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ACYLATED KAEMPFEROL GLYCOSIDES FROM *ACONITUM* (RANUNCULACEAE)

DAVID A. YOUNG* and ROBERT W. STERNER†

* Department of Botany, University of Illinois, Urbana, IL 61801, U.S.A.; † Department of Ecology and Behavioral Biology, University of Minnesota, Minneapolis, MN 55455, U.S.A.

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Key Word Index—*Aconitum noveboracense*; *Aconitum columbianum*; Ranunculaceae; flavonols; acylated kaempferol glycosides.

Abstract—Four new acylated kaempferol glycosides were isolated and identified from the leaves of *Aconitum noveboracense* and *A. columbianum*.

During a chemosystematic study of the *Aconitum noveboracense* A. Gray–*Aconitum columbianum* Nutt. in T. & G. complex of North America, six flavonol glycosides were isolated and characterized. The UV spectral properties of four of the compounds indicated that they were 3,7-substituted kaempferol glycosides and that they were acylated [1] (Table 1). The compounds were purified using a combination of 1D-PC and column chromatography (see Experimental), and were identified as follows (compounds **1**–**3** were isolated from *A. noveboracense* and **4** from *A. columbianum*).

1 (R_f (×100) 38/65; TBA, 15% HOAc). Acid hydrolysis of **1** yielded kaempferol, caffeic acid and glucose. Enzymatic hydrolysis with β-glucosidase yielded a 3-substituted kaempferol glycoside (**1a**, R_f 59/60) and glucose. These data suggested that the acyl group was located at the 3-position and that glucose was present at the 7-position. H_2O_2 oxidation of **1a** yielded glucose, suggesting that **1** was a 3-*O*-monoglucoside. Based upon these data, **1** was determined to be kaempferol 3-(caffeylglucoside)-7-glucoside.

2 (R_f 38/81). Acid hydrolysis yielded kaempferol, caffeic acid, rhamnose, arabinose and glucose; enzymatic hydrolysis with β-glucosidase yielded a 7-substituted kaempferol glycoside (**2a**, R_f 51/29) and glucose. These data indicated that the acyl group, rhamnose and arabinose were located at the 7-position. Oxidation of **2** yielded a disaccharide that co-chromatographed in four

Table 1. R_f values and UV spectral properties of the acylated kaempferol glycosides of *A. noveboracense* and *A. columbianum*

	Compound	R_f/R_{rutin} (×100) in TBA	15% HOAc	H_2O	BAW	BEW*
1	Kaempferol 3-(caffeylglucoside)-7-glucoside	38/86	65/118	34/121	50/98	38/88
2	Kaempferol 3-gentiobioside-7-(caffeylarabinosylrhamnoside)	38/83	81/145	53/204	44/76	45/88
3	Kaempferol 3-glucoside-7-(*p*-coumarylglucoside)	57/106	70/130	41/165	59/113	68/119
4	Kaempferol 3-(*p*-coumarylrutinoside)-7-glucoside	34/88	71/131	55/183	38/—	43/—

	$\lambda_{max\,(nm)}$ in MeOH	NaOMe	$AlCl_3$	$AlCl_3$/HCl	NaOAc
1	353sh†, 335, 300sh, 267, 245	380, 297sh, 267, 242	393, 347, 300, 272, 263sh	393, 332, 296, 273, 265sh	400sh, 353, 299sh, 269
2	343, 330sh, 290sh, 267, 243	406, 344sh, 305sh, 275, 244	394, 347, 298sh, 273, 265sh	394, 344, 255sh, 272, 265sh	405sh, 350, 290sh, 267
3	355sh, 320, 300sh, 268, 230sh	398sh, 364, 299sh, 275, 244	393, 350sh, 322, 300, 274, 267sh	392, 350sh, 325, 300, 275, 267sh	405sh, 360sh, 320, 299sh, 267
4	355sh, 320, 301sh, 268, 228sh	400sh, 360, 299sh, 272, 243	393, 350sh, 319, 298, 273, 265sh	395, 350sh, 320, 300, 275, 267sh	405sh, 355sh, 319, 297sh, 267

* For solvent composition see refs [5, 6].
† shoulder.

solvents with gentiobiose. These data indicated that **2** is kaempferol 3-gentiobioside-7-(caffeylarabinosylrhamnoside).

3 (R_f 57/70). Acid hydrolysis yielded kaempferol, *p*-coumaric acid and glucose; enzymatic hydrolysis with β-glucosidase yielded a 7-substituted kaempferol glycoside (**3a**, R_f 63/17) and glucose, indicating that the acyl group was located at the 7-position. Acid hydrolysis of **3a** yielded *p*-coumaric acid and glucose. Oxidation of **3** yielded glucose, which suggested that it is a 3-*O*-monoglucoside. Based upon these data, **3** was determined to be kaempferol 3-glucoside-7-(*p*-coumarylglucoside).

4 (R_f 34/71). Acid hydrolysis yielded kaempferol, *p*-coumaric acid, glucose and rhamnose; enzymatic hydrolysis with β-glucosidase yielded a 3-substituted kaempferol glycoside (**4a**, R_f 44/73) and glucose. These data suggested that the acyl group was located at the 3-position and that **4** is a 7-*O*-monoglucoside. Oxidation of **4a** yielded rutinose. From these results, **4** was determined to be kaempferol 3-(*p*-coumarylrutinoside)-7-glucoside. Besides **1**–**3**, quercetin 3-*O*-sophoroside and an unidentified quercetin glycoside (R_f 33/61) were detected in *A. noveboracense*.

To our knowledge, this is the first report of these acylated kaempferol glycosides from nature. Acylated flavonoids previously have not been reported from *Aconitum*, although they have been detected in other genera of Ranunculaceae (e.g. *Helleborus* [2], *Coptis* [3] and *Delphinium* [M. Warnock, personal communication]). Flavonoid surveys of additional genera of Ranunculaceae are needed before the distribution of acylated flavonoids in the family can be determined and their potential taxonomic significance evaluated.

EXPERIMENTAL

Plant material was collected by the authors from natural populations of the two species, and vouchers are deposited in the University of Illinois herbarium (ILL). Extraction, separation and purification of a leaf flavonoids of each species followed standard procedures of 1D- and 2D-PC and polyamide and Sephadex (LH-20 and G-10) column chromatography (eluted with 50–100% aq. MeOH, 80% aq. MeOH and 100% MeOH, respectively) [4, 5]. Purified compounds were identified by their R_f/R_{rutin} values in five solvents (TBA, 15% HOAc, BAW, BEW, H_2O; see [5] and [6] for solvent composition), color properties in UV light with and without NH_3 vapor, UV spectral properties [1, 5] and acid (1 N HCl for 1 hr over boiling H_2O bath) and enzyme (β-glucosidase) hydrolysis products. Sugars obtained from hydrolyses were identified by co-chromatography with known standards on PC in several solvents [6]. H_2O_2 oxidations followed standard procedures [6].

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