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GYMNOSPERMAE

PINACEAE

FLAVONOID CONSTITUENTS FROM *LARIX* NEEDLES

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Plant. Larix laricina (Du Roi) K. Koch.

Source. Arboretum University of Wisconsin, Madison, September 1968. Gimborn Arboretum, State University Utrecht, September 1969.

Previous work. Phenolic glucosides.[1]

Previous work on other species L. kaempferi Sargent. Kaempferol-3-glucoside.[2]

Present work. Freeze-dried needles were extracted with EtOH. The extract was dried and separated by $NaHCO_3$–BuOH partition, polyamide and/or silica column chromatography, followed by banding on silica TLC and paper giving kaempferol-3-glucoside, isorhamnetin-3-glucoside, 8-*O*-xylosylvitexin and glucosylxylosylvitexin. Hydrolysis products were identified by co-chromatography (five solvents, paper and TLC) and spectral comparison with the authentic compounds. The position of the sugars was determined from the spectral shifts before and after hydrolysis. In glucosylxylosylvitexin, only the 7–OH was substituted; enzyme hydrolysis (emulsin) gave a compound with free 7–OH and R_f similar to that of 8-*O*-xylosylvitexin. Thus, 7-glucosyl-8-*O*-xylosylvitexin seems indicated.

Acknowledgements—The gift of vitexin from the collection of Dr. M. Seikel and of isorhamnetin by Dr. T. Mabry is appreciated.

[1] G. J. NIEMANN, *Phytochem.* **8**, 2101 (1969).
[2] M. TAKAHASHI, T. ITO, A. MIZUTANI and K. ISOI, *J. Pharm. Soc. Japan* **80**, 1488 (1960).

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ANGIOSPERMAE

APOCYNACEAE

FLAVONOIDS OF *ANODENDRON AFFINE*

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(*Received* 21 *July* 1970)

Plant. Anodendron affine (Hook. et Arn.) Durce.

Uses. Not known.

Previous work. Alkaloid.[1]

Leaves. The methanol extract concentrated, diluted with H_2O and filtrated. The filtrate treated with Pb acetate and basic Pb acetate respectively. Each precipitated part

[1] K. SASAKI and Y. HIRATA, *Tetrahedron Letters* 4065 (1969).

chromatographed on silica gel, eluted by $CHCl_3$–MeOH (9:1). Kaempferol $C_{15}H_{10}O_6$ m.p. 271–273° (m.p., mixed m.p., u.v., i.r. and TLC): from basic Pb acetate part. Astragalin(kaempferol-3-glucoside) $C_{21}H_{20}O_{11}$ m.p. 224–225° (m.p., mixed m.p., u.v., i.r. and TLC): from both of Pb acetate and basic Pb acetate parts. Hydrolysed by heating at 100° in 5% H_2SO_4 for 90 min; the aglycone and sugar were identified as kaempferol and glucose. After methylation with diazomethane acid hydrolysis gave 3-hydroxy-5,7,4′-trimethoxyflavone.

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ISOLATION OF GLUCOSYRINGIC ACID FROM *ANODENDRON AFFINE*

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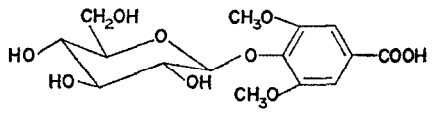
(*Received* 8 *August* 1970)

Abstract—Glucosyringic acid (4-β-D-glucopyranosyloxy-3,5-dimethoxybenzoic acid) has been isolated from *Anodendron affine* Durce. Its structure has been confirmed by synthesis.

IN THE investigation of water-soluble component of *Anodendron affine* we obtained one phenolic glycoside which was identified as glucosyringic acid. This paper describes of this glycoside which is the first reported isolation from a natural source.



(I)

The methanol extract of the stems was concentrated, diluted with water and filtrated. After extraction with ether and chloroform, respectively, the aqueous layer was concentrated to dryness and extracted with chloroform–methanol (2:1) by heating in a water bath. The residue was dissolved in water and treated with lead acetate and basic lead acetate. Then concentrated aqueous solution was chromatographed on activated charcoal. The combined fractions which were found by TLC to consist of one single compound, on recrystallization from methanol, furnished colorless needles (I) (m.p. 206–207°) analysing for $C_{15}H_{20}O_{10}$. Acid hydrolysis of (I) gave aglycone and sugar. The sugar was identified as glucose by R_f value on TLC and PC. In the NMR spectrum of the aglycone acetate, signals at 2·30 δ (3H, singlet, CH_3COO—), 3·86 δ (6H, singlet, 2 × CH_3O—), 7·30 δ (2H, singlet, 2 × aromatic H) and 9·85 δ (1H, broad —COOH) suggested it to be acetyl syringic acid. The aglycone was identified as syringic acid on the basis of the mixed m.p., u.v., i.r. and TLC with authentic sample. U.v. spectra (λ_{max}^{EtOH}, 257·5 mμ, $\lambda_{max}^{EtOH+NaOH}$, 248·5 mμ) of (I)