known glycosides were identified by co-chromatography with authentic markers and by hydrolytic studies, followed by identification of intermediates in the case of diglycosides. The glycoside **1**, a cream powder, mp 248–250°, from aq. EtOH, on acid hydrolysis gave kaempferol, glucose and rhamnose. The percentage of kaempferol in **1** was determined spectrophotometrically as 42% (39% required for a triglycoside). The glucose–rhamnose ratio was determined as 1:1.98 by GC of the sugar mixture, after trimethylsilylation. After complete methylation (Me_2SO_4, Me_2CO, K_2CO_3, 8 hr) of **1**, and acid hydrolysis, kaempferol 5-methyl ether was produced. This was identified by spectral and chromatographic comparison with a synthetic sample.

Enzymic hydrolyses were carried out in acetate buffers with β-glycosidase (emulsin) or with Sigma naringinase as a source of α-rhamnosidase. Partial acid hydrolysis was conducted on **1** with 1 M HCl at 100° for 2 min. The products were separated by PC in 15% HOAc and purified. They were analysed by co-chromatography, R_f determination, spectral measurements and by sugar analysis using both PC and GC. 2D-PC chromatograms were run in BAW followed by 15% HOAc.

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FLAVONOIDS IN THE BLACK RHIZOMES OF *BOESENBERGIA PANDURATA*

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Key Word Index—*Boesenbergia pandurata*; Zingiberaceae; black rhizomes flavonoids; flavonoid methyl ethers; flavanones.

Abstract—5-Hydroxy-7-methoxyflavanone, 5,7-dimethoxyflavanone, 5-hydroxy-7-methoxyflavone 5-hydroxy-7,4′-dimethoxyflavone, 5,7-dimethoxyflavone, 5,7,4′-trimethoxyflavone, 5,7,3′,4′-tetramethoxyflavone, 5-hydroxy-3,7-dimethoxyflavone, 5-hydroxy-3,7,4′-trimethoxyflavone, 3,5,7-trimethoxyflavone and 5-hydroxy-3,7,3′,4′-tetramethoxyflavone have been isolated from the black rhizomes of *Boesenbergia pandurata*.

INTRODUCTION

Following our previous work on constituents of the Zingiberaceae of Thailand [1, 2], the present report deals with the chemical constituents of the rhizomes of *Boesenbergia pandurata* (Roxb.) Schltr. (black rhizomes) (local name: krachai-dum) which is used in folk medicine for the treatment of colic disorders.

RESULTS AND DISCUSSION

The milled rhizomes of *B. pandurata* were extracted exhaustively with hexane in a Soxhlet apparatus. The crude extract was chromatographed on a column of Si gel using hexane–ether as eluants. Further purification by prep. TLC gave 5-hydroxy-7-methoxyflavanone (**1**), 5,7-dimethoxyflavone (**2**), 5-hydroxy-7-methoxyflavone (**3**), 5-hydroxy-7,4′-dimethoxyflavone (**4**), 5,7-dimethoxyflavone (**5**), 5,7,4′-trimethoxyflavone (**6**), 5,7,3′,4′-tetramethoxyflavone (**7**), 5-hydroxy-3,7-dimethoxyflavone (**8**), 5-hydroxy-3,7,4′-trimethoxyflavone (**9**), 3,5,7-trimethoxyflavone (**10**) and 5-hydroxy-3,7,3′,4′-tetramethoxyflavone (**11**). Compounds **1**–**11** were identified on the basis of their spectroscopic data and elemental analyses. Compound **5** has been isolated in pure form from a natural source and been fully characterized for the first time. Compounds **6** and **8** do not appear to have been found previously in nature.

It is interesting to note that even though the *B. pandurata* (black rhizomes) is a variation of *B. pandurata* (yellow rhizomes) [2, 3], their chemical constituents differ substantially. Three known flavonoids, **1**, 7-hydroxy-5-methoxyflavone and 5,7-dihydroxyflavone; two known chalcones, 2′,6′-dihydroxy-4′-methoxychalcone and 2′,4′-dihydroxy-6-methoxychalcone; and a new chromenoid chalcone derivative, boesenbergin A, have been isolated from the latter plant.

EXPERIMENTAL

A voucher specimen (BKF No. 73995) of the plant material has been lodged at the Forest Herbarium, Royal Forest Department,

Ministry of Agriculture, Bangkok, Thailand, ^{1}H NMR spectra were recorded in $CDCl_3$ with TMS as int. standard.

Extraction of the milled rhizomes of *B. pandurata* (2.0 kg) with hexane gave the crude material (61.0 g) and a portion of this extract (30.0 g) was chromatographed on Si gel (1.3 kg) using hexane–Et_2O as the eluting solvent to give **1**–**11** as powder (0.02, 0.12, 0.15, 0.25, 0.10, 2.00, 0.04, 3.89, 0.20, 1.22 and 0.04 g, respectively).

5-Hydroxy-7-methoxyflavone (**1**). Compound **1** was purified by prep. TLC with hexane–Et_2O (8:2) as the mobile phase, then crystallized from MeOH to give **1** as colourless plates, mp 99–101° (lit. mp 99–100°) [3]. (Found: C, 71.3; H, 5.4. Calc. for $C_{16}H_{14}O_4$: C, 77.1; H, 5.2%.) (Correct IR, ^{1}H NMR and UV spectra.)

5,7-Dimethoxyflavanone (**2**). Upon purification by repeated prep. TLC with hexane–Et_2O (8:2) as the mobile phase, then crystallization from aq. MeOH, **2** was obtained as colourless needles, mp 169–170° (lit. mp 159–160°) [4]. (Found: C, 71.8; H, 5.4. Calc. for $C_{17}H_{16}O_4$: C, 71.8; H, 5.6%.) (Correct IR, ^{1}H NMR and UV spectra.)

5-Hydroxy-7-methoxyflavone (**3**). Recrystallization of flavone **3** from $CHCl_3$–MeOH gave yellow needles, mp 172–174° (lit. 165–166°) [5]. (Found: C, 71.5; H, 4.6. Calc. for $C_{16}H_{12}O_4$: C, 71.6; H, 4.5%.) (Correct IR, ^{1}H NMR and UV spectra.)

5-Hydroxy-7,4′-dimethoxyflavone (**4**). Purification by prep. TLC with hexane–Et_2O (8:2) as the mobile phase and followed by crystallization from $CHCl_3$–MeOH gave flavone **4** as yellow needles, mp 177–179° (lit. 168°) [6]. (Found: C, 68.2; H, 4.7. Calc. for $C_{17}H_{14}O_5$: C, 68.5; H, 4.7%.) (Correct IR, ^{1}H NMR and UV spectra.)

5,7-Dimethoxyflavone (**5**). Recrystallization of **5** from hexane–$CHCl_3$ gave colourless needles, mp 149–150° (lit. oil, not pure)[7]. (Found: C, 72.3; H, 5.1. $C_{17}H_{14}O_4$ requires: C, 72.3; H, 5.0%.) IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1636, 1603. UV λ_{max}^{EtOH} nm (log ε): 262 (4.42), 307 (4.16). ^{1}H NMR: δ 3.92 (3H, *s*, 1 × OC<u>H</u>$_3$), 3.97 (3H, *s*, 1 × OC<u>H</u>$_3$), 6.38 (1H, *d*, *J* = 2.5 Hz, Ar<u>H</u>), 6.57 (1H, *d*, *J* = 2.5 Hz, Ar<u>H</u>), 6.65 (1H, *s*, ArCOC<u>H</u> = CAr), 7.48 (3H, *m*, 3 × Ar<u>H</u>), 7.88 (2H, *m*, 2 × Ar<u>H</u>). MS *m/z* (rel. int.): 282 (100), 254 (37), 236 (39), 224 (16), 209 (22), 108 (2), 150 (14), 102 (6).

5,7,4′-Trimethoxyflavone (**6**). Compound **6** was purified by prep. TLC using Si gel pretreated with oxalic acid as the adsorbent and $CHCl_3$–Et_2O (8:2) as the mobile phase and crystallized from $CHCl_3$–hexane to give a powder, mp 159–161° (lit. 154–155°) [8]. (Found: C, 69.0; H, 4.8. Calc. for $C_{18}H_{16}O_5$: C, 69.2; H, 5.2%.) IR ν_{max}^{nujol} cm^{-1}: 1640, 1603, 1465, 1350, 830. UV λ_{max}^{EtOH} nm (log ε): 264 (4.33), 324 (4.40). ^{1}H NMR: δ 3.85, 3.88, 3.93 (9H, all *s*, 3 × OC<u>H</u>$_3$), 6.35 (1H, *d*, *J* = 2.5 Hz, Ar<u>H</u>), 6.53 (1H, *d*, *J* = 2.5 Hz, Ar<u>H</u>), 6.55 (1H, *s*, ArCOC<u>H</u> = CAr), 6.98 (2H, *d*, *J* = 9.0 Hz, 2 × ArH), 7.81 (2H, *d*, *J* = 9.0 Hz, 2 × Ar<u>H</u>). MS *m/z* (rel. int.): 312 (23), 298 (4), 284 (10), 266 (13), 180 (2), 132 (27), 89 (27), 40 (100).

5,7,3′,4′-Tetramethoxyflavone (**7**). Purification by repeated prep. TLC with EtOAc–hexane–C_6H_6 (4:1:5) as the mobile phase, then crystallization from hexane–$CHCl_3$ to give **7** as a powder, mp 195–197° (lit. 192–194°) [9, 10]. (Found: C, 62.6; H, 5.7. Calc. for $C_{16}H_{18}O_6$: C, 62.7; H, 5.9%.) (Correct IR, ^{1}H NMR and UV spectra.)

5-Hydroxy-3,7-dimethoxyflavone (**8**). Compound **8** was purified by prep. TLC with hexane–Et_2O (4:1) as the mobile phase; further crystallization from $CHCl_3$–MeOH gave **8** as yellow needles, mp 129–130° [11]. (Found: C, 68.2; H, 4.9. Calc. for $C_{17}H_{14}O_5$: C, 68.5; H, 4.7%.) IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3000, 1649, 1598. UV λ_{max}^{EtOH} nm (log ε): 267 (4.45), 325 (4.06); + $AlCl_3$ + HCl 250 (4.24), 280 (4.42), 329 (4.16), 398 (3.89). ^{1}H NMR: δ 3.87 (6H, *s*, 2 × OC<u>H</u>$_3$), 6.37 (1H, *d*, *J* = 2.5 Hz, Ar<u>H</u>), 6.47 (1H, *d*, *J* = 2.5 Hz, Ar<u>H</u>), 7.50 (3H, *m*, 3 × Ar<u>H</u>), 8.08 (2H, *m*, 2 × Ar<u>H</u>), 12.53 (1H, *s*, O<u>H</u>). MS *m/z* (rel. int.): 298 (51), 269 (100), 255 (24), 239 (49), 225 (22), 77 (20).

5-Hydroxy-3,7,4′-trimethoxyflavone (**9**). Purification of **9** by prep. TLC with C_6H_6 as the mobile phase gave a solid which was crystallized from $CHCl_3$–MeOH to give yellow needles, mp 146–148° (lit. 145–147°) [12]. (Found: C, 65.8; H, 5.1. Calc. for $C_{18}H_{16}O_6$: C, 65.9; H, 4.9%.) (Correct IR, ^{1}H NMR and UV spectra.)

3,5,7-Trimethoxyflavone (**10**). Compound **10** was purified by repeated prep. TLC with hexane–Et_2O (4:1) as the mobile phase, then crystallized from $CHCl_3$–hexane, whereupon **10** was obtained as needles, mp 204–206° (lit. 199–200°) [13]. (Found: C, 69.8; H, 5.3. Calc. for $C_{18}H_{16}O_5$: C, 69.2; H, 5.1%.) (Correct IR, ^{1}H NMR and UV spectra.)

5-Hydroxy-3,7,3′,4′-tetramethoxyflavone (**11**). Compound **11** was purified by prep. TLC with C_6H_6 as the mobile phase, then crystallized from Et_2O–$CHCl_3$, whereupon **11** was obtained as yellow needles, mp 160–162° (lit. 160–161°) [14]. (Found: C, 64.0; H, 5.2. Calc. for $C_{19}H_{18}O_7$: C, 63.7; H, 5.1%.) (Correct IR, ^{1}H NMR and UV spectra.)

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