yellow crystals which were shown by TLC to be chiefly the compound of very high R_f. The crystals that remained after the washing with Et_2O were washed with sat. $NaHCO_3$. Upon acidification of the combined aqueous washings with 19% HCl, 0·1 g of norstictic acid was recovered. The solid (1·5 g) which was insoluble in $NaHCO_3$ was identified as stictic acid (TLC, m.p., IR).

All TLC analyses were done with silica gel HF_{254} using benzene–dioxane–HOAc, 90:25:4.

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APIGENIN-6,8-DI-*C*-GLYCOSIDE FROM *PORELLA PLATYPHYLLA**

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Key Word Index—*Porella platyphylla*; Hepaticae; flavone-*C*-glycoside; vicenin.

The occurrence of isovitexin and saponarin in *Porella platyphylla* has been established[1,2] and a third flavone, occurring in minor amounts, has now been isolated and purified by gel filtration.

UV absorption data in MeOH with diagnositc shift reagents indicated an apigenin derivative with free phenolic hydroxyls.[3] Attempted acid hydrolysis proved the absence of hydrolyzable sugar. The proton NMR spectrum of the TMS ether showed the typical pattern of the B-ring protons of apigenin derivatives,[3] and a singlet (1H) at δ 6·38 (CCl_4, rel. TMS) which shifted to δ 6·53 on partial hydrolysis showed the presence of 3-H. Since no A-ring protons were observed and the sugar proton region (δ 3·1–5·0) integrated to *ca.* 14H the compound could be classified as a vicenin type pigment.

Acid treatment gave no discernible isomerisation, an indication that the sugar groups are identical. Acetylation gave a product, the elemental analyses of which are in agreement with those calculated for a fully acetylated (11 acetyls) apigenin diglucoside, but limited supply of material prevented investigation of the nature of the sugar components.

* Part XIV in the series "Chemical Studies on Bryophytes". For part XIII see L. SVENSSON and G. BENDZ, *Phytochem.* **11**, 1172 (1972).

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EXPERIMENTAL

Plant material. Porella platyphylla was collected on cliffs in Nåsten, Uppsala.

Isolation of flavones. The plant was extracted at room temp. with 60% aq. MeOH (12 hr) and the evaporated residue was washed with Et_2O and $CHCl_3$. Gel filtration on Sephadex G25 with 50% aq. MeOH as eluant gave an enriched flavone fraction, which was resolved into three components by elution with MeOH from a Sephadex LH20 column. The flavones eluted in the order; saponarin, isovitexin, new flavone. Isovitexin could be removed by two more similar operations, giving the third compound in a chromatographically homogeneous state. R_f (TLC on Avicel): 0·26 (TBA), 0·45 (15% HOAc). M.p. > 350°.

Spectral data. IR: 1655, 1650, 1625, 1610, 1580, 835 cm^{-1}. UV (λ_{max}, nm): 276, 337 (MeOH); 285, 334, 403 (NaOMe); 266 (sh), 282, 307, 354, 380 ($AlCl_3$); 265 (sh), 282, 306, 350, 379, ($AlCl_3$–HCl); 285, 305 (sh), 395 (NaOAc); 278, 325, 346, 400 (sh) (NaOAc–H_3BO_3). NMR of TMS–ether (CCl_4, rel. TMS) δ 3·1–5 (14 H, sugar), δ 6·38 (*s*) H-3, δ 6·89 (*d*) H-3′ and H-5′, δ 7·92 (*d*) H-2′ and H-6′.

Acetate. From Ac_2O-pyridine, purified on a silica gel column with C_6H_6–EtOAc (3:1) as solvent and crystallization from CH_2Cl_2–C_6H_{12}. M.p. 163–165°. λ_{max} (MeOH) 256, 301 nm, unchanged with $AlCl_3$. Found: C, 55·9; H, 5·0. Calc. for $C_{49}H_{52}O_{26}$ (dihexosylapigenin-Ac_{11}): C, 55·68; H, 4·96%.

Hydrolysis. Treatment with boiling MeOH–2 M HCl (1:1) for 7 hr gave partial destruction of the flavone. TLC tests revealed no new flavonoid component or free sugar.

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PHENOLIC GLUCOSIDES FROM NEEDLES OF *LARIX LEPTOLEPIS**

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Key Word Index—*Larix leptolepis*; Pinaceae; phenolic glucosides.

Plant. Larix leptolepis (Sieb et Zucc.) Gord.. Voucher specimen No. GN 1, Botanical Museum and Herbarium, University Utrecht. *Source.* State Forest Service, Austerlitz, The Netherlands, August 1970. *Previous work on leaves.* Hydroxy acids;[1] *L. kaempferi* (flavonoids),[2] *L. laricina* (phenolic glucosides,[3] flavonoids[4,5] and aldehydes[5]), *L. sibirica* (phenolic glucosides,[6] flavonoid[7]).

Present work. Freeze-dried needles were extracted with light petrol., $CHCl_3$, $CHCl_3$–MeOH 2%, $CHCl_3$–MeOH 10%. The latter extract was dried and separated by repeated banding on paper and silica TL or by $NaHCO_3$–BuOH partition followed by Sephadex LH20 and polyamide column chromatography and by banding on paper. Four β-glucosides

* Part V in the series "Phenolics from *Larix* Needles". For Part IV see G. J. NIEMANN, *Acta Bot. Neerl.* **21**, 549 (1972).

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