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A NEW BIFLAVANONE GLUCOSIDE FROM *GARCINIA MULTIFLORA*

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Key Word Index—*Garcinia multiflora* Champ.; Guttiferae; biflavanoid glycoside; fukugiside; spicataside; xanthochymuside; 3,8″-binaringenin-7″-*O*-β-glucoside.

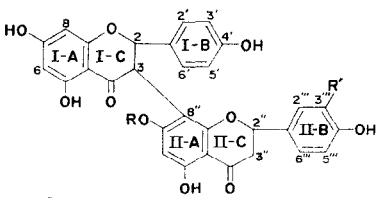
In an earlier communication [1], we reported that apigenin, 1,3,6,7-tetrahydroxyxanthone, GB-1a (3,8″-binaringenin) (**1**), GB-2a (**2**), volkensiflavone (**5**) and morelloflavone (**6**) were present in the heartwood-extractives of *G. multiflora*. Further studies on Fraction 4, [1] yielded three known biflavanoid glucosides, spicataside (**7**), fukugiside (**8**) and xanthochymuside (**4**), and a new biflavanone glucoside 3,8″-binaringenin-7″-*O*-β-glucoside (**3**) were isolated and characterized by chemical and spectral evidence.

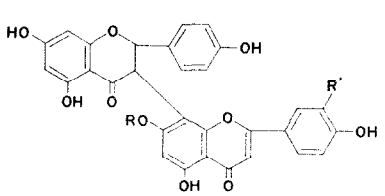
The first natural flavanoylflavone glycosides, fukugiside [2] and spicataside [3] were isolated from the fresh bark of *G. spicata* by Konoshima and Ikeshiro. The first biflavanone glycoside, xanthochymuside [3], was found recently in the wood and fresh leaves of *G. xanthochymus* Hook f. by the same authors. The present paper reports GB-1a-7″-*O*-glucoside (**3**), the second natural biflavanone glucoside from *G. multiflora*.

Fraction 4 on further chromatography over polyamide, yielded Fractions 4a, 4b and 4c; the latter was separated by preparative TLC on SiO_2 yielding Fractions $4c_1$ and $4c_2$. Recrystallization of each fraction from acetone-C_6H_6 yielded pure compounds **3**, **4**, **7** and **8**.

Compound **3**. Colourless crystals, mp 218–221°. $[\alpha]_D^{20}$ −31·68° (*c* 2·5, EtOH). Red with Mg–HCl. The UV spectra (Table 1) showed a bathochromic shift on addition of $AlCl_3$ or NaOAc indicating the presence of a flavanone with OH groups in 5 and 7 positions. ν_{max}(KBr) 3350, 1080 (OH), 1638 (conj. CO), 1600, 1520 cm^{-1} (arom.) NMR (Me_2CO-d_6) was very similar to that of GB-1a except eleven protons of a sugar residue appeared at δ 4·98 (*m*, 1 H) and 3·55 ~ 3·85 (*m*, 10 H). Hydrolysis with 10% HCl gave an aglycone which was confirmed as GB-1a (**1**) by comparison with an authentic samples (TLC, IR and mmp). The sugar was identified as glucose by comparison with authentic specimen (PPC, R_f 0·38 phenol sat. with H_2O).

Acetylation gave a nonaacetate, mp 148–149 (MeOH), ν_{max} (KBr) 1760, 1200 (ester CO), 1690 (flavanone CO), 1607, 1590, 1512 cm^{-1} (arom.). NMR showed four acetoxyl groups of a glucose moiety at δ 1·97 ~ 2·10 (12 H); five acetoxyl groups of GB-1a at δ 2·33 ~ 2·37 (15 H); H-3 and H-2 of the I-C ring as doublets (*J* 12 Hz) at δ 4·83 (1 H) and 6·03 (1 H); H-3 of the II-C ring at δ 3·0 (*m*, 2 *H*); seven protons of the glucose and H-2″ of the II-C ring at δ 4·30 (*b*, 2 H) and 5·2 ~ 5·5 (*m*, 6 H); eight protons (H-2′, 6′, 3′, 5′, 2‴, 6‴, 3‴, 5‴) in two





(**1**) GB-1a: R = R′ = H
(**2**) GB-2a: R = H, R′ = OH
(**3**) R = Glucosyl, R′ = H
(**4**) Xanthochymuside: R = Glucosyl, R′ = OH
(**5**) Volkensiflavone: R = R′ = H
(**6**) Morelloflavone: R = H, R′ = OH
(**7**) Spicataside: R = Glucosyl, R′ = H
(**8**) Fukugiside: R = Glucosyl, R′ = OH

Table 1. UV spectra of compounds **3**, **4**, **7** and **8** from the heartwood of *G. multiflora*

Solvent	Compound λ_{max}(log ϵ)			
	3 GB-1a-7″-*O*-glc	**4** Xanthochymuside	**7** Spicataside	**8** Fukugiside
MeOH	229 (4·63) 250 (4·25) 288 (4·50) 338 (sh, 3·85)	227 (3·46) 250 (sh, 4·01) 290 (4·40) 337 (sh, 3·80)	216 (4·60) 280 (4·32) 290 (4·33) 330 (sh, 4·10)	224 (4·71) 256 (sh, 4·24) 275 (4·45) 289 (4·47) 344 (4·39)
$AlCl_3$–MeOH	227, 256 sh 312, 392		223, 285 sh, 310, 350, 395	223, 281, 300 sh, 430
$AlCl_3$–HCl–MeOH	222, 256 sh 313, 392		222, 285 sh, 311, 352, 393	225, 281, 299, 350 sh, 395
NaOAc–MeOH	215, 250, 286, 326, 335 sh			224, 275, 291 sh, 330
NaOAc–H_3BO_3–MeOH	212, 250, 288, 333 sh		220, 289, 331	224, 270, 287 sh, 380

1,4-disubstituted benzene rings as two sets of A_2B_2 doublets (*J* 9 Hz) at δ 7·43 (2 H), 7·27 (2 H) and δ 7·38 (2 H), 7·07 (2 H); H-8 at δ 6·88 (*d*, *J* 2 Hz, 1 H); H-6 at δ 6·67 (*d*, *J* 2 Hz, 1 H); H-6″ at δ 6·50 (*s*, 1 H). From these data the compound H was suggested to be a GB-1a glucoside.

Dehydrogenation of the nonaacetate in CCl_4 with 1 mol of NBS–KOAc under irradiation gave a colorless flavanoflavone acetate, mp 153–155°, which was identified as spicataside acetate by comparison with the authentic sample (TLC, IR and mmp). As the structure of spicataside was confirmed as volkensiflavone 7″-*O*-β-glucoside by Konoshima *et al.* [3] hence **3** must be assigned as GB-1a 7″-*O*-β-glucoside. This is the second instance of the isolation of a new natural biflavanone glucoside.

Compound **4** (*xanthochymuside*). Colorless crystals, mp 223–225° (lit. [3] 219°). UV (Table 1). ν_{max} (KBr) 3400, 1090 (OH), 1635 (conj. CO), 1603, 1510 cm^{-1} (arom.). Hydrolysis with 10% HCl gave GB-2a (**2**) and glucose. Acetylation gave a decaacetate, mp 149–150° (EtOH). NMR showed four acetoxyl groups of a glucose moiety at δ 1·95 ~ 2·08 (12 H); six acetoxyl groups of GB-2a at δ 2·30 (*bs*, 18 H); seven protons of the glucose at δ 4·30 (*br*, 2 H) and 5·25 (*br*, 5 *H*). From these data the compound **4** was obviously xanthochymuside (**4**).

Compound **7** (*Spicataside*). Yellow crystals, mp 235–238° (lit. [3] 232 ~ 233). The UV spectra (Table 1) was very similar to that of volkensiflavone. ν_{max}(KBr) 3350, 1070, 1040 (OH), 1643 (conj. CO), 1605, 1580, 1520 cm^{-1} (arom.). NMR (Me_2CO-d_6) was very similar to that of volkensiflavone except the signal of eleven protons of the sugar residue at δ 3·7–5·49. Hydrolysis with 10% HCl gave a yellow aglycone which was identified as volkensiflavone (**5**) by comparison with an authentic sample (TLC, PPC, IR and mmp). The sugar from the mother liquor was identified as D-glucose by PPC as above.

Acetylation gave a nonaacetate, mp 156–158° (EtOH), ν_{max}(KBr) 1760, 1200 (ester CO), 1680 (flavanone CO), 1650 (flavone CO). NMR showed four acetoxyl groups of glucose at δ 1·98–2·13 (12 H); five acetoxyl groups of volkensiflavone at δ 2·23–2·42 (15 H); seven protons of the glucose at δ 5·57 (*m*, 5 H) and 4·25 (*m*, 2 H); eleven aromatic protons at δ 7·88–6·55; H-2 and H-3 protons of the flavanone C-ring at δ 6·12 (*b*, 1 H) and 4·95 (*b*, 1 H). From the above data the compound J was suggested to be a volkensiflavone-glucoside, which was confirmed as spicataside (**7**) by comparison with an authentic sample (IR and mmp) by the courtesy of Professor Y. Ikeshiro.

Compound **8** (*Fukugiside*). Yellow crystals, mp 240–242° (lit. [2] 242 ~ 243), $[\alpha]_D^{20}$ +24·68, UV (Table 1). ν_{max} (KBr) 3300, 1070 (OH), 1645 (conj. CO), 1603, 1520 cm^{-1} (arom.). NMR (Me_2CO-d_6) was very similar to that of morelloflavone except the eleven protons of a glucose at δ 3·57–5·0 (*m*, 11 H). Hydrolysis with 10% HCl gave morelloflavone (**6**) (i.e. fukugetin) and glucose. Hence the compound is fukugiside (**8**).

EXPERIMENTAL

UV spectra were measured in MeOH and IR spectra as KBr discs. NMR spectra, unless otherwise stated, were determined for soln in deuteriochloroform. TLC was performed with Si gel G and preparative TLC with Kieselgel (PF_{254}).

Separation of the Fraction 4. Fraction 4 (1 g) was chromatographed on polyamide (nylon 66, 100 g) eluting with MeOH–H_2O (3:7) to give Fraction 4a (0·1 g), 4b (0·05 g) and 4c (0·25 g). Fraction 4c was then separated by preparative TLC (SiO_2) with $CHCl_3$–MeOH (17:3) gave Fraction $4c_1$ (yellow band, R_f 0·33) and $4c_2$ (yellow band, R_f 0·17). Recrystallization of each fraction (4a, 4b, $4c_1$ and $4c_2$) from Me_2CO–C_6H_6 yielded compounds (**3**) (92 mg), (**4**) (34 mg), (**7**) (57 mg) and (**8**) (110 mg) respectively.

Dehydrogenation of **3** *nonaacetate.* The nonaacetate of **3** (11 mg), NBS (2 mg), benzoylperoxide (1 mg) in CCl_4 (10 ml) were refluxed under irradiation for 2 min. The soln became brown. KOAc (20 mg) was added and the whole refluxed for 5 min, during which brown red colour faded. After removal of CCl_4 *in vacuo*, added H_2O gave a ppt, mp 154–157° (EtOH), which was identical with an authentic spicataside (**7**) nonaacetate (TLC, IR and mmp).

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PENTACYCLIC TRITERPENIC ACIDS: MICROMERIC ACID FROM *SALVIA HORMINUM*

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INTRODUCTION

The presence of triterpenes in some Salvia species has long been known. Ursolic and oleanolic acids were isolated from *S. officinalis* [1–5], *S. triloba* [6–8] and *S. apiana* [9], other triterpenes were obtained from *S. officinalis* [10–12] and *S. apiana* [9] and a new triterpene, anagadiol, was found in *S. broussonetti* [13].

*S. horminum** which grows in Turkey, has not been investigated until now. From the upper ground parts of the plant ursolic, oleanolic and micromeric acids were isolated. Although micromeric, ursolic and oleanolic acids have been found together in other plants of the Labiatae, micromeric acid is reported for the first time in *Salvia*. The acid was first isolated from *Micromeria benthami* [14] and later, was found in the leaves of *Rosmarinus officinalis* [15].

* The plant was identified by Prof. Dr. A. Baytop (Istanbul). A voucher sample ISTE 8032 is deposited in the Herbarium of Faculty of Pharmacy, University of Ist.

EXPERIMENTAL

Salvia horminum was collected from the Mediterranean coast of Turkey. The dried and powdered plant was extracted successively with light petrol and $CHCl_3$. The petrol extract was fractioned on neutral Al_2O_3(activity III) giving five triterpenoid