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]

Acknowledgements We thank Dr. D. M. Yermanos, University of California, Riverside, for a sample of *S. californica* seed, Miss G. E. Secor for elemental analyses and Mrs. Mabry Benson for spin decoupled NMR spectra at 100 MHz.

[3] JACKMAN, L. M. and STERNHELL, S. (1966) *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd edn., pp. 176–180. Pergamon Press, New York.

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

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(*Received* 2 *April* 1974)

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]

[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.
[3] GARDNER, R. C. (1973) *Phytochemistry* **12**, 223.
[4] HARBORNE, J. B. (1967) *Comparative Biochemistry of the Flavonoids*. Academic Press, London.

Three major and three minor flavonoids have been identified as constituents of *Cirsium arvense* using the standard procedures of Mabry *et al.*[6] One of the major compounds was identified as tricin-5-*O*-glucoside (PC R_f: TBA, 0·10; 15% HOAc 0·16; H_2O, 0·01; PhOH, 0·72; BAW, 0·27; abbreviations refer to the standard solvent systems of Harborne and Mabry).[4,6] It appeared as a "whitish–yellow" chromatographic region when illuminated with near UV and became bright yellow when fumed with NH_3. Spectral data for this compound were: MeOH 346, 262 (sh), 240; NaOMe 406,259; $AlCl_3$ 390, 368, 310, 270; $AlCl_3$/HCl 384, 358, 306, 268; NaOAc 410, 310 (sh), 260; NaOAc/H_3BO_3 348, 259 (sh), 238. Hydrolysis of this glycoside yielded the sugar glucose and the aglycone tricin; the R_f and spectral properties of the latter were in agreement with Mabry *et al.*[6] Two additional major flavonoids were identified as quercetin-3-*O*-digalactoside (PC R_f: (solvents as listed), 0·33; 0·72; 0·20; 0·46; and 0·46) and quercetin-3-*O*-rhamnoglucoside (PC R_f: 0·44; 0·67; 0·12; 0·54; and 0·65). Both of these glycosides agreed spectrally and visibly as reported for quercetin-3-*O*-diglycosides.[6] Upon acidic hydrolysis both produced quercetin and their respective sugars; however, a minor flavonoid aglycone was identified from the hydrolyzate of each of the foregoing quercetin-diglycosides. The aglycone, pectolinaringen, was isolated as a hydrolytic product from quercetin-3-*O*-digalactoside while cirsimaritin was isolated as a hydrolytic product from quercetin-3-*O*-rhamnoglucoside. The spectral and chromatographic properties of these aglycones agreed with published data. Glycosides of the latter two compounds could not be separated from the quercetin-diglycosides. Since cirsimaritin has been identified as the 4′-*O*-rutinoside in *C. brevistylum*,[1] and since only rhamnose and glucose were obtained from the hydrolysis of the quercetin-glycoside, cirsimaritin probably exists as the 4′-*O*-rutinoside. Using similar rationale pectolinaringen probably occurs as a di- or tri-galactoside. Based on chromatographic (PC R_f: TBA, 0·73; 15% HOAc, 0·61), spectral, and sugar analysis, kaempferol-3-*O*-galactoside was also identified as a minor constituent.

EXPERIMENTAL

Leaf material (624 g) of *Cirsium arvense* was collected on the campus of the University of British Columbia during August 1969. The material was identified by the U.B.C. taxonomist, Dr. K. I. Beamish, and voucher specimens were deposited in the UBC Herbarium. The leaf material was thoroughly extracted with 10 l. of 80% EtOH. The extract was conc under vacuum to approx 10 ml and taken up in 200 ml H_2O. The aq. mixture was filtered through a bed of Celite and the filtrate was continuously extracted with EtOAc for 12 hr. The EtOAc was subsequently removed and the residue taken up in MeOH for chromatography. Paper Chromatography and UV spectral analysis, before and after hydrolysis, were according to Mabry *et al.*[6] The sugar moieties were analysed as their trimethylsilyl derivatives on 3% SE-52, 80/100 Chrom W (AW), and 3% Poly-A 101A, 100/200 GC Q. The trimethylsilyl derivatives were made using TRI-SIL (Pierce Chem. Co.). 68 monosaccharides and their derivatives were used as references.[7]

Acknowledgements—The author thanks the Western Carolina University Research Fund and the National Research Council of Canada for support of this work.

[5] HARBORNE, J. B. (1973) In *Phytochemistry* Vol. II L. P. Miller Ed., Van Nostrand Reinhold New York.
[6] MABRY, T. J. MARKHAM, K. R. and THOMAS, M. B. (1970) *The Systematic Identification of Flavonoids*, Springer, New York.
[7] WALLACE, J. W. (unpublished data).