UNUSUAL OCCURRENCE OF FULVOPLUMIERIN, AN ANTIBACTERIAL PIGMENT, IN THE MARINE MOLLUSK *NERITA ALBICILLA*

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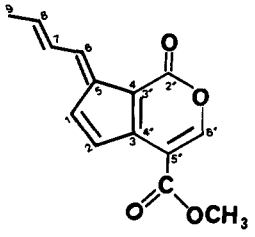
Marine mollusks have been reported to contain a wide variety of sterols and terpenes (1). Along with sterols and terpenes, they have also been shown to contain a number of other unusual compounds that may or may not have been acquired through dietary sources (2-5). In this communication, we report the isolation and identification of an antibacterial pigment, fulvoplumierin (6-8), from the snail *Nerita albicilla* L., which was also found to contain an unusually high concentration of benozic acid.



1

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were determined on a Fisher-Johns apparatus. Spectra were recorded on the following instruments: ir, Perkin-Elmer model 283; uv, Perkin-Elmer model 200; ^{1}H nmr and ^{13}C nmr, Nicolet NT-300 and Bruker WP-400; hplc, Waters Associates LC 1200 equipped with a 10μ silica gel cartridge in a Radial Compression Module model RCM 100 and a model 401 differential refractometer.

EXTRACTION AND ISOLATION.—The iPrOH extract of *N. albicilla* (organism identified by R.E. Schroeder), after concentration followed by lyophilization, gave a residue that was partitioned between hexanes, CCl_4, $CHCl_3$ versus increasing concentrations of MeOH in H_2O (9). The residue from the $CHCl_3$ layer, upon flash chromatography followed by hplc, gave compound **1** (0.001% of the iPrOH residue), which was recrystallized from C_6H_6 as orange needles, mp 150-151°. The uv spectrum (EtOH) of **1** showed absorptions at 272 and 365 mm, and the ir spectrum (CCl_4) exhibited bands at 1740, 1720, 1620 [γ-pyrones] (10), 1590, 1530, 1435 cm^{-1}. The molecular formula was established by hrms: $C_{14}H_{12}O_4$ (calcd. 244.073, found 244.075). The major ms fragments were found at *m/z* 212 ($C_{13}H_8O_3$, 22%), 156 ($C_{11}H_8O$, 39), 141 ($C_{11}H_9$, 39), 128 ($C_{10}H_8$, 100). ^{1}H nmr (400 MHz; δ, $CDCl_3$), 8.26 (1H, s, C6′-H), 7.94 (1H, d, J=11.8 Hz, C6-H), 7.30 (1H, d, J=5.2 Hz, C-2H), 7.20 (1H, d, J=5.2 Hz, C1-H), 6.83 (1H, dd, J=14.7, 11.8 Hz, C7-H), 6.54 (1H, dq, J=14.7, 7.0 Hz, C8-H), 3.89 (3H, s, -COOCH_3), 2.00 (3H, d, J=7.0 Hz, C9-H). ^{13}C nmr (75 MHz, ppm, $CDCl_3$): 163.61 (C-2′), 156.87 (-*C*OOCH_3), 155.98 (C-6′), 149.60 (C-4/3′), 144.90 (C-3/4′), 142.75 (C-2), 136.27 (C-5), 129.59 (C-6), 129.04 (C-5′), 126.77 (C-7), 112.68 (C-8), 109.35 (C-1), 51.48 (O*C*H_3), 19.00 (C-9). The ir, uv, ^{1}H-nmr spectral data matched with that reported for fulvoplumierin (6-8). The structure of **1** was finally confirmed by a direct comparison (mixed mp, ir, and ^{1}H nmr) of **1** with fulvoplumierin which was isolated from the roots of the plant *Plumeria rubra* by a method similar to that used for *N. albicilla*.

Details of isolation procedure and the spectral data are available on request to the senior author.

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FLAVONOIDS OF *PARIETARIA OFFICINALIS*

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The genus *Parietaria* (Urticaceae) comprises six species of which *Parietaria officinalis* L. is a medicinal plant (1,2). Previous chemical investigations indicated the presence of kaempferol-3-bioside and other unidentified flavonoids (3). This work is the first detailed report of flavonoids in the genus *Parietaria*.

The leaves and flowers of *P. officinalis* yielded ten flavonoids: the 3-glucosides and 3-rutinosides of quercetin, kaempferol and isorhamnetin, 3-sophorosides of quercetin and kaempferol, and 3-neohesperidosides of kaempferol and isorhamnetin.

EXPERIMENTAL

PLANT MATERIAL.—Flowering plants were collected in Poznań district, Poland. Voucher specimens are deposited at our department.

EXTRACTION AND ISOLATION.—Air-dried leaves and flowers (1000 g) were extracted five times with MeOH. Extracts were concentrated under reduced pressure, and the residue (145 g) was dispersed in hot H_2O. The H_2O-soluble portion was extracted with *n*-hexane, $CHCl_3$, Et_2O, EtOAc, and *n*-BuOH, successively. The two latter flavonoid-containing fractions (2.3 g and 8.0 g, respectively) were combined and chromatographed over a polyamide SC-6 column (100 g, 5×28.5 cm) with H_2O followed by an EtOH-H_2O gradient. Three fractions obtained were further separated on preparative polyamide 6D plates (20×20 cm) with $CHCl_3$-MeOH-methyl ethyl ketone, 9:4:2 (run twice). Bands were eluted with MeOH, and all individual compounds were finally purified over small Sephadex LH-20 columns in pure MeOH. Yields were low: 64 mg for quercetin-3-rutinoside, 20 mg for quercetin-3-sophoroside, 16 mg for isorhamnetin-3-neohesperidoside, and below 5 mg for the remaining compounds.

IDENTIFICATION OF THE FLAVONOIDS.—Flavonoids were identified by partial and total acidic hydrolysis, enzymatic hydrolysis, H_2O_2 oxidation, uv and ^{1}H-nmr spectroscopy (4,5), analysis of methylated sugars obtained from permethylated compounds, and tlc comparisons with authentic samples when available. Uv spectra were taken on a uv-Vis Specord (Zeiss, Jena) and ^{1}H-nmr spectra were recorded on a JEOL FX 90 Q.

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