Phytochemistry, Vol. 24, No. 9, p. 2133, 1985.
Printed in Great Britain.

0031-9422/85 $3.00 + 0.00
Pergamon Press Ltd.

METHYLATED FLAVONOLS FROM *WYETHIA BOLANDERI* AND *BALSAMORHIZA MACROPHYLLA*

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(*Received* 14 *September* 1984)

Key Word Index—*Wyethia bolanderi*; *Balsamorhiza macrophylla*; Compositae; Heliantheae; methylated flavonols.

Abstract—A leaf wash of *Wyethia bolanderi* afforded eight known methylated flavonols: santin, ermanin, jaceidin, 3,6-dimethoxyapigenin, kaempferide, isokaempferide, axillarin and quercetin 3-methyl ether. A leaf wash of *Balsamorhiza macrophylla* afforded six known methylated flavonols: centaureidin, quercetin 3,4'-dimethyl ether, axillarin, spinacetin, tamarexetin and quercetin 3-methyl ether. The chemotaxonomy of the two genera is discussed briefly.

As part of a chemical and morphological study on the related genera *Wyethia* and *Balsamorhiza* (Compositae, Heliantheae), the leaf surface flavonoids of *Wyethia bolanderi* (A. Gray) W. Weber and *Balsamorhiza macrophylla* Nutt. were examined. Separation of the two genera has largely rested upon the degree of stem leafiness.

The taxonomic history of *W. bolanderi* has been one of controversy. The species was placed in *Balsamorhiza* by Sharp [1] because of its epappose achenes. Weber, in a 1946 revision of the genus [2], placed it in *Wyethia* section *Agnorhiza*. His justification for this treatment was based on similarities of morphology and range restrictions. *Wyethia bolanderi*, like the five other species in the section, has cauline leaves but lacks true basal leaves. The lowermost leaves originate from the bases of the annual flowering shoots and not directly from the perennial underground stems that form at the apex of the taproot. All other species of both genera possess both basal and cauline leaves although the cauline leaves of *Balsamorhiza* are reduced. Of the six species placed in section *Agnorhiza*, five, including *W. bolanderi*, are California endemics.

Both members of *Wyethia* section *Alarconia*, *W. glabra* [3] and *W. helenioides* [4], produce isoflavones and prenylated flavanones. A preliminary examination of *W. angustifolia*, and other species in section *Wyethia*, indicates that the section produces similar isoflavones and prenylated flavanones.

Balsamorhiza macrophylla is placed in section *Balsamorhiza*. The six species in the section have pinnately toothed or divided basal leaves and a single pair of reduced, opposite cauline leaves. A preliminary flavonoid survey of *Balsamorhiza* suggests that the genus does not produce prenylated flavanones.

We report here the isolation and identification of eight methylated flavonols from a dichloromethane leaf wash of *W. bolanderi*: santin, ermanin, jaceidin, 3,6-dimethoxyapigenin, kaempferide, isokaempferide, axillarin and quercetin 3-methyl ether. A leaf wash of *B. macrophylla* afforded six quercetin and quercetagetin derivatives: centaureidin, quercetin 3,4'-dimethyl ether, axillarin, spinacetin, tamarexetin and quercetin 3-methyl ether. The absence of prenylated flavanones in *Wyethia bolanderi* suggests that the species may be chemically more closely related to members of *Balsamorhiza* than to members of *Wyethia*.

EXPERIMENTAL

Plant material. Leaves of *Wyethia bolanderi* were collected on May 1, 1984, 4.2 km W of Dobbins, California, Yuba Co. (voucher in UBC, Bohm#1786). Leaves of *Balsamorhiza macrophylla* were collected July 21, 1984 in Tony Grove, Cache National Forest, Cache Co., Utah (voucher in UBC, Robson & Barkworth, #8434).

Extraction and separation. Collections of *Wyethia bolanderi* (39 g) and *Balsamorhiza macrophylla* (19 g) were treated in the same fashion. Leaves were extracted with CH_2Cl_2 several times. The combined extracts were dried under red. pres. and chromatographed over a Polyclar AT column using CH_2Cl_2–MeOH (3:1) and increasing amounts of MeOH. Fractions from this column were further separated on polyamide TLC using toluene–petrol (bp 80–100°)–MeCOEt–MeOH (60:30:10:5) or toluene–MeCOEt–MeOH (60:25:15). Compounds were cleaned over LH-20 (MeOH) prior to spectral analysis. The flavonoids isolated from *W. bolanderi*, santin (25 mg), jaceidin (30 mg), ermanin (30 mg), 3,6-dimethoxy apigenin (60 mg), kaempferide (10 mg), isokaempferide (50 mg), axillarin (30 mg) and quercetin 3-methyl ether (30 mg), were identified using UV, MS and ^{1}H NMR techniques. The flavonoids isolated from *B. macrophylla*, centaureidin (12 mg), quercetin 3,4'-dimethyl ether (5 mg), axillarin (8 mg), spinacetin (5 mg), tamarixetin (8 mg) and quercetin 3-methyl ether (5 mg), were identified using UV, MS and, when sufficient quantities were present, ^{1}H NMR techniques.

Acknowledgements—This work was supported by operating and equipment grants from the Natural Science and Engineering Research Council of Canada. We would like to thank Mr. Felipe Balza for recording the mass spectra.

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