Flavonoids from the Leaf Resin of *Hymenoclea salsola* T. & G. (Asteraceae)

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Hymenoclea salsola (Asteraceae), a dominant shrub of the desert areas of California and Baja California, Mexico, secretes high amounts of resin on the leaf surface. Chemical analysis of the resin revealed the presence of a complex mixture of flavonoid aglycones. Among the compounds identified is the rare 2′,4′,6′-OH chalcone, previously not known to occur in the Asteraceae.

Introduction

Hymenoclea salsola T. & G. (Asteraceae, tribe Heliantheae) [1] is a dominant shrub of the Colorado and Mohave deserts of California [2] and the Sonoran desert of Baja California, Mexico [3]. Previous phytochemical analysis of *H. salsola* had indicated the presence of sesquiterpene lactones [4, 5].

In continuation of our phytochemical studies of resin secretions of arid land plants from California and Mexico, we report the flavonoid composition of the complex leaf resin of *H. salsola.*

Materials and Methods

Hymenoclea salsola was collected in March 1982 in the Anza Borrego desert, California, which forms part of the Colorado desert. A voucher specimen is on file in the UCI-herbarium. The phenolic leaf resin was extracted by dipping the leaves and stems in MeOH for about 30 s, yield of the crude resin was 10% of the dry weight. The resin (approximately 1 g) was chromatographed on a Sephadex LH-20 column (40×2.5 cm), eluted with MeOH. Fractions of 25 ml were collected and monitored on Polyamide TLC plates (Polyamide-DC 6, Macherey & Nagel), solvent system: benzene/MEK/MeOH/H_2O (55 : 22 : 20 : 3 v/v) and viewed under UV_{366}. Similar fractions were combined. Further purification was achieved by repeated preparative TLC on microcristalline Cellulose (Macherey & Nagel), solvent system: CH_3COOH/H_2O (40 : 60 v/v) and on Polyamide DC-6 with the described solvent system. The isolated compounds were purified on Sephadex LH-20, eluted with MeOH. UV spectra were recorded in MeOH according to standard procedures [6]. Compounds 1–13 (Fig. 1) were cochromatographed with authentic standards on Polyamide-DC 11 (Macherey & Nagel) solvent system: toluene/MEK/MeOH (60 : 25 : 15 v/v) [7].

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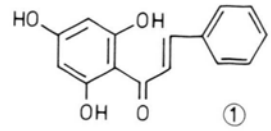
Results and Discussion

The needle like leaves of *Hymenoclea salsola* are covered by a thick film of resin which comprises up to 10% of the dry weight. Light microscopic analysis of the leaves showed the presence of yellow stained glandular trichomes which are probably involved in the secretion of the resin. The trichomes could only be observed after the resin had been rinsed off the leaves with MeOH.

Analysis of the leaf resin, which was obtained by dipping the leaves and stems in MeOH, indicated a complex mixture of flavonoid aglycones. By a combination of different chromatographic methods we were able to isolate the flavonoids 2′,4′,6′-OH chalcone (**1**), eriodictyol (**2**), chrysin (**3**), apigenin (**4**), luteolin (**5**) and luteolin 3′-methylether (**6**) and seven methylated flavonols of the quercetin type (**7**–**13**) (Fig. 1). The isolated flavonoids were identified by their UV-spectra, comparison with published data [6, 8, 9] and by cochromatography with authentic standards on Polyamide TLC plates. The 2′,4′-6′-OH chalcone (**1**) has so far only been found twice in nature, in the bud excretion of *Populus* spp. (Salicorniaceae) [10] and in the farinose exudate on fronds of *Adiantum sulphureum* (Polypodiaceae) [11]. This is the first report on the occurrence of this compound in the Asteraceae.



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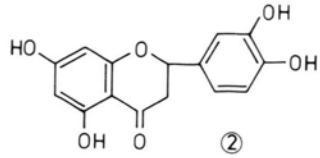

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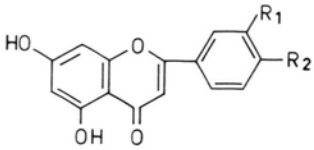
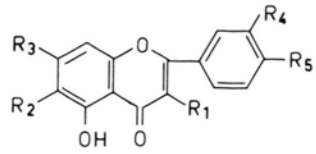


③ $R_{1,2} = H$
④ $R_1 = H$, $R_2 = OH$
⑤ $R_{1,2} = OH$
⑥ $R_1 = OMe$, $R_2 = OH$



⑦ $R_{1,3,4,5} = OH$, $R_2 = H$
⑧ $R_1 = OMe$, $R_2 = H$, $R_{3,4,5} = OH$
⑨ $R_{1,4,5} = OH$, $R_2 = H$, $R_3 = OMe$
⑩ $R_{1,3,5} = OH$, $R_2 = H$, $R_4 = OMe$
⑪ $R_{1,4} = OMe$, $R_2 = H$, $R_{3,5} = OH$
⑫ $R_{1,3} = OMe$, $R_2 = H$, $R_{4,5} = OH$
⑬ $R_{1,2,5} = OMe$, $R_{3,4} = OH$

Fig. 1. Structures of resin flavonoids isolated from *Hymenoclea salsola* (Asteraceae).

Flavonoids seem to be common constituents of external leaf resins of desert dominants in the Asteraceae (P. Proksch and E. Rodriguez, unpublished), but they also occur in members of other families growing under arid environmental conditions, like *Larrea tridentata* (Zygophyllaceae) [12]. The high yields of the secreted resins, often in the range of 10–20% of the dry weight, suggest important physiological functions which probably include the reduction of water loss through cuticular transpiration [13] and shielding against harmful UV radiation [14]. Recent experiments have shown that several flavonoid aglycones, including compounds **2, 5** and **7** (Fig. 1), act as feeding repellents against the insect *Heliothis zea* when added to artificial diets [15], indicating that common found flavonoid resin compounds may play an important role in plant animal interactions [13, 16].

Acknowledgements

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[1] T. F. Stuessy, The Biology and Chemistry of the Compositae, p. 621 (V. H. Heywood, J. B. Harborne, B. L. Turner eds.), Academic Press, London 1977.
[2] W. L. Jepson, A Manual of the Flowering Plants of California, p. 1108, University of California Press, Berkeley 1966.
[3] I. L. Wiggins, Flora of Baja California, p. 244, Stanford University Press, Stanford 1980.
[4] T. A. Geissman and F. P. Toribio, Phytochemistry, **6,** 1563 (1967).
[5] F. P. Toribio and T. A. Geissman, Phytochemistry, **7,** 1623 (1968).
[6] T. J. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Springer Verlag, Berlin 1970.
[7] E. Wollenweber, The Flavonoids: Advances in Research, p. 189 (J. B. Harborne and T.J. Mabry eds.), Chapman and Hall, London 1982.
[8] M. Jay, J.-F. Gonnet, E. Wollenweber, and B. Voirin, Phytochemistry, **14,** 1605 (1975).
[9] E. Wollenweber and K. Egger, Tetrahedron Lett., **1970,** 1601
[10] E. Wollenweber, Biochem. Syst. Ecol. **3,** 35 (1975).
[11] E. Wollenweber, Flora **168,** 138 (1979).
[12] M. Sakakibara, D. Difeo, N. Nakatani, B. Timmermann, and T. J. Mabry, Phytochemistry **15,** 727 (1976).
[13] E. Rodriguez, Plant Resistance to Insects, **Vol. 208,** p. 291 (P. A. Hedin ed.), American Chemical Society, Washington D.C. 1982.
[14] M. Caldwell, Photophysiology, **Vol. 6,** p. 131 (A. C. Giese, ed.), Academic Press, London 1971.
[15] C. A. Elliger, B. C. Chan and A. C. Waiss, Naturwissenschaften **67,** 358 (1980).
[16] J. B. Harborne, Introduction to Ecological Biochemistry, p. 146, Academic Press, London 1982.