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L-3-(3-CARBOXY-4-FURYL)ALANINE FROM *TRICHOLOMOPSIS RUTILANS*

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Key Word Index—*Tricholomopsis rutilans*; Tricholomataceae; Basidiomycetes; L-3-(3-carboxy-4-furyl)alanine.

Doyle and Levenberg [1] reported recently a new amino acid L-3-(3-carboxy-4-furyl)alanine from *Phyllotopsis nidulans* (Pers. ex Fr.) Sing. Independently we also isolated the same amino acid from another fungus, *Tricholomopsis rutilans* (Fr.) Sing.* Identification was based on IR and TLC comparison with an authentic sample from *Phyllotopsis*.

EXPERIMENTAL

The amino acid fraction obtained from the fruit bodies (3 kg) was fractionated with a column of Dowex 1 (AcO^-) and 0·5 N HOAc as an eluting agent, giving pure fractions. Yield: 695 mg. Mp 215–6° (decomp.) $[\alpha]_D^{30}$ −48° (*c* 1, H_2O), −28° (*c* 0·5, 3 N HCl). UV: $\lambda_{max}^{H_2O}$ 239 nm (ε 2100), pH 4·3. IR (furan): 3135, 875, 803 and 772 cm^{-1}. NMR (in 5% DCl, DSS): δ 3·3 (*m*), 4·36 (*q*), 7·45 (*s*) and 8·05 (*d*, *J* 1·2 Hz).

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* Vouchers are deposited in the Department of Biology, College of General Education, The University of Tokyo.

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MAIN FLAVONOIDS IN NEEDLES OF *LARIX DECIDUA**

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Key Word Index—*Larix decidua*; Pinaceae; Gymnospermae; flavonoids.

Plant. Larix decidua Mill. Voucher specimen No. GN3, Institute for Systematic Botany, University Utrecht. *Source.* Arboretum Schovenhorst, Putten, The Netherlands, Aug. 1973. *Previous work on leaves.* Lipids [1], sterols [2], *O*-methylinositols [3], and organic acids [4].

Present work. Freeze-dried needles were extracted with acetone–water [5]. Ether and butanol fractions [5] were separated by repeated banding on paper. Nine major flavonoids were isolated (in solution) and identified by chromatographic and UV spectral data of both the original and alkaline and/or acid hydrolysis/degradation [6] products as: the 3-glucosides of kaempferol, quercetin and isorhamnetin, the 3-rutinosides of quercetin, isorhamnetin and syringetin, kaempferol-3-(*p*-coumarylglucoside), and vitexin and its xyloside, 8-(xylosylglucosyl)apigenin. Besides the syringetin glycoside, other myricetin derivatives such as myricetin-3-glucoside were present in lower concentration.

As compared with *L. leptolepis* [7,8], *L. decidua* leaves seem rather similar in their flavonoid composition except for the quercetin glycosides forming major constituents in *L. decidua*, whereas quercetin-3-glucoside in a minor flavonoid in *L. leptolepis* leaves.

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* Part 9 in the series 'Phenolics from *Larix* needles'. For Part 8 see Niemann, G. J., *Planta Med.* **26,** 101.

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ACYLATED FLAVONOL GLYCOSIDES FROM *LARIX* NEEDLES*

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Key Word Index—*Larix decidua, L. leptolepis, L. laricina, L. sibirica, L. occidentalis, L. gmelinii, L. eurolepis*; Pinaceae; Gymnospermae; acylated flavonol glycosides.

Plants. Larix decidua Mill. (GN3), *L. leptolepis* (Sieb. et Zucc.) Gord. (GN1), *L. laricina* (Du Roi) K. Koch (GN5), *L. sibirica* Ledeb. (GN7), *L. occidentalis* Nutt. (GN9). *L. gmelinii* (Rupr.) Kuzeneva (GN4), *L. eurolepis* Gord./A. Henry (*L. dec.* × *L. lept.*, GN8). GN no.'s indicate voucher specimen at the Institute for Systematic Botany, University Utrecht. *Source.* State Forest Service, Austerlitz, August 1970—no. 1, Arboretum Schovenhorst, Putten, August 1973—no.'s 3–5, 7, Pinetum Blijdenstein, Hilversum, September 1973—no.'s 8–9; all in The Netherlands. *Relevant previous work.* Kaempferol-3-*p*-coumarylglucoside in needles of *L. leptolepis* [1], *L. decidua* [2] and *L. gmelinii* [3]. *Present work.* Kaempferol-3-*p*-coumarylglucoside (KCG) was isolated from ether fractions of acetone-extracted freeze-dried needles [4] of all larch species investigated. In each case, KCG was found as one of the main flavonoids, whereas often a variety of closely related, acylated flavonoids was present in either low to very low concentration. For example, the KCG complex of *L. leptolepis* needles [1] on alkaline hydrolysis produced traces of ferulic acid besides *p*-coumaric acid, indicating the possible presence of a kaempferol-3-ferulylglycoside (KFG). Because of the low concentration, KFG could not be isolated from *L. leptolepis* needles, but was obtained from *L. decidua*, a species with lower concentrations of KCG.

* Part 11 in the series "Phenolics From Larix needles". For Part 10 see G. J. Niemann, *Acta Bot. Neerl.* **24,** (in press).