OD): See Table 2.

Acknowledgments

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