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FLAVONOIDS OF *TOLMIEA MENZIESII**

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Key Word Index—*Tolmiea menziesii*; Saxifragaceae; kaempferol, quercetin and myricetin mono-, di- and triglycosides; flavonol glycoside gallate; chemotaxonomy; flavonoid variation.

Tolmiea is a genus in Saxifragaceae, tribe Saxifrageae, consisting of the single species *T. menziesii* (Pursh) T. & G. The plant is found in wet places in woods and along streams from southern Alaska to California [1]. *Tolmiea* is unique in its group of related genera in several ways: it has four petals instead of five; three stamens instead of five or ten; a form of vegetative reproduction characterized by the development of plantlets at the leaf bases; and a chromosome number of 2n = 28(2) instead of 2n = 14 as in other Heucheroid genera [3].

Published records of polyphenolic constituents of *Tolmiea* were reviewed by Hegnauer [4] who listed leucodelphinidin, myricetin and ellagic acid. It is the purpose of this note to describe the nature of flavonoid glycosides in this taxon as part of our study of the phenolics of the family.

The flavonoids of *Tolmiea* are based upon kaempferol, quercetin and myricetin; all glycosides are linked at position 3. The monosides consist of roughly equal mixtures of glucosides and galactosides plus smaller amounts of kaempferol and quercetin rhamnosides. A small amount of a compound was obtained which gave colour reactions characteristic of a myricedin-3-*O*-glycoside (UV, ammonia fumes, diphenylboric acid ethanolamine complex), but which had chromatographic behaviour reminiscent of the flavonol glycoside gallates seen in *Tellima* [5] and *Heuchera* [6, 7]. The compound was chromatographically identical to myricetin-3-*O*-glucoside-6″-gallate. This was confirmed by hydrolysis. No trace of either the kaempferol or the quercetin analogue was seen.

Kaempferol, quercetin and myricetin-3-*O*-rutinosides were the major constituents of the diglycoside fraction. The existence of quercetin-3-*O*-xylosylglucoside was indicated by means of partial and total hydrolyses. The position of attachment and stereochemistry of the outer sugar were not determined. The triglycoside fraction yielded kaempferol and quercetin as the only flavonoids and glucose, rhamnose and a trace of xylose as the sugars after acid hydrolysis. Rhamnose was present in larger amounts than was glucose. Chromatography of the mixture of glycosides against known kaempferol and quercetin 3-*O*-dirhamnosylglucosides (isolated from *Bensoniella oregona* [8]) showed good agreement. A trace of xylose-containing triglycoside was indicated but lack of material precluded any further work on the triglycoside fraction.

Six samples of *Tolmiea* were examined in this study, one in detail as described above, and five by means of TLC using the isolated compounds as standards. The six specimens showed no variation in the flavonoid patterns. This finding that the flavonoids represent a reliable set of characters is in agreement with observations on several species of related genera, e.g. *Tellima*, *Mitella* and *Heuchera* [9]. In the present study the sampling was small but represented, in the extreme case, sites that are separated by at least 500 miles.

Comparison of published data on flavonoid glycosides of Saxifragaceae, i.e. *Chrysosplenium* [10], *Elmera* [9], *Heuchera* [6, 7], *Jepsonia* [11], *Peltiphyllum* [12] and *Tellima* [13], along with unpublished results on *Boykinia*, *Leptarrhena*, *Saxifraga* and *Suksdorfia* shows that each genus possesses a unique combination of compounds. The flavonoid pattern of *Tolmiea* is such that it too can be distinguished from the other genera. Although the types of derivatives found in *Tolmiea* are seen in the other genera, the array is much simpler than in *Heuchera*, for example, where one finds mono-, di- and triglycosides based upon glucose, galactose, arabinose, xylose, rhamnose and various combinations of these. Similarly, in the case of flavonol glycoside gallate accumulation, *Tolmiea* is much simpler than either *Heuchera* [6, 7] or *Tellima* [5]. It seems possible that evolution of at least some of the herbaceous genera of Saxifragaceae was accompanied by an overall reduction in the diversity of flavonoids while the capacity for synthesis of the common pattern was retained [9].

EXPERIMENTAL

500 g fresh leaves, stems and flowers were obtained near bridal Veil Falls, Popkum, B.C. (BAB-1094). Smaller samples were collected from the following sites: Cape Perpetua Forest Camp, Lincoln Co., Oregon (RJG-0030); Grayback Forest Camp, Josephine Co., Oregon (RJG-0046); along Fall Creek 1.6 miles from Oregon Rt. 34, Lincoln Co., Oregon (BAB-1202); along Alsea River, beside U.S. Forest Service Rd. 1462, 1.0 mile from its junction with Oregon Rt. 34, Lincoln Co., Oregon; beside a stream at the north end of Spanish Banks, Vancouver, B.C. (BAB-1251). Vouchers are deposited in UBC.

Isolation and purification of compounds were done by procedures detailed in ref. [6]. Structure determinations were done using standard UV, ^{1}H NMR, hydrolytic, and co-chromatographic methods. All chromatographic comparisons were made using compounds whose structures had been determined by ^{1}H NMR. For the purpose of variation studies, 5 g quantities of dried plant material (without roots) were used. Solvent systems used were described by ref. [6].

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NEUE FLAVONE AUS *HETEROMMA SIMPLICIFOLIUM*

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Vertreter der südafrikanischen Gattung *Heteromma* (Tribus Astereae) sind bisher noch nicht untersucht worden. Wir haben daher zwei Arten, *H. decurrens* (DC.) O. Hoffm. und *H. simplicifolium* Wood et Evans, auf ihre Inhaltsstoffe untersucht. Beide Arten enthalten die C_{17}-Acetylenverbindungen **2** und **4**, während *H. decurrens* zusätzlich **1** und *H. simplicifolium* auch **3** ergibt. Aus *H. decurrens* isoliert man weiterhin neben Sesquiterpenkohlenwasserstoffen (**5–7**) die Triterpene **8–10** und aus den oberirdischen Teilen von *H. simplicifolium* drei Flavone, die offenbar nicht bekannt sind. Hauptinhaltsstoffe sind ein Penta- und ein Tetramethoxyflavonol.

Die Konstitutionen **11** und **12** folgen aus ihren ^{1}H-NMR-Daten und denen der durch Acetylierung erhaltenen Diacetate. Weiterhin zeigt die Verschiebung der UV-Maxima nach Zusatz von Aluminiumchlorid das Vorliegen einer freien 3-OH-Gruppe an. Da in dem NMR-Spektrum beider Flavone ein bei tiefen Feldern liegendes Singulett zu erkennen ist, muß weiterhin eine freie 5-OH-Gruppe vorliegen; die offenbar nicht von einer O-Funktion in 6-Stellung flankiert sein kann, da nach Acetylierung eine deutliche Tieffeldverschiebung des aromatischen Protons zu beobachten ist. Die Substitution am B-Ring folgt klar aus den NMR-Spektren (s. Tabelle 1).

Nur in sehr geringer Menge isoliert man schließlich noch ein weiteres Flavonol, dem offenbar die Struktur **13** zukommt, da nach Acetylierung neben dem 6-H nur das 5′-H zu tieferen Feldern verschoben wird. Bei der Benennung der drei Flavonole haben wir das Izalpinin (3,5-Dihydroxy-7-methoxyflavon) zu grunde gelegt.

Die Wurzeln der ebenfalls südafrikanischen *Microglossa mespilifolia* (Less) B. L. Robinson (Tribus Astereae) enthalten wieder **1** und **2** sowie *epi*-Friedelinol (**16**), während die oberirdischen Teile neben Linolensäure nur **5** ergaben.

Die isolierten Inhaltsstoffe deuten auf eine enge Beziehung der Gattungen *Heteromma* und *Microglossa* mit *Nidorella* [2] und *Myriactis* [1] hin, da in der Tribus nur in diesen Gattungen Verbindungen vom Typ **1–4** beobachtet wurden und für fast alle anderen Gattungen

Tabelle 1. ^{1}H-NMR-Daten von **11–15** ($CDCl_3$, 270 MHz, TMS als innerer Standard)

	11	**12**	**13**	**14**	**15**
6-H	*s* 6.43	*s* 6.43	*s* 6.43	*s* 6.79	*s* 6.79
2′-H	*d* 7.77	*s* 7.47	*d* 7.77	*s* 7.46	*d* 7.80
5′-H	*d* 7.03	—	*d* 7.07		*d* 7.18
6′-H	*dd* 7.81	*s* 7.47	*dd* 7.73	*s* 7.46	*dd* 7.75
OMe	*s* 4.03	*s* 4.02	*s* 4.01	*s* 4.03	*s* 3.98
	s 3.99	*s* 3.97	*s* 3.99	*s* 3.97	*s* 3.90
	s 3.98	*s* 3.95	*s* 3.88	*s* 3.95	*s* 3.83
	s 3.90	*s* 3.95		*s* 3.95	
		s 3.91		*s* 3.85	
OH	*s* 12.43	*s* 12.35	*s* 12.41	—	—
OAc	—	—	—	*s* 2.42	*s* 2.45
				s 2.39	*s* 2.37
					s 2.35

J(Hz): 2′,6′ = 2; 5′,6′ = 8.