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FLAVONOIDS OF *WYETHIA* SECTION *AGNORHIZA*

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Key Word Index—*Wyethia elata*; *W. ovata*; *W. reticulata*; *W. scabra*; *W. invenusta*; *Balsamorhiza*; Compositae; Heliantheae; flavonoids; 6-methoxyorobol 7-methyl ether.

Abstract—Five species of *Wyethia* section *Agnorhiza* were examined for external leaf flavonoids. Twenty flavonoids, including a new natural product, 6-methoxyorobol 7-methyl ether, were isolated. The systematics of the group are discussed briefly.

INTRODUCTION

As part of a chemical and morphological study of the related genera *Balsamorhiza* and *Wyethia* (Compositae, Heliantheae) [1–3], the leaf surface flavonoids of *Wyethia* section *Agnorhiza* were examined. Current separation of the two genera is based primarily on the degree of stem leafiness; species of *Wyethia* have better developed cauline leaves than *Balsamorhiza*. Chemically, species of *Wyethia* produce prenylated flavanones, dihydroflavanols, isoflavones and methylated flavones and flavonols, while *Balsamorhiza* species synthesize only simple flavonols and flavones [1–5].

The taxonomic history of *Wyethia* section *Agnorhiza* has been somewhat controversial. Two of the presently included species, *W. bolanderi* and *W. invenusta*, were previously placed by Sharp [6] in *Balsamorhiza* because they possess epappose achenes. Later, both species were removed from *Balsamorhiza* [7] and placed in *Wyethia* section *Agnorhiza* due to similarities of morphology and range restrictions. At present, *Agnorhiza* is largely characterized by species with basal leaves which are absent or smaller than the cauline leaves. Five of the six species in section *Agnorhiza*, *W. ovata*, *W. bolanderi*, *W. elata*, *W. invenusta* and *W. reticulata*, are California endemics, restricted to small ranges along the western slope of the Sierra Nevada or San Jacinto Mts *W. scabra* has a much larger range, occurring in desert areas from Utah to northern Arizona and New Mexico. The flavonoid chemistry of *W. bolanderi* was reported previously [1]. We report here on the leaf surface flavonoids of the remaining five species.

A total of 24 compounds were isolated from dichloromethane leaf washes of the six species in section *Agnorhiza*. The distribution of specific compounds is shown in Table 1. *W. bolanderi* produced only methylated flavonols [1]. *W. elata* yielded a dihydroflavonol, a methylated flavone and methylated flavonols. *W. reticulata* and *W. ovata* were both characterized by isoflavones and methylated flavonols. *W. invenusta* and *W. scabra* both produced isoflavones, prenylated flavanones and methylated flavonols.

One of the compounds isolated from *W. reticulata*, **4**, is a new natural product. It appeared dark under UV light indicating that there was a hydroxyl at the 5-position. No change in colour was noted after fuming with ammonia or after spraying with Naturstoffreagenz A (NA) solution. An isoflavone skeleton was suggested by a major absorbance at 269 nm and the appearance in the ^{1}H NMR spectrum of a one-proton singlet at 8.15 ppm. The mass spectrum of **4** had a molecular ion at *m/z* 330 requiring three hydroxyl groups and two methoxyl groups. A B_1 fragment at *m/z* 134 supported a B-ring with two hydroxyl groups. An $[A_1 + 1]$ fragment at *m/z* 193 was consistant with the A-ring having two methoxyls and one hydroxyl group. The large [M − 15] fragment supported a 6-methoxyl group. A one-proton singlet at 6.55 ppm which was consistant with an H-8 supported the assignment of the methoxyl to the 6-position. On the basis of the spectral data, **4** was identified as 6-methoxyorobol 7-methyl ether.

Section *Agnorhiza* exhibits quite a variable flavonoid distribution. The most characteristic compounds for the genus *Wyethia*, prenylated flavanones and isoflavones, are absent from some members of section *Agnorhiza*. A preliminary examination of additional species of *Balsamorhiza* indicate that, like *B. macrophylla* [1], they produce only simple flavonols and flavones. A cladistic analysis of *Wyethia* using the available flavonoid and morphological data, and using *Balsamorhiza* as an outgroup, suggests that the lack of isoflavones and/or prenylated flavanones in some members of *Agnorhiza* is due to secondary losses of their ability to synthesize these types of compound.

EXPERIMENTAL

Plant material. *Wyethia elata* was collected on 25 June 1984, north of Ahwahnee, Mariposa Co., California (Robson No. 8422). *W. ovata* was colledted on 15 July 1984, Lake Hemet, Riverside, Co., California (Robson No. 8429). *W. reticulata* was collected on 27 June 1984, Rescue, El Dorado Co., California

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Table 1. Distribution of flavonoids in *Wyethia* section *Agnorhiza*

	Flavonoid	Bol	Ela	Inv	Ova	Ret	Sca
1	Orobod 7methyl ether	−	−	+	+	+	+
2	Orobol 3′-methyl ether	−	−	+	−	−	+
3	Orobol 7,3′-dimethyl ether	−	−	+	+	−	−
4	6-Methoxyorobol 7-methyl ether	−	−	−	−	+	−
5	6-*C*-Prenyl naringenin	−	−	+	−	−	−
6	8-*C*-Prenyl naringenin	−	−	−	−	−	+
7	6-*C*-Prenyl eriodictyol	−	−	+	−	−	−
8	8-*C*-Prenyl eriodictyol	−	−	−	−	−	+
9	Eriodictyol	−	−	+	−	−	−
10	Dihydrokaempferol	−	+	−	−	−	−
11	Jaceidin (quercetagetin 3,6,3′-triMe)	+	+	+	−	−	−
12	Axillarin (quercetagetin 3,6-diMe)	+	+	+	−	+	−
13	Spinacetin (quercetagetin 6,3′-diMe)	−	−	+	−	−	−
14	Isorhamnetin	+	−	+	−	−	−
15	Quercetin 3-methyl ether	+	−	+	−	−	−
16	Kaempferide (kaempferol 4′-Me)	+	−	−	−	−	−
17	Isokaempferide (kaempferol 3-Me)	+	−	−	−	−	−
18	Ermanin (kaempferol 3,4′-diMe)	+	−	−	−	−	−
19	3,6-Dimethoxy apigenin	+	+	−	−	−	−
20	Santin (kaempferol 6-methoxy 3,4′-diMe)	+	−	−	−	−	−
21	6-Methoxy kaempferol	+	+	−	+	−	+
22	6-Methoxy apigenin	−	+	−	−	−	−
23	6-Methoxy luteolin	−	−	−	−	+	−
24	Chrysoeriol	−	−	−	+	−	−

Bol = *W. bolanderi*; Ela = *W. elata*; Inv = *W. invenusta*; Ova = *W. ovata*; Ret = *W. reticulata*; Sca = *W. scabra*.

(Ayres and Robson No. 8423). *W. invenusta* was collected on 11 July 1984, Alta Sierra, Kern Co., California (Robson No. 8428). *W. scabra* var *attenuata* was collected 17 July 1984, north of Kenab, Kane Co., California, (Robson No. 8431). Voucher specimens are deposited in the University of British Columbia Herbarium.

Extraction and Separation. Leaves (30 g) of each species were treated in the same fashion. The air-dried leaves were washed several times with CH_2Cl_2. The combined extracts were dried under red. pres. and then chromatographed over Polyclar columns using CH_2Cl_2–MeOH (3:1) and increasing amounts of MeOH. Fractions from this column were separated further on polyamide TLC using toluene–petrol (80–100°)–MeCOEt–MeOH (12:6:2:1) and/or toluene–MeCOEt–MeOH (12:5:3). Isolated compounds were cleaned over Sephadex LH-20 columns prior to spectral analysis. Individual compounds were identified on the basis of UV, MS, ^{1}H NMR and co-chromatography with standard compounds when available.

6-Methoxyorobol 7-methyl ether. UV MeOH (nm): 269, 296 sh, 344 sh; + NaOMe 340 sh, 270. EIMS (probe) 70 eV, *m/z*, rel. int.: 330 $[M]^+$ (87), 315 $[M - Me]^+$ (100), 197 $[A_1]^+$ (4), 181 $[A_1 - Me]^+$ (12), 153 $[A_1 - Me - CO]^+$ (69), 134 $[B_1]^+$ (75). ^{1}H NMR (90 MHz, TMS ether, CCl_4): 8.15 (1 H, *s*, H-2), 6.9–7.1 (3 H, *m*, H-2′, 5′, 6′), 6.55 (1 H, *s*, H-8), 3.93 (3 H, *s*, 7-OMe), 3.83 (3 H, *s*, 6-OMe).

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