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5-*O*-METHYLCYANIDIN 3-GLUCOSIDE FROM LEAVES OF *EGERIA DENSA*

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Egeria densa (Planch.) St. John has been described as producing a cyanidin diglucoside [1, 2]. However, we have found a new anthocyanin, 5-*O*-methylcyanidin 3-glucoside, in this species.

Detached leaves were immersed in 0.1 M sucrose soln and incubated at 24–26° for 4–5 days under continuous illumination (*ca* 4000 lx), whereupon they were tinged with red anthocyanin colour. The red leaves were dried over $CaCl_2$ *in vacuo* and extracted with 0.5% MeOH–HCl. The extract was purified by preparative PC. Bluish-purple needles (10 mg) were separated from the concentrated eluate.

Upon hydrolysis with 6N HCl, the anthocyanin gave glucose and a new aglycone (**1**) (R_f 0.65 in Forestal, 0.43 in HCOOH–HCl–H_2O (5:2:3)). A bathochromic shift by the addition of $AlCl_3$ (5% in EtOH) indicated the presence of an *o*-dihydroxylic B-ring. The absorption spectrum (in 0.01% MeOH–HCl) of **1** showed λ_{max} 272 and 534, and the ratio of $E_{440}/E_{vis\,max}$ was 14%, indicating that it is based on cyanidin.

Upon degradation with 2N NaOH, phloroglucinol monomethylether and protocatechuic acid were detected on TLC [3], suggesting that **1** is a monomethylcyanidin. Its fluorescence in UV-light suggested that the 5-hydroxyl was methylated [4]. This was confirmed by comparing the *Egeria*-aglycone with synthetic 5-*O*-methylcyanidin, when both compounds were identical in R_f and in visible and IR spectra.

The original anthocyanin was proved to be 3-monoglucoside of 5-*O*-methylcyanidin from the results of partial hydrolysis and H_2O_2-degradation. The new glucoside was also detected in a small amount from reddish spring shoots of *Egeria densa* and *Elodea Nuttallii* (Planch.) St. John.

EXPERIMENTAL

Plant material. Collected in early winter from the Botanical garden of Tokyo Kyoiku University.

ω-Hydroxy-3,4-diacetoxyacetophenone. A soln of ω-diazo-3,4-diacetoxyacetophenone (97 mg, synthesized from 3,4-diacetoxybenzoic acid chloride and CH_2N_2) in 50% HCOOH was stirred at room temp. for 30 min. After heating at 80° for 10 min., H_2O was added to the cooled reaction mixture. The EtOAc extract was dried, and evaporated to give pale yellow solids. Recrystallization from EtOH gave colorless needles (83.7 mg): mp 86–87° [5]; IR (ν_{max}^{KBr}) 3450 (br.), 1770, 1690, 1603 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 2.33 (6H, *s*), 4.86 (2H, *s*), 7.4–7.8 (3H).

Cyanidin 5-methyl ether. HCl was passed into a soln of 2,4-dihydroxy-6-methoxybenzaldehyde (34.5 mg) and ω-hydroxy-3,4-diacetoxyacetophenone (51.2 mg) in dry Et_2O (10 ml) on an ice bath for 90 min. The reaction mixture was stood overnight. The solids were thoroughly washed with Et_2O. The EtOH soln was poured into Et_2O and the red crystalline ppt. (24.1 mg) were collected; mp >300°, VIS (λ_{max}^{EtOH}) 537 nm, ($\lambda_{max}^{EtOH+AlCl_3}$) 571 nm; ν_{max}^{KBr} 3410, 3000 (br.), 1640, 1605, 1580, 1520, 1325, 1270, 1210 and 1038 cm^{-1}.

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