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SHORT COMMUNICATION

# FLAVONOIDS OF *BEILSCHMIEDIA MIERSII*

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**Abstract**—The occurrence of the rare quercetin 5-methyl ether, azaleatin, in the leaf of *Beilschmiedia miersii* has been confirmed; it is probably present as the 3-glucuronide. Other flavonoids in the leaf of this plant are quercetin 3-rhamnoside, quercetin 3-glucuronide and kaempferol 3-rhamnoside.

## INTRODUCTION

IN THE course of a survey of the Polycarpicae for flavonoids, Kubitzki and Reznik[1] noted, from a chromatographic study of leaf hydrolysates of fifty-two samples from thirty-three genera, the presence of azaleatin in only one member of the Lauraceae, *Beilschmiedia miersii* (Gay) Kosterm; together with quercetin, kaempferol and isorhamnetin. In view of the rarity in nature of azaleatin and related 5-*O*-methylated flavonoids[2] and of their taxonomic interest,[3] it seemed of some importance to confirm this finding by more rigorous procedures. A detailed study has therefore been made of the flavonoids in the leaf of this plant.

## RESULTS

Two-dimensional paper chromatography of leaf extract of *Beilschmiedia miersii* revealed the presence of five flavonoids with the usual dark brown colour in u.v. light of flavonol glycosides and a major component with blue to yellow green fluorescence characteristic of azaleatin derivatives. This derivative was unstable, and during purification by paper chromatography it was mostly converted to free azaleatin, which was readily identified by direct chromatographic and spectral comparison with authentic material. The instability of glycosidic links in azaleatin derivatives has previously been noted with the glycosides of azaleatin in *Eucryphia*[4] and, again in this case, has hindered full characterization. The glycoside in *Beilschmiedia* is different in $R_f$ from the known 3-rhamnoside, 3-glucoside or 3-galactoside of azaleatin. It gives glucuronic acid on acid hydrolysis and its $R_f$s, spectrum and colour reactions indicate that it is the 3-glucuronide.

Other leaf flavonoids of this plant were examined by standard procedures and two were readily identified as the commonly occurring 3-rhamnosides of quercetin and kaempferol. A third was identified as the 3-glucuronide of quercetin, an identification confirmed by direct

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comparison with material from *Phaseolus vulgaris* leaf.[5] Quercetin 3-glucuronide is rather uncommon, having been found previously only in *Euphorbia cyparissias* leaf (Euphorbiaceae)[6] *Vitis vinifera* fruit (Vitaceae),[7] *Populus grandidentata* leaf (Salicaceae)[8] and *Gaultheria miqueliana* leaf (Ericaceae).[9] With regard to the report of quercetin glucuronide in the last-named species, there has been some doubt about the position of attachment of the sugar residue. Re-investigation during the present work of the plant showed that it contains the 3-glucuronide, as in the case of all the other plants.

Although isorhamnetin was reported[1] as a constituent of *Beilschmiedia* during the preliminary survey, a more thorough examination of the flavonols formed on acid hydrolysis of leaf extracts failed to reveal this component. However, a further flavonoid, which was resistant to acid hydrolysis, was detected. This has not yet been identified, but preliminary observations suggest that it is a glycoflavone based on luteolin.

## EXPERIMENTAL

### *Plant Sources*

Leaves of *Beilschmeidia miersii* were collected by Dr. Otto Zoellner in Chile, near Quilpué, Prov. Valparaise, dried by him and airmailed to this country. Fresh leaves of *Phaseolus vulgaris* and *Gaultheria miqueliana* were available at the University Botanic Gardens, Ness.

### *Separation of Flavonoids*

Crushed leaf of *Beilschmiedia* was extracted overnight with 70% ethanol at room temp. The extract was washed with petrol. ether (X2), concentrated and chromatographed in butanol–acetic acid–water (4:1:5). The main flavonol bands were cut out, eluted and purified by successive paper chromatography in water and in butanol–ethanol–water (4:1:2·2).

### *Flavonoid Identifications*

Flavonoids were identified by comparison with authentic samples by u.v. spectral analysis and co-chromatography on paper in six solvents. The glycosides were further examined by acid and enzymic hydrolysis and by $H_2O_2$ oxidation (to confirm the attachment of sugar in the 3-position). Azaleatin was identified by comparison with material isolated from *Plumbago capensis*.[10] The azaleatin glycoside of *B. miersii*, the 3-glucuronide (?), had identical colour and spectral properties to azaleatin 3-galactoside and had $R_f$s of 0·26 in BAW and 0·32 in 15% HOAc (cf. azalein 0·56, 0·40 and azaleatin 3-galactoside, 0·40, 0·31). Quercetin 3-glucuronide was identified by comparison with material from *Phaseolus vulgaris*, as was the major flavonol glycoside in the leaf of *Gaultheria*. Identity in each case was confirmed by the rapid hydrolysis by glucuronidase to yield glucuronic acid and quercetin. $H_2O_2$ oxidation failed to yield any sugar, but this was due to the fact that glucuronic acid is attacked by this oxidizing agent. The unidentified flavonoid in *Beilschmiedia*, possibly a *C*-glycosylluteolin derivative, had $R_f$ 0·55 in BAW, 0·47 in PhOH and 0·32 in water (cf. quercetin 3-rhamnoside, 0·72, 0·53, 0·19; quercetin 3-glucuronide, 0·48, 0·19 and 0·17). In its spectral properties, it was identical with orientin, i.e. it had $\lambda_{max}$ at 257, 266 (sh) and 351 mn and gave the requisite shifts with alkali, $AlCl_3$, NaOAc and $H_3BO_3$.

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