(C$_4$), 166.0 (C$_7$), 163.8 (C$_5$), 163.4 (C$_9$), 148.6 (C$_{4'}$), 147.0 (C$_{3'}$), 131.7 (C$_{1'}$), 118.6 (C$_{6'}$), 114.5 (C$_{5'}$), 112.3 (C$_{2'}$), 104.1 (C$_{10}$), 101.3 (C$_{1''}$), 100.3 (C$_{1'''}$), 97.1 (C$_6$), 96.3 (C$_8$), 77.0, 76.4, 73.7, 73.0, 71.5, 71.0, 70.4, 69.0, 66.7 (sugar carbons cf Table 1), 56.1 MeO), 18.0 (C$_{6'''}$).

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O''-RHAMNOSOLISOSWERTISIN FROM OATS (*AVENA SATIVA*)

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Key Word Index—*Avena sativa*; Gramineae; oats; *C*-glycosylflavonoid; O''-rhamnosyl-isoswertisin.

Previous studies of oats have shown the presence of avenacin in roots [1], avenacoside in leaves [2] and flavonoids in leaves [3,4]*. A methanolic extract of finely ground primary leaves of Shokan 1 seedlings subjected to Si gel column chromatography has now yielded a pale yellow pigment. *O''*-rhamnosyl-8-*C*-β-D-glucopyranosylgenkwanin or (*O''*-rhamnosylisoswertisin, **1**).

Acidic hydrolysis of **1** gave rhamnose and an aglycone (**2**). The aglycone, **2** was identified as isoswertisin [5,6] from NMR, IR and MS [7] data and confirmed by direct comparison with an authentic sample. The NMR spectrum of the acetate of **1** exhibited two acetyls attached to aromatic ring at δ 2.35 and 2.42, indicating that rhamnose was attached to *C*-glucosyl moiety in **2**. Thus, **1** was identified as *O''*-rhamnosylisoswertsn, although the glycosyl linkage is not yet established.

EXPERIMENTAL

Extraction. Finely ground primary leaves (2.8 kg, fr. wt) of oat cultivar were extracted with 1.5 l. of MeOH. The MeOH soluble fraction was then evaporated to dryness. The resulting solid was successively extracted with 200 ml Et$_2$O and 200 ml MeOH. To the MeOH soln, 1.6 l. of Et$_2$O was added to form the Et$_2$O-insoluble ppt. (2.7 g). The ppt. was then chromatographed over Si gel column (3 × 45 cm) with CHCl$_3$–MeOH–H$_2$O (7:3:1), **1** separated and the crystallization from MeOH–CHCl$_3$ gave pale yellow powdery crystals (54 mg). Mp 199–204°, $[\alpha]_D^{18}$ − 108 (Py, *c* 0.64), (Found: C, 52.49; H, 5.92. C$_{28}$H$_{32}$O$_{14}$.2.5 H$_2$O requires: C, 52.75; H, 5.85%), UV λ_{max}^{EtOH} nm (log ε): 272 (4.18), 340 (4.20); + NaOMe: 260 (4.15), 270 (4.16), 404 (4.41): + NaOAc: no shift; + NaOAc + H$_3$BO$_3$: no shift: + AlCl$_3$: 280 (4.17), 306 (4.06), 340 (4.25), 392 (4.15): + AlCl$_3$ + HCl: 278 (4.16), 306 (4.06), 340 (4.25), 392 (4.11); IR ν_{max}^{KBr} cm^{-1}: 3400, 1660, 1600, 1450, 1050; NMR (90 MHz, DMSO-D$_6$ + D$_2$O); δ 8.04 (2H, *d*, *J* = 8.5 Hz, C-2′, 6′), 6.92 (2H, *d*, *J* = 8.5 Hz, C-3′, 5′), 6.82 (1H, *s*, C-6), 6.50 (1H, *s*, C-3), 5.8–3.0 (*m*), 3.92 (3H, *s*, OMe), 0.47 (3H, *d*, *J* = 6.8 Hz, rhamnose MeOH). NMR of the acetate of **1** (Mp 138–143°) (90 MHz, CHCl$_3$): δ 8.00 (2H, *d*, *J* = 9.0 Hz, C-2′, 6′), 7.26 (2H, *d*, *J* = 9.0 Hz, C-3′, 5′), 6.68 (1H, *s*, C-6), 6.60 (1H. *s*. C-3), 5.5–3.7 (*m*), 4.06 (3H, *s*, OMe), 2.42 (3H, *s*, aromatic acetyl), 2.35 (3H, *s*, aromatic acetyl), 2.1–1.8 (18H, 6 × sugar acetyl), 0.62 (3H, *d*, *J* = 6.8 Hz, rhamnose Me). Acid hydrolysis of **1** gave rhamnose and the aglycone **2**, mp shrinking at 200–230° and melting with decomp. at 290–293° (lit. [5]); MS (80 eV) *m/e* (rel. int.): 326 (11), 311 (10), 297 (100), 179 (30), 121 (9), 118 (5); IR ν_{max}^{KBr} cm^{-1}: 3350, 1650, 1580, 1100–1050; NMR (90 MHz, DMSO-d$_6$ + hexaduetroacetone): δ 8.03 (2H, *d*, *J* = 8.5 Hz, C-2′, 6′), 6.95 (2H, *d*, *J* = 8.5 Hz, C-3′, 5′), 6.63 (1H, *s*, C-6), 6.43 (1H, *s*, C-3), 4.87 (1H, *d*, *J* = 10 Hz, C-1″), 3.91 (3H, *s*, OMe), 4.2–3.0 (*m*) was identified as isoswertisin by direct comparison with NMR and IR of authentic sample and mmp (293°).

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* The compound described by Weissenboeck as 'apigenin-7-methoxy(?)-8-*C*-β-rhamnosylglucosylglucoside' in *Aventa sativa* L, leaves ('gellhafer') was suggested to be *O''*-rhamnosylisoswertisin i.e. **1** (Prof. J. Chopin, personal communication).

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6,8-DI-*C*-GLUCOSYLFLAVONES FROM *LARREA TRIDENTATA* (ZYGOPHYLLACEAE)

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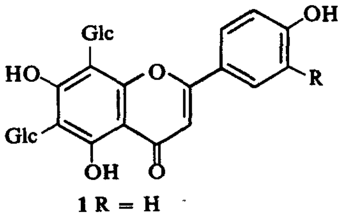
Key Word Index—*Larrea tridentata*; *L. divaricata*; Zygophyllaceae; 6,8-di-*C*-glucosylapigenin; 6,8-di-*C*-glucosylchrysoeriol; scoparin; glycoflavones.

We previously described 19 flavonoid aglycones from *Larrea tridentata* and *L. divaricata* [1–3]. In continuation of our investigations of *L. tridentata*, we now report the isolation and characterization of two *C*-glucosyl-flavones, 6,8-di-*C*-glucopyranosylapigenin (vicenin-2) (**1**) and a new flavonoid from nature [4], 6,8-di-*C*-β-D-glucopyranosylchrysoeriol (**2**).

Compound **1** was isolated as pale yellow crystals (from MeOH), mp above 238° (dec); λ_{max} (MeOH): 274, 302, 330 nm. All the standard [5] UV data and R_f values as well as the NMR spectrum of the trimethylsilyl ether of **1** were in accord with an apigenin 6,8-di-*C*-hexoside. It was therefore directly compared with an authentic sample of 6,8-di-*C*-β-D-glucopyranosylapigenin [6] by IR and co-chromatography and shown to be identical with it.



1 R = H
2 R = OMe

Compound **2** was isolated as yellow pellets (from MeOH), mp 110–150° (gradual dec); λ_{max} (MeOH): 273, 347 nm. All the standard [5] UV data and R_f values supported a chrysoeriol 6,8-di-*C*-hexoside structure. Furthermore, the MS of the PDM derivative showed the expected M^+ at m/e 811 and a fragmentation pattern for a undecadeuterio 6,8-di-*C*-hexosylchrysoeriol [7]. An authentic sample of 6,8-di-*C*-β-D-glucopyranosylchrysoeriol was prepared by *C*-glucosylation of scoparin [8] and the synthetic material was shown to be identical with compound **2** by IR and co-chromatography and by co-chromatography of their PM derivatives.

EXPERIMENTAL

Mps were uncorr. UV spectra were carried out by standard procedures [5]. The NMR spectrum of the TMS ether of **1** was measured at 60 MHz in CCl_4 with tetramethylsilane as an internal standard. Air-dried and ground leaf material (500 g) from a diploid population of *L. tridentata* (collected near Alpine, Texas, July, 1973) was extracted with 85% aq. MeOH; the extract was filtered and the filtrate was concd to an aq. suspension: the latter was extracted with ether repeatedly until the ether layer was colorless. The aq. layer was taken to dryness *in vacuo*. The residue was dissolved in MeOH and the soln filtered. More than 200 PCs of the MeOH solution were run with TBA. The bands with R_f values of from 0.05 to 0.30 were eluted with MeOH. From the concd extract 100 PCs were run with 15% HOAc; the bands with R_f values from 0.35 to 0.50 and from 0.50 to 0.60 were extracted separately with MeOH. Both extracts were evaporated and two residues were each chromatographed through a polyamide column using MeOH for elution. Recrystallization from MeOH of the column-chromatographed material (originally from bands of 0.35 to 0.50 R_f values on paper) gave pale yellow crystals of 6,8-di-*C*-glucosylapigenin (**1**): bands from paper of R_f values between 0.50 and 0.60 gave

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