Phytochemistry, Vol. 20, No. 7, pp. 1757–1758, 1981.
Printed in Great Britain.

0031-9422/81/071757-02 $02.00/0

4‴-*O*-ACETYLSAROTANOSIDE, A NOVEL FLAVANONE GLYCOSIDE FROM *NIEREMBERGIA HIPPOMANICA*

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(*Received* 21 *October* 1980)

Key Word Index—*Nierembergia hippomanica*; Solanaceae; flavanone glycosides; 4‴-*O*-acetylsarotanoside; sarotanoside.

Abstract—A new flavanone glycoside was isolated from the aerial parts of *Nierembergia hippomanica* and identified as the 4‴-acetate of pinocembrin 7-neohesperidoside.

From *Nierembergia hippomanica* Miers, sarotanoside (**1**) and a new flavanone glycoside were isolated. On acid hydrolysis the latter compound gave pinocembrin, glucose, and rhamnose. The IR and ^{1}H NMR spectra indicated the presence of an *O*-acetyl group. Reaction with NaOMe in MeOH afforded sarotanoside (**1**), acetylation gave hepta-*O*-acetylsarotanoside. Acetylated flavonoid glycosides have already been described, e.g. derivatives containing 6-*O*-acetyl-β-D-glucopyranose [1] or 2-*O*-acetyl-α-L-rhamnopyranose [2]. Acyl groups cannot be located by permethylation and hydrolysis, because they are replaced by methyl during the Kuhn procedure [1]. We now show by NMR analysis that the new glycoside is the 4‴-*O*-acetyl derivative of sarotanoside (**2**).

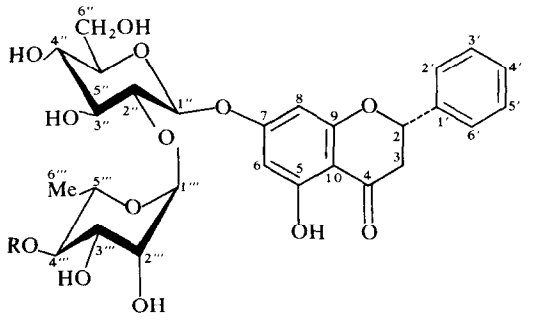
The ^{13}C NMR spectra of **1** and **2** (Table 1) differ in the rhamnose signals, indicating that the additional acetyl group is attached to this sugar. This is corroborated by an intense acetylrhamnosyl fragment in the MS of **2**. A triplet in the ^{1}H NMR spectrum at 5.13 ppm for the CHOAc proton with $J = 10$ Hz proves the 4‴-*O*-position of the acetyl group. In positions 2‴ or 3‴ double doublets are to be expected with $J = 3$ and 2 Hz or $J = 10$ and 3 Hz, respectively [2]. The ^{13}C NMR spectrum of **2** agrees with the 4‴-attachment of acetyl showing a downfield shift of +2.2 ppm for C-4‴ and an upfield shift of −2.6 ppm for C-3‴ and C-5‴ in comparison with the spectrum of **1**. The corresponding values for cyclohexanol and its acetate are $\Delta\delta$ +2.3 and −3.8 ppm, respectively [3].

Table 1. ^{13}C NMR spectra of sarotanoside (**1**) and 4‴-*O*-acetylsarotanoside (**2**) in DMSO-d_6 at 50 MHz*

Carbon	1	2	Carbon	1	2
2	77.1	77.0	1″	97.4	97.7
3	42.2	42.1	2″	78.6	78.6
4	196.7	196.8	3″	76.1‡	75.5‡
5	162.9†	163.0†	4″	69.6§	69.5§
6	96.4	96.4	5″	76.9‡	77.0‡
7	164.9	164.8	6″	60.4	60.4
8	95.2	95.1	1‴	100.4	99.7
9	162.5†	162.6†	2‴	70.4§	70.2§
10	103.2	103.4	3‴	70.5§	67.9
1′	138.5	138.4	4‴	71.8	74.0
2′	126.7	126.6	5‴	68.2	65.6
3′	128.6	128.5	6‴	18.0	17.5
4′	128.6	128.6	Me (Ac)		20.8
			CO(Ac)		169.8

*In ppm downfield from TMS; assignment by comparison with the chemical shifts of flavonoids [4,5], glucosides and rhamnosides [6], as well as shift differences by glycosylation [7] and *O*-acetylation [3], in accordance with the multiplicities in the off-resonance decoupled spectra.

†‡§May be interchanged.



1 R = H
2 R = Ac

EXPERIMENTAL

Seeds of *Nierembergia hippomanica* Miers, cv Veilchenblau, a common ornamental plant, were purchased from VEB Saat- und Pflanzgut, Quedlinburg, GDR. The plants were grown in the field in Halle (Saale) and harvested in September and October. A voucher specimen is retained in the Institute of Plant Biochemistry, Halle.

4‴-O-*Acetylsarotanoside* (**2**). Dried (50–60°) and ground plants including blossoms were extracted with MeOH at room temp. After evaporation *in vacuo* the residue was partitioned

between H_2O and C_6H_6–Et_2O (1:1). The aq. layer was extracted with $CHCl_3$–EtOH (2:1). Evaporation of the organic solvents gave the crude product, which was chromatographed over Si gel with $CHCl_3$–MeOH (9:1). Crystallization from MeOH afforded **2**, yield 0.21%; mp 220–5°, $[\alpha]_D^{20}$ – 103.1° (pyridine, *c* 0.75), R_f 0.36, Si gel, $CHCl_3$–MeOH (4:1), detection by anisaldehyde–H_2SO_4 at 120°. ν_{max}^{KBr} cm^{-1}: 1728 (OAc), 1640 (ketone), 1577, 1503 (aromatic compound). λ_{max}^{EtOH} nm (log ε): 329 (3.47), 285 (4.25), 227 sh (4.33), 213 (4.50). ORD (EtOH): $[\phi]_{348}$ 0° (peak), $[\phi]_{315}$ – 3800° (sh), $[\phi]_{290}$ – 7150° (trough), $[\phi]_{263}$ + 6700° (peak). ^{1}H NMR (100 MHz, DMSO-d_6/D_2O, TMS external): δ 1.42 (*d*, *J* = 7 Hz, 3 H, 6‴-H), 2.32 (*s*, 3 H, OAc), 5.13 (*t*, *J* = 10 Hz, 1 H, 4‴-H), 5.56 (*m*, 2 H, 1″-H and 1‴-H), 5.98 (*dd*, *J* = 12 and 3 Hz, 1 H, 2-H), 6.46 (*d*, *J* = 2 Hz, 1 H, 6-H), 6.53 (*d*, *J* = 2 Hz, 1 H, 8-H), 7.81 (*m*, 5 H, 2′-H to 6′-H); in DMSO-d_6 without D_2O δ 12.26 (*s*, 1 H, 5-OH). MSEI, 6–16 eV *m/z* (rel. int.): 256 (aglycone; 92), 189 (Ac-rhamnosyl [8]; 84), 179 (aglycone–C_6H_5; 100), 171 (189 – H_2O; 84), 129 (189 – HOAc [8]; 90).

Sarotanoside (**1**). Further elution of the Si gel column with $CHCl_3$–MeOH (9:1) and crystallization from EtOH gave **1**, yield 0.42%. Hydrolysis of **2** with 0.1 N NaOMe in MeOH (48 hr, 20°) afforded **1**, yield 57%; identified according to mp [9, 10], $[\alpha]_D$ [9, 10], UV [9].

Hepta-O-acetylsarotanoside. Synthesized from **2** (Ac_2O–pyridine) and identified according to mp [9], $[\alpha]_D$ [9], ^{1}H NMR [9]. MSEI, 6–16 eV, *m/z* (rel. int.): 816 (M – CH_2CO; 3), 561 (rhamnosylglucosyl hexaacetate; 69), 501 (561 – HOAc; 7), 441 (501 – HOAc; 10), 273 (rhamnosyl triacetate; 100), 256 (aglycone; 54), 213 (273 – HOAc; 62), 153 (213 – HOAc; 92).

Acid hydrolysis of **2** gave pinocembrin [N HCl in EtOH–H_2O (9:1), 3 hr, reflux], identified according to mp [11], $[\alpha]_D$ [11], UV [12], ^{1}H NMR, and high resolution MS, D-glucose and L-rhamnose [N H_2SO_4 in H_2O–EtOH (1:1), 1.5 hr, reflux], detected by PC.

Acknowledgement—I am very grateful to Dr. A. Preiß, Halle, for the ^{13}C NMR measurements.

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