Anal. Calcd for $C_{11}H_{14}NO_3P$: C, 55.22; H, 5.91; N, 5.86. Found: C, 55.38; H, 6.00; N, 5.83.

Registry No. 3, 73466-84-9; 4, 57020-81-2; 5a, 73466-85-0; 5b, 73466-86-1; 5c, 73466-87-2; 6a, 73466-88-3; 6b, 73466-89-4; (*E*)-7a, 73481-48-8; (*Z*)-7a, 73466-90-7; 7b, 73466-91-8; 7c, 73466-92-9; CH_3COCl, 75-36-5; 3-$CF_3C_6H_4COCl$, 2251-65-2; $EtOC(O)Cl$, 541-41-3; CH_3NCO, 624-83-9; 3-$CF_3C_6H_4NCO$, 329-01-1; $HONH_2$·HCl, 5470-11-1; 4-$ClC_6H_4NHNH_2$·HCl, 1073-70-7; $MeONH_2$·HCl, 593-56-6.

Structures of Satratoxin F and Satratoxin G, Metabolites of *Stachybotrys atra*: Application of Proton and Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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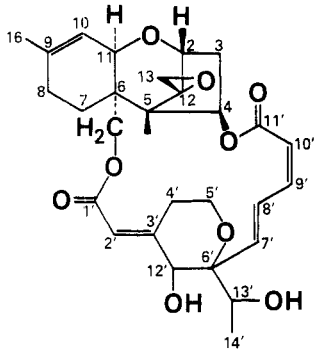
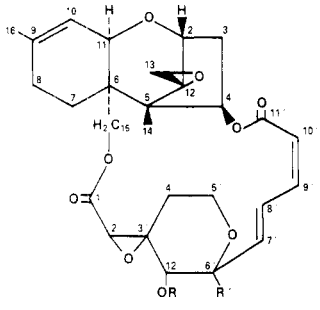
Received January 14, 1980

Recent work in our laboratories has demonstrated that two known trichothecenes of the roridin class[1] are produced by the mold *Stachybotrys atra*, viz., roridin E[2] and satratoxin H (1).[3] We now describe spectral studies which



show that the structures of two new *S. atra* metabolites, designated satratoxins F and G, are **3** and **2**, respectively.

MS, IR, and proton and carbon-13 NMR spectral data of **2** were observed to be quite similar to those of **1** (Tables



I and II). In particular, characteristic NMR signals due to (i) methyl protons at 0.83 and 1.74 ppm, (ii) epoxide methylene protons centered at 2.98 ppm, (iii) the methyl carbinol pendant group at 1.12 and 4.45 ppm, and (iv) the cis–trans diene group at 5.90, 5.93, 6.68, and 7.00 ppm clearly indicate that **2** is a trichothecene compound belonging to the roridin group and is closely related to **1**. Its molecular weight of 544 is 16 mass units greater than that of **1**, suggesting incorporation of an oxygen into the satratoxin H system.

Table I. ^1H NMR Data[a] of Satratoxins H (1), G (2), and F (3)

position	1	2	3
2	3.9 (m)	3.90 (d, 5)	3.85 (d, 5)
3A	2.45 (dd, 7.5, 15)	2.5 (m)	2.5 (m)
3B	2.20 (dt, 4,5, 15)	2.0 (m)	2.0 (m)
4	5.9 (m)	6.0 (m)	5.9 (m)
7	1.9 (m)	2.0 (m)	2.0 (m)
8	2.1 (m)	2.0 (m)	2.0 (m)
10	5.46 (d, 5)	5.46 (d, 5)	5.43 (d, 5)
11	3.62 (d, 5)	3.61 (d, 5)	3.59 (d, 5)
13	2.98[b] (AB, 4)	2.98[b] (AB, 4)	2.98[b] (AB, 4)
14	0.83	0.87	0.83
15	4.22[b] (AB, 12)	4.02[b] (AB, 12)	3.88[b] (AB, 12)
16	1.74	1.74	1.73
2′	5.85 (d, 2)	3.43	3.38
4′A	3.74 (dt, 3, 10)	2.5 (m)	2.5 (m)
4′B	2.6 (m)	2.5 (m)	2.5 (m)
5′	3.9 (m)	3.9 (m)	4.15 (m)
7′	6.09 (d, 17.5)	5.90 (d, 16.5)	5.60 (d, 15.5)
8′	7.36 (dd, 10.5, 17.5)	7.00 (dd, 7.5, 16.5)	6.81 (dd, 6, 15.5)
9′	6.63 (t, 10.5)	6.68 (dd, 7.5, 10.5)	6.57 (dd, 6, 10.5)
10′	5.91 (d, 10.5)	5.93 (d, 10.5)	5.92 (d, 10.5)
12′	3.97	4.35	4.24
13′	4.38 (q, 7)	4.45 (q, 7)	
14′	1.16 (d, 7)	1.12 (d, 7)	2.30

[a] In $CDCl_3$ in parts per million from Me_4Si; peak descriptions and J values (Hz) in parentheses. [b] Center of AB system.

Table II. ^{13}C NMR Data[a] of Satratoxins H (1), G (2), and F (3)

position	1	2	3
2	79.1 (d)	79.3 (d)	79.2 (d)
3	34.4 (t)	34.4 (t)	34.6 (t)
4	74.2 (d)	73.7 (d)	74.3 (d)
5	49.0	49.3	49.5
6	43.4	43.3	43.2
7	20.4 (t)	20.2 (t)	20.1 (t)
8	27.6 (t)	27.5 (t)	27.5 (t)
9	140.2	140.3	140.4
10	119.0 (d)	118.8 (d)	118.6 (d)
11	68.2 (d)	68.1 (d)	67.9 (d)
12	65.4	65.4	65.3
13	48.0 (t)	48.1 (t)	48.0 (t)
14	7.6 (q)	8.0 (q)	8.0 (q)
15	64.2 (t)	64.9 (t)	65.1 (t)
16	23.3 (q)	23.3 (q)	23.3 (q)
1′	166.2	166.9	166.1
2′	119.0 (d)	61.0 (d)	58.9 (d)
3′	155.1	65.4	63.9
4′	25.3 (dd)	22.7 (t)	22.7 (t)
5′	60.4 (t)	60.3 (t)	61.2 (t)
6′	81.4	81.5	87.1
7′	132.2 (d)	132.0 (d)	130.2 (d)
8′	134.2 (d)	131.5 (d)	130.5 (d)
9′	143.0 (d)	144.2 (d)	143.2 (d)
10′	120.4 (d)	120.0 (d)	121.2 (d)
11′	167.0	166.9	166.9
12′	73.7 (d)	72.6 (d)	73.7 (d)
13′	69.7 (d)	70.1 (d)	217.0
14′	15.7 (q)	16.1 (q)	29.7 (q)

[a] In $CDCl_3$ in parts per million from Me_4Si.

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A proton-noise-decoupled (PND) ^{13}C NMR spectrum revealed the presence of the same number of carbons (29) as for 1 and, together with a single-frequency off-resonance decoupled (SFORD) spectrum, demonstrated the presence of only six olefinic carbons (vs. eight for 1) and, notably, the absence of signals previously assigned to C-2′ and C-3′ in 1. Signals attributable to these two carbons appeared at 61.0 and 65.4 ppm and are both in the range expected for methine and quaternary carbons bonded to oxygen.[4] This observation suggested that the 2′,3′-acrylic ester double bond of 1 had been replaced with an epoxide function. The following evidence supported this conclusion and argued against epoxide formation at either the 7,8 site as in epoxyisororidin E and epoxyroridin H[5] or the 9,10 double bond as in baccharin and isobaccharin.[6] First, existence of the cis–trans diene system was mandated by the observation of proton and carbon-13 NMR signals in 2 (vide supra) which were essentially identical with respect to both chemical shift and multiplicity with those of the 7′,8′,9′,10′-diene system in 1 and the other roridins.[7] Second, the chemical shifts of H-10, 16-CH_3, C-9, and C-10 are virtually identical in 1 and 2, thus supporting the belief that this moiety exists unaltered in 2. This similarity in ^{13}C NMR data also extends to those signals assigned to C-4′, C-5′, C-6′, and C-12′ of the pyran ring in structures 1 and 2.

Satratoxin G, like 1, formed a diacetate derivative (mol wt 628), indicating the presence of two hydroxyl groups. The ^1H NMR spectrum of 2 also exhibited loss of two protons upon addition of D_2O, confirming the previous observation. The data presented thus far support the belief that 2 is an epoxidized variation of 1. Analogous epoxidations at the acrylic ester double bond have been reported for verrucarin B, roridin D[1], and a series of baccharin trichothecenes.[6]

MS, IR, and ^1H and ^{13}C NMR spectral data of 3 were found, in turn, to be very much like those of 1 and 2 (Tables I and II). Most of the arguments which were made concerning similarities between the NMR spectra and, therefore, the structures of 1 and 2, viz., common trichothecene and diene moieties, can be made for 3. Inspection of the ^{13}C NMR data of 3 reveals, moreover, the presence of two signals at 58.9 and 63.9 ppm, indicating that 3 possesses an epoxide group at C-2′ and C-3′, like 2, and not an acrylic ester double bond, like 1. However, two notable differences in the ^1H NMR spectrum of 3 are the appearance of a methyl, single-resonance line at δ 2.30, the concomitant absence of a methyl doublet at δ 1.20, and a methine quartet at ca. δ 3.7, which are characteristic of the methyl carbinol group found in most of the roridins.[1,5,6]

In addition, the molecular weight of 3 of 542 is just 2 mass units less than that of 2. This NMR and mass spectral data suggested that the methylcarbinol group at C-6′ of 2 had been oxidized to a ketone function in 3, an inference which was supported by the following evidence. First, 3 formed a monoacetate derivative of mol wt 584, indicating the presence of only one hydroxyl group. Second, a quartet at 29.7 ppm and a single line at 217 ppm appeared in an SFORD ^{13}C NMR spectrum. The former is in the range expected for an acyl methyl carbon, while the latter can be assigned to a ketonic carbonyl carbon.[4]

These data support the belief that 3 is an oxidized variation of 2. Satratoxin F is the first known member of the roridin family to possess an acyl group at C-6′ in place of the more common methylcarbinol function.

Comparison of the SFORD ^{13}C NMR spectra of these compounds reveals that the signal assigned to C-4′, which is observed as a triplet in 2 and 3, appears as a doublet of doublets in 1. Conversion of the acrylic ester double bond to an epoxide apparently changes the conformation of the macrocyclic ring in 2 and 3 sufficiently that both of the C-4′ methylene protons are relatively equidistant from the acrylic ester lactonic oxygen and, therefore, have similar chemical shifts. This is not the case in 1 where H-4′A (3.74 ppm) is considerably closer to the lactonic oxygen than H-4′B (2.6 ppm). It is this unusual difference in geminal proton chemical shift values which is responsible for the atypical appearance of the C-4′ signal in the SFORD spectrum of 1.[8]

Experimental Section

Satratoxins F and G were isolated according to the method of Eppley and Bailey.[2] Additional purification was achieved on silica gel with a Waters Prep LC/Systems 500 high-pressure liquid chromatograph. Elution with 3% methanol–chloroform gave complete separation into two fractions.

Satratoxin F (3). The residue from the first fraction was crystallized from chloroform–hexane to give 3: 40 mg; mp 140–143 °C; IR (KBr) 3460, 1748, 1715, 1183 cm^{-1}; mass spectrum (electron impact), m/e 542 ($M^{+\cdot}$) calcd for $C_{29}H_{34}O_{10}$.

Satratoxin G (2). Crystallization of the second fraction from chloroform-hexane gave 2: 87 mg; mp 132–136 °C; IR (KBr) 3450, 1747, 1710, 1185 cm^{-1}; mass spectrum (electron impact), m/e 544 ($M^{+\cdot}$) calcd for $C_{29}H_{36}O_{10}$.

General Methods. Melting points were determined on a Kofler hot stage and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 180 recording spectrophotometer. Mass spectra of 2 and 3 were determined on a Varian MAT CH-5DF spectrometer and that of satratoxin G diacetate on a Finnigan 3300 by simultaneous pulsed positive/negative ion chemical ionization. Proton magnetic resonance spectra were recorded at 300 MHz for 1[3] and at 90 MHz on a Varian EM-390 spectrometer for 2 and 3. Carbon-13 magnetic resonance spectra were determined on a Varian CFT-20 spectrometer operating at 20 MHz. Signals were assigned by using SFORD and selective proton-decoupling experiments and chemical shift correlations[4] and by comparison with each other.

Registry No. 1, 53126-64-0; 2, 73513-00-5; 3, 73513-01-6.

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Marine Natural Products: Two New Acyclic Sesquiterpene Hydrocarbons from the Gorgonian *Plexaurella grisea*

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Received November 30, 1979

Although a variety of novel cyclic sesquiterpenes have been isolated from marine coelenterates, no simple farnesene derivatives or other acyclic sesquiterpenes appear to have been reported[1] from these organisms. Inci-

0022-3263/80/1945-2523$01.00/0