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Note

Diterpenes from the seeds of locally grown of *Zea mays*

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Chemical investigation of the hexane soluble of the methanol-hexane (1:1) extract of the seeds locally grown plant *Zea Mays* collected from Kushtia district results in the isolation of two new diterpenes, orthosiphol F and ceriopsin C. The structures of the two diterpenes are elucidated with the help of ^{1}H NMR, ^{13}C NMR, COSY, DEPT 45, DEPT 90, DEPT 135 and mass spectral data.

Keywords: Diterpenes, seeds, Zea *mays*, hexane soluble, Kushtia district.

IPC: Int.Cl.^{8} A61K

Traditional medicines are widely used along with modern medicine in many countries of Southeast Asia and play an important role in promoting a health care system[1]. *Zea mays* is a small tree, which grows in tropical and sub-tropical Asian countries as well as all over the world. It is locally known as 'Bhutta'. Maize is a potential allergen source from early infancy as it is an ingredient in infant's diets in many parts of the world. A relatively low degree of relation is thought to exist between maize and the other cereals[2] although maize and rice antigens show similarities[3]. The psychotropic activity of this mint species has been attributed to a neoclerodane diterpenes found in the leaves, salvinorin A[4]. It has been demonstrated that salvinorin A is an extraordinary potent drug in humans. The site of action and mechanism of pharmacological activity of salvinorin A remain unknown[5]. The recent surge of interest in chemistry of this plant has led to the isolation of more than 20 components including flavonoids, terpenoids and caffeic acid derivatives with different biological acitivies[6-7]. During the course of our investigation on the biologically active constituents of *Graminae* plants, we examined the constituents of the seeds of *Zea mays* widely cultivated in Bangladesh and isolated two new diterpenes, orthosiphol F **1** and ceriopsin C **2** together with a known compound, salvinorin **3**. This paper describes the structure elucidation of the new diterpenes.

Experimental Section

IR spectra were recorded (KBr discs) on a FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker R-32 (300 MHz) instrument in $CDCl_3$ with TMS as an internal standard (chemical shifts in δ, ppm). UV spectra were recorded on a HATACHI, U-2000 spectrophotometer Ultrospeck in methanol (nm). EIMS spectra were obtained using a JEOL JMS-DX 302. TLC was performed with silica gel GF_{254}. All solvents were analytical reagent grade.

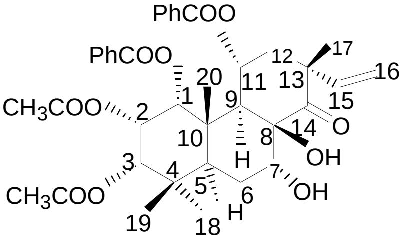
*Plant Material.*The ripe seeds of Zea mays were collected from the Kushtia district of Bangladesh in June 2004. The plant was identified and voucher specimen number was deposited at Bilik Herba of School of Pharmaceutical Sciences, Penang, Malaysia with 051.

Extraction. The dried and milled seeds (500 g) were extracted with methanol (1L) in a Soxhlet extractor for 72 hr. The extract was evaporated in a rotatory evaporator and dried under vacuum. The methanolic extract (5 g) was suspended in water and extracted successively with petrol, hexane, chloroform and ethyl acetate to yield petrol (0.320 g), hexane (1.23 g), chloroform (1.50 g) and ethyl acetate-soluble (0.63 g) fractions, respectively. Hexane soluble fraction (1.20 g) was subjected to column chromatography on silica gel (60-120 mesh, Merck) and eluted with dichloromethane-acetone (13:3) solvent system. Repeated chromatography afforded five major fractions namely fraction 1, 098 g; fraction 2, 0.119 g; fraction 3, 0.208 g; Fraction 4, 0.041 g and fraction 5, 0.107 g

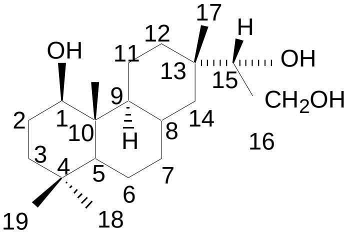
Chromatographic separation. Fraction 1. The active hexane fraction (0.098 g) was chromatographed on LH-20 (160 cm × 5 cm; methanol) to yield fractions **A-D.** They were combined (0.062 mg) and rechromatographed on Sephadex LH-20 (methanol) to yield **E-G.** Fraction E was crystallized from petrol to give compound **1.** Fraction F and G were crystallized separately from dil methanol and dichloromethane to give compounds **2** and **3,** respectively.

Compound 1: **Orthosiphol F**: Colourless amorphous solid; $[\alpha]_D^{25}$ -82.8° (*c* =2.10, $CHCl_3$); UV: 228 nm; (M^+ 677); IR (KBr): 3540, 3470, 1740, 1455, 1376, 1289, 1114, 1045 cm^{-1}. ^1H NMR and ^{13}C NMR:are shown in **Table I**.

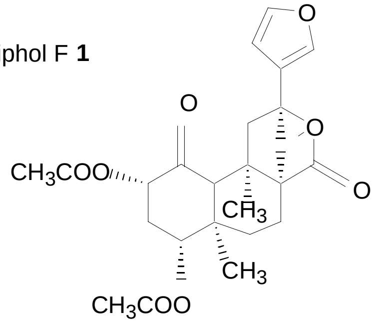
Compound 2: **Ceriopsin C 2**: It was a colourless oil. $[\alpha]_D^{25}$+50.6° (*c* =1.5, $CHCl_3$); UV: 232 nm; EIMS



Orthosiphol F **1**



Ceriopsin **2**



Salvinorin A **3**

Table I — ^1H NMR and ^{13}C NMR data for Orthosiphol F

Position	δ_H	Position carbon	δ_C	HMBC
1	5.28 d (3 Hz)	1	71.80	2, 3, 9, 20
2	5.51 t (3)	2	66.29	1, 3
3	5.00 d (3.5)	3	76.00	1, 2, 18, 19
5	2.68 dd (13, 2.5)	4	37.87	3, 5, 18, 19
6	2.03 dd(14, 13)	5	35.6	1, 3, 7, 18, 19, 20
7	4.21 t (2.5)	6	23.31	5
9	3.08 d (4.5)	7	69.01	9
11	5.61 dd (4.5, 4)	8	78.1	7,9
12	2.21 dd (15, 2.5)	9	42.2	7, 12
15	4.75 d (12)	10	47.88	12,15,16,17
16	4.88 d (17.5)	11	68.88	9, 12
17	1.26 s	12	39.00	15, 17
18	0.98 s	13	47.88	12, 15, 16, 17
19	1.21 s	14	214.9	9, 12, 15, 17
20	1.46 s	15	141.6	12, 16, 17
1-OCOPh		16	113.00	
2′, 6′	7.51 dd (8, 1)	17	27.9	12, 15
3′, 5′	7.08 t (8)	18	27.9	3, 5, 19
4′	7.55 d (8)	19	22.65	5, 18
2- $OCOCH_3$				
1″	1.84 s	20	17.43	5, 9
3- $OCOCH_3$				
1‴	1.47 s	1-OCOPh		
11-OCOPh		1′	130.30	3′, 5′
2‴, 6‴	7.49 d (7.5)	2′, 6′	128.11	3′, 4′, 5′
3‴, 5‴	6.89 t (7)	3′, 5′	127.9	
4‴	7.29 d (8)	4′	132.90	2′, 6′

—*Contd*

Table I — ^{1}H NMR and ^{13}C NMR data for Orthosiphol F—*Contd*

Position	δ_H	Position carbon	δ_C	HMBC
		CO	164.5	1′, 2′, 6′
		2- $OCOCH_3$		
		1″	173.0	
		CO	19.2	2, 1″
		3- $OCOCH_3$		
		1′′′′	172.9	
		CO	19.90	3, 1″
		11-OCOPh		
		1′′′′	130.54	
		2′′′′, 6′′′′	129.4	3′′′′, 4′′′′
		3′′′′, 5′′′′	126.98	
		4′′′′	134.90	2′′′′, 6′′′′
		CO	166.98	11, 2′′′′, 6′′′′

Table II — ^{1}H NMR and ^{13}C NMR data for Ceriopsin C **2**

Position	δ_H	Position carbon	δ_C	HMBC
1α	3.42 dd (10.8, 4.5)	1	80.80	
1β	-	2	28.29	
2α	1.62 m	3	34.00	
2β	1.25 m	4	32.67	
3α	1.29 m	5	55.58	
3β	1.44 m	6	18.81	
5	1.08 m	7	39.11	
6α	1.43 m	8	82.70	
6β	1.96 m	9	54.22	
7α	5.55 s	10	42.88	
7β	-	11	24.55	
9	1.91 m	12	39.30	
11α	2.15 m	13	40.33	
11β	1.32 m	14	51.91	
12α	1.26 m	15	84.43	
12β	1.60 m	16	63.98	
14α	1.64 m	17	19.92	
14β	2.41 m	18	32.99	
15α	-	19	22.65	
15β	3.72 dd (10.5, 3)	20	8.4	
16	3.44 dd (10.5, 9.5)			
17	0.82 s			
18	0.84 s			
19	0.90 s			
20	0.88 s			

m/z 323 $[M+H]^+$, 305, 291, 273, 257, 245, 105; IR (Nujol): 3420-3410, 1610, 1596, 1473, 1379, 1100, 1059, 900 cm^{-1}; Found: C, 74.3; H, 10.3. $C_{20}H_{34}O_3$ requires C, 74.6; H, 10.5%; ^{1}H NMR and ^{13}C NMR data are included in **Table II**.

Compound 3: **Salvinorin 3**: It was crystallized from dichloromethane to give yellow crystals and identified as salvinorin **3** (Co-TLC, Co-IR, Co-^{1}H NMR data).

Results and Discussion

Maize is the only cereal of American origin and it formed the staple diet of the American Indians. The USA produces nearly 50% of the world's maize. Its popularity as a table vegetable is increasing as fresh, frozen and canned. It is widely used in starch manufacture and for whiskey distilling. Orthosiphol F **1** was obtained as a colourless amorphous solid. High resolution mass of **1** indicated the molecular formula $C_{38}H_{44}O_{11}$ (m/z 676). Its IR spectrum showed absorption due to hydroxyl (3540, 3470), and ester carbonyl cm^{-1} (1740) groups. The ^{1}H NMR and ^{13}C NMR data (**Table I**) similar to those of Orthosiphol A which was confirmed by the ^{1}H-^{1}H shift correlation spectroscopy (COSY) and heteronuclear multiple bond correlation (HMBC) spectra (**Table I**).

Ceriopsin C **2** was isolated as colourless oil from dil methanol and its molecular formula was assigned as $C_{20}H_{34}O_3$ from elemental analysis and EIMS at m/z 322. The IR spectrum showed multiple hydroxyl absorptions at (3420-3410 cm^{-1}). In ^{1}H NMR spectra showed the presence of four tertiary methyls at 0.82, 0.84, 0.90 and 0.88. The details of ^{1}H NMR and ^{13}C NMR data are given in **Table II**.

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