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.

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

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

Phytochemistry, 1975, Vol. 14, pp. 1437–1438. Pergamon Press. Printed in England.

ACYLATED FLAVONOL GLYCOSIDES FROM *LARIX* NEEDLES*

GERARD J. NIEMANN

Botanical Laboratory, University Utrecht, The Netherlands

(*Received* 28 *November* 1974)

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.

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

Freeze-dried needles of *L. decidua* were extracted with 70% EtOH; chlorophyll etc. was removed with CCl_4, and the extract was separated on a polyamide column and on paper. In addition to KCG, 4 new acylated glycosides were isolated and identified by standard methods as: the 3-ferulylglucosides of kaempferol, quercetin, isorhamnetin and syringetin. A fifth compound could not be completely freed from KCG, but was identified as kaempferol-3-*p*-coumarylarabinoside-KCA. Traces of KCA were also found in needles of *L. laricina*.

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

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Phytochemistry, 1975, Vol. 14, pp. 1438–1439. Pergamon Press. Printed in England.

DIMERIC ALKALOIDS OF SECODINE-TYPE FROM *AMSONIA TABERNAEMONTANA* ROOTS

BÉLA ZSADON and MÁRIA SZILASI
Eötvös Loránd University, Department of Chemical Technology, H-1088 Budapest, Muzeum krt. 6-8, Hungary

JÓZSEF TAMÁS
Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary

and

PÁL KAPOSI
Research Institute for Medicinal Plants, Budakalász, Hungary

(*Received* 8 *August* 1974)

Key Word Index—*Amsonia tabernaemontana*; Apocynaceae; indolalkaloids; tetrahydrosecamine; tetrahydropresecamine; decarbomethoxy-tetrahydrosecamine; eburnamine.

Plant. Amsonia tabernaemontana Walt. *Source.* Cultivated in Budakalász, Hungary. *Previous work.* Alkaloids [1].

Recent work. Roots. Alkaloids were extracted with MeOH from the air-dried ground roots (500 g) collected in the early autumn. The crude basic material (5·2 g) was fractionated by a combination of column chromatography on alumina of activities II and III giving two dimeric alkaloids of the secodine-type, tetrahydrosecamine (800 mg) and tetrahydropresecamine (115 mg) in addition to eburnamine (182 mg) and other alkaloids reported previously [1]. The secodine-type alkaloids from *Amsonia* roots proved to be identical with those isolated earlier from *Rhazya* species [2–4].

Tetrahydrosecamine. High resolution MS gave a molecular ion peak at *m/e* 680 (680·4305 corr. to $C_{42}H_{56}N_4O_4$) and base peak at *m/e* 126. Amorphous: λ (EtOH) 224, 284, 292 nm; ν_{max}($CHCl_3$) 3420 (NH), 1738 (satd. ester) cm^{-1}; $[\alpha]_D^{20}$ 0° (EtOH). *Tetrahydropresecamine.* $C_{42}H_{56}N_4O_4$. High resolution MS gave the molecular ion peak of the monomer 15,20-dihydrosecodine at *m/e* 340 (340·2148 corr. to $C_{21}H_{28}N_2O_2$), base peak at *m/e* 126 and another characteristic peak at *m/e* 281. Amorphous glass, which easily transforms into tetrahydrosecamine on standing at room temp. in strong acid solutions for several hours. λ (EtOH) 224, 288, 295, 328 nm; ν ($CHCl_3$) 3360 (NH), 1738 (satd. ester), 1680 and 1610 (β-anilinoacrylic ester); $[\alpha]^{20}$ −12 (EtOH). *Eburnamine.* High resolution MS gave a molecular ion (base) peak at *m/e* 296 (296·1891 corr. to $C_{19}H_{24}N_2O$) and other significant peaks at *m/e* 296, 295, 278, 267, 249, 226, 208, 206, 193. λ (EtOH) 229, 276, 282, 290. The sample could be transformed into (+)-eburnamonine by oxidizing with CrO_3 or into eburnamenine by dehydrating in HOAc (cf. reference [5]).

A new dimeric alkaloid of the secodine-type