Phytochemistry, Vol. 26, No. 4, pp. 1085–1089, 1987.
Printed in Great Britain.

0031-9422/87 $3.00+0.00

DITERPENOIDS WITH A NOVEL SKELETON FROM THE LIVERWORT *ANASTROPHYLLUM MINUTUM**

JÜRGEN BEYER†, HANS BECKER, MASAO TOYOTA‡ and YOSHINORI ASAKAWA‡

Institut für Pharmazeutische Biologie der Universität Heidelberg, Im Neuenheimer Feld 364, D-6900 Heidelberg, F.R.G.; ‡Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Yamashiro-cho, Tokushima 770, Japan

(*Received* 24 *July* 1986)

Key Word Index—*Anastrophyllum minutum*; Jungermanniales; Hepaticae; sesquiterpene hydrocarbons; diterpenoids with novel carbon skeleton; sphenolobane diterpenoids; plant growth inhibitory activity.

Abstract—Six diterpenoids with a novel carbon skeleton were isolated from the liverwort *Anastrophyllum minutum*. Their structures were determined by means of high field NMR spectroscopy including proton–proton and proton–carbon shift correlation 2D-techniques, NOE difference spectroscopy and high resolution mass spectrometry. Sphenolobane is the proposed name of the new skeletal type and its biogenetic origin is briefly considered. Inhibitory activity against the growth of shoots and roots of rice was shown by 3α,4α-epoxy-5α-acetoxy-18-hydroxysphenoloba-13*E*,16*E*-diene.

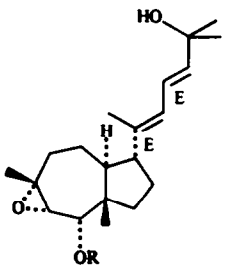
INTRODUCTION

Liverworts are known to have oil bodies which contain mainly terpenoids. Comparison of these constituents with those of algae, pteridophytes and higher plants may reveal important information about the evolutionary relationships of plants. In addition to the known sesquiterpene hydrocarbons anastreptene, β-barbatene and bicyclogermacrene, we have isolated and elucidated the structures of six diterpenoids from *Anastrophyllum minutum* (Schreb.) Schust. (syn. *Sphenolobus minutus* (Schreb.) Berggr.) Jungermanniales (Hepaticae). The carbon skeleton of these diterpenoids represents a new type for which we propose the name sphenolobane. The major compound **1** showed growth inhibitory activity against rice seedlings.

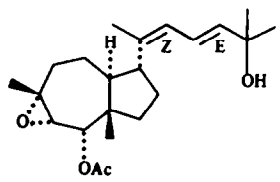
RESULTS AND DISCUSSION

A combination of low and high pressure LC of the CH_2Cl_2 extract of *Anastrophyllum minutum* yielded, in addition to the known sesquiterpene hydrocarbons anastreptene, β-barbatene and bicyclogermacrene, six novel diterpenoids (**1**–**6**). Separation of anastreptene and β-barbatene was achieved by low temperature HPLC. For details of the low temperature separation see ref. [1]. The structures of these hydrocarbons were derived from MS and ^{1}H NMR spectra which were identical to those of the literature [2–5].

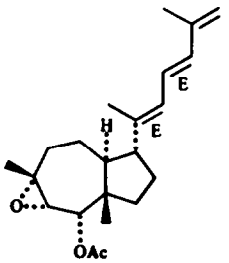
The major compound (**1**) showed hydroxyl (3620 and 3500 cm^{-1}) and acetate (1760 and 1230 cm^{-1}) absorption in the IR spectrum. The UV spectrum (λ_{max} 243 nm) indicated the presence of a conjugated diene. The molecular formula, $C_{22}H_{34}O_4$, was determined by means of high resolution mass spectrometry. Furthermore the mass spectrum exhibited the characteristic fragments *m/z* 344 $[M-H_2O]^+$ and *m/z* 59 which indicated partial structure R^1 (Fig. 1). The ^{1}H NMR coupling pattern (Table 2) of three olefinic protons δ_H 5.96 (*br d*, $J_{15,16}$ = 11 Hz, H-15),



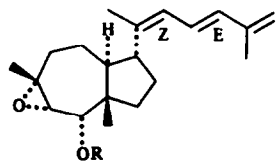
1 R = Ac
2 R = H



3



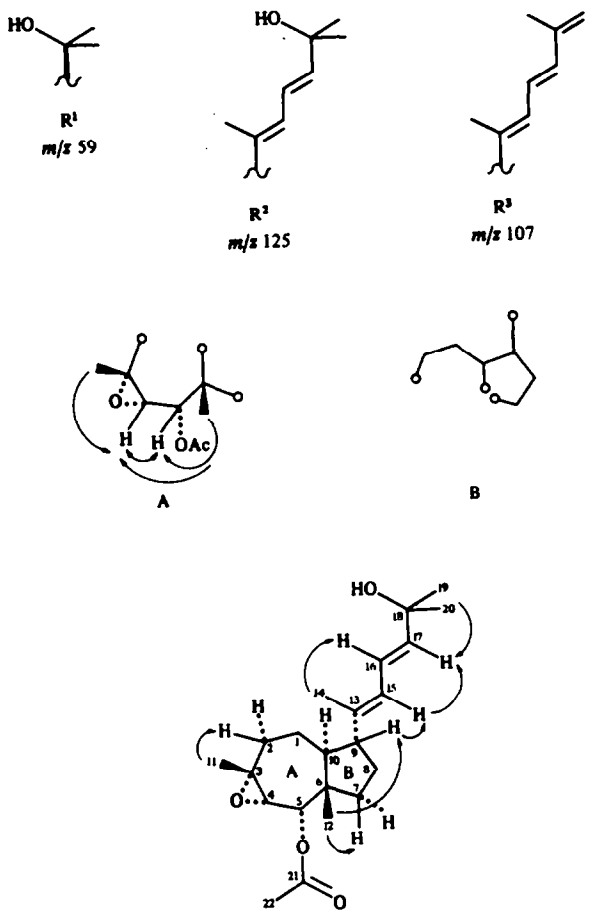
4



5 R = Ac
6 R = H

* Part of this work was presented at the 30th Symposium of the Chemistry of Terpenes, Essential Oils and Aromatics of Japan, Hiroshima, October 1986.

†Author to whom correspondence should be addressed.



1

Fig. 1. → = NOE.

Table 1. ^{13}C NMR (100 MHz) spectral data of compounds 1 and 4 (TMS int. stand.)

C No.	1 (C_6D_6)	4 ($CDCl_3$)
1	23.5 (CH_2)	23.1 (CH_2)
2	34.8 (CH_2)	34.4 (CH_2)
3	59.6 (C)	60.2 (C)
4	59.7 (CH)	59.7 (CH)
5	71.8 (CH)	71.8 (CH)
6	46.8 (C)	46.7 (C)
7	35.7 (CH_2)	35.5 (CH_2)
8	25.8 (CH_2)	25.6 (CH_2)
9	52.4 (CH)	52.1 (CH)
10	48.0 (CH)	47.8 (CH)
11	23.3 (CH_3)	23.3 (CH_3)
12	16.2 (CH_3)	16.4 (CH_3)
13	139.0 (C)	140.6 (C)
14	12.8 (CH_3)	13.2 (CH_3)
15	126.4 (CH)	126.4* (CH)
16	123.0 (CH)	125.4* (CH)
17	140.4 (CH)	133.8* (CH)
18	70.4 (C)	142.4 (C)
19	30.3 (CH_3)	115.9 (CH_2)
20	30.3 (CH_3)	18.6 (CH_3)
21	169.4 (C)	170.3 (C)
22	20.4 (CH_3)	20.8 (CH_3)

Chemical shifts in ppm.
* Interchangeable assignments; multiplicities were determined by the INEPT pulse sequence.

δ_H 6.63 (*dd*, $J_{16,15}$ = 11 Hz, $J_{16,17}$ = 15 Hz, H-16) and δ_H 5.76 (*d*, $J_{17,16}$ = 15 Hz, H-17) as well as the presence of a vinyl methyl δ_H 1.62 (3H, *d*, $J_{14,15}$ = 1.5 Hz, H-14) which exhibited allylic coupling (J = 1.5 Hz) with H-15 suggested partial structure R^2, a characteristic mass fragment (m/z 125) present in the mass spectra of compounds 1–3. The ^{13}C NMR spectrum (Table 1) revealed the presence of six methyls, four methylenes, seven methines and five quaternary carbons. An epoxide was indicated by the signals at δ_C 59.6 (C, C-3) and δ_C 59.7 (CH, C-4) as well as by the resonance at δ_H 2.66 (*d*, $J_{4,5}$ = 5.5 Hz, H-4). The epoxide methine was shown to be α to a secondary acetate (δ_H 5.13, *d*, $J_{5,4}$ = 5.5, H-5) by the presence of the expected coupling. NOEs were observed between methyl H-11 (δ_H 1.09, *br s*) and H-4, between methyl H-12 (δ_H 0.64, *br s*) and H-5 and between methyl H-12 and H-4. Furthermore saturation of H-4 revealed an NOE upon H-5. These results suggested partial structure A (Fig. 1). Partial structure B (Fig. 1) was determined by means of a two dimensional proton–proton correlated COSY experiment. The linkage of A and B was clearly shown in the 2D COSY spectrum by long range couplings (^4J) between H-2α (δ_H 1.53, *m*) and methyl H-11 and between H-7α (δ_H 1.61, *m*) and methyl H-12. Additionally H-9 (δ_H 2.26, *m*) was long range coupled (^4J) with H-7β (δ_H 1.15, *m*). Models show that these latter couplings are due to W-arrangements of these protons. The above results indicate structure 1 (Fig. 1) which was confirmed by a proton–carbon shift correlated 2D-experiment. Hence complete assignment of both the ^1H and ^{13}C NMR spectra of 1 was possible. The relative configurations were established by means of extensive difference NOE spectroscopy. The most important resonances observed are indicated in Fig. 1. It clearly follows from the NOE difference spectra that the five and seven membered rings are *trans*-fused as saturation of the methyl H-12 did not reveal an NOE upon H-10 (δ_H 1.91, *m*). In addition to the NOE results the 13*E* geometry of 1 is supported by the allylic coupling of H-15 with methyl H-14 ($J_{14,15}$ = 1.5 Hz).

The ^1H NMR spectrum of 2 was very similar to that of 1. However the H-5 resonance now occurred at higher field (δ_H 3.84) suggesting that C-5 in 2 bore a hydroxyl group. This was supported by the disappearance of the acetate methyl in the ^1H NMR spectrum, the lack of carbonyl stretch in the IR spectrum and the molecular formula ($C_{20}H_{32}O_3$). No other major differences were observed between the spectra of 1 and 2 and thus 2 was formulated as the deacetyl derivative of 1. Confirmation came from the conversion of 1 into 2 by $LiAlH_4$ reduction. The assignments of the ^1H NMR resonances of 2 were again obtained from a 2D COSY experiment.

The structure of the third compound (3) followed immediately from consideration of its ^1H NMR spectrum which was very similar to that of 1. The H-9 resonance had

Table 2. ^{1}H NMR (400 MHz) spectral data of diterpenoids 1–6 (TMS int. stand.)

H No.	1 (C_6D_6)	2 (C_6D_6)	3 (C_6D_6)
1α	1.38 *m*	1.35 *m*	*
1β	0.96 *m*	0.91 *m*	*
2α	1.53 *m*	1.46 *m*	*
2β	1.77 *m*	1.70 *m*	*
4	2.66 *d* (5.5)	2.55 *d* (5.5)	2.62 *d* (5.5)
5	5.13 *d* (5.5)	3.84 *d* (5.5)	5.11 *d* (5.5)
7α	1.61 *m*	2.15 *m*	*
7β	1.15 *m*	1.22 *m*	*
8α	1.44 *m*	1.55 *m*	*
8β	1.69 *m*	1.78 *m*	*
9	2.26 *m*	2.30 *m*	3.08 *m*
10	1.91 *m*	2.16 *m*	1.97 *m*
11	1.09 *br s*	1.06 *br s*	1.03 *br s*
12	0.64 *br s*	0.61 *br s*	0.64 *br s*
14	1.62 *d* (1.5)	1.64 *d* (1)	1.68 *s*
15	5.96 *br d* (11)	5.97 *br d* (11)	6.02 *d* (11)
16	6.63 *dd* (11; 15)	6.58 *dd* (11; 15)	6.77 *dd* (11; 15)
17	5.76 *d* (15)	5.71 *d* (15)	5.67 *d* (15)
19	1.25 *s*	1.21 *s*	1.19† *s*
20			1.20† *s*
22	1.81 *s*	—	1.80 *s*

H No.	4 ($CDCl_3$)	5 ($CDCl_3$)	6 ($CDCl_3$)
1α	1.90 *m*	*	*
1β	1.18 *m*	*	*
2α	1.44 *m*	*	*
2β	1.96 *m*	*	*
4	2.85 *d* (5.5)	2.86 *d* (5.5)	2.93 *d* (5.5)
5	5.00 *d* (5.5)	5.02 *d* (5.5)	4.01 *d* (5.5)
7α	1.67 *m*	*	*
7β	1.37 *m*	*	*
8α	1.85 *m*	*	*
8β	1.52 *m*	*	*
9	2.38 *m*	3.02 *m*	3.02 *m*
10	1.94 *m*	*	*
11	1.31 *d* (2.5)	1.32 *br s*	1.36 *br s*
12	0.99 *br s*	1.04 *br s*	0.95 *br s*
14	1.74 *d* (1)	1.75 *s*	1.75 *s*
15	5.91 *br d* (11)	5.97 *d* (11)	5.98 *d* (11)
16	6.42 *dd* (11; 15.5)	6.42 *dd* (11; 15)	6.43 *dd* (11; 15)
17	6.25 *d* (15.5)	6.23 *d* (15)	6.22 *d* (15)
19a	4.95 *br s*	4.94 *br s*	4.93 *br s*
19b	4.96 *br s*	4.96 *br s*	4.95 *br s*
20	1.90 *s*	1.89 *s*	1.89 *s*
22	2.10 *s*	2.09 *s*	—

Chemical shifts in ppm; numbers in parentheses are coupling constants in Hz.
*Not assigned; signals indicated as *m* were unresolved or overlapped multiplets.
†Assignment may be reversed.

shifted downfield (δ_H 3.08) and there was no allylic coupling between H-15 and methyl H-14 suggesting that **3** is the 13*Z* isomer of **1**. The 16–17 double bond remains *trans* as revealed by the magnitude of $J_{16,17}$ (15 Hz). Difference NOE measurements verified the stereochemistry of **3** with conclusive NOEs between H-15 and H-14 as well as between H-16 and H-9.

Compound **4**, $C_{22}H_{32}O_3$, is a conjugated triene as was easily seen from the UV spectrum (λ_{max} 278 nm). The IR spectrum contained bands characteristic of an acetate group (1760 and 1230 cm^{-1}). Furthermore the fragment *m/z* 125 (R^2, Fig. 1), present in the mass spectra of **1–3**, was now replaced by base peak *m/z* 107. Comparison of the ^{13}C NMR shifts (Table 1) of **4** with those of **1** revealed

that the only difference was in the nature of the side chain. The presence of a vinyl methyl (δ_H 1.90, *br s*, H-20) which was long range coupled to an exomethylene (δ_H 4.95 and 4.96, each *br s*, H-19a and H-19b) in the ^{1}H NMR spectrum of **4** suggested that **4** is formally a dehydration product (R^3, Fig. 1) of **1**. The allylic coupling of H-15 with methyl H-14 as well as NOEs between H-9 and H-15, H-14 and H-16, H-15 and H-17, and H-20 and H-16 confirmed the 13*E*,16*E* geometry. Final proof of the proposed structure came from dehydration of **1** ($POCl_3$/pyridine) which afforded **4**.

The structure of compound **5**, the 13*Z*,16*E* isomer of **4**, was revealed by ^{1}H NMR and NOE difference spectroscopy. Thus the appropriate NOEs were observed between H-9 and H-16 and between H-14 and H-15. In addition there was no allylic coupling between methyl H-14 and H-15, and H-9 showed the expected downfield shift (δ_H 3.02).

The ^{1}H NMR spectrum of the final compound **6** was similar to that of **5**. However the upfield shift of H-5 (δ_H 4.01) indicated that **6** was simply the deacetyl derivative of **5**. The mass spectrum and the results of NOE difference experiments were in accordance with this structure.

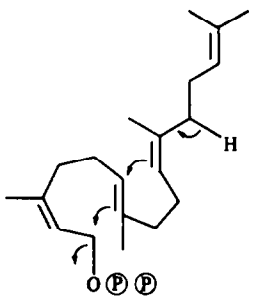
The sphenolobane skeleton can be considered to be an isoprenylogue of the carotane skeleton and presumably arises by folding of geranylgeranyl pyrophosphate as shown in Scheme 1. It is of interest that hercynolactone, the only carotane hitherto reported from the Hepaticae, occurs in the closely related species *Barbilophozia lycopodioides* and *B. hatcheri* [6].

Compound **1** significantly decreased shoot and root elongation of rice seedlings (*Oryza sativa*) at concentrations between 20 and 500 ppm. 500 ppm solutions additionally inhibited germination of 30% of the seedlings. Thus **1** possesses only low growth inhibitory activity against rice seedlings.

EXPERIMENTAL

Mps uncorr.; the solvents used for spectral determinations were CCl_4 (IR), EtOH and Et_2O (UV), EtOH and $CHCl_3$ ($[\alpha]_D$), TMS–C_6D_6 and TMS–$CDCl_3$ [^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz)]; MS by EI at 100 and 70 eV.

Plant material. Anastrophyllum minutum was collected at Eppenbrunn, F.R.G. in April, 1985 (voucher deposited in the Herbarium of the Institut für Pharmazeutische Biologie, Universität Heidelberg).



Scheme 1. Proposed cyclization of geranylgeranyl pyrophosphate to afford the sphenolobane skeleton.

Isolation of sesquiterpenoids and diterpenoids. Fresh plant material (220 g) was homogenized with CH_2Cl_2 and extracted for 1 day at ambient temp. Extraction was repeated twice. The crude extract (1.9 g) was separated by CC (SI, 200 g, particle size 0.040–0.063 mm) employing a *n*-hexane–EtOAc gradient. Fraction A (*n*-hexane, 100%) was a colourless oil (159 mg). Low temperature HPLC (SI, *n*-hexane–*n*-pentane) of A gave anastreptene (52 mg), β-barbatene (37 mg) and bicyclogermacrene (24 mg) [1]. Separation of fraction B (*n*-hexane–EtOAc, 85:15), yellow oil (129 mg), could only be achieved by means of HPLC on a CN-phase column (*n*-hexane–EtOAc, 98:2, flow 1.0 ml per min) and afforded **5** (49 mg), **4** (8 mg) and **6** (3 mg). Fraction C (*n*-hexane–EtOAc, 60:40), yellow oil (140 mg), was rechromatographed on HPLC (SI, *n*-hexane–*iso*-propanol, 96:4, flow 5.0 ml per min) to give **1** (110 mg) and **2** (6 mg). Fraction D (*n*-hexane–EtOAc, 50:50), yellow oil (21 mg), containing **3** (9 mg) was purified by means of HPLC (SI, *n*-hexane–*iso*-propanol, 95:5, flow 5.0 ml per min). Columns: Spherisorb SI (250 × 8 mm, particle size 5 μm), Nucleosil CN (200 × 4 mm, particle size 5 μm). Compounds were detected using a UV detector and a differential refractometer.

3α,4α-*Epoxy*-5α-*acetoxy*-18-*hydroxysphenoloba*-13E,16E-*diene* (**1**). Mp 46–48° (EtOAc–*n*-hexane); IR ν_{max} cm^{-1}: 3620 and 3500 (OH), 2960, 1760 (C=O), 1460, 1370, 1230 (C–O), 1100, 1040, 970; UV λ_{max}^{EtOH} nm (log ε): 243 (4.38); $[\alpha]_D^{23}$ +22.3 (EtOH; *c* 4.640); EIMS at 100 eV, *m/z* (rel. int.): 362.2456 [M]$^+$ (16) ($C_{22}H_{34}O_4$, requires: 362.2457), 344.2341 [M − H_2O]$^+$ (5) ($C_{22}H_{32}O_3$, requires: 344.2351), 259 (4), 175 (8), 159 (9), 147 (10), 133 (10), 125 [R^2]$^+$ (28), 109 (31), 107 (25), 93 (17), 59 [R^1]$^+$ (9), 55 (17), 43 (100), 41 (17).

3α,4α-*Epoxy*-5α,18-*dihydroxysphenoloba*-13E,16E-*diene* (**2**). Colourless oil; IR ν_{max} cm^{-1}: 3600 and 3520 (OH), 2950, 1460, 1370, 1110, 960; UV λ_{max}^{EtOH} nm (log ε): 243 (4.35); $[\alpha]_D^{22}$ +28.3 (EtOH; *c* 0.450); EIMS at 100 eV, *m/z* (rel. int.): 320.2338 [M]$^+$ (26) ($C_{20}H_{32}O_3$, requires: 320.2351), 302 [M − H_2O]$^+$ (5), 259 (3), 219 (12), 201 (12), 175 (13), 159 (20), 147 (29), 135 (22), 125 [R^2]$^+$ (43), 109 (63), 107 (46), 93 (40), 55 (27), 43 (100), 41 (23).

3α,5α-*Epoxy*-5α-*acetoxy*-18-*hydroxysphenoloba*-13Z,16E-*diene* (**3**). Yellow oil; IR ν_{max} cm^{-1}: 3620 and 3480 (OH), 2960, 1760 (C=O), 1460, 1370, 1230 (C–O), 1100, 1040, 970; UV ν_{max}^{EtOH} nm (log ε): 242 (4.35); $[\alpha]_D^{23}$ −11.5 (EtOH; *c* 0.590); EIMS at 100 eV, *m/z* (rel. int.): 362.2449 [M]$^+$ (12) ($C_{22}H_{34}O_4$, requires: 362.2457), 259 (8), 175 (14), 159 (17), 147 (16), 133 (16), 125 [R^2]$^+$ (11), 121 (17), 109 (43), 93 (28), 43 (100), 41 (12).

3α,4α-*Epoxy*-5α-*acetoxysphenoloba*-13E,16E,18-*triene* (**4**). Yellow oil; IR ν_{max} cm^{-1}: 2920, 1760 (C=O), 1460, 1370, 1230 (C–O), 1100, 1040, 970; UV $\lambda_{max}^{Et_2O}$ nm (log ε): 278 (4.52); $[\alpha]_D^{25}$ +13.0 ($CHCl_3$; *c* 0.620); EIMS at 70 eV, *m/z* (rel. int.): 344.2363 [M]$^+$ (39) ($C_{22}H_{32}O_3$, requires: 344.2351), 159 (13), 145 (13), 134 (21), 121 (10), 119 (38), 107 [R^3]$^+$ (100), 93 (38), 55 (27), 44 (83).

3α,4α-*Epoxy*-5α-*acetoxysphenoloba*-13Z,16E,18-*triene* (**5**). Yellow oil; IR ν_{max} cm^{-1}: 3100, 3050, 2920. 1760 (C=O), 1450, 1370, 1230 (C–O), 1100, 1040, 960; UV λ_{max}^{EtOH} nm (log ε): 277 (4.51); $[\alpha]_D^{24}$ +3.2 ($CHCl_3$; *c* 2.420); EIMS at 70 eV, *m/z* (rel. int.): 344.2352 [M]$^+$ (29) ($C_{22}H_{32}O_3$, requires: 344.2351), 159 (12), 145 (11), 134 (19), 121 (11), 119 (32), 107 [R^3]$^+$ (100), 93 (33), 55 (20), 44 (69).

3α,4α-*Epoxy*-5α-*hydroxysphenoloba*-13Z,16E,18-*triene* (**6**). Mp 77–79° (EtOAc–*n*-hexane); IR ν_{max} cm^{-1}: 3520 (OH), 2920, 1460, 1370, 1110, 1040, 960; UV λ_{max}^{EtOH} nm (log ε): 278 (4.52); $[\alpha]_D^{25}$ −51.1 ($CHCl_3$; *c* 0.250); EIMS at 70 eV, *m/z* (rel. int.): 302.2221 [M]$^+$ (29) $C_{20}H_{30}O_2$, requires: 302.2246), 159 (6), 119 (21), 107 [R^3]$^+$ (100), 93 (27), 55 (14), 42 (23).

Deacetylation of **1**. Compound **1** (6.7 mg) in dry Et_2O (3.0 ml) was stirred with $LiAlH_4$ (50 mg) at 0° for 0.5 hr. Usual work up afforded 5.3 mg of **2**. ^{1}H NMR (C_6D_6): δ0.61 (3H, *br s*, H-12),

1.06 (3H, *br s*, H-11), 1.21 (6H, *s*, H-19 and H-20), 1.64 (3H, *d*, J = 1 Hz, H-14), 2.16 (1H, *m*, H-10), 2.30 (1H, *m*, H-9), 2.55 (1H, *d*, J = 5.5 Hz, H-4), 3.84 (1H, *d*, J = 5.5 Hz, H-5), 5.71 (1H, *d*, J = 15 Hz, H-17), 5.97 (1H, *br d*, J = 11 Hz, H-15), 6.58 (1H, *dd*, $J_{16,15}$ = 11 Hz, $J_{16,17}$ = 15 Hz, H-16).

Dehydration of **1**. Compound **1** (20.0 mg) in dry pyridine (1.5 ml) was stirred with $POCl_3$ (0.1 ml) at 15° for 2 hr. Extraction with Et_2O afforded **4** (15.2 mg). ^{1}H NMR ($CDCl_3$): δ0.99 (3H, *br s*, H-12), 1.31 (3H, *d*, J = 2.5 Hz, H-11), 1.74 (3H, *d*, 1 Hz, H-14), 1.90 (3H, *br s*, H-20), 2.10 (3H, *s*, H-22), 2.38 (1H, *m*, H-9), 2.85 (1H, *d*, J = 5.5 Hz, H-4), 4.95 (1H, *br s*, H-19a), 4.96 (1H, *br s*, H-19b), 5.00 (1H, *d*, J = 5.5 Hz, H-5), 5.91 (1H, *br d*, J = 11 Hz, H-15), 6.25 (1H, *d*, J = 15.5 Hz, H-17), 6.42 (1H, *dd*, $J_{16,15}$ = 11 Hz, $J_{16,17}$ = 15.5 Hz, H-16).

Bioassay with Oryza sativa. Growth inhibitory activity was examined for **1** in the range of 0.5–500 ppm by Kato's method [7].

Acknowledgements—We thank Mr. Rubik, Institut für Biochemie (Director Prof. Dr. Hecker), DKFZ, for running high resolution MS and Dr. Kramer and Mrs. Jost, Pharm. Chem. Inst. (Director Prof. Dr. Neidlein), Universität Heidelberg, for running ^{1}H NMR spectra. We are grateful to Dr. Mues, Botanisches Institut der Universität Saarbrücken, for identifying the plant species.

REFERENCES

1. Beyer, J., Becker, H. and Martin, R. (1986) *J. Liq. Chromatogr.* **9**, 2433.
2. Andersen, N. H., Ohta, Y., Moore, A. and Tseng, C. W. (1978) *Tetrahedron* **34**, 41.
3. Anderson, N. H., Costin, C. R., Kramer, C. M., Ohta, Y. and Huneck, S. (1973) *Phytochemistry* **12**, 2709.
4. Nishimura, K. (1969) *Tetrahedron Letters* 3097.
5. Nishimura, K., Horibe, I. and Tori, K. (1973) *Tetrahedron* **29**, 271.
6. Huneck, S., Cameron, A. F., Connolly, J. D., McLaren, M. and Rycroft, D. S. (1982) *Tetrahedron Letters* **23**, 3959.
7. Kato, T., Tsunakawa, M., Sasaki, N., Aizawa, H., Fujita, K., Kitahara, Y. and Takahashi, N. (1977) *Phytochemistry* **16**, 45.