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A New Ceramide from the Basidiomycetes *Armillaria mellea*

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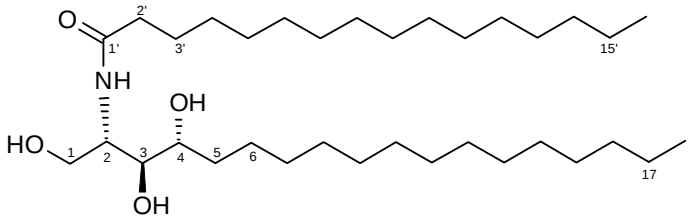
Abstract: A new phytosphingosine-type ceramide, armillaramide **1**, has been isolated from the fruiting bodies of Basidiomycetes *Armillaria mellea* (Vahl ex Fr.) Quél. . Its structure was established as (2*S*, 3*S*, 4*R*)-2-N-(palmitoyl)-phytosphingosine by spectroscopic and chemical methods.

Keywords: *Armillaria mellea*, basidiomycetes, ceramide, armillaramide.

As one part of our study on the bioactive metabolites of the higher fungi in Yunnan Province, the chemical constituents of *Armillaria mellea* (Tricholomataceae) collected at Zhong Dian in Yunnan Province have been investigated. The present report deals with the structural elucidation of a new ceramide **1**, named armillaramide, isolated from the AcOEt extract of the fruiting bodies of this fungus.

Figure 1 The structure of armillaramide **1**



Compound **1**, white amorphous powder, mp 113~117°C, $[\alpha]_D^{26}$ + 14.35 (c 0.21, pyridine). The molecular formula of **1** was determined as $C_{34}H_{69}NO_4$ by high resolution EI-MS (555.5187 $[M]^+$, calcd. 555.5226). Its IR spectrum revealed the absorptions of hydroxyls at 3376 cm^{-1}, a secondary amide at 1557,1615 cm^{-1}, and the long alphatic chains at 721 cm^{-1}. The ^1H NMR spectrum of **1** showed the presence of two terminal methyls at δ 0.90 (6H, br t), and methylenes at δ 1.30 (ca.36H, br s), an amide proton signal at δ 8.13 (1H, d, J = 6.7 Hz). The ^{13}C NMR (DEPT) spectrum of **1** further furnished 1×C, 3×CH, n×CH_2, 2×CH_3 (**Table 1**), in which one quaternary carbon at δ 173.44 (CONH), three methines at δ 53.79 (CHNH), 76.86 (CHOH), 73.18 (CHOH), and one methylene at 62.28 (CH_2OH) were given, respectively. All of the above spectral

data revealed that **1** was a phytosphingosine-type ceramide[1]. The chemical shifts and coupling constants of H-1, H-2, H-3, and H-4 in **1** were in agreement with those of the synthetic ceramide[2], (2*S*, 3*S*, 4*R*)-2-N-(2′-hydroxytricosanoyl)-phytosphingosine (**Table 1**). The above fact and the comparison of the optical rotations of **1** and the synthetic compound ($[\alpha]_D$+9.1) suggested that they have the same absolute configuration at 2, 3, 4 chiral centers. Methanolysis of **1** yielded methyl palmitate detected by GC/MS as the fatty acyl carbon chain[3]. The part of phytosphingosine is therefore an C_{18} aliphatic amino alcohol unit containing three hydroxyls and an amino group. Thus, the above evidence led to the establishment of the structure of **1** as (2*S*, 3*S*, 4*R*)-2-N-(palmitoyl)-phytosphingosine (**Figure 1**).

Table 1 ^{1}H and ^{13}C NMR spectral data for **1** (400 / 500 MHz, C_5D_5N)

C/H	**1**		^{1}H-^{1}H COSY
	C (DEPT)	H (J in Hz)	selected
1	62. 28 (CH_2)	4.57 (dd, 12.4, 3.8)	H-2
		4.40 (dd, 12.4, 4.0)	
2	53.79 (CH)	4.98 (m)	H-1, H-3, NH
3	76.86 (CH)	4.31 (dd, 4.8, 3.9)	H-2, H-4
4	73.18 (CH)	4.23 (m)	H-3, H-5
5	34.09 (CH_2)	1.93 (m)	H-4
6	26.68 (CH_2)	2.20 (m)	
7~15	29.66~30.36 ($9CH_2$)	1.30 (brs)	
18	14.29 (CH_3)	0.90 (t, 5.6)	
NH		8.13 (d, 6.7)	H-2
1′	173.44 (C)		
2′	36.91 (CH_2)	2.43 (t, 6.0)	H-3′
3′	26.44 (CH_2)	1.83 (m)	
4′~13′	29.66~30.36 ($9CH_2$)	1.30 (brs)	
16′	14.29 (CH_3)	0.90 (t, 5.6)	

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