

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*.

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

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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 $\text{C}_{42}\text{H}_{56}\text{N}_4\text{O}_4$) 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} ;

$[\alpha]_{\text{D}}^{20}$ 0° (EtOH). *Tetrahydropresecamine.* $\text{C}_{42}\text{H}_{56}\text{N}_4\text{O}_4$. High resolution MS gave the molecular ion peak of the monomer 15,20-dihydrosecodeine at m/e 340 (340.2148 corr. to $\text{C}_{21}\text{H}_{28}\text{N}_2\text{O}_2$), 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_{max} (CHCl_3) 3360 (NH), 1738 (satd. ester), 1680 and 1610 (β -anilinoacrylic ester); $[\alpha]_{\text{D}}^{20}$ -12 (EtOH). *Eburnamine.* High resolution MS gave a molecular ion (base) peak at m/e 296 (296.1891 corr. to $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}$) and other significant peaks at m/e 296, 295, 278, 267, 249, 226, 208, 206, 193. λ (EtOH) 229, 276, 282, 290 nm. 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

(11 mg) was isolated from the basic extract (1.55 g) of *A. tabernaemontana* roots (500 g) collected late in the winter. This proved to be *decarbomethoxytetrahydrosecamine*. Its high resolution MS gave a molecular ion peak at m/e 622 (622.4248 corr. to $C_{40}H_{54}N_4O_2$) and base peak at m/e 126. Amorphous; $[\alpha]_D^{20}$ 0° (EtOH); λ_{max} (EtOH) 224, 284, 292 nm; ν_{max} (CHCl₃) 3360 (NH), 1738 (satd. ester) cm^{-1} . (The latter is of much smaller intensity than the corr. peak of tetrahydrosecamine.)

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ANTHOCYANIN OF *ACANTHOPANAX DIVARICATUS*

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Key Word Index—*Acanthopanax divaricatus*; Araliaceae; delphinidin 3-xylosylgalactoside.

Preparative chromatography of the fruit extract of *Acanthopanax divaricatus* (Sieb. et Zucc.) Seeman revealed the presence of two anthocyanins, one of which was a new pigment. On complete acid hydrolysis, the new anthocyanin yielded delphinidin, xylose and galactose. The absorption spectrum (in 0.01 % MeOH-HCl) of the glycoside showed λ_{max} (nm) 283 and 532 and a bathochromic shift of 13 nm by the addition of AlCl₃ indicating the presence of a free *o*-dihydroxylic grouping in the B-ring. The ratios of $Eu.v_{max}/Evis_{max}$ and $E440/Evis_{max}$ were 58 and 22, respectively. These values suggest that the pigment is the 3-glycoside [1]. By H₂O₂ oxidation the glycoside yielded the disaccharide which was identified paper chromatographically as lathyrose. On partial acid hydrolysis delphinidin 3-galactoside was detected as an intermediate. The pigment must therefore be delphinidin 3-xylosylgalactoside (3-lathyroside), which has not been reported before. Recently, cyanidin 3-lathyroside has been found in the ripe berries of *Aralia elata* [2] and its variety *canescens* [3], and *A. cordata* [2]. Therefore, the glycosidic similarity of the anthocyanins

in the plants in the family Araliaceae may be of systematic interest.

EXPERIMENTAL

The anthocyanin extract of the ripe black fruits was separated into two components by PC in HOAc-HCl-H₂O (15:3:82). Diagnostic chromatography of the new anthocyanin, its anthocyanidin and sugars were carried out by standard procedures [4]. The quantity of the second anthocyanin was too small to examine in detail. Chromatographic identification of lathyrose followed H₂O₂ oxidation of the glycoside [5]. Delphinidin 3-galactoside as the partial hydrolysate was identified by direct comparison with empetrin from *Empetrum nigrum* L. var. *japonicum* K. Koch [6].

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