

EXPERIMENTAL

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

Isolation of flavones. The plant was extracted at room temp. with 60% aq. MeOH (12 hr) and the evaporated residue was washed with Et₂O and CHCl₃. 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 ($\lambda_{\max}$, nm): 276, 337 (MeOH); 285, 334, 403 (NaOMe); 266 (sh), 282, 307, 354, 380 (AlCl₃); 265 (sh), 282, 306, 350, 379, (AlCl₃-HCl); 285, 305 (sh), 395 (NaOAc); 278, 325, 346, 400 (sh) (NaOAc-H₃BO₃). NMR of TMS-ether (CCl₄, 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 Ac₂O-pyridine, purified on a silica gel column with C₆H₆-EtOAc (3:1) as solvent and crystallization from CH₂Cl₂-C₆H₁₂. M.p. 163-165°. $\lambda_{\max}$ (MeOH) 256, 301 nm, unchanged with AlCl₃. Found: C, 55.9; H, 5.0. Calc. for C₄₉H₃₂O₂₆ (dihexosylapigenin-Ac₁₁): 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.

Acknowledgements—A grant from the Swedish Natural Science Research Council (to Dr. G. Bendz) is gratefully acknowledged. Ultramicro elemental analyses were performed by the Microanalytical Laboratory at the Agricultural College of Sweden, Uppsala.

Phytochemistry, 1973, Vol. 12, pp. 723 to 724. Pergamon Press. Printed in England.

PHENOLIC GLUCOSIDES FROM NEEDLES OF *LARIX LEPTOLEPIS**

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(Received 20 October 1972. Accepted 8 November 1972)

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 aldehydes⁵), *L. sibirica* (phenolic glucosides,⁶ flavonoid⁷).

Present work. Freeze-dried needles were extracted with light petrol., CHCl₃, CHCl₃-MeOH 2%, CHCl₃-MeOH 10%. The latter extract was dried and separated by repeated banding on paper and silica TL or by NaHCO₃-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).

¹ G. J. NIEMANN, *Acta Bot. Neerl.* 20, 397 (1971).

² M. TAKAHASHI, T. ITO, A. MIZUTANI and K. ISOI, *J. Pharm. Soc. Japan* 80, 1488 (1960).

³ G. J. NIEMANN, *Phytochem.* 8, 2101 (1969).

⁴ G. J. NIEMANN and R. BEKOBY, *Phytochem.* 10, 893 (1971).

⁵ G. J. NIEMANN, *Acta Bot. Neerl.* 21, 549 (1972).

⁶ S. A. MEDVEDEVA, N. A. TJUKAVKINA and Z. IVANOVA, *Khim. Prir. Soedin.* 844 (1971).

⁷ S. A. MEDVEDEVA, N. A. TJUKAVKINA and Z. IVANOVA, *Khim. Prir. Soedin.* 123 (1972).

were isolated (in solution) and identified as the glucosides of vanillic- (GV), *p*-hydroxybenzoic- (GPH), ferulic- (GF) and *p*-coumaric acid (GPC) by chromatographic and UV spectral data of both the original and the enzymatic and acid degradation products. A trace of a fifth compound was tentatively (R_f and colour reactions only) identified as arbutin.

GPH has previously been isolated from *L. laricina*³ and designated the α -structure because of its comparatively high stability towards emulsin hydrolysis (GPH could be isolated from a mixture of GPH and GPC by degrading GPC with β -glucosidase, leaving a considerable residue of GPH). Nevertheless, it has to be the β -glucoside since it was not affected by α -glucosidase.

After isolating GF from *L. leptolepis* the previous extracts of *L. laricina* needles³ were reinvestigated for GF. A trace of the compound could be detected. In *L. leptolepis* similar amounts to the other glucosides were present. Also, in *L. sibirica* needles GV, GPH and GPC have been reported⁶ and not GF.

Acknowledgement—The assistance of Judith Koerselman-Kooij is appreciated.

Phytochemistry, 1973, Vol. 12, pp. 724 to 725. Pergamon Press. Printed in England.

DIMETHYL-3,4'-KAEMPFEROL DE *CORDIA BOISSIERI*

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(Reçu le 23 octobre 1972. Accepté le 8 novembre 1972)

Key Word Index—*Cordia boissieri*; Boraginaceae; allantoin; D-pinitol; calcium oxalate; kaempferol-3,4'-dimethyl ether.

Plante étudiée. La *Cordia boissieri* (anacahuite) est connue dans le nord du Mexique où elle abonde, dans le centre du Mexique et au Texas. On l'utilise en médecine populaire contre les affections des bronches, comme diurétique et comme tonifiant général.^{1,2} On a étudié les extraits éthanoliques de la fleur, récoltée en particulier pendant les mois de juin et juillet. Le matériel végétal est originaire de l'état du Nuevo León, Mexique. *Etudes antérieures.* Sur des espèces voisines,³ et sur les carbohydrates de *C. boissieri*.⁴

Oxalate de calcium. Pendant les mois de mars et avril, les extraits éthanoliques de la fleur contiennent 48 % de sels, dont le principal a été identifié comme l'oxalate de calcium.

Allantoïne. L'extrait éthanolique concentré à sec et repris par CHCl_3 donne l'allantoïne, p.f. 238–240°, $M^+ = 158$, $\text{C}_4\text{H}_6\text{N}_4\text{O}_3$. Le produit est identifié par UV, IR, RMN.⁵ Cette observation confirme sur le plant chimiotaxonomique les observations antérieures faites sur les Boraginacées.⁶

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² D. S. CORRELL et C. J. MARSHAL, dans *Manual of the Vascular Plants of Texas*, Texas Research Foundation, Texas (1970).

³ M. K. SEIKEL et J. W. ROWE, *Phytochem.* 3, 27 (1964).

⁴ R. E. CHAPPA, Thèse présentée à l'I.T.E.S.M. (1967).

⁵ Lit. p.f. 238–240°, *Dictionary of Organic Compounds*, Oxford University Press, Oxford (1953).

⁶ K. PAECH et M. V. TRACEY, dans *Moderne Methoden der Pflanzenanalyse*, Vol. 4, Springer, Berlin (1955).