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LINARIN MONOACETATE FROM *THALICTRUM AQUILEGIFOLIUM**

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Key Word Index—*Thalictrum aquilegifolium*; Ranunculaceae; ^{13}C NMR; flavonoid glycoside; linarin monoacetate; linarin.

Abstract—Linarin monoacetate, a new flavonoid glycoside, has been isolated from *Thalictrum aquilegifolium* and the position of the acetyl group has been determined by ^{13}C NMR spectral data.

In a previous paper [1] we reported a novel glycoside containing a nitro group, thalictoside from *Thalictrum aquilegifolium*. Recently, a new flavonoid glycoside **1**, and linarin (**2**) have been isolated from this plant. We wish to describe **1** in this paper.

Compound **1** was analysed for $C_{30}H_{34}O_{15}\cdot 1.5H_2O$. ^{1}H NMR (100 MHz, C_5D_5N; δ, TMS internal reference): 1.30 (3H, *d*, $J = 6.0$ Hz, $CH_3CH<$), 2.02 (3H, *s*, MeCOO—), 3.74 (3H, *s*, MeO—). IR ν_{max}^{KBr} cm^{-1}: 3350 (OH), 1720 (ester C=O), 1650 (ketone C=O), 1610 (C=C), 1590, 1560, 1500 (aromatic ring). UV λ_{max}^{MeOH} nm ($\log\varepsilon$): 270 (4.02), 328 (4.06).

Acetylation of both **1** and **2** with Ac_2O–pyridine afforded the same compound, linarin heptaacetate (**3**) [2]. Alkaline hydrolysis of **1** gave **2** which was identified with an authentic sample of linarin [3] by TLC, IR and mmp. Furthermore, UV ($\lambda_{max}^{MeOH+AlCl_3}$: 280, 303, 348, 385) revealed diagnostic bathochromic shifts indicating the presence of the free phenolic hydroxyl group at the C-5 position. From these results it follows that **1** is linarin monoacetate and the acetyl group is attached to the sugar moiety.

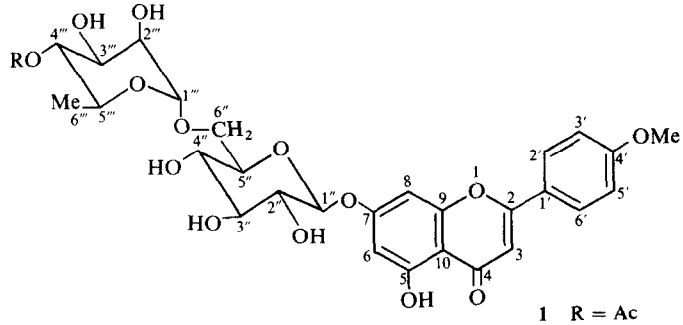
Recently, the position of the acyl group of linarin 2-methylbutyrate was determined by ^{13}C NMR data [4], and ^{13}C NMR signals of sugar carbons of several flavonoid diglycosides were assigned [5]. Table 1 presents

Table 1. ^{13}C NMR data* of the sugar carbons of **1** and **2**

Carbon	**2**	**1**
1″	99.9	99.7
2″	73.0	73.0
3″	76.3†	76.2‡
4″	69.6	69.4
5″	75.6†	75.3‡
6″	66.1	65.7
1‴	100.4	100.0
2‴	70.2	70.2
3‴	70.7	68.1
4‴	72.0	73.9
5‴	68.2	65.7
6‴	17.7	17.2
CH_3CO	—	20.8
$MeCO$	—	169.8

*The spectra were measured with a JNM FX-100 spectrometer (25 MHz) in DMSO-^{12}C-d_6 with TMS as an internal reference, using a 5 mm glass tube.

†, ‡Assignments bearing the same superscript in each spectrum may be reversed.



*Part I in the series "Studies on the Constituents of Ranunculaceae Plants".

^{13}C NMR data of sugar carbons of **1** and **2**. All signals of **2** are in good agreement with the assignments for **2** made in the literature [4]. Each signal due to the glucose carbons of **1** is in good agreement with that of **2**, but the rhamnose carbons of **1** are quite different from those of **2**. The acetyl group, therefore, must be on the rhamnose moiety. Positions C-2‴, C-3‴ and C-4‴ (rhamnose C-2, C-3 and C-4) might each contain the acetoxyl group. It is well known [6, 7] that acylation of a sugar hydroxyl group shifts the signal of the carbon bearing the hydroxyl group by *ca* +2.0 ppm and those of the two contiguous carbons by *ca* −2.0 ppm. The signals of C-1‴ and C-3‴ must shift upfield if the acetoxyl group is attached to C-2‴, but they did not move upfield. The signals at 73.9, 65.7 and 70.2 ppm may be assigned to C-3‴, C-2‴ and C-4‴, respectively, if the acetoxyl group is assumed to be attached to C-3‴. However, both shifts of C-3‴ and C-2‴ (by +3.2 and −4.5 ppm, respectively) seem to be too large for C-3‴ to be the position of the acetoxyl group. On the other hand, when the position of the acetoxyl group is assumed to be C-4‴, the shifts of C-4‴, C-3‴ and C-5‴ (by +1.9, −2.6 and −2.5 ppm, respectively) are in good accordance with previous observations [6, 7] on rhamnose with an acetoxyl group at C-4‴. Thus we conclude that linarin monoacetate is acacetin 7-*O*-(4‴-*O*-acetyl)-α-L-rhamnopyranosyl-β-D-glucopyranoside (**1**).

EXPERIMENTAL

Mps were uncorr. Plants were collected in Shizuoka Prefecture (the central district of Japan).

Extraction and isolation of **1** *and* **2**. Dried whole plant (including roots, 630 g) of *Thalictrum aquilegifolium* was extracted with hot MeOH and the MeOH soln was concd *in vacuo* to 300 ml. The methanolic extract was extracted with 300 ml of 5% HOAc.* The aq. HOAc soln was extracted with EtOAc and the ppt. was filtered off from the conc EtOAc extract. The ppt. was chromatographed on a Si gel column (Merck 60, 70–230 mesh ASTM) and eluted with $CHCl_3$–MeOH (20:1) to give **1** as colourless needles (28 mg) and **2** (53 mg). TLC analysis on Si gel 60 F_{254} Merck plates, $CHCl_3$–MeOH (5:2), exposure to I_2 or spray with 2% $FeCl_3$: **1** (R_f 0.68), **2** (R_f 0.53). Compound **1** was recrystallized from MeOH, mp 262–263°, $[\alpha]_D^{23}$ − 93.6° (*c* 0.083, MeOH). Compound **2** was recrystallized from pyridine–H_2O, mp 273–275° (lit. [3] 253–254°).

Linarin heptaacetate (**3**). Treatment of **1** with Ac_2O–pyridine for 24 hr at room temp. afforded **3**, mp 124–125° (lit. [2] 123–125°).

Alkaline hydrolysis of **1**. Treatment of **1** with 1% KOH in MeOH overnight gave **2**.

*Part of the methanolic extract was extracted with an equivalent vol. of H_2O and the aq. soln was extracted with EtOAc. The spot of **1** included in the EtOAc extract on TLC was detected by comparison with the sample of **1** obtained from 5% HOAc extract: these facts indicate that **1** is not an artefact.

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