Identification of Flavones in Sixteen *Compositae* Species

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In the previous papers,¹⁾ we described the investigation for flavones of the genus *Gramineae*. The present paper describes the identification of flavones in sixteen *Compositae* species by paper chromatography and ultraviolet spectroscopy. In this work, the presence of apigenin (1), apigenin 7-O-glucoside (2), apigenin 7-O-rhamnoglucoside (3), acacetin 7-O-glucoside (4), acacetin 7-O-rhamnoglucoside (5), luteolin (6), luteolin 7-O-glucoside (7), luteolin 7-O-rhamnoglucoside (8), quercetin 3-O-galactoside (9), quercitrin (10), isorhamnetin 3-O-galactoside (11) has been demonstrated in the plants. The methods used for identification are outlined below. Methanol extracts of fresh plants were separated by two-dimensional paper chromatography, and the developed chromatograms were eluted separately with methanol. The ultraviolet spectral characteristics of the eluates were compared with the data reported for known compounds for the identification of the flavones in the plant. For the identification of glycoside, the eluate from chromatogram was subjected to acid hydrolysis to yield aglycone and sugar which was identified by paper chromatography and ultraviolet spectroscopy. The identified flavones are shown in Table I in which the compounds marked with ^{a)} have not yet been reported in those plants. The ultraviolet spectral data and the data of acid hydrolysis shown in Table II agreed with those reported for known compounds.²⁾

EXPERIMENTAL

Fresh stems and leaves were extracted with methanol for 40~50 hr. Evaporation of methanol under reduced pressure yielded a sticky residue, which was dissolved in a small portion of methanol. Spots of the extracts on Whatman 3 MM chromatographic paper (46×57 cm) was developed by descending two-dimensional chromatography using TBA (tertiary butanol: glacial acetic acid: water=3:1:1 v/v) as the first solvent and HOAc (glacial acetic acid: water=15:85 v/v) as the second solvent. All of the detected spots were cut off from the paper and eluted separately with methanol.

TABLE I. THE FLAVONES OF SIXTEEN
Compositae SPECIES

Species	Compounds identified
<i>Artemisia japonica</i> Thunb	Apigenin 7-O-glucoside ^{a)} Luteolin 7-O-glucoside ^{a)}
<i>Aster leiophyllus</i> Fr. et Sav	Apigenin 7-O-glucoside ^{a)}
<i>Chrysanthemum morifolium</i> Ramat	Apigenin 7-O-glucoside Luteolin 7-O-glucoside Acacetin 7-O-rhamnoglucoside
<i>Cirsium nipponicum</i> (Maxim.) Makino	Apigenin 7-O-glucoside ^{a)} Luteolin 7-O-glucoside ^{a)}
<i>Cirsium purpuratum</i> (Maxim.) Matsum	Apigenin ^{a)} Apigenin 7-O-glucoside ^{a)} Acacetin 7-O-glucoside ^{a)} Quercitrin ^{a)}
<i>Cosmos bipinnatus</i> Cav	Apigenin 7-O-glucoside Quercitrin ^{a)}
<i>Dahlia pinnata</i> Cav	Apigenin 7-O-glucoside
<i>Erigeron acris</i> L	Luteolin 7-O-glucoside ^{a)}
<i>Erigeron annuus</i> (L.) Pers	Apigenin 7-O-rhamnoglucoside ^{a)} Quercitrin ^{a)}
<i>Hypochoeris radicata</i> L	Luteolin 7-O-glucoside ^{a)}
<i>Kalimeris pinnatifida</i> (Maxim.) Kitam	Isorhamnetin 3-O-galactoside ^{a)} Apigenin 7-O-glucoside ^{a)}
<i>Lactuca indica</i> L	Apigenin 7-O-glucoside ^{a)} Luteolin 7-O-glucoside ^{a)} Quercetin 3-O-galactoside ^{a)}
<i>Sonchus asper</i> (L.) Vill	Apigenin 7-O-rhamnoglucoside ^{a)} Luteolin 7-O-glucoside ^{a)} Luteolin 7-O-rhamnoglucoside ^{a)}
<i>Sonchus oleraceus</i> L	Luteolin ^{a)} Luteolin 7-O-glucoside ^{a)} Apigenin 7-O-glucoside ^{a)}
<i>Taraxacum platycarpum</i> Dahlst	Apigenin 7-O-glucoside ^{a)}
<i>Youngia denticulata</i> (Houtt.) Kitam	Luteolin 7-O-glucoside ^{a)} Luteolin 7-O-glucoside ^{a)}

^{a)} First identified by our work.

In this way, chromatograms of about 30 sheets of chromatographic paper in each plant have been developed. The eluate thus obtained was used for spectral analyses. The ultraviolet spectra were measured in methanol, sodium methylate, methanolic aluminum chloride, methanolic aluminum chloride-hydrochloric acid, methanolic sodium acetate, and methanolic sodium acetate-boric acid solution by an application of the method of Mabry *et al.*²⁾ Substance which was suspected to be a glycoside was subjected to acid hydrolysis. The combined eluate from about 30 chromatograms was concentrated almost to dryness and was

TABLE II. IDENTIFICATION OF FLAVONES

Substance	UV spectral data				Products by acid hydrolysis	Identity
	MeOH	NaOMe	AlCl ₃	AlCl ₃ /HCl		
Sbst. 1	267	275	276	276		Apigenin
	336	325	300	299		
		393	348	340		
			385	380		
Sbst. 2	268	270	276	277	Apigenin	Apigenin 7-O-glucoside
	333	298sh	300	299	Glucose	
		385	348	340		
			386	382		
Sbst. 3	267	245	275	276	Apigenin	Apigenin 7-O-rhamnoglucoside
	333	267	298	299	Glucose	
		300sh	346	341	Rhamnose	
		385	382	380		
Sbst. 4	268	285	277	278	Acacetin	Acacetin 7-O-glucoside
	324	359	300	300	Glucose	
			345	338		
			384	381		
Sbst. 5	268	286	277	278	Acacetin	Acacetin 7-O-rhamnoglycoside
	324	358	300	300	Glucose	
			345	340	Rhamnose	
			384	382		
Sbst. 6	253	266	273	263		Luteolin
	267sh	329sh	300sh	275		
	290sh	400	328	295		
	348		426	355		
				385		
Sbst. 7	255	263	274	274	Luteolin	Luteolin 7-O-glucoside
	267sh	300sh	298sh	294sh	Glucose	
	348	394	330sh	357		
			432	387		
Sbst. 8	255	263	272	272	Luteolin	Luteolin 7-O-rhamnoglucoside
	265sh	300sh	296sh	295	Glucose	
	349	394	330sh	359	Rhamnose	
			432	388		
Sbst. 9	257	272	275	268	Quercetin	Quercetin 3-O-galactoside
	269	327	305sh	300sh	Galactose	
	300sh	408	330sh	365sh		
	360		436	403		
Sbst. 10	256	270	275	272	Quercetin	Quercitrin
	265sh	326	303sh	303sh	Rhamnose	
	300sh	395	333	353		
	350		430	400		
Sbst. 11	255	272	270	267	Isorhamnetin	Isorhamnetin 3-O-galactoside
	267sh	327	300sh	300sh	Galactose	
	300sh	415	365sh	357		
	357		407	403		

mixed with 6% aqueous hydrochloric acid (3~5 ml) using a minimum of methanol to effect complete solution. The solution was heated on a steam bath for 2~3 hr and then cooled and extracted with ether. Evaporation of the aqueous layer yielded sugars which were identified by paper chromatography in two

solvent systems; *n*-butanol:acetic acid:water=4:1:5 v/v, and ethyl acetate:pyridine:water=2:1:2 v/v. Authentic samples of sugar were chromatographed alongside as check. The ether layer, after drying over sodium sulfate yielded aglycones which were identified by ultraviolet spectroscopy by the procedure de-

scribed above.

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