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# IRIDOID AND PHENOLIC GLYCOSIDES OF *FRAXINUS GRIFFITHII*

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**Key Word Index**—*Fraxinus griffithii*; Oleaceae; iridoid glucoside; ligstroside; syringin; 3-(4-glucosyl-3,5-dimethoxyphenyl)-2-propenal; sinapaldehyde glucoside.

Extracts of bark and leaves of *Fraxinus griffithii* Clarke have been found on the black market in certain areas in Indonesia as an adulterant of illegal opium [1]. These extracts have a slight acute toxic effect on mice [2]. *Fraxinus griffithii* grows in several regions in Indonesia [3] and in the Himalayas [4]. Boorsma [5] isolated mannitol and other unidentified substances from the leaves. No further investigations on the constituents of this plant are known until this time.

Material used for the present work was dried bark collected in May 1976 from plants used as shade trees at a coffee plantation near Prajekan, East Java. For the isolation of the glucosides the method of Inouye [6] for the isolation of iridoid and other glucosides from bark of *Fraxinus japonica* Blume was applied in a modified form to give the iridoid glucoside ligstroside. Column chromatography of the aqueous fraction produced the pure glucoside syringin, isolated from *Fraxinus griffithii* for the first time, and its aldehyde derivative, sinapaldehyde glucoside, a new substance, Sinapaldehyde is known as a monomeric unit of some lignins, but has never been obtained before as its glucoside.

## EXPERIMENTAL

The fractions from the column were monitored by qualitative TLC on Si gel plates (E. Merck) with EtOAc–MeCOEt–HCOOH–$H_2O$ (5:3:1:2).

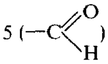
*Extraction of bark* Dried ground bark (kg) was percolated at 20° for 5 days with EtOH (95%) to prepare 5 l. extract. This was evapd nearly to dryness and successively extracted with $H_2O$ (150 ml) and $Et_2O$ (100 ml). The $Et_2O$ fraction was discarded. The $H_2O$ fraction was extracted with $CHCl_3$ (5 × 100 ml) and EtOAc (10 × 100 ml) to prepare the $H_2O$ fraction (B) and the EtOAc fraction (A).

*Ligstroside* To EtOAc fraction (A) 25 g Si gel was added and the solvent was evapd *in vacuo*. The powdered residue was placed on a column of Si gel (85 g) packed in $CHCl_3$–MeOH (47:3) and eluted with the same solvent mixture Fractions of 50 ml were monitored by TLC. The fractions containing glucosides were combined and the solvent evapd. Residue (5.4 g) was mixed with 10 g Si gel and chromatographed on Si gel column eluated with $CHCl_3$–MeOH (47:3). Fractions showing substances with $R_f$ 0.45–0.55 on the TLC plates were collected and evapd. A yellowish residue of crude ligstroside was obtained (1 g) and pure ligstroside was obtained by PLC on Si gel plates (E. Merck), using $CHCl_3$–MeOH (7:3) The purity was confirmed by TLC and detection of glucose after enzymatic hydrolysis by $\beta$-glucosidase. Found C 55.83, H 6.26, $C_{25}H_{32}O_{12}\cdot H_2O$ required: C 55.35, H 6.32. MS *m/e* (Field desorption spectra, Varian MAT 711–Electron impact spectra, direct insertion probe, Finnigan 3300): 525 (M + 1), 387, 224, 163, 138, 107 IR $\nu_{max}^{KBr}$ cm$^{-1}$: 770–910, 1000–1170, 1505, 1630, 1700, 1740. UV $\lambda_{max}^{EtOH}$ nm: 227, 208. NMR ($CD_3OD$) $\delta$· 1.5 (*d*, 10-$H_3$), 2.4 (*t*, 14-$H_2$), 3·4 (*t*, 13-$H_2$), *m* 5.7, 6.5–6.9 (*m*, arom. protons), 7.2 (*s*, 3-H).

*Isolation of other glucosides.* The $H_2O$ fraction (B) was chromatographed on $Al_2O_3$ eluted with EtOH (95%). The fractions containing glucosides were collected and evapd to dryness *in vacuo*. Repeated recrystallization from EtOH of the residue produced a substance giving 2 spots on TLC. Separation by chromatography on a Si gel column eluted with $CHCl_3$–MeOH (47:3). Syringin and the glucoside of sinapaldehyde, were obtained

*Syringin(3-(4-glucosyl-3,5-dimethoxyphenyl)-2-propenol).* Purity confirmed by TLC. Detection of glucose after enzymic hydrolysis by $\beta$-glucosidase. Found· C 53.02, H 6.84; $C_{17}H_{24}O_9$ required: C 54.81, H 6.50. MS *m/e*: 372, 210, 182, 167, 154, 149. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 627, 1020–1140, 1242, 1340, 1420, 1465, 1505, 1585, 3400. UV $\lambda_{max}^{EtOH}$ nm: 265, 222 NMR ($CD_3OD$) $\delta$ *s* 3.3 (*br*), *m* 3.8, *s* 3.9, *d* 4.3, *s* 4.8, *s* 6.5, *s* 6.7. Mp 192–193°.

*Sinapaldehyde glucoside(3-(4-glucosyl-3,5-dimethoxyphenyl)-2-propenal).* Found: C 54.17, H 6.24; $C_{17}H_{22}O_9$ required: C 55.11, H 5.99. MS *m/e*: 208, 180, 177, 165, 163, 137. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 810, 1020–1140, 1248, 1340, 1420, 1470, 1505, 1583, 1630, 3400. UV $\lambda_{max}^{EtOH}$ nm: 315, 237, 210. NMR (aglucone obtained by enzymic hydrolysis) $\delta$· *s* 3.8 (br), *s* 4.6 (br), 6.6, *s* 6.8, *d* 9.4, 9 5 (



$-\mathrm{C}\begin{smallmatrix}=\mathrm{O}\\ -\mathrm{H}\end{smallmatrix}$ )

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