Lentinellic Acid, a Biologically Active Protoilludane Derivative from *Lentinellus* Species (Basidiomycetes) [1]

A. Stärk, T. Anke,

LB Biotechnologie der Universität, Paul-Ehrlich-Straße 23, D-6750 Kaiserslautern, Bundesrepublik Deutschland

U. Mocek, W. Steglich,

Institut für Organische Chemie und Biochemie der Universität, Gerhard-Domagk-Straße 1, D-5300 Bonn, Bundesrepublik Deutschland

A. Kirfel and G. Will

Mineralogisches Institut der Universität, Poppelsdorfer Schloß, D-5300 Bonn, Bundesrepublik Deutschland

Z. Naturforsch. **43c,** 177–183 (1988); received October 16, 1987

Dedicated to Professor Helmut Doerfel on the occasion of his 60th birthday

Lentinellus, Basidiomycetes, Sesquiterpenoids, Protoilludanes, Lentinellic Acid, Antibiotics

A new antimicrobial and cytotoxic sesquiterpenoid, lentinellic acid (**1**), has been isolated from submerged cultures of *Lentinellus ursinus* and *L. omphalodes*. The structure of the antibiotic was elucidated by spectroscopic methods and a single crystal X-ray analysis. **1** may be formed biogenetically by condensation of a protoilludane aldehyde **4** with a malonate unit.

Introduction

Species of the genus *Lentinellus* are of widespread occurrence, their usual habitat being decaying wood. They are characterized by tough carpophores with toothed lamellae and spores with amyloid spines. The hymenium contains gloeocystidia staining blue with sulfovanillic acid. The component responsible for this color reaction has been identified as the sesquiterpenoid stearoylvelutinal [2]. The taxonomy of the genus *Lentinellus* and its relationship to the Aphyllophorales has been discussed by Singer [3]. During our investigation of the secondary metabolism of mycelial cultures of *Lentinellus* species several antibiotic and cytotoxic compounds have been isolated [4, 5]. In the following we wish to describe a new antibiotic, lentinellic acid (**1**), derived from fermentations of *Lentinellus omphalodes* and *L. ursinus*.

Reprint requests to Prof. Dr. T. Anke or Prof. Dr. W. Steglich.

Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen
0341–0382/88/0003–0177 $ 01.30/0

Experimental

Lentinellus omphalodes (Fr.) P. Karst. and L. ursinus (Fr.) Kühn.

Mycelial cultures were obtained from spore prints or tissue plugs from specimens collected in Germany (*L. ursinus* 80163, *L. omphalodes* 8075, 80272), Canada (*L. omphalodes* 80116, 80131), or USA (*L. omphalodes* 8349).

Fermentation and isolation

For the maintenance on agar slants the strains were grown in a yeast extract-malt extract-glucose medium composed of (g/liter): yeast extract 4, malt extract 10, glucose 4, and agar 20. For the production of lentinellic acid the medium contained (g/liter): glucose 50, peptone 2, yeast extract 5, KH_2PO_4 1, and $MgSO_4 \times 7H_2O$ 1. The fermentations were carried out in a Biolafitte fermentation apparatus (1 l air/min, 200 rpm, 22 °C). 200 ml of a well grown seed culture were used as inoculum for 20 l of medium. Antibiotic production was followed by paper-disc/agar-diffusion assay using *Bacillus brevis* as test organism. After fermentation the mycelia were separated from the culture fluid by filtration. Lentinellic acid was extracted from the culture fluid (19 l) with 5 l of ethyl acetate. After evaporation of the solvent the crude product (4.4 g) was applied to a column of

silica gel (Merck 60) and eluted with dichloromethane. The fractions containing lentinellic acid were combined to yield 1.8 g of a yellow precipitate. Pure lentinellic acid (0.95 g) was obtained by crystallization from methanol.

Physical and spectroscopic data

NMR spectra were recorded on a Bruker WM-400 spectrometer. The high-resolution mass spectra were determined with an AEI MS-50 spectrometer. Analytical thin-layer chromatography (TLC) was performed with Merck 5554 silica plates. Melting points were obtained on a Reichert hot plate microscope and are uncorrected.

Lentinellic acid (**1**): Yellow crystals, soluble in methanol, acetone, chloroform; m.p. 174–176 °C; R_f 0.38 (benzene/acetone/acetic acid = 70:30:1); $[\alpha]_D^{20}$ −187.1° (c = 0.19, in $CHCl_3$); UV (MeOH) λ_{max} (log ε) 317 (4.21), 242.5 nm (3.74); CD (MeOH) $[\theta]_{385}$ -10.78×10^3, $[\theta]_{349}$ 0, $[\theta]_{315}$ $+43.94\times10^3$, $[\theta]_{275.5}$ 0, $[\theta]_{240}$ -14.58×10^3, $[\theta]_{213}$ -33.16×10^3; IR (KBr) cm^{-1} 3480–3400 (m, br), 2955 (st), 2910 (sh), 2870 (w, br), 2770 (w), 1760 (sst), 1725 (w), 1680 (st, br), 1645 (m), 1605 (sh), 1592 (m), 1465 (w), 1430 (m, br), 1402 (st), 1342 (w), 1310 (w, br), 1255 (w), 1220 (w), 1188 (m), 1150 (st), 1112 (st), 1080 (sh), 1062 (w), 1038 (w), 850 (m, br), 803 (m); ^1H and ^{13}C NMR spectra see Table I; MS (direct inlet, 180 °C) *m/z* 316.1315 (8.7%, calc. for $C_{18}H_{20}O_5$ 316.1310), 274 (100, $C_{16}H_{18}O_4$), 272 (5.4, $C_{17}H_{20}O_3$), 259 (6.7, $C_{15}H_{15}O_4$), 241 (5.2, $C_{15}H_{13}O_3$), 230 (17.7, $C_{15}H_{18}O_2$), 229 (8.2, $C_{15}H_{17}O_2$), 215 (6.5, $C_{14}H_{15}O_2$), 200 (12.2, $C_{12}H_8O_3$), 174 (10.6, $C_{11}H_{10}O_2$), 115 (10.4, C_9H_7), 91 (13.8), 77 (11.0), 44 (22.4), 41 (15.5).

Methyl lentinellate (**2**): To a solution of 6 mg **1**, 2 ml methanol, and 3 mg 4-(dimethylamino)pyridine in 5 ml of dichloromethane at 0 °C 8.5 mg dicyclohexylcarbodiimide were added and the solution was stirred for 5 min at 0 °C and 3 h at 20 °C. After filtration of the deposite the solvent was removed in vacuo and the residue was purified by preparative TLC on silica gel plates (eluant: chloroform). Yield: 6.2 mg, yellow oil; R_f 0.34 (cyclohexane/ethyl acetate/formic acid = 120:40:5); ^1H NMR ($CDCl_3$): δ = 1.03, 1.19, 1.26 (each s, 3H), 1.49–2.08 (m, 3H), 2.32–2.88 (m, 3H), 2.99 (br. s, 2H), 3.91 (s, 3H), 4.99 (d, J = 9.0 Hz, 1H), 8.01 (s, 1H); MS (DI 180 °C): *m/z* 330.1472 (62.9%, calc. for $C_{19}H_{22}O_5$ 330.1467).

Crystal structure determination by X-ray diffraction

Single crystals suitable for a crystal structure investigation were obtained from acetone/petroleum ether. The crystal data are: orthorhombic symmetry, with a = 6.506 (1), b = 10.807 (3), c = 22.706 (5) Å, V = 1596.5 (1.0) $Å^3$ (standard deviations in parentheses). Space group $P2_12_12_1$, Z = 4, D_x = 1.315 g/cm^3, (CuK_α) = 7.5 cm^{-1}, $F_{(000)}$ = 672, T = 293 K.

The intensity measurements were carried out on an automatic four circle diffractometer (SYNTHEX $P2_1$) in the ω-mode using graphite monochromated CuK_α radiation (λ = 1.5413 Å); lattice constants were determined from angular settings of 25 independent reflections (2 θ ≤ 50°); the range was $\sin\theta_{max}/\lambda$ = 0.54 $Å^{-1}$. A standard reflection was remeasured after every 33 records with an intensity variation of ± 1%; the number of reflections measured was 1216, with 305 considered unobserved [I < 2.56(I)]; the number of unique observed reflexions was 911. No absorption correction was applied.

The structure was solved by use of the direct method program MULTAN [6] and refined on | F | by full matrix least squares calculations. In the final stage of refinement the hydrogen atoms were treated as riding on the carrier atoms with B(H) = 1.2 B(C). Hydrogen bonded in OH was located from difference Fourier maps and refined for positional parameters only. An isotropic extinction factor g was included in the list of variables. In total 212 refined parameters were used. Refinement converged at R = 0.034, R_w = 0.045 (omitting unobserveds), s = 1.12. The weighting function was $w = (\sigma^2(F) + 0.001\ F^2)^{-1}$; the final parameter shifts were less than 0.30 and peaks in the final difference Fourier map were max 0.11 $e/Å^3$, min −0.11 $e/Å^3$; atomic scattering factors were taken from International Tables for X-ray Crystallography (1974); all calculations were done with SHEL X76 [7]. Further details of the crystal structure determination have been deposited at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2. Any request for this material should be accompanied by a full literature citation and the reference number CSD.

Biological assays

The antimicrobial spectra and macromolecular syntheses in cells of the ascitic form of Ehrlich carcinoma were measured as described previously [8, 9].

Results and Discussion

When grown in submerged culture isolates of *Lentinellus ursinus* and *L. omphalodes* from Europe, U.S.A., and Canada produced lentinellic acid in almost equal amounts (50–80 mg/l of culture). This finding suggests that the biosynthetic pathway leading to lentinellic acid might be a suitable taxonomic character. A typical fermentation of *L. ursinus* is shown in Fig. 1. The antibiotic content of the culture is highest 13 days after inoculation. Under the same conditions *L. omphalodes* yielded the highest amounts of lentinellic acid (70 mg/l of culture) after 16 days of fermentation.

Lentinellic acid (**1**), purified from the culture fluid as described in the experimental section, was obtained in form of yellow crystals. Esterification with methanol yielded the methyl ester **2** which exhibited enhanced antimicrobial activity.

According to the mass spectrum **1** has the molecular formula $C_{18}H_{20}O_5$. The mass spectrum is dominated by a ketene elimination from the molecular ion *m/z* 316 which leads to the base peak at *m/z* 274. Lentinellic acid exhibits two strong IR bands (KBr) in the carbonyl region at 1760 and 1680 cm^{-1}. Two UV maxima (MeOH) at 242.5 and 317 nm point to the presence of an extended chromophore. In the ^1H NMR spectrum (Table I) seven well separated multiplets and two methyl singlets at $\delta = 0.98$ and 1.14 can be assigned to the protons of partial structure A. The presence of a 3,4-disubstituted 1,1-dimethylcyclopentane ring in A is in agreement with the characteristic 1.9 Hz W-coupling between the α-protons of the two methylene groups. The structure **1** of lentinellic acid was finally solved by an X-ray analysis. The ^{13}C NMR signals (Table I) were assigned by 2D ^{13}C-^1H shift correlations and selective decoupling experiments. According to the chemical shifts of the olefinic carbons the lactone and carboxylic carbonyl groups exert a strong electron withdrawing effect whereas the cyclobutanone carbonyl is much less effective due to its out of plane conformation.

Lentinellic acid afforded crystals suitable for the X-ray structural determination by crystallization from acetone–petroleum ether. The structure was solved by direct methods using the SHEL X76 program and refined. Dispersion corrections and anisotropic temperature factors have been applied for the no-hydrogen atoms. The conformation and relative configuration of lentinellic acid is depicted in the stereoplot (Fig. 2). Selected structural parameters are given in Tables II–V*. From the bond lengths of the double bonds a mesomeric interaction in the dienoic acid moiety is revealed and the carboxylic proton is partially chelated to the lactone carbonyl group. The molecules are bond in the crystal by Van der Waals forces only.

The absolute configuration of lentinellic acid (**1**) was not determined and is assumed to correspond to that of other natural protoilludane derivatives [10]. The CD spectrum of **1** is depicted in Fig. 3.

1 may be formed in the fungus by condensation of aldehyde **4** with a malonate unit. **4** can be derived

---

+ The numbering system is that used for the protoilludane skeleton [10d].

* The numbering used in Tables II–IV is indicated in Fig. 2. It differs from that given in formula **1**.

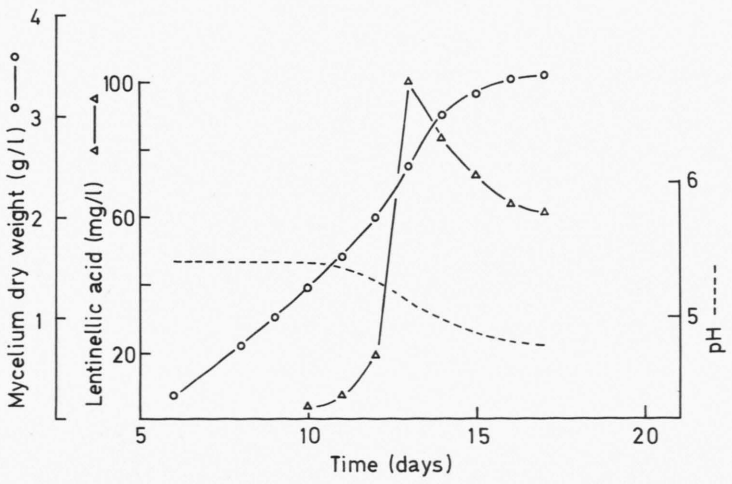
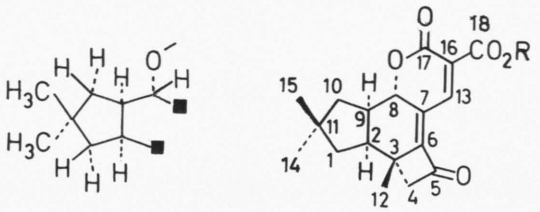


Fig. 1. Time course of a fermentation of *Lentinellus ursinus* 80163. Dry weight of the mycelium, pH, and lentinellic acid content of the culture fluid, determined photometrically after isolation from a 100 ml sample.



A

1, R = H†
2, R = CH_3

Table I. ^1H and ^{13}C NMR data of lentinellic acid (**1**) (400 and 100.62 MHz, respectively; $CDCl_3$ as solvent and internal standard).

H-atom	δ	multiplicity, *J* [Hz]	C-atom	δ	multiplicity, *J* [Hz]
1α	1.61	ddd 12.9/8.1/1.9	1	40.70	Tm 125
1β	1.49	dd 12.9/10.2	2	44.72	Dm 130
2	2.45	ddd 10.2/8.1/7.5	3	41.03*	m
4a	2.91	AB-system 18	4	61.83	Tqd 137/4.6/4.6
4b	2.98	AB-system 18	5	192.48	td 6/1.5
8	5.05	d 9.3	6	162.92	m
9	2.75	dddd 10.8/9.3/7.5/7.2	7	125.43	dd 4/2
10α	2.02	ddd 12.6/7.2/1.9	8	82.60	Dtd 153/5/2.5**
10β	1.33	dd 12.6/10.8	9	50.91	Dm 130
12	1.22	s	10	46.07	Tm 129
13	8.37	s	11	39.20*	m
14	0.98***	s	12	19.34	Qqd 128/4/4
15	1.14***	s	13	142.60	Dd 170/2
CO_2H	12.30	br. s	14	26.65	Qm 126
			15	29.20	Qm 124
			16	118.02	d 1.5
			17	165.18	dd 9/2
			18	161.70	d 5.6

* Signals may be interchanged.
** $J_{2\text{-H},8\text{-C}} = 2.5$ Hz.
*** Assignment according to [10c].

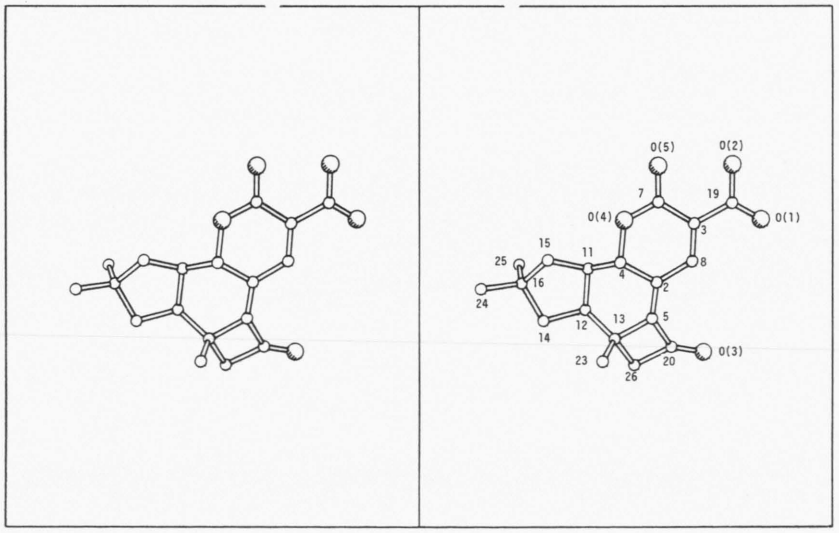


Fig. 2. Stereoplot of lentinellic acid (**1**).

Table II. Fractional atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) (e.s.d.'s in parentheses).

Atom	*x*	*y*	*z*	U
O(4)	1667(5)	2383(2)	1285(1)	57(1)*
C(2)	1655(6)	4306(3)	688(2)	43(1)*
C(3)	1688(6)	2308(4)	217(1)	45(1)*
C(4)	1408(6)	3724(3)	1287(1)	44(1)*
C(5)	1786(7)	5541(4)	692(2)	48(1)*
O(1)	1767(5)	2000(3)	−817(1)	69(1)*
C(7)	1701(7)	1714(4)	795(2)	51(1)*
C(8)	1727(6)	3545(4)	176(1)	47(1)*
O(5)	1816(6)	591(3)	854(1)	76(1)*
O(2)	1710(5)	319(3)	−268(1)	70(1)*
C(11)	2971(6)	4233(3)	1722(1)	40(1)*
C(12)	3338(7)	5672(3)	1690(2)	49(1)*
C(13)	1953(7)	6338(3)	1231(2)	50(1)*
C(14)	3157(9)	6115(4)	2333(2)	73(2)*
C(15)	2499(6)	3991(4)	2367(1)	53(1)*
C(16)	3635(7)	4990(3)	2715(2)	55(1)*
O(3)	2672(7)	6700(3)	−221(1)	87(1)*
C(19)	1728(7)	1542(4)	−336(2)	54(1)*
C(20)	2499(7)	6568(4)	305(2)	62(2)*
C(23)	−176(8)	6711(4)	1459(2)	80(2)*
C(24)	5938(7)	4721(4)	2743(2)	78(2)*
C(25)	2793(9)	5141(4)	3343(2)	86(2)*
C(26)	2974(9)	7366(4)	841(2)	73(2)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U tensor.

Table III. Selected bond distances (Å) with e.s.d.'s in parentheses.

O(4)−C(4)	1.459(4)	O(4)−C(7)	1.326(4)
C(2)−C(4)	1.507(5)	C(2)−C(5)	1.337(5)*
C(2)−C(8)	1.425(5)	C(3)−C(7)	1.462(5)
C(3)−C(8)	1.341(5)*	C(3)−C(19)	1.504(5)
C(4)−C(11)	1.521(5)	C(5)−C(13)	1.500(5)
C(5)−C(20)	1.490(6)	O(1)−C(19)	1.200(5)
C(7)−O(5)	1.224(5)	O(2)−C(19)	1.331(5)
O(2)−Ho(2)	0.997(35)	C(11)−C(12)	1.575(5)
C(11)−C(15)	1.518(5)	C(12)−C(13)	1.555(5)
C(12)−C(14)	1.541(5)	C(13)−C(23)	1.533(7)
C(13)−C(26)	1.568(6)	C(14)−C(16)	1.526(5)
C(15)−C(16)	1.529(5)	C(16)−C(24)	1.527(7)
C(16)−C(25)	1.535(5)	O(3)−C(20)	1.208(5)*
C(20)−C(26)	1.522(6)		

* Double bonds.

Table IV. Selected bond angles (°) with e.s.d.'s in parentheses.

C(4)−O(4)−C(7)	123.1(3)	C(4)−C(2)−C(5)	114.6(3)
C(4)−C(2)−C(8)	120.0(3)	C(5)−C(2)−C(8)	125.4(3)
C(7)−C(3)−C(8)	120.0(3)	C(7)−C(3)−C(19)	120.5(3)
C(8)−C(3)−C(19)	119.4(3)	O(4)−C(4)−C(2)	113.5(3)
O(4)−C(4)−C(11)	106.5(3)	C(2)−C(4)−C(11)	111.4(3)
C(2)−C(5)−C(13)	125.8(3)	C(2)−C(5)−C(20)	139.3(4)
C(13)−C(5)−C(20)	91.8(3)	O(4)−C(7)−C(3)	120.9(3)
O(4)−C(7)−O(5)	116.8(3)	C(3)−C(7)−O(5)	122.3(3)
C(2)−C(8)−C(3)	121.2(3)	C(19)−O(2)−Ho(2)	104.5(21)
C(4)−C(11)−C(12)	115.3(3)	C(4)−C(11)−C(15)	115.4(3)
C(12)−C(11)−C(15)	104.2(3)	C(11)−C(12)−C(13)	113.6(3)
C(11)−C(12)−C(14)	104.6(3)	C(13)−C(12)−C(14)	116.6(3)
C(5)−C(13)−C(12)	108.8(3)	C(5)−C(13)−C(23)	111.2(4)
C(12)−C(13)−C(23)	114.7(3)	C(5)−C(13)−C(26)	88.7(3)
C(12)−C(13)−C(26)	117.5(4)	C(23)−C(13)−C(26)	112.8(3)
C(12)−C(14)−C(16)	106.0(3)	C(11)−C(15)−C(16)	106.2(3)
C(14)−C(16)−C(15)	99.8(3)	C(14)−C(16)−C(24)	112.0(4)
C(15)−C(16)−C(24)	111.2(3)	C(14)−C(16)−C(25)	111.7(3)
C(15)−C(16)−C(25)	112.5(3)	C(24)−C(16)−C(25)	109.4(4)
C(3)−C(19)−O(1)	122.2(4)	C(3)−C(19)−O(2)	116.8(3)
O(1)−C(19)−O(2)	121.0(4)	C(5)−C(20)−O(3)	134.4(4)
C(5)−C(20)−C(26)	90.8(3)	O(3)−C(20)−C(26)	134.8(4)
C(13)−C(26)−C(20)	88.0(3)		

Table V. Atomic coordinates ($\times 10^4$) for the hydrogen atoms and isotropic temperature factors ($Å^2 \times 10^3$).

Atom	*x*	*y*	*z*	U
H(4)	26	3924	1401	49
H(8)	1805	3926	−206	55
H(11)	4162	3781	1595	47
H(12)	4668	5884	1538	60
H(14a)	1791	6408	2411	83
H(14b)	4126	6765	2409	83
H(15a)	1047	4047	2436	62
H(15b)	2979	3185	2479	62
H(23a)	−26	7224	1802	97
H(23b)	−941	5981	1560	97
H(23c)	−896	7161	1158	97
H(24a)	6464	4618	2351	94
H(24b)	6168	3978	2965	94
H(24c)	6631	5399	2931	94
H(25a)	1350	5323	3325	101
H(25b)	3499	5807	3536	101
H(25c)	3004	4388	3559	101
H(26a)	4412	7491	913	100
H(26b)	2277	8149	847	100

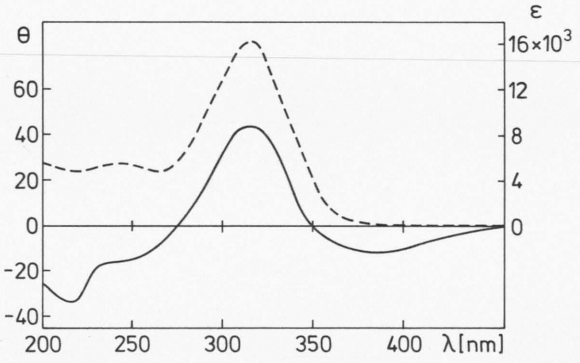
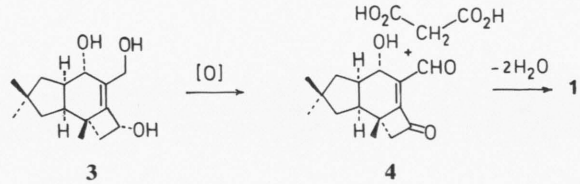


Fig. 3. Circular dichroism spectrum (——) and UV spectrum (– – –) of lentinellic acid (**1**) in methanol.

from armillol (**3**) [10b] by oxidation of two of its hydroxyl groups. Esters of **3** with orsellinic acid and related aromatic acids have recently been isolated from cultures of *Armillariella mellea* [10b, 11].



The antibacterial activity of lentinellic acid in the serial dilution assay is shown in Table VI. The antibiotic inhibits the growth of Gram-negative and Gram-positive bacteria at concentrations ranging from 1 to 100 μg/ml. In the same assay the yeasts *Candida albicans, Nadsonia fulvescens, Saccharomyces cerevisiae,* and *Rhodotorula glutinis* were not affected by concentrations of up to 100 μg/ml. The antifungal activity of lentinellic acid is quite low. The results of the plate diffusion assay are shown in Table VII. Only *Absidia glauca* and *Nematospora coryli* were sensitive at high concentrations. The antifungal but not the antibacterial activities of the methyl ester (**2**), however, were much higher (Table VI). The effect of lentinellic acid on macromolecular syntheses in cells of the ascitic form of Ehrlich carcinoma is shown in Fig. 4. The incorporation of the precursors thymidine, uridine, and leucine into the 5% trichloroacetic acid insoluble fraction of cells (DNA, RNA, and protein) was inhibited at almost the same concentrations. The same effect was observed with cells of *Bacillus brevis.*

Table VI. Antifungal spectra of lentinellic acid (**1**) and its methyl ester (**2**) in the plate diffusion assay.

	Diameter inhibition zone [mm] μg/disc			
	1		**2**	
	50	100	50	100
Absidia glauca	–	10	10	20
Alternaria porri	–	–	11	20
Ascochyta pisi	–	–	–	13
Aspergillus ochraceus	–	–	12	17
Curvularia lunata	–	–	–	10
Eurotium cristatum	–	–	11	13
Mucor miehei	–	–	23	28
Nematospora coryli	20	26	13	21
Neurospora crassa	–	–	–	9
Paecilomyces varioti	–	–	9	17
Penicillium islandicum	–	–	–	15
Penicillium notatum	–	–	11	15
Phytophthora infestans	–	–	10	20
Pleospora herbarum	–	–	11	20
Pythium debaryanum	–	–	14	26
Saprolegnia ferax	–	–	–	9
Ustilago nuda	–	–	–	11
Venturia cerasi	–	–	–	–
Zygorhynchus moelleri	–	–	10	15

Table VII. Antibacterial spectrum of lentinellic acid (**1**) (serial dilution assay).

Test organism	MIC [μg/ml]
Acinetobacter aerogenes	20– 50
Aerobacter aerogenes	1– 5
Bacillus brevis	1– 5
Bacillus subtilis	20– 50
Corynebacterium insidiosum	1– 5
Escherichia coli K-12	> 100
Leuconostoc mesenteroides	> 100
Micrococcus luteus	10– 20
Mycobacterium phlei	50–100
Proteus vulgaris	20– 50
Pseudomonas fluorescens	> 100
Staphylococcus aureus	20– 50
Streptomyces sp. ATCC 23836	10– 20

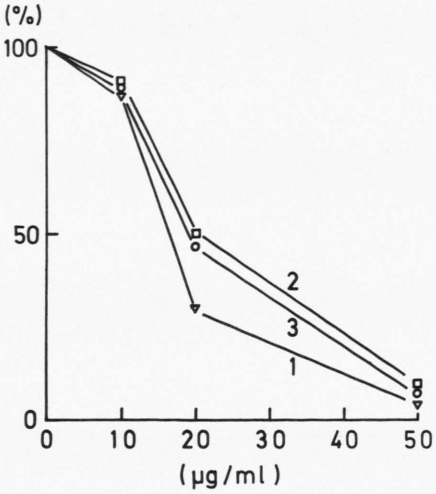


Fig. 4. Effect of lentinellic acid (**1**) on macromolecular syntheses in Ehrlich carcinoma ascitis cells in % of the controls without antibiotic. (1) Protein synthesis; (2) RNA synthesis; (3) DNA synthesis. Controls without antibiotic (= 100%); incorporation per 10^6 cells: [^{14}C]leucine 28.653 cpm; [^{14}C]uridine 12.171 cpm; [^{14}C]thymidine 3.908 cpm.

Acknowledgements

Financial support of this work by the Deutsche Forschungsgemeinschaft and the Bundesministerium für Forschung und Technologie is gratefully acknowledged. We thank Dr. B. Steffan, Bonn, for NMR spectra.

[1] Antibiotics from Basidiomycetes XXVII. XXVI: H. Anke, I. Casser, W. Steglich, and E.-H. Pommer, J. Antibiotics **40,** 443 (1987).
[2] K. Gluchoff-Fiasson and R. Kühner, C. R. Acad. Sc. Paris **294,** 1067 (1982).
[3] R. Singer, The Agaricales in Modern Taxonomy, 4th Edit., Koeltz Scientific Books, Koenigstein 1986.
[4] A. Stärk, Dissertation, University of Kaiserslautern, 1985.
[5] E. Hillen-Maske, Dissertation, University of Bonn, 1986.
[6] G. Germain, P. Main, and M. M. Woolfson, Acta Cryst. **A 27,** 368 (1971).
[7] G. M. Sheldrick, SHEL X76, Program for Crystal Structure Determination, Cambridge 1976.
[8] T. Anke, F. Oberwinkler, W. Steglich, and G. Schramm, J. Antibiotics **30,** 806 (1977).
[9] J. Kupka, T. Anke, F. Oberwinkler, G. Schramm, and W. Steglich, J. Antibiotics **32,** 130 (1979).
[10] a) Absolute configuration of fomannosin: D. E. Cane, R. B. Nachbar, J. Clardy, and J. Finer, Tetrahedron Letters **1977,** 4277; b) armillyl orsellinate: D. M. X. Donnelly, J. Polonsky, T. Prangé, and C. Pascard, J. Chem. Soc., Chem. Commun. **1982,** 135; c) sulcatine: A. Arnone, G. Nasini, G. Assante, H. J. Roeijmans, and G. W. Van Eijk, Phytochemistry **26,** 1739 (1987); d) see also W. A. Ayer and L. M. Brown, Tetrahedron **37,** 2199 (1981) and literature cited therein.
[11] D. M. X. Donnelly, D. J. Coveney, N. Fukuda, and J. Polonsky, J. Nat. Prod. **49,** 111 (1986).