

One New and Two Rare Alkamides from Two Samples of the Fruits of *Piper longum*[†]

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Abstract – Two samples of the fruits of *Piper longum* have been chemically investigated. From one sample a new alkamide, pergumidiene and from other sample two rare alkamides, brachystamide B and piperderdine have been isolated. The known compounds, piperine, piperlonguminine, pellitorine, (+)-sesamine and 3-(3', 4', 5'-trimethoxyphenyl)-propionic acid were the common constituents of both the samples.

Key words – *Piper longum*, Piperaceae, alkamide, pergumidiene, brachystamide B, piperderdine.

Introduction

Piper longum Linn (Piperaceae) is a slender aromatic climber found in different parts of India (Thakur et. al., 1989). The fruits of the plant are frequently used to treat bronchial trouble and as carminative and analgesic (Thakur et. al., 1989). Recently we have collected two different samples of the fruits of the plant from two different regions of India (one from Andhra Pradesh and other from West Bengal) for chemical investigation. Several alkamides together with a lignan and a propionic acid derivative have been isolated. Here, we report the isolation and characterization of these chemical constituents.

Experimental

Spectra were recorded with the following instruments: IR, Nicolet 740 FTIR spectrophotometer; UV, Shimadzu 240 spectrophotometer; ¹H- and ¹³C-NMR, Varian Gemini-200 MHz; MS, VG Micromass 7070H (70 eV).

Column Chromatography was performed on silica gel (BDH, 100-200 mesh) and TLC with silica gel G.

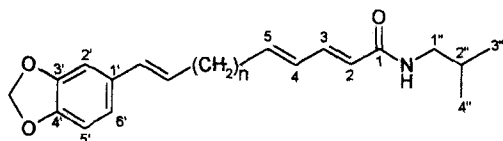
Plant material: The first sample of the fruits of *P. longum* was collected from Andhra Pradesh in October, 1995 and the second sample from West Bengal in August, 1996. The voucher specimens (Nos PL-F₁ and PL-F₂ respectively) are deposited in our laboratory.

Isolation of Constituents of the Fruits of *P. longum* (1st sample): The dried fruits (500 gm) of *P. longum* (1st sample) were powdered and extracted with CH₂Cl₂-MeOH (1:1) for 120 hr. The concentrated extract (1.50 gm) was chromatographed over silica gel (30 gm), the column being eluted with Pet. ether and Pet. ether-EtOAc mixture. The following compounds were eluted according to the increasing order of polarity: pellitorine (147 mg), (+)-sesamine (352 mg), pergumidiene (1 (72 mg), piperine (138 mg) and 3-(3', 4', 5'-trimethoxyphenyl)-propionic acid (408 mg).

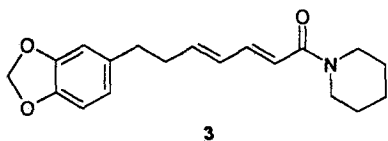
Isolation of Constituents of the Fruits of *P. longum* (2nd sample): The dried powdered fruits of *P. longum* (2nd sample) were ex-

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1. $n = 9$
2. $n = 8$



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tracted with CH_2Cl_2 -MeOH (1:1) and extract was purified by column chromatography by following the above-mentioned method. The compounds eluted according to the increasing order of polarity are as follows: peltitorine (122 mg), (+)-sesamine (285 mg), brachystamide B (82 mg), piperderdine (28 mg), piperine (47 mg) and 3-(3', 4', 5'-trimethoxyphenyl)-propionic acid (364 mg).

Results and Discussion

Chemical investigation on the two sam-

ples of the fruits of *P. longum* has resulted in the isolation of several compounds including alkamides, a lignan and a propionic acid derivative. A new alkamide, pergumidiene (**1**) was isolated as an amorphous solid from the first sample. Its UV [$\lambda_{\text{max}}^{\text{EtOH}}$ 258 and 208 nm ($\log \epsilon$ 4.45 and 4.12)] and IR spectrum ($\nu_{\text{max}}^{\text{KBr}}$ 3330, 1655, 1625, 1000 cm^{-1}) indicated (Banerji and Das, 1989) the presence of an E, E-dienamide function. Further characteristic bands in the IR spectrum were observed for a 1, 2, 4-trisubstituted benzene ring (1615, 850, 810 cm^{-1}), a methylenedioxy group (1250, 1040, 920 cm^{-1}) and another *trans* (E)-double bond (960 cm^{-1}). The $^1\text{H-NMR}$ spectral data of **1** (Table 1) were very similar to those of the known alkamide, brachystamide B (**2**) (Banerji and Das, 1989) but a proton count indicated that a methylene group is more in **1**. This was also suggested from the mass spectrum, which showed the molecular ion peak at m/z 425 (24%) (corresponding to $\text{C}_{27}\text{H}_{39}\text{NO}_3$) along with the intense peaks at m/z (%): 397 (28), 180 (22), 161 (43), 152 (51), 131 (100), 103 (59). The peak at m/z 161 was the

Table 1. $^1\text{H-NMR}$ (200 MHz, CDCl_3) and $^{13}\text{C-NMR}$ (50 MHz, CDCl_3) spectral data of Pergumidiene (**1**)

C	$^1\text{H-NMR}$ Chemical shifts (ppm)	$^{13}\text{C-NMR}$ Chemical shifts (ppm)
1	-	166.38
2	5.71 (1H, d, $J=15.0$ Hz)	121.94
3	7.27 (1H, dd, $J=15.0$ & 11.0 Hz)	142.78
4	6.13-5.88 (2H, m)	128.28
5		140.95
6, 14	2.25-2.08 (4H, m)	32.77
7-13	1.50-1.22 (14H, m)	29.25-28.53
15	6.01 (1H, m)	129.21
16	6.27 (1H, d, $J=16.0$ Hz)	129.29
1'	-	132.42
2'	6.73 (2H, brs)	105.33
5'		108.09
3'	-	147.94
4'	-	146.56
6'	6.86 (1H, brs)	120.07
1''	3.18 (2H, t, $J=6.5$ Hz)	46.88
2''	1.82 (1H, m)	29.25
3'', 4''	0.92 (6H, d, $J=6.5$ Hz)	20.04
-OCH ₂ O-	5.94 (2H, s)	100.78
-NH-	5.39 (1H, brt, $J=6.5$ Hz)	-

indicative of the presence of double bond at C-15-C-16. Thus, the structure **1** was settled for the new alkamide, pergumidiene. The structure was finally confirmed from the analysis of its ^{13}C -NMR spectral data (Table 1) which were again compared with those of brachystamide B (**2**) (Banerji and Das, 1989).

The second sample of the fruits of *P. longum* afforded two rare alkamides, brachystamide B (**2**) and piperderdine (**3**). This is the first report of the isolation of these two compounds from the title plant. Previously they were reported from the aerial parts of *P. brachystachyum* (Banerji and Das, 1989) and from the stems of *P. tuberculatum* (DeAraujo et. al., 1997) respectively. The known alkamides, piperine (Dutta et. al., 1977), piperlonguminine (Chatterjee and Dutta, 1967) and pellitorine (Dhar and Atal, 1967), a known lignan, (+)-sesamine (Atal et. al. 1966) and 3-(3', 4', 5'-trimethoxyphenyl)-propionic acid (Belletire and Mahmoodi, 1989) were found to be the common constituents of both the samples. The known compounds were identified from their spectral data and by comparison of their physical and spectral properties with those reported for the compounds in the literature.

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