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Two Flavonol Glycosides from the Underground Parts of *Vancouveria hexandra*

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The genus *Vancouveria* (Berberidaceae) contains three species, *V. hexandra*, *V. chrysantha*, and *V. planipetala*, distributed along the Pacific coast of North America from northern Washington to central California. The genus is closely related morphologically to the genus *Epimedium*. In the course of our chemotaxonomic studies on *Epimedium*, the chemical constituents of the roots and rhizomes of *V. hexandra* were investigated. From the *n*-butanol soluble portion of a methanolic extract, two new flavonol glycosides were isolated. The glycosides were determined by chemical and spectral means to be anhydroicaritin 3-galactosyl (1→3) rhamnoside 7-glucoside and anhydroicaritin 3-[6-O-acetyl-galactosyl (1→3) rhamnoside] 7-glucoside.

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Structure Confirmation for an Unusual Flavanone from *Encelia stenophylla*

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Lately the first natural flavonoid with 3'-O-substituted B-ring has been reported, namely, 5,7,3'-trihydroxyflavanone, isolated from the leaf and stem exudate of *Encelia stenophylla* as a minor constituent. We deemed it very important to confirm the identity of this unusual product by synthesis. Condensation of 2-hydroxy-4,6-diisopropoxyacetophenone with 3-isopropoxybenzaldehyde gave 2'-hydroxy-3,4',6'-triisopropoxychalcone, which was led to a flavanone derivative by phosphoric acid in 2-methoxyethanol. Deisoprenylation of the resulting flavanone afforded the desired flavanone. All spectral data of the synthetic product are in accordance with those of the natural flavanone and we take it as granted, therefore, that 5,7,3'-trihydroxyflavanone from *Encelia* is the first flavonoid with 3'-O-substituted B-ring found in nature.

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Synthesis and Structure Confirmation of the Complex Flavonoids in *Pityrogramma calomelanos*

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From the farinose exudate of *Pityrogramma* species (Gymnogrammoideae), several compounds with a new C₆-C₃-C₆-C₃-C₆ skeleton (complex flavonoids) were isolated. These compounds have been reported to play an important role in the chemotaxonomy of the genus *Pityrogramma*. To confirm the structures of two complex flavonoids, 8-(3-phenylpropionyl)-5,7-dihydroxyneoflavanone [8-(3-phenylpropionyl)-5,7-dihydroxy-4-phenylchroman-2-one] and 8-(2-carboxyl-1-phenylethyl)-5,7-dihydroxyflavone δ -lactone were synthesized. The prepared complex flavonoids were well agreed with the natural ones after direct comparison.