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# TRIANGULARIN, A NEW CHALCONE FROM *PITYROGRAMMA TRIANGULARIS*

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**Key Word Index**—*Pityrogramma triangularis*, Adiantaceae; flavonoid exudate; chalcone; flavanone.

**Abstract**—2′,6′-Dihydroxy-4′-methoxy-3′-methylchalcone has been isolated from the exudate farina of the ceroptin chemotype of *Pityrogramma triangularis*. The analogous flavanone was also detected as a minor component in the extract.

## INTRODUCTION

Ferns of the genus *Pityrogramma* exude a colored waxy-flavonoid powder primarily on the abaxial side of fronds. Exudate colors which exist in a range of hues: bright white, pale yellow, greenish-yellow, golden-yellow, orange-yellow, orange and pink, often serve as a basis for taxonomic delimitation. To date, ten flavonoids have been identified in the exudates of five species: the flavonols galangin and izalpin from *P. chrysoconia* [1]; 3,5,7-trihydroxy-4′-methoxyflavone and 3,5-dihydroxy, 7-4′-dimethoxyflavone and pityrogrammin from *P. triangularis* [2]; rhamnocitrin, genkwanin and 2′,6′-dihydroxy-4,4′-dimethoxydihydrochalcone from *P. tartarea* [3]. This dihydrochalcone as well as 2′,6′-dihydroxy-4′-methoxydihydrochalcone were reported from *P. chrysophylla* var. *marginata* [4]. The latter is also the major exudate flavonoid of *P. calomelanos* [3]. A novel chalcone-like compound, ceroptin, was described from *P. triangularis* [5], and, to date, two chalcones 2′,6′-dihydroxy-4′-methoxychalcone and 2′,6′-dihydroxy-4, 4′-dimethoxychalcone have been reported from the orange exudate of *P. chrysophylla* var. *heyderi* [6] and the latter chalcone also from *P. calomelanos* [7].

In earlier work, we reported the existence of two exudate chemotypes of *Pityrogramma triangularis*, one in which kaempferol methyl ethers are the major components, and the other in which ceroptin is the primary constituent [2]. As part of a continuing study of *Pityrogramma* we report here a new chalcone from the ceroptin exudate chemotype of *P. triangularis*.

## RESULTS

Red prisms of the new chalcone crystallized spontaneously from a concentrated methanolic extract which had been washed with hexane and from which the crystalline ceroptin fraction was removed by filtration. These red crystals were identified, as 2′,6′-dihydroxy-3′-methyl-4′-methoxychalcone (which we name triangularin) on the basis of UV, NMR, and MS data. The UV spectrum in MeOH supports a chalcone structure for the compound [8]: $\lambda_{max}$: 240, 290 and 340 nm. The lack of a shift in Band II in NaOAc indicates that the A-ring 4′ position is substituted. A bathochromic shift of Band I in $AlCl_3$ relative to the MeOH spectrum of 30 nm (from 342 to 372 nm) suggests a free hydroxyl group at the 6′ position in the A-ring.

NMR data establish an unsubstituted B-ring; a multiplet at $\delta$ 6.85–7.75 integrating for 7 aromatic or vinyl protons, 5 of which can be assigned to the B-ring and two to the $\alpha$- and $\beta$- protons. One aromatic signal at $\delta$ 5.91 can be attributed to a proton at either C-3′ or C-5′. The C-methyl group which appears as a singlet at $\delta$ 1.96 can also be assigned to either C-3′ or C-5′. The methoxyl group at $\delta$ 3.77 is assigned to the A-ring 4′-position based upon a shift of 0.37 ppm in benzene relative to the spectrum in $CCl_4$. Two singlets of about 35% relative intensity adjacent to signals for the methoxyl and *C*-methyl groups, indicate that in $CCl_4$ the chalcone exists as a mixture of two isomers, i.e. the *cis*- and *trans*-forms of 2′,6′-dihydroxy-3′-methyl-4′-methoxychalcone.

A strong molecular ion at *m/e* 284 confirms the molecular formula of $C_{17}H_{16}O_4$. That the chalcone contains a 2′-hydroxyl group was confirmed by the fragmentation pattern since 2′-hydroxychalcones can isomerize at high temperature [9] to the flavanone and give flavanone fragment peaks, here found at *m/e* 180 (65%), 104 (51%), 207 (62%), and 152 (69%). Fragment peaks for the chalcone were at *m/e* 181 (48%), 131 (27%), 153 (37%), 137 (41%) and 283 (73%). Indeed, traces of the flavanone were present in all samples of triangularin, and could be separated by Si gel TLC as 5-hydroxy-6-methyl-7-methoxyflavanone, an expected cyclization product from the chalcone. The flavanone which was characterized by UV, and MS may be an artifact of the chalcone isolation procedure or a natural product [5, 7]; we propose that the chalcone is the natural product because the red crystals appeared spontaneously in the extract, but upon standing, particularly in solution, there was a slow conversion to the flavanone.

The demonstration of A-ring C-methylation in triangularin along with the C-methylated ceroptin and pityrogrammin further establishes the biosynthetic differentiation of the ceroptin chemotype from its cogeners which produce other flavonoid methyl ethers.

## EXPERIMENTAL

The new chalcone was isolated from the *Pityrogramma triangularis* exudate· deep red crystals from MeOH. $R_f$ 0.80 in

$CHCl_3$–MeOH–MeCOEt (12:2:1) on polyamide TLC; purple color on paper in UV light to purple with UV + $NH_3$; mp 192–196°. UV spectral data: $\lambda_{max}^{MeOH}$; 240*s*, 290*s*, 342 nm; $\lambda_{max}^{NaOMe}$: 298, 353 nm; $\lambda_{max}^{AlCl_3}$: 330*s*, 372 nm; $\lambda_{max}^{AlCl_3/HCl}$: 315*s*, 366 nm; $\lambda_{max}^{NaOAc}$: 290*s*, 342 nm; $\lambda_{max}^{NaOAc/H_3BO_3}$: 290, 352 nm. The flavanone was separated by Si/gel TLC, $C_6H_6$–EtOAc–$Me_2CO$ (8:1:1); $R_f$ 0.86; purple on paper over UV light, remaining purple with $NH_3$. UV data: $\lambda_{max}^{MeOH}$: 290, 340 nm; $\lambda_{max}^{NaOMe}$: 293, 355 nm; $\lambda_{max}^{AlCl_3}$: 222, 314, 385 nm; $\lambda_{max}^{AlCl_3/HCl}$: 225, 314, 385 nm; $\lambda_{max}^{NaOAc/H_3BO_3}$: 291, 335 nm. MS: *m/e* 284 ($M^+$; 100%); *m/e* 207 (62%), *m/e* 180 (65%), *m/e* 104 (51%) and *m/e* 152 (69%).

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# DIDYMOCARPIN, A NEW FLAVANONE FROM *DIDYMOCARPUS PEDICELLATA*

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**Key Word Index**—*Didymocarpus pedicellata*; Gesneriaceae; didymocarpin; 7-hydroxy-5,6,8-trimethoxyflavanone.

In continuation of our studies on the genus *Didymocarpus* [1–3], we further examined *D. pedicellata*, which elaborates a number of polymethoxylated chalcones, a flavanone and quinochalcones [4–7]. A new flavanone, didymocarpin, has now been isolated from the leaves of *D. pedicellata*, collected from the Western Himalayan regions [8]. It has been identified as 7-hydroxy-5,6,8-trimethoxyflavanone.

## EXPERIMENTAL

The dried powdered leaves of *D. pedicellata* were successively extracted with petrol (bp 60–80°), $C_6H_6$ and $CHCl_3$. The $C_6H_6$ extract on chromatography over Si gel furnished a compound crystallizing from petrol–$C_6H_6$ as pale yellow needles, mp 103–104°, $[\alpha]_D$ −12.8° ($c$ = 0.7, $CHCl_3$), $C_{18}H_{18}O_6$ ($M^+$ 330). The colour reaction (+ve Shinoda) coupled with the appearance of a double doublet ($C_2$-1H, 5.40 $\delta$, $J$ = 4 Hz) and a rough triplet ($C_3$-2H, 3.00 $\delta$) in the NMR spectrum confirmed the presence of a flavanone system. Functional group analysis revealed the presence of three OMe groups (3H-singlets at 4.17, 3.97, 3.90 $\delta$), a phenolic OH (1H-singlet at 5.57 $\delta$, exchangeable with $D_2O$; $\gamma_{max}^{KBr}$ 3430 $cm^{-1}$) and a conjugated $>C=O$ ($\gamma_{max}^{KBr}$ 1680 $cm^{-1}$). The IR spectrum disclosed a complex aromatic substitution pattern (1600, 1460, 1430, 1360, 1300, 1240, 1170 $cm^{-1}$) and an unsubstituted benzene [6] ring (710, 630 $cm^{-1}$). A 5H-singlet at 7.47 $\delta$ indicated the presence of five aromatic protons. The two peaks at *m/e* 253 ($M^+ - 77$; $M^+ - C_6H_5$) and at *m/e* 226 ($M^+ - 104$; $M^+ - C_6H_5$—$CH{=}CH_2$) corresponding to the loss of phenyl and styrene fragments respectively from the $M^+$ ion confirmed that the B-ring is unsubstituted. Didymocarpin exhibited two other fragments at *m/e* 211 (*m/e* 226–15; *m/e* 226–Me) and *m/e* 183 (*m/e* 211–28; *m/e* 211–CO). The ready solubility of the flavanone in aq. $Na_2CO_3$ [9] coupled with the UV spectrum [$\lambda_{max}^{EtOH}$ 282 (log ε 4.7) nm; $\lambda_{max}^{EtOH-0\ 1(N)NaOH}$ 296 (log ε 4.6) nm] showing a bathochromic shift of 14 nm suggested the presence of an —OH group in the 7-position of didymocarpin. The reduced activity of the 7-OH group towards NaOAc showing no bathochromic shift [$\lambda_{max}^{EtOH-NaOAc}$ 282 nm] of the maximum is presumably due to the presence of two oxygen substituents at 6 and 8 positions [10, 11]. The absence of a shift with $AlCl_3$ indicates that the 5-OH is methylated.

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