

Exudate Flavonoids from *Grindelia tarapacana* of Chile

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Ten methylated flavonols have been identified in the lipophilic resinous exudate found on aerial parts of *Grindelia tarapacana*, a gumweed species of Chile.

Introduction

Grindelia, a New World plant genus with approximately 60 species of annual, biennial and perennial shrubs and herbs, is a member of the subtribe Solidagininae, tribe Astereae, family Asteraceae. *Grindelia* is well represented in North America, with 45 species and 66 varieties and forms [1]. The largest concentration of species occurs in the southwestern United States. The genus does not occur in Central America, but reappears in South America in Chile [2], Peru, Uruguay, Paraguay, southern Brazil and Argentina [3]. Most of the species are well-adapted to regions where annual precipitation is 25 cm or less.

The common name “gumweed” used for most North American species of *Grindelia* refers to the conspicuous accumulation of hydrophobic, non-volatile resins on the plants surfaces as part of the cuticular layer. The production and accumulation of these resins appears to be associated with resin

glands which occur in shallow pits on the surfaces of the leaves, stems, and involucre of the flower heads (multicellular resin ducts occur in the leaf mesophyll and stem cortex) [4–6]. Heavy resinous coatings may be a phytochemical and ecological adaptation to the arid and semi-arid environments where these plants grow [4].

Phytochemical investigations of the resins of *Grindelia* show that while all species have distinct chemical patterns, they are all characterized by the presence of bicyclic diterpene acids of the labdane type [7–10]. A few reports on the presence of flavonoids are available in the literature for several species of *Grindelia* [9, 11–14]. The diterpene acids produced by *Grindelia* were shown to have physical properties nearly identical with those of pine resins used in the naval stores industry and several applications of the resins from *G. squarrosa* have, in fact, been patented [15–17].

As part of a search for new cash crops for arid lands and a broad evolutionary and biochemical-systematic investigation of *Grindelia*, we analyzed a taxon native to the arid lands of northern Chile. This report is the first of a series on the flavonoid chemistry of South American *Grindelia* and describes the isolation and characterization of 10 flavonoid aglycones from the resin of the leaves, stems and flower heads of *G. tarapacana* Phil.

Material and Methods

Aerial parts of *Grindelia tarapacana* were collected in Chile, region of Tarapaca, Tiguamar at 3,000 meters above sea level in March, 1991. A herbarium specimen has been deposited at the Pontificia Universidad Católica de Chile. Leaves, stems and flower heads were collected separately, air-dried, and stored at 5 °C prior to extraction. The material corresponding to leaves (100 g), stems (503 g) and flower heads (575 g) of *G. tarapacana* were extracted with dichloromethane at room temperature. The extracts were filtered and concentrated to afford 25.7 g (25.7%), 37.0 g (7.4%) and 95.0 g (16.5%), respectively, of resinous material. Each extract was taken up in methanol and eluted from Sephadex LH-20 with methanol to separate the flavonoid aglycones from the dominating terpenoids. Some of the flavonoid containing fractions were combined and subject to preparative TLC on silica (solvent A, toluene–

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methylethyl ketone 9:1). Individual flavonoids were identified by direct comparisons with markers on polyamide TLC (solvent B, toluene–petrol_{100–140}–methylethyl ketone–methanol 12:6:6:1) and on silica (solvent A, or solvent C, toluene–dioxane–HOAc 90:25:5). Spots were visualized under UV₃₆₆ before and after spraying with “Naturstoffreagenz A”. Discrimination of quercetin-3,3'-dimethyl ether *versus* quercetin-3,4'-dimethyl ether was done by fuming the thin layer plate with ammonia.

Result and Discussion

The individual dichloromethane extracts of leaves, stems and flower heads of *Grindelia tarapacana* Phil. were analyzed for flavonoids. According to all our previous results, flavonoid aglycones, whenever present in members of the Asteraceae, are constituents of a complex lipophilic exudate that consists mainly of terpenoids [9, 18, 19]. We assume, therefore, that the flavonoids reported here are also accumulated externally.

The flavonoid patterns observed in extracts of leaves, stems, and flower heads are qualitatively the same; there are only minor quantitative differences. In each case the following flavonoids can be detected: kaempferol-3-methyl ether and kae-3,7-dimethyl ether (isokaempferide and kumatakenin), the 3,6,7- and the 3,6,4'-trimethyl ethers of

6-hydroxykaempferol (penduletin and santin), the 3,7-, the 3,3'- and the 3,4'-dimethyl ethers and the 3,7,3'-trimethyl ether of quercetin, the 3,6,4'-trimethyl and the 3,6,7,3'-tetramethyl ether of quercetagetin (centaureidin and chrysosplenetin). Although none of these flavonols is a rare natural product, this is the first time that their occurrence as exudate flavonoids is reported for *Grindelia tarapacana*.

To our knowledge some nine species of *Grindelia* have so far been studied for flavonoids [9, 13, 14 and refs. therein]. The products so far found include kaempferol-3-methyl and kaempferol-3,7-dimethyl and 3,4'-dimethyl ethers, quercetin and its 3-methyl, 3,3'-dimethyl and 3,7,3'-trimethyl ethers, luteolin, apigenin-4'-methyl ether and taxifolin-7,3'-dimethyl ether. Flavonols are clearly dominating also in *G. tarapacana*, so our present results fit in this pattern. This is the first time, however, that derivatives of quercetagetin have been encountered in *Grindelia*.

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