

chromatographed on silica gel, eluted by  $\text{CHCl}_3$ -MeOH (9:1). Kaempferol  $\text{C}_{15}\text{H}_{10}\text{O}_6$  m.p.  $271$ – $273^\circ$  (m.p., mixed m.p., u.v., i.r. and TLC): from basic Pb acetate part. Astragalín(kaempferol-3-glucoside)  $\text{C}_{21}\text{H}_{20}\text{O}_{11}$  m.p.  $224$ – $225^\circ$  (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  $100^\circ$  in 5%  $\text{H}_2\text{SO}_4$  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*

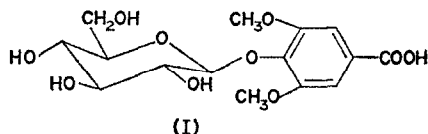
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**Abstract**—Glucosyringic acid (4- $\beta$ -D-glucopyranosyloxy-3,5-dimethoxybenzoic acid) has been isolated from *Anodendron affine* Durce. Its structure has been confirmed by synthesis.

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.



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.  $206$ – $207^\circ$ ) analysing for  $\text{C}_{15}\text{H}_{20}\text{O}_{10}$ . 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  $2.30\delta$  (3H, singlet,  $\text{CH}_3\text{COO}$ —),  $3.86\delta$  (6H, singlet,  $2 \times \text{CH}_3\text{O}$ —),  $7.30\delta$  (2H, singlet,  $2 \times$  aromatic H) and  $9.85\delta$  (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 ( $\lambda_{\text{max}}^{\text{EtOH}}$ ,  $257.5\text{ m}\mu$ ,  $\lambda_{\text{max}}^{\text{EtOH} + \text{NaOH}}$ ,  $248.5\text{ m}\mu$ ) of (I)

supported the position of attachment of glucose to the aromatic hydroxy group.<sup>1</sup> The above results suggested glucosyringic acid (4- $\beta$ -D-glucopyranosyloxy-3,5-dimethoxybenzoic acid) for (I). Glucosyringic acid was synthesized from syringic acid and  $\alpha$ -acetobrom-D-glucose for identification. The resulting acetylglucoside proved to be identical to acetate of (I) with respect to m.p.,  $R_f$  value on TLC and i.r. spectrum. The m.p., u.v. and i.r. spectrum of its deacetylated product were also identified to those of (I). After methylation of synthetic acetylglucosyringic acid with diazomethane acid hydrolysis gave methyl syringate, which was identified with authentic sample.

<sup>1</sup> Y. HAYASHI, *Yakugaku Zasshi* **82**, 1025 (1962).

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### $\alpha$ -YOHIMBINE FROM *ASPIDOSPERMA EXCELSUM*

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*Plant.* *Aspidosperma excelsum* Benth<sup>1</sup> from Venezuela.

*Previous extraction.* Yohimbine, *O*-acetyl-yohimbine and excelsinine (10-methoxycorynanthine) were isolated previously.<sup>2</sup>

*Isolation.* The mother liquors from the previous extraction showed by TLC (silica gel G: CHCl<sub>3</sub> 10-MeOH 1) small quantities of a fourth alkaloid. The crude base (4 gm) was chromatographed slowly over a column of TLC silica gel G yielding (after certain highly coloured impurities): *O*-acetyl-yohimbine (200 mg),  $\alpha$ -yohimbine (10 mg), yohimbine (1.53 gm) and excelsinine (29 mg).

*Identification.* m.p. 233–235° (decomp.);  $[\alpha]_D^{20}$  -18° (pyridine).  $\lambda_{\max}^{\text{EtOH}}$  227.5 (40,800), 284 (8310) and 292 (6920) nm; i.r. peaks at 3550 (OH), 3400 (NH) and 1740 (ester) cm<sup>-1</sup>; NMR peaks at 7.98 (1H: indolic NH), 7.22 (4H: mult. aromatic) and 3.83 (COOCH<sub>3</sub>)  $\delta$ . Mass spectrum: 354 (M<sup>+</sup>), 336 (M-H<sub>2</sub>O), 295 (M-COOCH<sub>3</sub>) and typical tetrahydrocarboline peaks at 184, 170, 169 and 156 *m/e*.

Comparison of these properties with those published for  $\alpha$ -yohimbine<sup>3</sup> suggested identity which was confirmed by comparison with an authentic sample† (TLC, i.r. and mixed m.p.).

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<sup>1</sup> R. E. WOODSON, *Ann. Missouri Botan. Garden*, **38**, 162 (1951).

<sup>2</sup> P. R. BENOIN, R. H. BURNELL and J. D. MEDINA. *Can. J. Chem.* **45**, 725 (1967).

<sup>3</sup> M. HESSE. *Indolalkaloide in Tabellen* (and references cited), Springer-Verlag, Berlin (1964).