Phytochemistry, Vol. 30, No. 8, pp. 2777–2780, 1991
Printed in Great Britain.

0031-9422/91 $3.00+0.00

ISOFLAVANS AND A PTEROCARPAN FROM *ASTRAGALUS MONGHOLICUS*

ANAS SUBARNAS, YOSHITERU OSHIMA* and HIROSHI HIKINO†

Pharmaceutical Institute, Tohoku University, Aoba-yama, Sendai 980, Japan

(*Received* 28 *November* 1990)

Key Word Index—*Astragalus mongholicus*; Leguminosae; roots; isoflavans; 7-*O*-methylisomucronulatol; isomucronulatol 7,2′-di-*O*-glucoside; 5′-hydroxyisomucronulatol 2′,5′-di-*O*-glucoside; pterocarpan; 3,9-di-*O*-methylnissolin.

Abstract—Three new isoflavans, 7-*O*-methylisomucronulatol, isomucronulatol 7,2′-di-*O*-glucoside, 5′-hydroxyisomucronulatol 2′,5′-di-*O*-glucoside, and one new pterocarpan, 3,9-di-*O*-methylnissolin were isolated from *Astragalus mongholicus* roots. Their structures were established by spectral analyses and chemical conversions.

INTRODUCTION

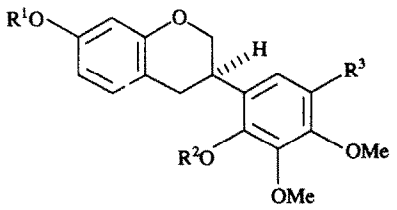
The roots of *Astragalus mongholicus*, and certain species of *Astragalus* (Leguminosae), are used as an antiperspirant, a diuretic or a tonic in Oriental medicines [1]. This crude drug is reported to contain flavonoids [2, 3] and triterpenoid glycosides [1, 4, 5] as well as active principles, γ-aminobutyric acid responsible for hypotensive activity [6] and L-canavanine showing inhibitory activity against silkworm metamorphosis [7]. Among *Astragalus* species, *A. mongholicus* is rarely investigated chemically. Therefore, we carried out a phytochemical investigation on the roots of this species. The work resulted in the isolation of three new isoflavans, 7-*O*-methylisomucronulatol (**1**), isomucronulatol 7,2′-di-*O*-glucoside (**2**) and 5′-hydroxyisomucronulatol 2′,5′-di-*O*-glucoside (**3**), and one new pterocarpan, 3,9-di-*O*-methylnissolin (**4**), in addition to the known isomucronulatol (**5**) and isomucronulatol 7-*O*-glucoside (**6**).

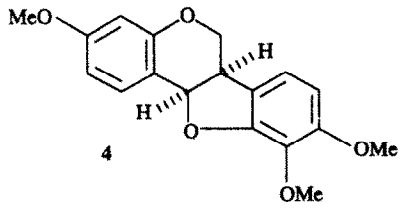
RESULTS AND DISCUSSION

7-*O*-Methylisomucronulatol (**1**) analysed for the molecular formula $C_{18}H_{20}O_5$ from its $[M]^+$ ion peak at *m/z* 316 in the EI mass spectrum and the number of hydrogens and carbons in its ^1H and ^{13}C NMR spectra. The IR spectral band at 3400 cm^{-1} indicated the presence of a hydroxyl group in the molecule. The ^1H NMR spectrum of **1** showed signals at δ2.92 (1H, *dd*, *J* = 5 and 16 Hz), 3.0 (1H, *dd*, *J* = 10 and 16 Hz), 3.50 (1H, *m*), 4.04 (1H, *t*, *J* = 10 Hz) and 4.32 (1H, *dd*, *J* = 3 and 10 Hz), characteristic for the $-CH_2-CH-CH_2-O$ group of an isoflavan skeleton [8–10]. Furthermore, its ^1H NMR spectrum revealed five aromatic hydrogen signals at δ6.42 (1H, *d*, *J* = 2.5 Hz), 6.44 (1H, *d*, *J* = 8 Hz), 6.48 (1H, *dd*, *J* = 2.5 and 8 Hz), 6.74 (1H, *d*, *J* = 8 Hz) and 6.98 (1H, *d*, *J* = 8 Hz), in addition to three aromatic methoxyl signals at δ3.74, 3.82 and 3.90 (3H, each *s*). The above indicate that **1** has 1,2,4-tri- and 1,2,3,4-tetrasubstituted benzene rings. The mass fragment ion peaks generated by retro-Diels–Alder type fission clearly displayed the number of hydroxyl and methoxyl groups in each benzene ring. Thus, a prominent ion at *m/z* 180 was attributed to the B-ring having one hydroxyl and two methoxyl groups, and an ion peak at *m/z* 137 was supposed to be generated from the monomethoxylated A-ring. NOE difference spectra were further measured for the assignment of the positions of oxygen functions in the benzene rings. By irradiation of the methoxyl signal at δ3.74 distinct NOE's were observed on the aromatic hydrogen signals at δ6.42 and 6.48. This fact, supported by the evidence that the chemical shifts of the A-ring hydrogen signals were similar to those of 7-hydroxyisoflavan [11, 12], suggested that the methoxyl group in the A-ring is at C-7. Moreover, saturation of the methoxyl signal at δ3.82 caused a significant enhancement of the doublet at δ6.44, and no NOE was detected on irradiation of the remaining methoxyl signal at δ3.90. These observations and the fact that isomucronulatol (**5**) and isomucronulatol 7-*O*-glucoside (**6**) were isolated from the same source suggests that isoflavan **1** has a 2′-hydroxy-3′,4′-dimethoxy substituted B-ring. The CD spectrum of **1** exhibited a negative Cotton effect at 227 nm ($[\theta]$ −10030) indicating that it has the 3*R* configuration [12–14]. Finally, its structural confirmation was obtained by monomethylation of isomucronulatol (**5**) with diazomethane to afford a product identical with **1**.

Isomucronulatol 7,2′-di-*O*-glucoside (**2**) was determined to have the molecular formula $C_{29}H_{38}O_{15}$ by FAB mass spectral measurement (*m/z* 649 $[M+Na]^+$ and *m/z* 627 $[M+H]^+$) and an analysis of its ^1H and ^{13}C NMR data. Compound **2** was thought to be an isoflavan glycoside from the signals due to the $-CH_2-CH-CH_2-O$ group at δ2.84 (2H, *br d*), 3.50 (1H, *m*) and 4.30 (2H, *m*), and two anomeric hydrogen signals at δ4.60 and 4.80 (1H each *d*, *J* = 7.2 Hz) in its ^1H NMR spectrum. Moreover, a comparative study of the aromatic hydrogen signals of **2** [δ6.56 (1H, *d*, *J* = 2 Hz), 6.60 (1H, *dd*, *J* = 2 and 8 Hz), 6.80 (2H, *s*) and 6.96 (1H, *d*, *J* = 8 Hz)] with those of **5** and **1**, suggested that they have the same oxygenation patterns

*Author to whom correspondence should be addressed.
†Deceased on 8 December 1988.





4

	R^1	R^2	R^3
1	Me	H	H
2	Glc	Glc	H
3	H	Glc	O-Glc
3a	Ac	Glc(OAc)$_4$	O-Glc(OAc)$_4$
3b	H	H	OH
5	H	H	H
6	Glc	H	H

Table 1. ^{13}C NMR data of compounds **1**, **2**, **3a** and **5**

C	1	2*	3a	5
2	69.9 *t*	70.8 *t*	69.9 *t*	69.8 *t*
3	32.3 *d*	31.2 *d*	29.2 *d*	32.1 *d*
4	30.0 *t*	29.8 *t*	30.6 *t*	30.0 *t*
4a	114.5 *s*	116.5 *s*	118.3 *s*	113.7 *s*
5	130.2 *d*	130.5 *d*	129.1 *d*	130.2 *d*
6	107.3 *d*	108.9 *d*	112.6 *d*	108.1 *d*
7	159.5 *s*	155.6 *s*	148.7 *s*	155.8 *s*
8	101.5 *d*	105.0 *d*	108.7 *d*	102.9 *d*
8a	155.2 *s*	157.7 *s*	153.7 *s*	154.8 *s*
1′	120.4 *s*	129.2 *s*	130.8 *s*	120.6 *s*
2′	147.5 *s*	148.8 *s*	145.1 *s*	147.6 *s*
3′	135.5 *s*	142.3 *s*	142.2 *s*	135.5 *s*
4′	151.2 *s*	152.9 *s*	141.6 *s*	151.2 *s*
5′	103.7 *d*	109.3 *d*	146.9 *s*	103.5 *d*
6′	121 9 *d*	121.9 *d*	110.3 *d*	121.8 *d*
1″	—	102.0 *d*	99.3 *d*	—
2″	—	73.4 *d*	70.0 *d*	—
3″	—	78.5 *d*	71.2 *d*	—
4″	—	71 5 *d*	67.1 *d*	—
5″	—	75.5 *d*	71.2 *d*	—
6″	—	62.1 *t*	60.3 *t*	—
1‴	—	102.0 *d*	100.0 *d*	—
2‴	—	73.4 *d*	70.7 *d*	—
3‴	—	78.1 *d*	71.4 *d*	—
4‴	—	71.0 *d*	68.6 *d*	—
5‴	—	74.7 *d*	71.4 *d*	—
6‴	—	61.5 *t*	61.0 *t*	—
OMe	55.4 (*q*)	55.7 *q*	60.1 *q*	55.7 *q*
	55.9 *q*	61.1 *q*	60.3 *q*	60.8 *q*
	61.1 *q*	—	—	—

*Spectrum was measured in pyridine-d_5, and others in chloroform-*d*.

in the benzene rings. In addition to the above signals, two 3H singlets at δ3.88 and 3.90 were assigned for two aromatic methoxyls. The ^{13}C NMR spectrum of **2**, on comparison with that of **5**, revealed downfield shifts of the signals at C-4a ($\Delta\delta$ +2.8 ppm), C-6 ($\Delta\delta$ +0.8 ppm) and C-8 ($\Delta\delta$ +2.1 ppm) on the A-ring and those at C-1′ ($\Delta\delta$ +8.6 ppm), C-3′ ($\Delta\delta$ +6.8 ppm) and C-5′ ($\Delta\delta$ +5.8 ppm) on the B-ring due to the glycosylation effects of the hydroxyl group at C-7 [15] and C-2′, respectively. A negative Cotton effect at 227 nm ([θ] −5630) in its CD spectrum indicated the *R* configuration at C-3 [12–14]. Acid hydrolysis of **2** yielded an isoflavan identical with **5** together with glucose. The configurations of the glycosidic linkages were determined as β by the anomeric hydrogen doublets with large coupling constants (J = 7.2 Hz, each). From these findings, compound **2** was identified as isomucronulatol 7,2′-di-*O*-glucoside.

5′-Hydroxyisomucronulatol 2′,5′-di-*O*-glucoside (**3**) showed an absorption band at 3350 cm^{-1} in its IR spectrum, indicating the presence of hydroxyl groups in the molecule. The FAB mass spectrum gave ions at *m/z* 665 [M+Na]$^+$ and 643 [M+H]$^+$ which gave the molecular formula $C_{29}H_{38}O_{16}$. Like the other isoflavans, its ^{1}H NMR spectrum revealed five aliphatic hydrogen and two methoxyl signals. In addition, two anomeric hydrogen signals were observed at δ5.63 and 5.67 (1H each *d*, J = 7 Hz) which suggested that compound **3** is an isoflavan glycoside with two sugar moieties. Three aromatic hydrogen signals at δ6.76 (1H, *dd*, J = 2 and 8 Hz), 6.80 (1H, *d*, J = 2 Hz) and 6.97 (1H, *d*, J = 8 Hz)] in the ^{1}H NMR spectrum of **3** were similar to those of the isoflavans **1**, **2**, **5** and **6**, an observation which indicates that they have the same substituted A-ring. Another signal appearing as a singlet at δ7.42 suggested the presence of an isolated hydrogen in the B-ring. In order to clarify the oxygenation patterns of the aromatic rings, the ^{13}C NMR spectral data of the acetylated product (**3a**) and the previous isoflavans (**2** and **5**) were compared. In the ^{13}C NMR spectrum of **3a**, carbon signals of the A-ring appearing at δ118.3 (C-4a), 129.1 (C-5), 112.6 (C-6), 148.7 (C-7), 108.7 (C-8) and 153.7 (C-8a) shifted from those of the corresponding carbons of isomucronulatol (**5**) by +4.6, −1.1, +4.5, −7.1, +5.8 and −1.1 ppm, respectively. The differences of these chemical shifts were considered to be due to the acetylation effect of the hydroxyl group at C-7 [16]. Moreover, from biogenetic considera-

tions the two methoxyl groups on the B-ring were assumed to be attached to C-3′ and C-4′, and no NOE on irradiation of the two aromatic methoxyl signals suggested that the single aromatic hydrogen was present at C-6′. Consequently, the sugar moieties might be assigned to C-2′ and C-5′ hydroxyls, as the chemical shifts of sugar carbon signals excluded the presence of a disaccharide structure. The ^{13}C NMR spectrum showing significant shifts of the signals at C-2′ ($\Delta\delta$ −3.7 ppm), C-4′ ($\Delta\delta$ −11.3 ppm), C-5′ ($\Delta\delta$ +37.6 ppm) and C-6′ ($\Delta\delta$ −11.6 ppm) compared with those of isomucronulatol 7,2′-di-*O*-glucoside (**2**), confirmed the positions of the oxygen functions in the B-ring. Acid hydrolysis of **3a** afforded the aglycone **3b** and glucose. The anomeric hydrogen signals at δ5.63 and 5.67 with large coupling constant values (J = 7 Hz, each) indicated β-configurations for the glycosidic linkages. The *R* configuration at C-3 was assigned from its negative Cotton effect at 227 nm ([θ] −4250) in the CD spectrum [12–14]. The structure of the compound was therefore elucidated as indicated in formula **3**.

For 3,9-di-*O*-methylnissolin (**4**) the $[M]^+$ at *m/z* 314 in the EI mass spectrum, and the 18 carbon atoms from the ^{13}C NMR spectrum defined its molecular formula as $C_{18}H_{18}O_5$. Compound **4** was recognized as a pterocarpan derivative from the characteristic ^{1}H NMR signals associated with the O–CH_2–CH–CH–O unit [10, 17] at δ3.56 (1H, *m*), 4.20 (2H, *m*) and 5.50 (1H, *d*, J = 6 Hz). Its ^{1}H NMR spectrum revealed the presence of five signals in the aromatic region at δ6.42 (1H, *d*, J = 8 Hz), 6.44 (1H, *d*, J = 2 Hz), 6.60 (1H, *dd*, J = 2 and 8 Hz), 6.82 (1H, *d*, J = 8 Hz) and 7.46 (1H, *d*, J = 8 Hz), which showed 1,2,4-tri-and 1,2,3,4-tetrasubstituted benzene rings, and three aromatic methoxyl signals at δ3.78, 3.82 and 3.90 (3H, each *s*). The chemical shifts of the aromatic hydrogen signals led to the assumption that **4** is 3,9,10-trimethoxypterocarpan. The coupling constant (J = 6 Hz) of the C-11a hydrogen signal at δ5.50 indicated a *cis* relationship between the two asymmetric centres [17], and the absolute configurations at C-6a and C-11a were defined as *R* by its negative optical rotation [17, 18] and the CD spectrum showing Cotton effects identical to those of related compounds [19]. Furthermore, hydrogenation of **4** afforded an isoflavan which matched well with 7-*O*-methylisomucronulatol (**1**). Thus, the structure of the compound was confirmed as shown in formula **4**.

EXPERIMENTAL

General. Mps are uncorr. ^{1}H and ^{13}C NMR spectra were measured on at 500 MHz and 25 MHz, respectively, (TMS as int standard).

Extraction and isolation. Dried roots of *A. mongholicus* Bunge (10 kg) were extracted ×3 with MeOH and the solvent evapd under red. pres. to give an extract (780 g). Partition of the MeOH extract with EtOAc–H_2O (1:1) afforded EtOAc (140 g) and H_2O layers. The H_2O layer was further extracted with *n*-BuOH and concd to yield *n*-BuOH and water sol. extract (120 and 500 g, respectively). The EtOAc extract (50 g) was subjected to reversed-phase CC over polyamide and eluted with H_2O–EtOH mixts of decreasing polarity. Rechromatography of the H_2O–EtOH (2:3) fr. by silica gel CC (*n*-hexane–EtOAc, 19:1, 9:1 and 4:1) gave 7-*O*-methylisomucronulatol (**1**, 10 mg) and 3,9-di-*O*-methylnissolin (**4**, 10 mg). The *n*-BuOH extract (100 g) was subjected to silica gel CC and eluted with EtOAc–MeOH mixts of increasing polarity. The EtOAc–MeOH (7:3) fr. was repeatedly chromatographed by silica gel CC (EtOAc–MeOH, 4:1 and 3:1) to yield isomucronulatol 7,2′-di-*O*-glucoside (**2**, 20 mg) and 5′-hydroxyisomucronulatol 2′,5′-di-*O*-glucoside (**3**, 6 mg).

7-O-*Methylisomucronulatol* (**1**). Needles, mp 140–141°. $[\alpha]_D$ −11.0° ($CHCl_3$; *c* 0.4). CD (MeOH; *c* 0.02): $[\theta]_{216}$ −14 110, $[\theta]_{227}$ −10 030, $[\theta]_{282}$ +3760. EIMS *m/z*: 316 $[M]^+$, 180, 167, 165, 137. UV λ_{max}^{MeOH} nm (log ε): 218 (4.11), 280 (3.70). IR ν_{max}^{Nujol} cm^{-1}: 3400, 1615, 1505, 1460; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.92 (1H, *dd*, J = 5, 16 Hz, H-4), 3.0 (1H, *dd*, J = 10, 16 Hz, H-4), 3.50 (1H, *m*, H-3), 3.74, 3.82, 3.90 (3H, each *s*, OMe), 4.04 (1H, *t*, J = 10 Hz, H-2), 4.32 (1H, *dd*, J = 3, 10 Hz, H-2), 6.42 (1H, *d*, J = 2.5 Hz, H-8), 6.44 (1H, *d*, J = 8 Hz, H-5′), 6.48 (1H, *dd*, J = 2.5, 8 Hz, H-6), 6.74 (1H, *d*, J = 8 Hz, H-6′), 6.98 (1H, *d*, J = 8 Hz, H-5). ^{13}C NMR: see Table 1.

Isomucronulatol 7,2′-di-O-glucoside (**2**). Needles, mp 150–151°: $[\alpha]_D$ −24.3° (MeOH; *c* 0.5). CD (MeOH; *c* 0.03): $[\theta]_{213}$ −13 500, $[\theta]_{227}$ −5630, $[\theta]_{281}$ +1040. FABMS *m/z*: 649 $[M+Na]^+$, 627 $[M+H]^+$, 465, 303. UV λ_{max}^{MeOH} nm (log ε): 212 (4.66), 278 (3.94). IR ν_{max}^{Nujol} cm^{-1}: 3350, 1615, 1500, 1460. ^{1}H NMR (100 MHz, pyridine-d_5) δ: 2.84 (2H, *br s*, H-4), 3.50 (1H, *m*, H-3), 3.88, 3.90 (3H, each *s*, OMe), 4.30 (2H, *m*, H-2), 4.60, 4.80 (1H, each *d*, J = 7.2 Hz, anomeric H), 6.56 (1H, *d*, J = 2 Hz, H-8), 6.60 (1H, *dd*, J = 2, 8 Hz, H-6), 6.80 (2H, *s*, H-5′, H-6′), 6.96 (1H, *d*, J = 8 Hz, H-5). ^{13}C NMR: see Table 1.

5′-Hydroxyisomucronulatol 2′,5′-di-O-glucoside (**3**). Needles, mp 160–162°. $[\alpha]_D$ −17.7° (MeOH; *c* 0.3). CD (MeOH; *c* 0.03): $[\theta]_{210}$ −7890, $[\theta]_{227}$ −4250, $[\theta]_{280}$ +1820. FAB-MS *m/z*: 665 $[M+Na]^+$, 643 $[M+H]^+$, 481, 369, 319. UV λ_{max}^{MeOH} nm (log ε): 225 (4.60), 276 (4.0). IR ν_{max}^{Nujol} cm^{-1}: 3350, 1620, 1505, 1460. ^{1}H NMR (500 MHz, pyridine-d_5) δ: 2.94 (1H, *dd*, J = 5, 16 Hz, H-4), 3.14 (1H, *dd*, J = 10, 16 Hz, H-4), 3.82 (1H, *m*, H-3), 3.96 (6H, *s*, OMe), 4.24 (1H, *t*, J = 10 Hz, H-2), 4.75 (1H, *dd*, J = 4, 10 Hz, H-2), 5.63, 5.67 (1H, each *d*, J = 7 Hz, anomeric H), 6.76 (1H, *dd*, J = 2, 8 Hz, H-6), 6.80 (1H, *d*, J = 2 Hz, H-8), 6.97 (1H, *d*, J = 8 Hz, H-5), 7.42 (1H, *s*, H-6′).

3,9-*Di*-O-*Methylnissolin* (**4**). Needles, mp 136–137°. $[\alpha]_D$ −200.0° ($CHCl_3$; *c* 0.4). CD (MeOH; *c* 0.02): $[\theta]_{212}$ −157 000, $[\theta]_{234}$ −39 250, $[\theta]_{284}$ +19 190. EIMS *m/z*: 314 $[M]^+$, 299, 284, 267, 191, 178, 161. UV λ_{max}^{MeOH} nm (log ε): 223 (4.10), 279 (3.71), 284 (3.71). IR ν_{max}^{Nujol} cm^{-1}: 1615, 1500, 1455. ^{1}H NMR (100 MHz, $CDCl_3$) δ: 3.56 (1H, *m*, H-6a), 3.78, 3.82, 3.90 (3H, each *s*, OMe), 4.20 (2H, *m*, H-6), 5.50 (1H, *d*, J = 6 Hz, H-11a), 6.42 (1H, *d*, J = 8 Hz, H-8), 6.44 (1H, *d*, J = 2 Hz, H-4), 6.60 (1H, *dd*, J = 2, 8 Hz, H-2), 6.82 (1H, *d*, J = 8 Hz, H-7), 7.46 (1H, *d*, J = 8 Hz, H-1). ^{13}C NMR (25 MHz, $CDCl_3$) δ: 130.5 (*d*, C-1), 108.9 (*d*, C-2), 155.6 (*s*, C-3), 105.0 (*d*, C-4), 157.7 (*s*, C-4a), 70.8 (*t*, C-6), 31.2 (*d*, C-6a), 129.2 (*s*, C-6b), 121.9 (*d*, C-7), 109.3 (*d*, C-8), 152.9 (*s*, C-9), 151.4 (*s*, C-10), 153.2 (*s*, C-10a), 79.2 (*d*, C-11a), 112.4 (*s*, C-11b), 55.5, 56.5, 60.8 (*q*, 3 × OMe).

Methylation of compound **5**. A soln of **5** (5 mg) was treated with Et_2O–CH_2N_2 and kept standing at 0° for 1 hr. Removal of solvent left the crude Me ether which was purified by silica gel CC to give **1** (2 mg) as needles, whose mass and ^{1}H NMR spectra were identical to those of authentic **1**.

Acid hydrolysis of compound **2**. A soln of **2** (8 mg) in 0.5 M H_2SO_4 (3 ml) was heated at 70° for 4 hr. Usual work-up of the reaction mixt. afforded **5** (3 mg) and glucose. *Compound* **5**. Needles. EIMS *m/z*: 302 $[M]^+$, 180, 167, 123. ^{1}H NMR (100 MHz, $CDCl_3$) δ: 2.96 (2H, *br d*, J = 7.2 Hz, H-4), 3.56 (1H, *m*, H-3), 3.83, 3.90 (3H, each *s*, OMe), 4.05 (1H, *t*, J = 10 Hz, H-2), 4.32 (1H, *dd*, J = 3, 10 Hz, H-2), 6.35 (1H, *d*, J = 2 Hz, H-8), 6.37 (1H, *dd*, J = 2, 8 Hz, H-6), 6.44 (1H, *d*, J = 8 Hz, H-5′), 6.76 (1H, *d*, J = 8 Hz, H-6′), 6.92 (1H, *d*, J = 8 Hz, H-5). Glucose was identified by GC comparison with an authentic sample after acetylation with Ac_2O and pyridine.

Acetylation of compound **3**. A soln of crude **3** (30 mg) in Ac_2O–pyridine (5 ml, 1:1) was kept standing at room temp. overnight. Usual work-up of the reaction mixt. gave a crude product which was purified by silica gel CC to yield **3a** (10 mg) as needles. EIMS *m/z*: 691 $[M-C_{14}H_{17}O_9]^+$, 503, 429, 360, 331, 169. ^1H NMR (500 MHz, $CDCl_3$) δ: 1.97, 1.99, 2.00, 2.01, 2.02, 2.04, 2.06, 2.08, 2.26 (3H, each *s*, OAc). 2.72 (1H, *dd*, $J=10$, 16 Hz, H-4), 2.92 (1H, *dd*, $J=5$, 16 Hz, H-4), 3.62 (1H, *m*, H-3), 3.80, 3.82 (3H, each *s*, OMe), 3.92 (1H, *t*, $J=10$ Hz, H-2), 5.14, 5.26 (1H, each *d*, $J=7$ Hz, anomeric H), 6.52 (1H, *d*, $J=2$ Hz, H-8), 6.58 (1H, *dd*, $J=2$, 8 Hz, H-6), 6.64 (1H, *s*, H-6'), 7.01 (1H, *d*, $J=8$ Hz, H-5). ^{13}C NMR: see Table 1.

Acid hydrolysis of compound **3a**. A soln of **3a** (8 mg) in 0.5 M H_2SO_4 was heated at 70° for 4 hr. Usual work-up of the reaction mixt. afforded the aglycone **3b** (3 mg) and glucose. *Compound* **3b**. Needles. EIMS *m/z*: 318 $[M]^+$, 196, 149, 123. ^1H NMR (500 MHz, $CDCl_3$) δ: 2.77 (1H, *dd*, $J=5$, 16 Hz, H-4), 2.83 (1H, *dd*, $J=10$, 16 Hz, H-4), 3.43 (1H, *m*, H-3), 3.79, 3.82 (3H, each *s*, OMe), 3.91 (1H, *t*, $J=10$ Hz, H-2), 4.19 (1H, *ddd*, $J=2$, 4, 10 Hz, H-2), 6.26 (1H, *d*, $J=2$ Hz, H-8), 6.32 (1H, *dd*, $J=2$, 8 Hz, H-6), 6.36 (1H, *s*, H-6'), 6.80 (1H, *d*, $J=8$ Hz, H-5). Glucose was identified as described for compound **5**.

REFERENCES

1. Kitagawa, I., Wang, H.-K., Takagi, A., Fuchida, M., Miura, I. and Yoshikawa, M. (1983) *Chem. Pharm. Bull.* **31**, 689.
2. Kurabayashi, M. and Ogiso, A. (1969) *The 89th Annual Meeting of Pharmaceutical Society of Japan*, Nagoya, Abstract paper, p. 320.
3. Shimada, T., Saito, Y., Shibata, S., Ogiso, A. and Kurabayashi, M. (1976) *The 96th Annual Meeting of Pharmaceutical Society of Japan*, Nagoya, Abstract paper II, p. 289.
4. Kitagawa, I., Wang, H.-K., Saito, M. and Yoshikawa, M (1983) *Chem. Pharm. Bull.* **31**, 709.
5. Gan, L.-X., Han, K.-B. and Chen, Y.-Q. (1986) *Phytochemistry* **25**, 1437.
6. Hikino, H., Funayama, S. and Endo, K. (1976) *Planta Med.* **30**, 297.
7. Isogai, A., Murakoshi, S., Suzuki, A. and Tamura, S. (1973) *Nippon Nogeikagaku Kaishi* **47**, 449.
8. Kurosawa, K., Ollis, W. D., Redman, B. T., Sutherland, I. O., Braga de Oliveira, A., Gottlieb, O. R. and Alves, H. M. (1968) *J. Chem. Soc. Chem. Commun.* 1263.
9. Braga de Oliveira, A., Gottlieb, O. R., Ollis, W. D. and Rizzini, C. T. (1971) *Phytochemistry* **10**, 1863.
10. Kurosawa, K., Ollis, W. D., Sutherland, I. O., Gottlieb, O. R. and Braga de Oliveira, A. (1978) *Phytochemistry* **17**, 1405.
11. Pelter, A. and Amenicchi, P. I. (1969) *J. Chem. Soc. C*, 887.
12. Manners, G. D. and Jurd, L. (1979) *Phytochemistry* **18**, 1037.
13. Donnelly, D. M. X., Keenan, P. J. and Prendergast, J P. (1973) *Phytochemistry* **12**, 1157.
14. Yahara, S., Ogata, T., Saijo, R., Konishi, R., Yamahara, J., Miyahara, K. and Nohara, T. (1989) *Chem. Pharm. Bull.* **37**, 979.
15. Markham, K. R., Ternai, B., Stanley, R., Geiger, H. and Mabry, T. J. (1978) *Tetrahedron* **34**, 1389.
16. Pelter, A., Ward, R. S. and Gray, T. L. (1976) *J. Chem. Soc., Perkin I*, 2475.
17. Pachler, K. G. R. and Underwood, W. G. E. (1967) *Tetrahedron* **23**, 1817.
18. Cook, J. T., Ollis, W. D., Sutherland, I. O. and Gottlieb, O. R. (1978) *Phytochemistry* **17**, 1419
19. Bezuidenhoudt, B. C. B., Brandt, E. V. and Ferreira, D. (1987) *Phytochemistry* **26**, 531