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The Occurrence of Yangonin, 4-Methoxy-6-(*p*-methoxystyryl)-2-pyrone, in *Ranunculaceae*

Tamotsu SHIBATA,[1] Tsuyoshi SHIBUYA, and Kozo DOI
Department of Chemistry, Faculty of Science, Hirosaki University, Hirosaki

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Since the isolation of protoanemonin from the essential oil,[2] little is known about the constituents of *Ranunculus quelpaertensis* Nakai (Kitsunenobotan in Japanese), belonging to *Ranunculaceae*. Recently we have reinvestigated the extractive of stems and leaves of the plant, and have isolated and characterized the following substances as the constituents: fumaric, palmitic, and stearic acids from the acidic fraction, and a long-chain saturated hydrocarbons mixture containing C_{23}—C_{31}, stigmasterol, β-sitosterol, hexacontanol, unidentified C_{27}-alcohol, and yangonin,[3] 4-methoxy-6-(*p*-methoxystyryl)-2-pyrone, from the neutral fraction. As far as we know, yangonin had been isolated only from the root of *Piper methysticum* Forst.[3] (*Piperaceae*), and it is of interest from the stand of chemotaxonomy to occur also in *Ranunculaceae*. The details of the work will be described in the following section.

Experimental

All melting points are uncorrected. The IR spectra were determined as KBr pellets on a Hitachi model EPI-S spectrophotometer. The mass spectra[4] were taken on a Hitachi model RMU-7 mass spectrometer at 70 eV. Gas-liquid chromatographic analyses (glc) were made at 180—220°C, using a Yanagimoto model GCG-5DH apparatus with a hydrogen flame ionization detector (3 mm × 1.5 m column, 10% SE-30/Chromosorb W).

Extraction and Fractionation. Dried stems and leaves (4.2 kg) of the plant were ground and extracted with hot methanol, and the extract were evaporated *in vacuo* to give dark green residue, which was extracted again with ether. The ether solution was then fractionated into the hydrogen carbonate-soluble, carbonate-soluble, and neutral fractions. The former two fractions were extracted respectively with ether after acidifications.

The Hydrogen Carbonate-soluble Fraction. The ether extract was evaporated *in vacuo* to give crystalline residue, from which was isolated fumaric acid, colorless needles (80 mg), mp and mixed mp 284°C (sealed tube), after vacuum sublimation followed by recrystallization from ethanol.

The Carbonate-soluble Fraction. After evaporation of the solvent *in vacuo* followed by crystallization from ethanol, the ether extract afforded a mixture (120 mg) of palmitic and stearic acids, identification of which was made with glc of their methyl esters.

The Neutral Fraction. The *n*-hexane solution of the neutral fraction (22 g) was chromatographed through a column packed with alumina (200 g), an effluent (1200 m*l*) from the same solvent was collected, and the remain was recovered with methanol (1900 m*l*). The former effluent was evaporated *in vacuo* to give colorless crystals (10 g), mp 57—64°C, identified as a mixture of long-chain saturated hydrocarbons containing C_{23}—C_{31}, consisting of mainly C_{27} and C_{29}, from the comparison of glc with standard sample of hydrocarbons.[5] The fraction recovered with methanol, after evaporation *in vacuo*, deposited colorless leaflets (1.6 g), mp 146—148°C, from ethanol. The IR spectrum shows maxima at 970 and 959 cm^{-1}, and the mass spectrum two molecular ion peaks at *m/e* 414 and *m/e* 412. From the comparison of glc, this was proved to be a mixture of stigmasterol and β-sitosterol (2: 1).[6]

The fraction removed from the above sterols was chromatographed through a column packed with alumina (300 g) and developed with a mixed solvent of benzene and ether. An effluent from the system (benzene–ether (99:1)) afforded colorless crystals (10 mg) by recrystallization from methanol, mp 68.5—69.5°C, $\nu_{\max}$: 3250, 1053, 720, and 710 cm^{-1}. The mass spectrum indicates base peak at *m/e* 31 ($CH_2{=}O^{+}H$) and two molecular ion peaks at *m/e* 392.403 (Calcd for $C_{27}H_{52}O$: 392.402) and *m/e* 382.418 (Calcd for $C_{26}H_{54}O$: 382.417), indicative of a mixture of alcohols containing at least hexacontanol.

An effluent from the system (benzene–ether (97:3)) gave pale yellow prisms by recrystallization from ethanol, mp 152—

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[1] Present address: Aomori-kenritsu Aomori Nishi High School, Shinjo, Aomori.

[2] Y. Asahina and A. Fujita, *Acta Phytochim. Japan*, **1**, 1 (1922).

[3] W. Borsche and C. K. Bodenstein, *Ber.*, **62**, 2515 (1929) and previous papers. For the structure, see I. Chmielewska, J. Cieslak, K. Gorczynska, B. Kontnik, and B. Pitakowska, *Tetrahedron*, **4**, 36 (1958). J. D. BuLock and H. G. Smith, *J. Chem. Soc.*, **1960**, 502.

[4] We are indebted to Mr. H. Sato, Hitachi Seisakusho, for measurements of the spectra.

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153°C. Its mass spectrum shows peaks at *m/e* 258 (M^+) and *m/e* 230.092 (M^+–CO) (Calcd for $C_{14}H_{14}O_3$: 230.094), establishing its molecular formula, $C_{15}H_{14}O_4$. The IR spectrum indicates the presence of 2-pyrone ring (1720, 1624, and 1556 cm^{-1}), 1,4-disubstituted phenyl with conjugation (1602, 1575, 1512, 1176, 1110, 1025, 1000, and 827 cm^{-1}), and an extra *trans*-disubstituted ethylene (960 cm^{-1}). The spectral pattern resembles closely that of naturally occurring yangonin. In fact, this constituent showed no depression of mixed melting point with authentic sample.[7] The other mass spectral peaks at *m/e* 215(M^+–CO–CH_3), 202(M^+–2 × CO), 187(M^+–2 × CO–CH_3), 159(M^+–3 × CO–CH_3), 144(M^+–3 × CO– 2 × CH_3), are also compatible to the structure of yangonin.

An effluent from the system (benzene–ether (1:1)) afforded further a mixture of stigmasterol and β-sitosterol.

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