

## Main Flavonoids from *Pseudolarix amabilis* Leaves

Gerard J. Niemann

Botanical Laboratory, University of Utrecht, The Netherlands

(Z. Naturforsch. **30 c**, 550 [1975]; received May 5, 1975)

Pinaceae, *Pseudolarix amabilis*, Flavonoids

Needles of *Pseudolarix amabilis* contain one principal flavonoid, which was identified as myricetin-3-rhamnoside. Myricetin-3-glucoside, quercetin-3-rhamnoside, kaempferol-3-glucoside, kaempferol-3-(ferulylglucoside) and kaempferol-3-(p-coumarylglucoside) were present in much lower concentration.

Pinaceae are marked accumulators of flavonoids. According to Hegnauer<sup>1</sup> it seems that each genus went its own way in this connection. This opinion is mainly based on heartwood and bark flavonoids of a limited number of genera and species. Little is known of the leaf constituents<sup>2</sup> except that most Pinaceae leaves contain quercetin, kaempferol and, to a lesser extent, myricetin and dihydroquercetin in bound form<sup>3</sup>. For *Pseudolarix* leaves Takahashi *et al.*<sup>3</sup> reported quercetin and kaempferol, present as (unidentified) glycosides. No other flavonoids have been reported for *Pseudolarix amabilis*, the only species in the genus.

On the other hand in needles of *Larix* species a rich array of flavonoids was found with great similarity in the flavonoid pattern of different species<sup>4</sup>. Comparison of *Larix* with other Pinaceae based on leaf C-glycosides indicated that *Larix* might be rather different in its leaf flavonoid composition<sup>5</sup>. To substantiate this view needles of *Pseudolarix amabilis*, a species which closely resembles larch and with *Cedrus* and *Larix* belongs to the subfamily Laricoideae, were investigated.

### Material and Methods

Needles of *Pseudolarix amabilis* (J. Nels) Rehd. (= *P. kaempferi* Gordon) were collected at the Pinetum Blijdenstein, Hilversum, The Netherlands, in September 1973. A voucher specimen No GN 10 was deposited at the Institute for Systematic Botany, University of Utrecht.

Freeze-dried needles were extracted with acetone-water; chlorophyll and other lipophilic constituents were removed with light petrol. After concentration,

the solution was further separated by extraction with ether followed by butanol<sup>6</sup>. Ether and butanol fractions were purified by repeated banding on Whatman no 1 chromatography paper. The compounds were obtained in solution and identified by  $R_F$  values, UV spectral data inclusive spectral shifts, acid hydrolysis/degradation<sup>7</sup>, and in some cases by alkaline hydrolysis or peroxide oxidation<sup>8</sup>.

### Results and Discussion

One- and two-dimensional chromatography showed the presence of one principal flavonoid, accompanied by a number of other components present in comparatively low concentration. The main component was isolated and identified as myricetin-3-rhamnoside. The other flavonoids identified were: Myricetin-3-glucoside, quercetin-3-rhamnoside and kaempferol-3-glucoside and the acylated compounds kaempferol-3-(ferulylglucoside) and kaempferol-3-(p-coumarylglucoside). The method of isolation implies that, whatever the relative concentration of the isolated compounds, they still must be considered as major flavonoids. Many more minor ones may occur, which has to be kept in mind when the genus is compared with other Laricoideae.

When compared with *Larix* a striking difference in flavonoid pattern becomes apparent. Some correspondence is also found; the ubiquitous kaempferol-3-glucoside is present in both genera and the same holds for the acylated glycosides. Reports on the latter compounds are relatively scarce<sup>2</sup>. It seems quite probable, however, that the acylated flavonoids have often been overlooked, and, once recognised, will appear rather common.

3-Glycosylation is the main pattern in both genera, but whereas rhamnosides and glucosides were found in *Pseudolarix*, *Larix* has glucosides and rutinosides. O-methylation, a main feature in *Larix*<sup>4,9</sup>, is totally absent among the major flavonoids of *Pseudolarix*. Together with the absence of C-glycoflavones, these aspects seem to put *Pseudolarix* chemically further apart from *Larix* than expected from their morphological resemblance. Hegnauer's view<sup>1</sup> that each genus in the Pinaceae went its own way in flavonoid biosynthesis seems supported in this case.

The assistance of Judith Koerselman-Kooij and of Betty Boonzaaijer-van Dijk is much appreciated.

<sup>4</sup> G. J. Niemann, Acta Bot. Neerl. **24**, 65 [1975].

<sup>5</sup> G. J. Niemann and H. J. Miller, Biochemical Systematics and Ecology **2**, 169 [1975].

<sup>6</sup> M. Tissut and K. Egger, Phytochemistry **11**, 631 [1972].

<sup>7</sup> G. J. Niemann, J. Chromatogr. **74**, 155 [1972].

<sup>8</sup> B. V. Chandler and K. A. Harper, Aust. J. Chem. **14**, 586 [1961].

<sup>9</sup> G. J. Niemann, Planta Med. **26**, 101 [1974].

Requests for reprints should be sent to Dr. G. J. Niemann, Botanical Laboratory, University of The Netherlands, Utrecht, Lange Nieuwstraat 106.

<sup>1</sup> R. Hegnauer, Chemotaxonomie der Pflanzen, Bd. 1, Birkhäuser Verlag, Basel u. Stuttgart 1962.

<sup>2</sup> J. B. Harborne, Comparative Biochemistry of the Flavonoids, Academic Press, London and New York 1967.

<sup>3</sup> M. Takahashi, T. Ito, A. Mizutani, and K. Isoi, J. Pharm. Soc. Japan **80**, 1488 [1960].

