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A new flavonoid from the bract of *Zea mays* L.

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Abstract

A new flavonoid was isolated from the bract of *Zea mays* L. The structure of the compound was identified as 4′,5,7-trihydroxy-3′,5′-dimethoxyflavone 7-*O*-[*β*-D-apiofuranosyl (1 → 2)]-*β*-D-glucopyranoside on the ground of chemical and spectroscopic methods.

Keywords: *Zea mays* L.; Flavonoid; Bract

Zea mays (maize), a member of the *Poaceae*, is the most economically important crop in China and the third most important crop plant in the world, and has many biological activities [1]. In our study, a novel flavonoid was isolated for the first time from the bract of *Zea mays* L. The air-dried bract of *Zea mays* was extracted with 95% ethanol at room temperature. The extract was subjected to Diaion AB-8 column chromatography eluted with ethanol–H_2O, and the eluate was further chromatographed on silica gel and Sephadex LH-20 columns repeatedly to yield the new compound **1**.

Compound **1**, yellow amorphous powder, produced positive reactions to $AlCl_3$ reagent and Molish reagent, had the molecular formula $C_{28}H_{32}O_{16}$ determined by HRESIMS ($[M+H]^+$ 625.1760, calcd. 625.1763). Acid hydrolysis gave two kinds of monosaccharides, one of which was identified as D-glucose by paper chromatography comparison with authentic D-glucose. The IR spectrum of **1** indicated the presence of hydroxyl (3420 cm^{-1}), a carbonyl (1650 cm^{-1}) and an aromatic (1609 cm^{-1}) groups. UV maxima occurred at 349 nm (band I) and 269 nm (band II), characteristic of a flavonoid system. All the above data suggested that **1** was a flavonoid glycoside. The ^1H NMR spectrum (400 MHz, DMSO-d_6) showed two hydroxyl active proton signals at δ 12.96 (brs, 1H, 5-OH), 9.38 (brs, 1H, 4′-OH) in the lower field; five aromatic proton signals at δ 7.36 (brs, 2H, H-2′,6′), 7.08 (s, 1H, H-3), 6.91 (d, 1H, J = 2.0 Hz, H-8), 6.44 (d, 1H, J = 2.0 Hz, H-6), two methoxy proton signals at δ 3.88 (s, 6H, 3′,5′-OCH_3). From the above information, the aglycone was identified as tricin, 4′,5,7-trihydroxy-3′,5′-dimethoxyflavone, on further comparing corresponding ^{13}C NMR data with the reported [2]. The coupling constant of the anomeric proton of glucose at δ 5.16 (d, 1H, J = 6.0 Hz) indicated that glucose moiety was in β-configuration. Besides the signals attributed to glucose moiety, there were four

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Table 1
^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), HMQC and HMBC data of compound **1** (DMSO-d_6, δ).

No.	δ_C	δ_H	HMBC (H → C)	No.	δ_C	δ_H	HMBC (H → C)
2	164.1			7-O-sugar			
3	103.8	7.08 (s, 1H)	182.0, 164.1, 120.2, 105.4	glc			
4	182.0			1″	98.3	5.16 (d, 1H, J = 6.0 Hz)	162.7, 76.1
5	161.1			2″	77.2	3.47 (m, 1H)	108.7, 98.3
6	99.4	6.44 (d, 1H, J = 2.0 Hz)	161.1, 105.4, 95.2	3″	76.1	3.75 (t, 1H, J = 4.2 Hz)	
7	162.7			4″	69.9	3.17 (m, 1H)	
8	95.2	6.91 (d, 1H, J = 2.0 Hz)	105.4, 99.4	5″	75.9	3.51 (m, 1H)	
9	156.9			6″	60.6	3.73, 3.44 (m, each 1H)	
10	105.4			api			
1′	120.2			1□	108.7	5.35 (s, 1H)	74.0, 79.2
2′,6′	104.5	7.36 (s, 2H)	164.1, 148.2, 140.1, 120.2, 104.5	2□	76.8	3.56 (m, 1H,)	
3′,5′	148.2			3□	79.2		
4′	140.1			4□	74.0	3.92, 3.66 (d, each 1H, J = 9.2 Hz)	79.2
3′,5′-OCH_3	56.4	3.88 (s, 6H)	148.2	5□	64.2	3.23 (m, 2H)	

All assignments based on the extensive 1D and 2D NMR spectra (HMQC, HMBC, ^{1}H–^{1}H COSY).

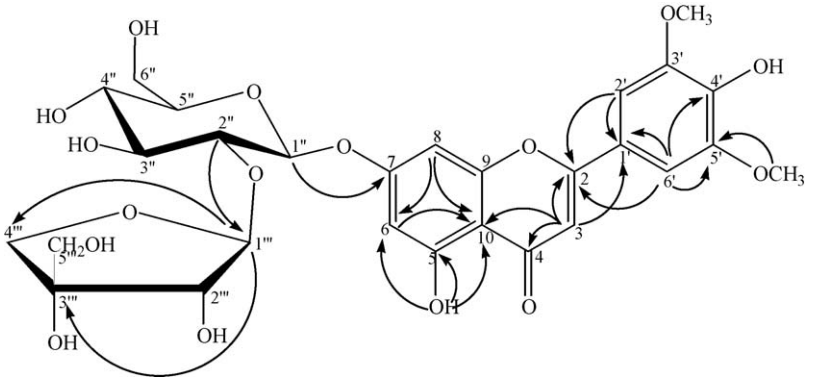

Fig. 1. The key HMBC correlation of compound **1** (arrows point from proton to carbon).

signals at δ 76.8, 79.2, 74.0, 64.2 in the region between δ 60.5 and 70.9, and one signal at δ 108.7 in the anomeric region between δ 95.1 and 108.8, which were attributed to β-D-apiose by comparing with the reported [3]. The complete assignment of the signals of compound **1** was based on 2D NMR of ^{1}H–^{1}H COSY, HMQC and HMBC. The down field about 4 ppm of the signal of C-2″ of glucose (δ 77.2) showed that apiose was linked to C-2″ of glucose, which was further confirmed by the HMBC correlation of 2″-H (δ_H 3.47) to C-1 (δ_C 108.7). The HMBC correlation of 1″-H (δ_H 5.16) to C-7 (δ_C 162.7) showed that glucose was linked to C-7 of alycone, which was further confirmed by free active hydroxyl protons of C-5 (δ_H 12.96) and C-4′ (δ_H 9.38) and the HMBC correlation of 5-OH (δ_H 12.96) to C-6 (δ_C 99.4). For all the remaining assignments of ^{1}H NMR and ^{13}C NMR see Table 1, and for all the remains of HMBC correlation see Fig. 1. Therefore, the structure of compound **1** was elucidated as 4′,5,7-trihydroxy-3′,5′-dimethoxyflavone 7-*O*-[β-D-apifuranosyl (1 → 2)]-β-D-glucopyranoside.

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