

FURTHER STUDIES OF FLAVONOIDS OF THE BLACK RHIZOMES

BOESENBERGIA PANDURATA

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Abstract

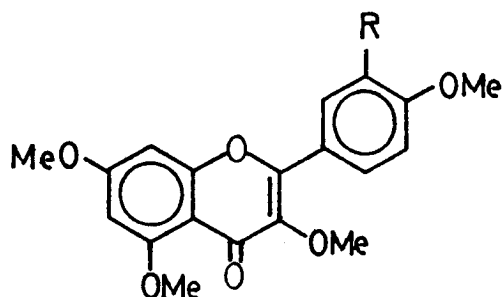
*From the black rhizomes of *Boesenbergia pandurata*, two rare flavones, 3, 5, 7, 3', 4' -pentamethoxyflavone and 3, 5, 7, 4' -tetramethoxyflavone, together with 5-hydroxy-7, 4' -dimethoxyflavanone and two chalcones, 2' -hydroxy-4', 6' -dimethoxychalcone and 2' -hydroxy-4, 4', 6' -trimethoxychalcone have been isolated.*

In continuation of our research on *Boesenbergia pandurata* (Roxb.) Schltr. (black rhizome)¹, we now report the isolation and identification of five additional compounds (1-5).

The milled rhizomes (2.0 kg) of *B. pandurata* were successively extracted in a Soxhlet with hexane and chloroform to give the crude hexane and chloroform extracts (61.0 and 101.5 g, respectively). A portion of the chloroform extract (50.0 g) was chromatographed on a silica gel column (1.5 kg) with gradients of hexane-CHCl₃ and CHCl₃-MeOH as eluents. Ten fractions were obtained. The second one (0.80 g, yellow solid) was further purified on preparative TLC with benzene-hexane (10:1) to give 2' -hydroxy-4', 6' -dimethoxychalcone (4) as a yellow solid (8 mg), 5-hydroxy-7, 4' -dimethoxyflavanone (3) as a slightly yellow solid (28 mg) and 2' -hydroxy-4, 4', 6' -trimethoxychalcone (5) as a yellow solid (28 mg). Preparative TLC of the third fraction (1.24 g, yellow semisolid) with benzene gave 3, 5, 7, 4' -tetramethoxyflavone (2) as a slightly yellow solid (0.29 g). The sixth fraction (9.0 g, yellow semisolid) was further chromatographed on a silica gel column (400 g) using a gradient of hexane-EtOAc as the eluting solvent to give 3, 5, 7, 3', 4' -pentamethoxyflavone (1) as a slightly yellow solid (2.02 g).

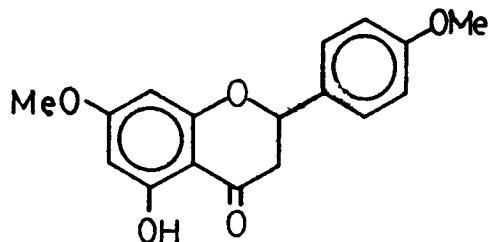
Compounds (1) - (5) were identified on the basis of their spectroscopic data and comparison with authentic specimens. In our case, authentic specimens were prepared from the phenolic derivatives previously isolated.¹ Flavones (1) and (2) do not appear to have been isolated from natural sources but they are known as synthetic products.^{2,3}

Analyses were carried out by Scientific and Technological Research Equipment Center, Chulalongkorn University, Bangkok, Thailand. Infrared spectra were obtained with a Jasco A-302 spectrophotometer. Ultraviolet spectra of ethanol solutions were

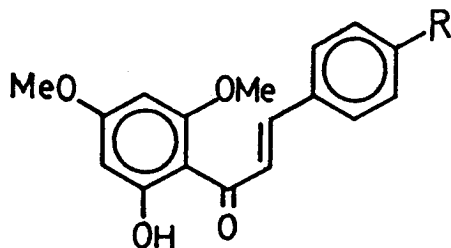


(1): R = OMe

(2): R = H



(3)



(4): R = H

(5): R = OMe

measured with a Jasco Uvidec-650 spectrophotometer. NMR spectra of CDCl_3 solutions were recorded with Varian EM 360L (60 MHz). Plates for thin-layer chromatography (TLC) or preparative thin-layer chromatography (prep. TLC) were prepared from Merck silica gel PF₂₅₄ and were activated by drying at 100° for 2 h.

3, 5, 7, 3', 4' -Pentamethoxyflavone (1): Compound (1) was crystallized from methanol as colorless needles, m.p. 160-161° (lit.² 152°). (Found: C, 64.2; H, 5.3. Calc. for $\text{C}_{10}\text{H}_{20}\text{O}_7$: C, 64.5; H, 5.4%). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1624, 1605, 1515, 1450, 1325, 1268, 1233, 1212, 1154, 1108, 815. UV $\lambda_{\text{max}}^{\text{EtOH}}$ (log ϵ): 340.4 (4.22), 300 (s) (4.11), 249.2 (4.23), 240 (s) (4.20). ¹HNMR: δ 3.90 (3H, s, OCH₃), 3.97 (12H, s, 4 × OCH₃), 6.33 (1H, d,

J 2.0 Hz, ArH), 6.50 (1H, d, J 2.0 Hz, ArH), 6.97 (1H, d, J 9.0 Hz, ArH), 7.73 (2H, m, 2×ArH). The IR, ¹HNMR spectra and TLC behaviour of the natural and synthetic products (1) were identical.

3, 5, 7, 4' -Tetramethoxyflavone (2): Compound (2) was crystallized from methanol as colorless rhombics, m.p. 167.5 - 168° (lit.⁴ 153°). (Found: C, 66.3; H, 5.2. Calc. for C₁₉H₁₈O₆: C, 66.7; H, 5.3%). IR $\nu_{\max}^{\text{Nujol}}$ cm⁻¹: 1620, 1595, 1450, 1370, 1244, 1205, 1005, 835, 820, UV $\lambda_{\max}^{\text{EtOH}}$ nm(log ϵ): 334.4(4.31), 300(s) (4.15), 264.4 (4.29), 255 (s) (4.25). ¹HNMR: δ 3.88 (9H, s, 3×OCH₃), 3.93 (3H, s, OCH₃), 6.28 (1H, d, J 2.0 Hz, ArH), 6.47 (1H, d, J 2.0 Hz, ArH), 6.97 (2H, d, J 8.0 Hz, 2×ArH), 8.03 (2H, d, J 8.0 Hz, 2×ArH). The IR, ¹HNMR spectra and TLC behaviour of the natural and synthetic products (2) were identical.

The fully methylated flavones (1) and (2) were prepared by treatment of 5-hydroxy-3, 7, 3', 4' -tetramethoxyflavone¹ and 5-hydroxy-3, 7, 4' -trimethoxyflavone¹ respectively, with Me₂SO₄/K₂CO₃, followed by purification by preparative TLC using benzene-EtOAc(7:3).

5-Hydroxy-7, 4' -dimethoxyflavanone (3): Compound (3) was crystallized from methanol as colorless needles, m.p. 117.5 - 119° (lit.⁵ 115.5 - 115.9°). (Found: C, 68.1; H, 5.5. Calc. for C₁₇H₁₆O₅: C, 68.0; H, 5.3%). (IR, ¹HNMR and UV spectra were consistent with the proposed structure).

2' -Hydroxy-4, 4', 6' -trimethoxychalcone (5): Compound (5) was crystallized from methanol as yellow rhombics, m.p. 115° (lit.⁶ 114-115°). (Found: M⁺, 314.1140. Calc. for C₁₈H₁₈O₅, 314.1153). (IR, ¹HNMR and UV spectra were consistent with the proposed structure).

The spectral data (IR, ¹HNMR, UV) of (4) were identical with those of the authentic sample.

Treatment of 2', 6' -dihydroxy-4' -methoxychalcone⁷ with MeI/K₂CO₃ in acetone at room temperature, followed by purification on preparative TLC using hexane-EtOAc (8:2), gave the authentic specimen (4).

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บทคัดย่อ

จากการสกัดและตรวจหาสูตรโครงสร้างของสารในหัวกระชายดำ (*Boesenbergia pandurata* (Roxb.) Schltr. (black rhizome)) พบสารเพิ่มอีก 5 ชนิด คือ 3, 5, 7, 3', 4' -pentamethoxyflavone, 3, 5, 7, 4' -tetramethoxyflavone, 5-hydroxy-7, 4' -dimethoxyflavanone, 2' -hydroxy-4', 6' -dimethoxychalcone และ 2' -hydroxy-4, 4', 6' -trimethoxychalcone.