

External Flavonoids in Two *Grindelia* Species

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A series of methylated flavonols and two methyl flavones have been identified in the exudate of the American gumweed species *Grindelia glutinosa* and *Grindelia robusta*. They resemble the flavonoid patterns observed in other species of this genus, which thus shows a tendency for accumulation of methylated flavonols.

Introduction

In a previous publication (Wollenweber *et al.*, 1993a), some of us have reported on the flavonoid components found in the resinous material accumulated on the surface of the aerial parts of *Grindelia tarapacana* Phil., a species native to Chile. We now have analyzed the lipophilic exudate of *Grindelia glutinosa* (Cav.) Dunal, native to the Desert of Atacama in Chile, and of cultivated *Grindelia robusta* Nutt., a species native to Mexico and South America.

The term “resin” is defined here on the basis of simple physicochemical properties different enough to distinguish them from other types of

plant products such as latex, essential oils, gums and waxes. The major components of *Grindelia* resin are numerous bicyclic diterpene acids of the labdane type and namely grindelic acid and its derivatives (Timmermann *et al.*, 1983, 1985, 1986a, 1986b, 1987a, 1988).

The South American *Grindelia tarapacana* and *G. glandulosa* afford very high yields of resins, exceeding 10% of the plant's dry weight. The crude resin yields range from 17% in *G. glutinosa* to 26% in *G. tarapacana* (Castro *et al.*, 1994). In contrast, *G. robusta* yields approximately 6% of crude resin (Timmermann *et al.*, 1987b). Most wild collections of the promising North American tetraploid *G. camporum* Greene yield approximately 10% crude resin (Hoffmann *et al.*, 1984). This species has been identified as a potential resin cash crop for the U.S. Southwest that could be used as feedstocks for specialty chemicals and other commodities (Timmermann and Hoffmann, 1985).

Some of the species (including *G. robusta* and *G. squarrosa*) were formerly officinal drugs, being antispasmodic and stomachic, administered in asthma and externally, to relieve the irritation caused by poison ivy (Kearney and Peebles, 1964).

Materials and Methods

Leaves and stems of *Grindelia glutinosa* were collected separately in Chile, Poconchile, Valle de Liuta, region of Tarapaca at 800 m above sea level on March 29, 1991. A herbarium specimen has been deposited at the Pontificia Universidad Católica de Chile, Santiago, Chile. Aerial parts of *Grindelia robusta* were collected from plants cultivated at the Botanischer Garten der Universität Wien. A voucher is kept at the herbarium of the Institut für Botanik, University of Vienna (WU) in Vienna, Austria. Air-dried plant material was rinsed with dichloromethane (*G. glutinosa*) or with acetone (*G. robusta*) at room temperature to dissolve the exudate material. In both species most of the resin consists of terpenoids. In *G. glutinosa* the flavonoid content in the stem wash appeared higher than in the leaf wash. Since the flavonoids composition seemed to be the same in both organs, we analyzed the stem exudate only. The organic solutions were filtered and concentrated and further processed by column chromatography

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on Sephadex LH-20, eluted with methanol. Fractions were monitored and comparisons with authentic samples were done by thin layer chromatography on polyamide and on silica as reported previously (Wollenweber *et al.*, 1993a, 1993b). All markers were available in E. W.'s lab.

Results and Discussion

In the stem exudate of *Grindelia glutinosa* we identified the following flavonoid aglycones: kaempferol-3,4'-dimethyl ether (ermanin), kaempferol-3,7,4'-trimethyl ether (santin), 6-hydroxykaempferol-3,6,4'-trimethyl ether, 6-hydroxykaempferol-3,6,7,4'-tetramethyl ether, apigenin-4'-methyl ether (acacetin) and scutellarein-6,4'-dimethyl ether (pectolinarigenin). The exudate of *Grindelia robusta* yielded 9 flavonols: kaempferol-3-methyl ether (isokaempferid), kaempferol-3,4'-dimethyl ether (ermanin), quercetin-3,3'-dimethyl ether, quercetin-3,7,3'-trimethyl ether (pachypodol), quercetin-3,3',4'-trimethyl ether, 6-hydroxykaempferol-3,6-dimethyl ether (trace amount only), 6-hydroxykaempferol-3,6,7-trimethyl ether (penduletin), quercetagenin-3,6,4'-trimethyl ether (centaureidin) and quercetagenin-3,6,7,3'-tetramethyl ether (chrysosplenetin). Due to the lack of additional material, a few spots remain unidentified. In particular in *G. glutinosa* the percentage of flavonoids in the exudate is so small that the resinous material would need to be processed in relatively large scale to allow for the identification of the minor phenolic components.

Most of the flavonoid aglycones found in the two *Grindelia* species analyzed here have pre-

viously been reported from other species of this genus (Wollenweber *et al.*, 1993a and ref. therein). It becomes clear that *Grindelia* has a strong tendency to accumulate methylated flavonols. The flavonoid pattern of *G. robusta* is pretty close to that observed in *G. tarapacana* (Wollenweber *et al.*, 1993a). Analysis of externally accumulated flavonoids in further species is desirable. Also the constancy of flavonoid patterns in plant material of different origin should be checked, however, before any chemosystematic conclusions can be drawn.

It should be mentioned that there is some uncertainty with regard to the correctness of the species names used here. According to Steyermark's 1934 monograph (Steyermark, 1934) the older and hence valid name for both materials is *Grindelia rubricaulis* DC. *G. glutinosa* (Cav.) Dunal would correspond to *G. rubricaulis* DC var. *latifolia* (Kellogg) Steyermark and *G. robusta* Nutt. would correspond to *G. rubricaulis* DC var. *robusta* (Nutt.) Steyermark. The important difference between the two exudate flavonoid patterns found in these two taxa is not necessarily in contrast to such treatment.

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