

GLC was carried out in a  $0.32 \times 122$  cm. column packed with 1% SE-54 on Gas Chrom Z and programmed from 100 to 300° in 15 min. GLC retention times were compared to fatty acid methyl ester, hydrocarbon, and aliphatic alcohol standards from Applied Science, Inc. Other standards were synthesized in our own laboratories.

Oxidation of the  $\beta$ -diketone was according to the procedure of Downing and Greene,<sup>11</sup> except that the methyl esters were prepared using  $\text{CH}_2\text{N}_2$ .<sup>12</sup> Alkaline hydrolysis of the  $\beta$ -diketone was done by adding 2 ml of 0.5 M aqueous NaOH to 5 mg of  $\beta$ -diketone, and heating at 60° for 6 hr. After acidification with 1 N HCl and extraction with hexane, the methyl esters of the fatty acids were prepared using  $\text{CH}_2\text{N}_2$ .<sup>12</sup> Acetylation of the alcohol was done in acetic anhydride-pyridine (1:1, v/v). The i.r. spectrum of the alcohol acetate was taken using NaCl plates, and compared with the i.r. spectrum of 1-cetyl acetate and 2-cetyl acetate.

Mass spectra were determined with a Varian Mat CH-5 mass spectrometer operating at ionizing voltage 30eV, collector current 100  $\mu\text{A}$ . The heated sample inlet was operated up to 200°.

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<sup>11</sup> D. T. DOWNING and R. S. GREENE, *Lipids* 3, 96 (1968).

<sup>12</sup> H. SCHLENK and J. L. GELLERMAN, *Anal. Chem.* 32, 1412 (1960).

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## FLAVONOIDS OF *STIPA LEMMONII*

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**Abstract**—The presence of a number of flavonoid *O*-glycosides along with two *C*-glycosides is confirmed in *Stipa lemmonii*. The identified glycosides are: tricin 5-glucoside, 7-glucoside and 7-glucuronide; chrysoeriol 7-glucoside, 7-glucuronide and 7-rutinoside; luteolin 7-glucoside; iso-orientin and its glucoside; kaempferol and quercetin 3-acylglucosides(?).

IN THE course of a survey of certain grasses for flavonoids, a number of *O*-glycosides of tricin, chrysoeriol, luteolin, kaempferol and quercetin were found to occur along with iso-orientin and its glucoside in *Stipa lemmonii* Vasey.

Two dimensional paper chromatography of extracts of the plant revealed the presence of about fourteen flavonoids. Luteolin 7-glucoside and iso-orientin were readily identified by paper chromatography with authentic samples. The second *C*-glycoside gave glucose and a mixture of iso-orientin and orientin on acid hydrolysis, the u.v. was identical with that of iso-orientin, giving shifts with  $\text{AlCl}_3$ , sodium acetate and boric acid, suggesting that the glucose is attached through the glycosyl residue of iso-orientin and not through a phenolic hydroxyl group. The only other such glycoside reported is 2''-*O*- $\beta$ -D-xylopyranosylvitexin.<sup>1</sup> No other *C*-glycosides were found in *S. lemmonii*.

<sup>1</sup> R. M. HOROWITZ and B. GENTILI, *Chem. & Ind.* 625 (1966).

Tricin was found to occur in the free form along with three of its glycosides. It was identified through its chromatographic and u.v. characteristics and demethylation which gave the corresponding 5,7,3',4',5'-pentahydroxyflavone which in turn was found to be identical in properties with those reported in the literature.<sup>2</sup>

Both tricin 5-glucoside and 7-glucoside along with the 7-glucuronide were identified through the standard methods of identification, along with chrysoeriol 7-glucoside, chrysoeriol 7-glucuronide and chrysoeriol 7-rutinoside. The identity of chrysoeriol was confirmed through u.v. and chromatographic properties along with demethylation which gave luteolin. A number of these glycosides have been previously reported in grasses.<sup>3</sup>

The presence of kaempferol and quercetin glycosides is rare in grasses and only one report of their glucosides in *Panicum bulbosum* and *Lolium perrene* is recorded.<sup>2</sup> Both glycosides appear to be polyglycosides giving kaempferol 3-glucoside and quercetin 3-glucoside as intermediates. The u.v. data indicate that glycosylation occurs at position 3 only; however insufficient material prevented any further studies. The possibility is that they are acylated derivatives, as they failed to co-chromatograph with authentic samples of 3-mono-glucosides or 3-diglucosides.

Two other flavonoids of minor concentration were present but could not be identified due to lack of material.

#### EXPERIMENTAL

*Source of Plants.* 6 miles west of Cle Elum, Kittitas Co., Washington, Collection No. Maze and Bohm 501. Vouchers have been deposited in the U.B.C. Botany Department Herbarium. Plants were maintained in cultivation in the U.B.C. Botany Department gardens until used.

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<sup>2</sup> J. B. HARBORNE, *Comparative Biochemistry of Flavonoids*, Academic Press, London (1967).

<sup>3</sup> J. B. HARBORNE and E. HALL, *Phytochem.* 3, 421 (1964).

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### FRUCTOSYLRAFFINOSE, A TETRASACCHARIDE IN WHEAT BRAN

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**Abstract**—A new tetrasaccharide has the structure *O*- $\alpha$ -D-galactopyranosyl-(1 $\rightarrow$ 6)- $\alpha$ -D-glucopyranosyl-(1 $\rightarrow$ 2)-[*O*- $\beta$ -D-fructofuranosyl-2 $\rightarrow$ 1]- $\beta$ -D-fructofuranoside.