

group(s). It gave a diacetate (m.p. 143°). On treatment with acid (1 hr, 4% alcoholic HCl), **2** gave a colourless crystalline compound **5** (m.p. 101°), which was identified as 5-hydroxy-7-methoxyflavanone (pinostrobin). Hence **2** has been assigned the structure 2',6'-dihydroxy-4'-methoxychalcone. MS is in complete agreement with the assigned structure.

A small amount of (\pm) pinostrobin was also isolated from the light petroleum extract. Presumably this has been formed from **2** during isolation.

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FLAVONOIDS FROM *ALNUS CRISPA*, *A. JAPONICA*, *A. KOEHNEI* AND *A. SINUATA*

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Key Word Index—*Alnus* species; Betulaceae; bud excretion; flavonoid aglycones.

Plants. *Alnus crispa* Pursh.; *A. japonica* Sieb. et Zucc.; *Alnus x koehnei* Call.; *A. sinuata* Rydbg. *Source.* Botanic gardens of Darmstadt (*A. crispa*, *A. koehnei*) and Heidelberg (*A. japonica*, *A. sinuata*). *Previous work.* Two flavones from *Alnus japonica*;¹ comp.²

Present work. Lipophilic material, excreted by winter buds of all the *Alnus* species examined contains, besides triterpenoids, a number of flavonoid aglycones.

RESULTS

Alnus crispa. The bud excretion of this tree contains: kaempferol 3,7-dimethyl ether (kumatakenin), quercetin 3,7-dimethyl ether and quercetin-3,7,4'-trimethyl ether (ayanin).

Alnus japonica. Buds of this species produce many more flavonoids. The occurrence of the rare compounds luteolin 7,4'-dimethyl ether (pilloin) and scutellarein-6,7,4'-trimethyl ether (salvigenin) has already been reported.¹ Further aglycones are: kaempferide, isohamnetin, rhamnazin, quercetin-7,3',4'-trimethyl ether, the 3,6,4'-trimethyl ether of 6-hydroxykaempferol (3-methylbetuletol), acacetin, apigenin-7,4'-dimethyl ether and scutellarein-6,4'-dimethyl ether (pectolinarigenin).

Alnus koehnei. The following compounds were found: kaempferol, kaempferide, rhamnetin, isorhamnetin, quercetin-3,7-dimethyl ether, quercetin-3,3'-dimethyl ether, quercetin-7,3',4'-trimethyl ether; the 3,6-dimethyl ether, 6,4'-dimethyl ether (betuletol) and 3,6,4'-trimethyl ether of 6-hydroxykaempferol; quercetagenin-3,6,4'-trimethyl ether (centaureidin); acacetin and salvigenin.

Alnus sinuata. Buds contain only: kumatakenin, quercetin-3,7-dimethyl ether and genkwanin.

¹ WOLLENWEBER, E. and WASSUM, M. (1972) *Tetrahedron Letters*, 797.

² WOLLENWEBER, E., FAVRE-BONVIN, J. and JAY, M. (1974) *Phytochemistry*, **13**, (in press).

Besides some common flavonoids, buds of alder-trees produce many rather rare compounds as aglycones. Quercetin 7,3',4'-trimethyl ether had been known before only from buds of *Aesculus hippocastanum*.³ The methyl ethers of 6-hydroxykaempferol were first found in *Betula ermani*⁴ and *Alnus glutinosa*.⁵ Quercetin 3,7-dimethyl ether and quercetin 3,3'-dimethyl ether have just been reported to occur together in buds of several *Populus* species.⁶ The flavonoid patterns of the *Alnus* species described here are all different (see also²). A chemotaxonomic survey on more than one dozen other *Alnus* species is in preparation.

EXPERIMENTAL

The lipophilic material was recovered by extraction with acetone. The solution was evaporated and the residue taken up in C_6H_6 . Separation was brought about either on columns of silica gel, eluted with C_6H_6 and increasing quantities of EtOAc and MeOH, or by preparative TLC. Solvents for TLC were (a) C_6H_6 -petrol.-EtOAc-MeOH 60:26:7:7 or (b) C_6H_6 -dioxane-MeOH 8:1 for polyamide, and (c) C_6H_6 -Me₂CO 9:1 for silica gel. All flavonoids were identified by co-chromatography with authentic substances, appearance in UV light and colour reactions with spray reagents and by their UV spectra, as already published in previous papers of this series.^{1,3-6}

³ WOLLENWEBER, E. and EGGER, K. (1970) *Tetrahedron Letters*. 1601.

⁴ WOLLENWEBER, E. and LEBRETON, P. (1971) *Biochimie* **53**, 935.

⁵ WOLLENWEBER, E., BOUILLANT, M.-L., LEBRETON, P. and EGGER, K. (1971) *Z. Naturforsch* **26b**, 1188.

⁶ WOLLENWEBER, E. (1974) *Phytochemistry* **13**, 760.

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CYANOMETHYLENECYCLOHEXYL GLUCOSIDES FROM *SIMMONDSIA CALIFORNICA*

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Key Word Index—*Simmondsia californica*; Buxaceae; jojoba; simmondsin; cyanomethylenecyclohexyl glucosides.

Plant. *Simmondsia californica* Nutt. [*Simmondsia chinensis* (link) Schneider], common name; jojoba. *Source.* University of California, Riverside. *Previous work.* Wax esters of seed,¹ cyanomethylenecyclohexyl glucoside from seed.²

Present work. Milled seed was extracted in succession with petrol, C_6H_6 and EtOAc. Chromatography of the EtOAc extract on silica gel using a gradient from $CHCl_3$ to 20% MeOH/ $CHCl_3$ yielded three fractions showing characteristic conjugated nitrile absorption at $ca\ 2220\ cm^{-1}$ in the IR spectra of the crude materials. The major component (of intermediate polarity) was simmondsin [2-(cyanomethylene)-3-hydroxy-4,5-dimethoxycyclohexyl β -D-glucoside].² The faster running material consisted of a mixture of *cis* and *trans*

¹ (a) MIWA, T. K. (1971) *J. Am. Oil Chemists' Soc.* **48**, 259. (b) MIROV, N. T. (1952) *Econ. Bot.* **6**, 41.

² ELLIGER, C. A., WAISS, A. C. and LUNDIN, R. E. (1973) *J. Chem. Soc. Perkin Trans. I*, No. 19, 2209.