Isolation of Acacetin-7-O-Rutinoside and Martynoside from Buddleja Davidii

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Summary: The methanol extract of fresh leaves of Buddleja davidii yielded two compounds which were indentified as acacetin-7-O-rutinoside (I) and martynoside (II). This is the first report of their presence as constituents of B. davidii.

Introduction

The genus Buddleja (Baddlejaceae) is found in the temperate regions of America, Asia and South Africa. Buddleja davidii Franchet (B. variabilis Hemsley) is the only species found in Switzerland in both its wild and cultivated states [1]. Several members of the genus Buddleja are known to be toxic to fish; buddledin A and B two such substances isolated from B.dividii, are piscicidal sesquiterpenes [2]. Several known pharmacological activities and folkoric uses are also attributed to the genus. For exampls B. asiatica, which is indigenous to China, India, and Java, is known for its uses as an abortifacient, for treatment of skin diseases, and for uses in the preparation of fermented liquor [3]. Flowers and buds of B. asiatica produce a yellow coloured essential oil which is active against several pathogenic fungi [4]. In central and southern region of Chile, an aqueous extract of B. globosa is used to treat stomach ulcers, wounds and burns [5]. Due to these and other attributed medicinal activities, as yet undescribed chemical constituents of B. davidii were characterized.

Results and Discussion

After additional fractionation, a Craig fraction, of methanol extracted fresh leaves of B. davidii yielded two compounds. Compound I was insoluble in most of the organic solvents tested, but dissolved well in DMSO. Compound I yielded a yellow spot on TLC plate

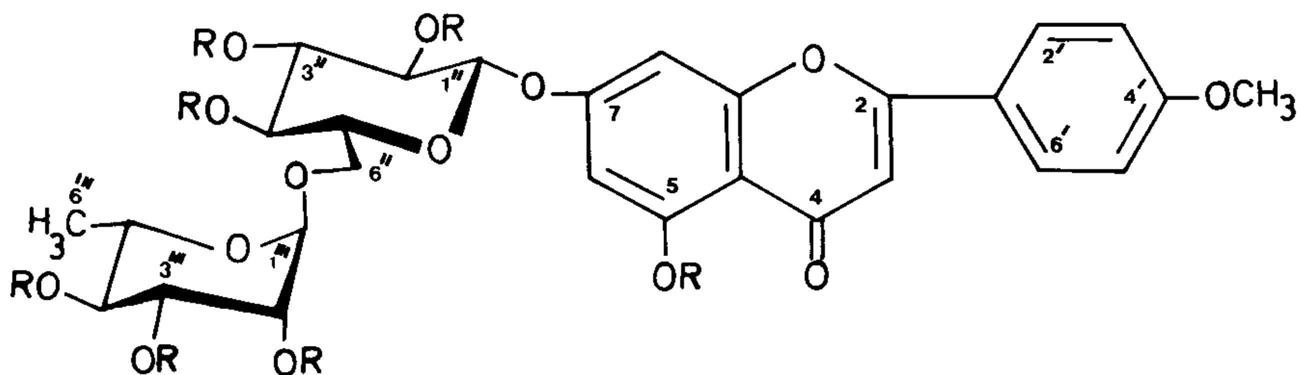

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Table-1: ^{1}H- and ^{13}C-NMR data for acacetin-7-O-rutinoside

H at C/C atom	ppm	J in Hz	ppm	
2	-		162.85	s
3	6.90 s		103.70	d
4	-		181.91	s
5	-		161.06	s
6	6.44,d	2.0	99.60	d
7	-		163.85	s
8	6.77, d	2.1	94.74	d
9	-		156.87	s
10			105.40	s
OCH_3	3.85,s		55.50	q
OH	12.9,s		-	
1"	5.05,d,	7.1	100.47	d
2"			73.04	d
3"			76.22	d
4"	3.14 - 5.19*		70.71	d
5"			75.63	d
6"			66.05	t
1"'	4.56,s		99.9	d
2"'			70.32	d
3"'			69.57	d
4"'	3.14 - 5.19*		72.03	d
5"'			68.29	d

Table-1: (Contd.) ^{1}H- and ^{13}C-NMR data for acacetin-7-O-rutinoside

H at C/C atom	ppm	J in Hz	ppm	
6'''	1.08, d	6.2	17.78	q
1'	-		122.56	s
2'	8.04,d	8.9	128.35	d
3'	7.14,d	9.0	114.62	d
4'	-		162.33	s
5'	7.14, d	9.0	114.62	d
6'	8.04, d	8.9	128.35	d

The spectra were recorded in DMSO-d_6 (TMS) at 300 (^{1}H-NMR) and 75.5 (^{13}C-NMR) MHz respectively.

*The signals were not clear due to overlapping.

sprayed with a vanillin-H_2SO_4 reagent and was found to be chromatographically pure. On the bases of ^{1}H- and ^{13}C-NMR, UV, IR and MS spectra, Compound I was identified as the flavonoid glucoside, acacetin-7-O-rutinoside [6] (see Table 1).

Compound II was isolated as a white amorphous powder with the chemical composition $C_{31}H_{41}O_{15}$ (molecular weight 653). Its UV spectrum showed maxima at 217, 230, 282 and 326 nm (log ε = 3.85, 3.78, 3.80, 3.78 respectively). Its infrared (IR) spectrum showed a broad band at 3440 cm^{-1} indicating the presence of hydroxyl functions, while peaks at 1695, 1625, 1585 and 1510 cm^{-1} suggested the presence of C=O, C=C and aromatic rings. Compound II was identified as martynoside on the basis of ^{1}H- and ^{13}C-NMR data as well as on comparison with an authentic sample of its heptaacetate. The presence of martynoside and acacetin-7-O-rutinoside in B. davidii has not been previously reported.

Experimental

UV and IR spectra were recorded on a Perkin-Elmer spectrophotometer (Model 550) and a Perkin-Elmer grating spectrometer (Model 257), respectively. ^{1}H- and ^{13}C-NMR spectra were made on a Bruker Spectrospin WM 300 spectrometer. The isolation of pure compounds from a prepurified Craig fraction was carried out on DCCC (DCCC-A Tokyo-Rikakikai Co. Ltd.) and by HPLC (Waters pump, Model M-45 solvent delivery system; Waters injector Waters Model U6A, detector; Perkin-Elmer spectrophotometer LC 55, W+W recorder series 1100. column Kanuer-C_{18}, 30 cm x 3.9 mm I.D).

Extraction and Isolation

Dried leaves of B. davidii (443 g) were collected near Zollikon, Switzerland, in September 1982. The leaves

Fig.1: ^{1}H-NMR spectrum (CD_3OD, 300 MHz) of martynoside.

Table-2: ^{1}H- and ^{13}C-NMR data for martynoside

H at C/C-atom	ppm	J in Hz	ppm	
1	-		132.93	s
2	6.76, d	2.3	112.91	d
3	-		147.39	s
4	-		147.57	s
5	6.79, d	8.2	117.14	d
6	6.70, dd,	2.1,8.2	121.24	d
α-CH_2	4.04,m,		72.16	t
	3.75, m,			
β-CH_2	2.82,t	7.4	36.63	t
OCH_3	3.81, s		56.53	q
1'	4.37,d,	7.9	104.26	d
2'	3.40, dd,	9.1,7.9	76.25	d
3'	3.30 - 4.10*		81.62	d
4'	4.93, t,	9.2	70.69	d
5'	3.30 - 4.10*		76.08	d
6'	3.75*		62.45	t
	3.60*			
1"	5.20, d,	1.7	103.04	d
2"			72.41	d
3"	3.30-4.00*		72.16	d
4"			73.86	d
5"			70.48	d
6"	1.09, d	6.2	18.57	q

Table-2:(Contd.)

H at C/C-atom	ppm	J in Hz	ppm	
1'"	-		127.47	s
2'"	7.18,d	1.9	111.82	d
3'"	-		148.03	s
4'"	-		149.52	s
5'"	6.82, d,	8.2	116.67	d
6'"	7.08,dd,	1.9,8.2	124.49	d
α-CH	6.34,d,	15.9	114.96	d
β-CH	7.65,d,	15.9	148.03	d
OCH_3	3.88,s,		56.53	q
C=O	-		168.36	s

The spectra were recorded in CD_3OD (TMS) at 300 (^{1}H-NMR) and 75.5 (^{13}C-NMR) MHz respectively.
*The signals were not clear due to overlapping.

were crushed into small pieces, then extracted with methanol under reflux at 40°C. The extract was concentrated under vacuum, water was added, and the insoluble material was removed by filtration through celite. The filtrate was then extracted with petroleum ether; the soluble part was discarded. The aqueous phase was concentrated under reduced pressure and lyophilized, yielding crude glycosides (85.30g) whichwere subjected to Craig distribution (37 g) (chloroform-methanol-water 43:37:20).

Craig fraction I (3g) yielded compound I (216 mg) upon fractionation in chloroform-methanol-water (43:37:20). The residue of this fraction was subjected to DCCC (chlroform-methanol-water 43:37:20) and compound II was collected. It was purified on semipreparative RP-HPLC (methanol-water 45:55, flow rate 8 ml/min).

Compound I

Acacetin-7-O-rutinoside, $C_{28}H_{32}O_{14}$, molecular weight 592, melting point 254.5°C, optical rotation $[\alpha]_D^{20}$ = -85.3° (pyridine). UV λ_{max}^{DMSO} = 270.2, 232.8 (log ε = 4.09 and 4.16) nm, IR (KBr) = 3400 (br, OH), 1710 (C=O), 1600 (C=C), 1520 and 1465 (aromatic ring) cm^{-1}. For ^{1}H- and ^{13}C-NMR see Table 1.

Compound II

Martynoside, $C_{31}H_{41}O_{15}$, molecular weight 653 (EI-MS), optical rotation

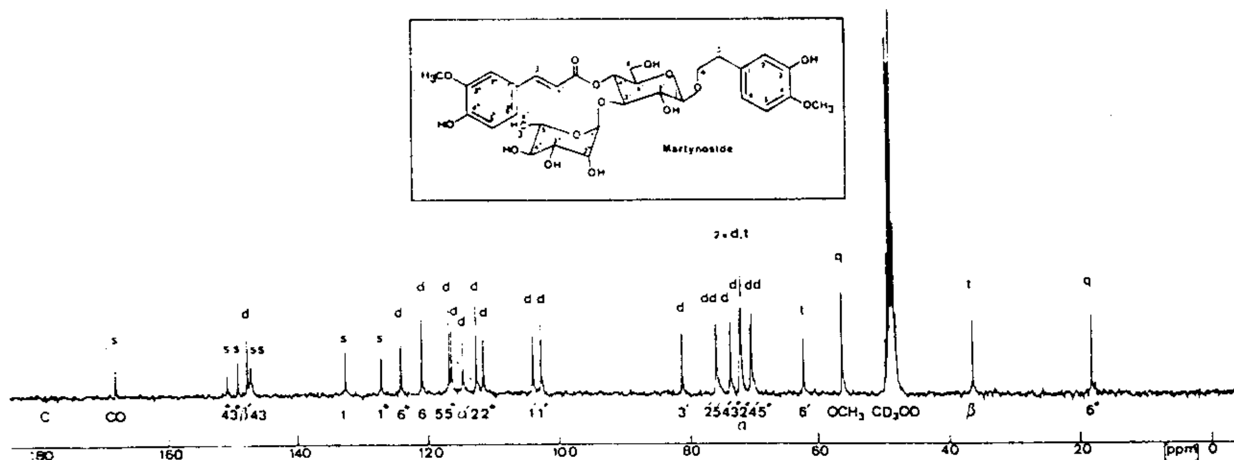

Fig.2: ^{13}C-NMR spectrum (CD_3OD, 75.5 MHz) of martynoside.

$[\alpha]_D^{20} = - 68.7°$ (c = 0.69; MeOH), UV λ_{max}MeOH = 217,230,282 and 326 (log ε = 3.85, 3.78, 3.80, 3.78) nm, IR (KBr) = 3410 (br.OH), 1695 (C=O), 1625 (C=C), 1585 and 1510 (aromatic ring) cm^{-1}. ^{1}H- and ^{13}C-NMR date are given in Table-2. See Fig. 1 & 2. The heptaacetate of II which was prepared on the usual way was identical with an authentic sample of martymoside heptaacetate [7].

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