FLAVONOIDS FROM SEEDS OF *Maclura aurantiaca* GROWING IN GEORGIA

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Maclura aurantiaca Nutt. is known to contain biologically active compounds [1-4]. The flavonoid and lipid compositions of fruit pulp, which has antitumor activity, have been studied [2, 5]. Flavonoids from seeds of *M. aurantiaca* growing in Georgia have not been studied. Column chromatography of the aqueous alcohol (80%) extract of defatted seeds isolated total phenolic compounds with 0.28% flavonoid content. Column chromatography over silica gel isolated three compounds from the total extract.

Compounds **1** and **2** did not give a Synod reaction [6]. Absorption maxima in the UV spectra were typical of isoflavones. Compound **3** was a flavonol glycoside.

Compound 1, mp 188-191°C ($CHCl_3$), UV spectrum (CH_3OH, λ_{max}, nm): 270. IR spectrum (KBr, ν, cm^{-1}): 3417 (–OH), 3070, 2969, 2923, 2854 (aliphatic $–CH_2$ and CH_3), 1643 (>C=O), 1573, 1519 (aromatic CH=CH), 1434, 1365 [$C–(CH_3)_2$], 1326 (>C–OH). Acetyl derivative of **1**, mp 165-167°C. The analytical results indicated that **1** was osajin [1].

Compound 2, mp 173-175°C ($CHCl_3$). UV spectrum (CH_3OH, λ_{max}, nm): 270. IR spectrum (KBr, ν, cm^{-1}): 3425 (–OH), 3070, 2969, 2907, 2854 (aliphatic $–CH_2$ and CH_3), 1643 (>C=O), 1565, 1519 (aromatic CH=CH), 1442, 1380 [$C–(CH_3)_2$], 1326 (>C–OH). Acetylation product of **2**, mp 127-130°C ($CHCl_3$). The melting point of the acetate product differed from that of pomiferin acetate (134.5°C) [1]. This may have been due to the effect of the crystallization medium or its conformational features.

Table 1 lists PMR and ^{13}C NMR analysis of correlation spectra. It can be seen that these compounds differ in the structure of ring B. Compound **1** is unsubstituted at position C-3′ whereas it has a hydroxyl in the 2-position. This was confirmed by the singlet for C-2′ at 7.05 ppm in the PMR spectrum and the resonance at 147.0 ppm corresponding to C-3′ as a result of a weak-field shift of this resonance from 116.0 to 147.0 ppm compared with **1**.

Methyls on the pyran ring resonated at 28.3-28.0 ppm; aliphatic, at stronger field of 26.4-26.5 and 17.2-17.0 ppm; correlating atoms C-3‴ and C-2‴. The CH_2 C atom at 22.4 ppm correlated with C-2‴, C-3‴, and C-7.

PMR and ^{13}C NMR correlation spectra agreed completely with the structures of osajin (**1**) and pomiferin (**2**) [7], the structures of which were also established by chemical transformation [1, 2] and crystallographic analysis [8].

Compound **3** was needle-like yellow crystals, mp 226-228°C (alcohol). UV spectrum (C_2H_5OH, λ_{max}, nm): 355, 265; $+CH_3COONa$: 367, 270. IR spectrum (KBr, ν, cm^{-1}): 3400 (–OH), 1640 (>C=O), 1575, 1540, 1520 (aromatic CH=CH). Compound **3** was hydrolyzed by acid and base to form the aglycon, which was characterized as kaempferol. PC of the carbohydrate part detected L-rhamnose, which was bonded to C-7. Thus, **3** was identified as kaempferol-7-*O*-α-L-rhamnoside [9].

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TABLE 1. Chemical Shifts of **1** and **2** (CD_3OD, δ, ppm)

C atom	**1**			**2**		
	δ_H	δ_C	HMBC	δ_H	δ_C	HMBC
2	8.12, s	154.4	3, 4, 9	8.06, s	154.4	3, 4, 9
3	-	125.0		-	125.0	
4	-	182.6		-	182.6	
5	-	158.8		-	159.0	
6	-	115.0		-	114.8	
7	-	157.5		-	157.5	
8	-	102.5		-	102.5	
9	-	152.3		-	152.2	
10	-	116.7		-	116.6	
1′	-	123.0		-	124.0	
2′	7.39, d	131.5	1′, 3′, 4′	7.05, s	117.3	1′, 3′, 4′
3′	6.86, d	116.0	1′, 4′	-	147.0	
4′	-	158.5		-	147.5	
5′	6.86, d	116.0	6′, 4′	6.83, d	116.2	6′, 4′
6′	7.39, d	131.5	5′, 4′	6.85, d	121.5	5′, 4′, 1′
1″	6.75, d	115.4	3″, 8, 7	6.74	115.5	
2″	5.70, d	128.0	8, 3″, Me	5.68	128.3	
3″	-	80.2		-	80.0	
1‴	3.33, m	22.4	2‴, 3‴, 7	3.31, m	22.1	2‴, 3‴, 7
2‴	5.20, m	123.0	1‴, 3‴, Me	5.20	123.0	1‴, 3‴, Me
3‴	-	131.5		-	131.5	
Me	1.48×2, s	28.3×2	3″, 2″	1.46×2	28.0×2	3″, 2″
	1.68, s	26.4	3‴, 2‴, Me	1.67	26.5	3‴, 2‴, Me
	1.82, s	17.2	3‴, 2‴, Me	1.82	17.0	3‴, 2‴, Me

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