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 also[2]). 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–Me_2CO 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.

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Phytochemistry, 1974, Vol. 13, pp. 2319 to 2320. Pergamon Press. Printed in England.

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.

simmondsin 2′-ferulate, λ_{max}^{EtOH}, 328,218 nm (log ϵ = 4·05, 4·20); $\lambda_{max}^{EtOH,\ basic}$, 380 nm (log ϵ = 4·21) whose NMR spectrum is essentially a superposition of those of simmondsin and of ferulic acid. Base hydrolysis yielded ferulic acid, identical to an authentic sample, as well as 2-hydroxy-3-methoxyphenylacetonitrile (also produced from simmondsin under basic conditions). Treatment with aqueous ammonia removed the feruloyl residue to give simmondsin which was identical in all respects to authentic material. Satisfactory elemental analyses were obtained on the penta-acetate (m.p. 170–171°, aq. EtOH) and on the 4′,6′-benzylidine derivative. That the substituent feruloyl group was attached at position 2 of the glucosyl unit was inferred from the chemical shift [δ = 4·81 (deuteroacetone)] of the corresponding proton.[3]

The mixture of substances which was eluted in the most polar column fraction was acetylated and rechromatographed on silica gel with a gradient from hexane to ethyl acetate. Obtained in this way were hexaacetates of the two monodesmethylsimmondsins. Although these materials did not crystallize and were never obtained in pure form, it was possible to characterize them as acetates of 2-(cyanomethylene)-3,4-dihydroxy-5-methoxycyclohexyl β-D-glucoside and 2-(cyanomethylene)-3,5-dihydroxy-4-methoxycyclohexyl β-D-glucoside. These structural assignments were based upon their NMR spectra in comparison with that of simmondsin penta-acetate which clearly reveals the respective methoxyl or acetoxyl substitution. Additionally, base treatment of the former hexa-acetate yielded 2,3-dihydroxyphenylacetonitrile while treatment of the latter provided 2-hydroxy-3-methoxyphenylacetonitrile. These results parallel the behavior of simmondsin under similar conditions.[2]

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Phytochemistry, 1974, Vol. 13, pp. 2320 to 2321. Pergamon Press. Printed in England.

TRICIN-5-*O*-GLUCOSIDE AND OTHER FLAVONOIDS OF *CIRSIUM ARVENSE*

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Key Word Index—*Cirsium arvense* (L.) Scopili (*Carduus arvensis* (L.) Robson); Compositae; Tricin-5-*O*-glucoside; Quercetin-3-*O*-rhamnoglucoside; Quercetin-3-*O*-digalactoside; cirsimaritin; pectolinaringen.

Relatively few reports concerning the phenolic chemistry of the large genus *Cirsium* Mill. have been published.[1–3] Tricin glycosides have only been reported as constituents of the "more advanced" monocots[4,5] while the aglycone, tricin, has been identified as a constituent in the seeds of one of the parasitic dicots.[4]

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[1] EARLIER REFERENCES CITED IN WALLACE, J. W. and BOHM, B. A. (1971) *Phytochemistry* **10**, 452.

[2] MCGOWAN, S. G. and WALLACE, J. W. (1972) *Phytochemistry* **11**, 1503.

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