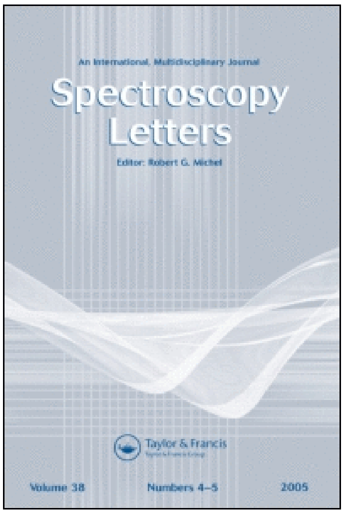

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Spectroscopic Studies of a Less Abundant Flavone, Genkwanin

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SPECTROSCOPIC STUDIES OF A LESS ABUNDANT FLAVONE, GENKWANIN

Key Words: Genkwanin, Flavone, NMR, IR,
UV, Mass Spectrum

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Abstract

A rare flavone, Genkwanin, was isolated by column and preparative thin layer chromatography of a chloroform extract of the leaves of *Vernonia fasciculata* Michx. Spectral studies (NMR, IR, UV and MS) and a comparison with data for closely related compounds has been made.

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INTRODUCTION

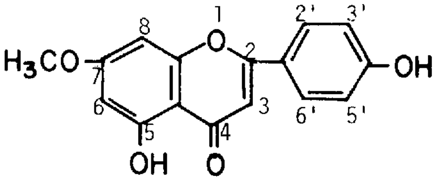
During the search for physiologically active compounds from Vernonia fasciculata Michx, a rare flavone, Genkwanin, was isolated and characterized from a chloroform extract of the leaves of the plant[1]. Genkwanin spectral data as reported in the literature is incomplete (only few reports of inconsistent uv data, Table 2). I wish to report here additional spectral data of this uncommon flavone and its differentiation from structurally similar flavones. This compound has not been reported previously as constituent of vernonia fasciculata Michx[2].

EXPERIMENTAL

All m.p.'s were taken on a Fisher-Johns apparatus. IR spectra were recorded with Beckman IR-12 and Perkin-Elmer 237B model number IR spectrophotometers. The samples were measured as KBr pellets. NMR spectra were taken on Varian A-60 and JOEL-100 MHz instruments. All spectra were taken in DMSO-d_6 with TMS as an internal standard. The positions of the signals are given in δ scale with the internal standard resonance signal set at 0.0, coupling constants (J) are expressed in Hz. For multiplets the values given represent the center of the signals. UV spectra were measured in MeOH and EtOH on Cary-14, 15 spectrophotometers. Mass spectra were obtained on Perkin-Elmer-Hitachi model RMU-6E spectrometer at 70 eV.

RESULTS AND DISCUSSIONS

Genkwanin, 1, has m.p. 292-295° (lit.,[3-9] 282-283°, 287-290°, 283-284°, 280°, 282°, 285°, 273-275°), analyzed for $C_{16}H_{12}O_5$ and parent ion at 284.



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A 60 MHz NMR of genkwanin (Table 1) had a singlet at δ 3.8 (3H) revelaing the presence of a methoxyl group. Two sharp doublets at δ 6.4 and 6.8 (J=2.5 Hz) and a singlet at δ 7.0 were assigned to protons at C-6, C-8, and C-3, respectively. Additionally, two doublets at 8.0 (J=8.5 Hz) and 7.1 (J=8.5 Hz) accounted for the four protons of ring B at C'2, C'3, C'5, and C'6 and constituted an A_2B_2 system. The two singlets at δ 13.0 and δ 10.4 which disappeared when shaken with D_2O confirmed the protons on the two hydroxyl groups. The former is typical of a C-5 hydroxyl group hydrogen bonded to the carbonyl group at C-4[10] while the latter could be due to an isolated hydroxyl group anywhere else in the rings. The absence of a characteristic signal for the C-2 proton excluded an isoflavonoid for genkwanin[10]. Moreover, a careful account of all the signals in the NMR implied the substitutions to be at C-7 and C'-4, the latter is satisfying the requirements of an A_2B_2 system.

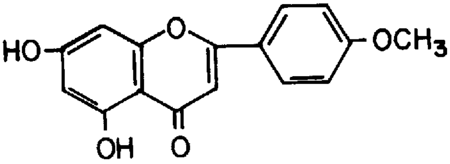
TABLE 1

Proton Magnetic Resonance Data of Genkwanin in DMSO-d_6

Signal position (δ)	J (Hz)	Number of Protons	Proton Position
3.8 (s)		3H	$-OCH_3$
6.4 (d)	2.5	1H	C-6
6.8 (d)	2.5	1H	C-8
6.8 (s)		1H	C-3
7.0 (d)	8.5	2H	C'-3, C'-5
8.0 (d)	8.5	2H	C'-2, C'-6
10.4 (s)		1H	-OH
13.0 (s)		1H	C-5 OH Chelated to C-4-C=O group

Chemical Shifts are given on the δ scale. The symbols "s" and "d", are used to refer to singlets and doublets.

Other possible structures which would fit the data can also be postulated and are represented by 2, 3, and 4.



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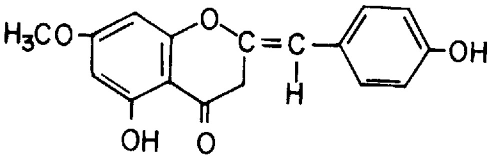
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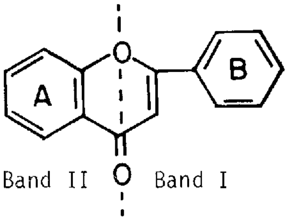

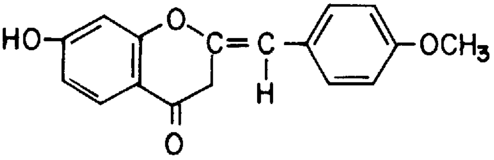
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The lack of a characteristic uv band at longer wavelengths (370-430 nm)[11] excluded the possibility of a structure with an aurone 3 or chalcone 4 skelton. Furthermore, genkwanin did not form any red or orange color with sodium methoxide characteristic of aurones or chalcones.

A bathochromic shift of 60 nm in the presence of sodium methoxide without any decrease in intensity is diagnositc of a free C'-4 hydroxyl group in genkwanin. Of the 130 flavone and flavonol ultraviolet spectra done in the presence of sodium methoxide, 47 had a 40-60 nm bathochromic shift for band I without a decrease in the intensities. All of those except three were flavonoids containing C'-4 hydroxyl groups[10]. A comparative study of the bathochromic shift of genkwanin with acacetin 2 is included in the Table 2. However, the reported uv data of genkwanin were not consistent (Table 3).

Table 2. Comparative uv shift studies of genkwanin and acacetin.

Shift reagent	Acacetin		Genkwanin	
	Band I	Band II	Band I	Band II
MeOH	269	303(sh)[a] 327	242(sh)	268 333
NaOMe	276	295(sh) 364	232(sh) 255	269 395
$AlCl_3$	259; 277	292(sh) 302, 344 382	250(sh)	277 302, 351
$AlCl_3$/HCl	260; 279	294(sh) 300, 338 379	247(sh)	278 301, 345
NaOAc	276	297(sh) 358	256	268 295 (weak)
NaOAc/H_3BO_3	269	309, 331		268 335

[a] sh = shoulder

Table 3. Comparative uv data of 5,7,4'-trisubstituted flavones.

Compound	Neutral ETOH Band I	Band II	N/500 (NaOEt, ETOH) Band I	Band II	Band II Δ OEt$^-$	Reference
Apigenin	269(18,800)	340(20,900)	277(21,900)	400(31,700)	+60	11
	300^a(13,500)		330(13,000)			
Acacetin	269^a(20,300)	330(20,800)	278(32,600)	376(14,200)	+46	
	298^a(16,400)		295^a(21,000)			
Genkwanin	269(17,000)	337(17,000)	269(13,600)	397(23,800)	+60	
	300^a(14,000)		292^a(10,500)			
Genkwanin	256(19,050)	355(23,990)				13
	290^a(13,490)					
Genkwanin	268	337 + $AlCl_3$	278^b, 301,			14
			346, 386			
Genkwanin[(C)]	268(21,520)	336(26,634)	273(21,307)	360^a(29,119)	+24	
			300^a(12,074)	382(34,801)	+46	Present Study
408 x 10^{-5}]			+NaOAc/ETOH	344^a(30,597)	+8	
			368(20,952)	396(16,690)	+60	

[a] Inflection, [b] Close to acacetin, see Table 2

Table 4. Comparative Ms data of apigenin, acacetin, genkwanin.

Compound	1 M	M-1 M+1	I-Co I-28	A	A-Co A-28	B	C	Other Peaks	Reference
Apigenin	270 (100)	269 (S)	242 (S)	152 (S)	124(S)	118(S)	121(S)	241(M) 153(S) 133(W) 128(W)	15, 18
Acacetin	284(S) (100)	283(M) 285(S)	256(M)	152(M)	124(M)	132(S)	135**	241(M) 213(W) 128(W) 117(W) 89(W)	18
Genkwanin (expected values)	284 (100)	285 283	256	166	138	118	121		
Genkwanin	284 (100)	283(M)	242(abs)	152 (abs)	124(abs)	132(VVW)	135(abs)	255(S) 241(M) 213(W) 212(W-M)	Present Study
			256(M)	166(M)	138(W-M)	118(W-M)	121(W-M)	149(M) 167(M) 128(M) 123(W-M)	

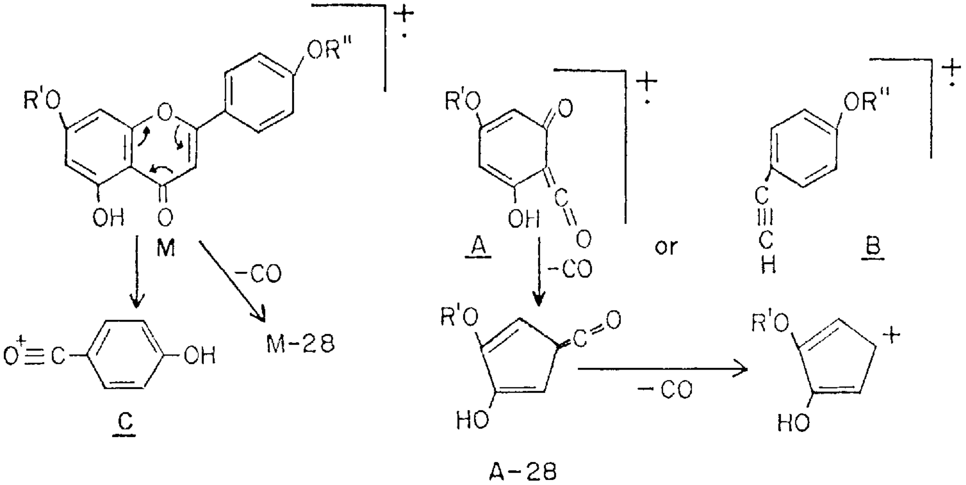
abs = absent, S = strong, M = medium, W-M = weak-medium.

*See Scheme 1 for signal interpretation (M-1, etc.)

**Not mentioned (VVW).

The IR spectrum of genkwanin had characteristic peaks at 3270 (OH), 1650 and 1692 cm^{-1} (chromone) comparable to literature[12] values of 1655 and 1680 cm^{-1} for the chromone system. Other peaks at 1575 (s=strong), 1488 (s), 1440 (w=weak), 1379 (m=medium), 1330 (m), 1280 (w), 1270 (m), 1210 (s) and 825 (m) cm^{-1} further supported the general structure.

Genkwanin showed the presence of an intense molecular ion (M^+ 284); an (M^+-1) ion of uncertain origin; and (M-CO) ion; an (A-CO) ion (Scheme 1); and an aroyl cation C composed of ring B and a carbonyl group from ring C. The latter is significant



Apigenin; R'=OH, R"=OH

Acacetin; R'-OH; R"=OCH_3

Genkwanin; R'=OCH_3; R'=OH

Scheme 1.--Mass spectral fragmentation pattern of flavones in the case of flavones containing an OH group in ring B. An ion D with mass A + 1 is the result of a retro-Diels-Alder reaction (RDA)[15,16]. The comparison of retro-Diels-Alder fragments of apigenin;[17,18] acacetin,[18] and the expected values of genkwanin confirmed the identity of genkwanin (Table 4). The mass spectra of the flavones can best be interpreted *via* a retro-Diels-Alder reaction as illustrated in Scheme 1.

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