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4′-HYDROXYWOGONIN 7-NEOHESPERIDOSIDE FROM *GARCINIA ANDAMANICA*

M. SARWAR ALAM, M. KAMIL and M. ILYAS

Department of Chemistry, Aligarh Muslim University, Aligarh 202001, India

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Key Word Index—*Garcinia andamanica*; Guttiferae; 4′-hydroxywogonin 7-neohesperidoside.

Abstract—A new flavone glycoside 4′-hydroxywogonin 7-neohesperidoside has been characterized from leaves of *Garcinia andamanica* by chemical and spectral studies.

INTRODUCTION

In a recent communication [1] we reported a new flavone glycoside, Sorbifolin 6-galactoside from the methanolic extract of the leaves of *Garcinia andamanica* King. In the present paper we report the isolation and characterization of another new glycoside (**1**) from the same extract.

RESULT AND DISCUSSION

The new flavone glycoside (**1**) analysed for $C_{28}H_{32}O_{15}$ responded to the Shinoda test [2], gave a ferric reaction and positive Molisch test. The UV spectrum showed absorption maxima at 272, 330 nm and the IR spectrum displayed a strong band at 3350 cm (OH) and 1640 cm (C=O). Hydrolysis with 7% aq. H_2SO_4 yielded glucose, rhamnose and an aglycone (**1a**), which gave a shift of + 12 nm with NaOAc (absent in glycoside) thus showing that a sugar is linked to the 7-position of the aglycone. This is further supported by the fact that the aglycone but not the glycoside gave a positive colour test specific for 5,7-dihydroxyl system with the vanillin–hydrochloric acid reagent [3]. The aglycone was characterized as 4′-hydroxywogonin by spectral and chromatographic comparison with an authentic sample [4].

The glycoside (**1**) formed a crystalline octaacetate (**1b**). The ^1H NMR of **1b** indicated it to be a rhamnoglucoside as it showed two aromatic acetoxyls at $\delta 2.31$ (3H) and $\delta 2.48$ (3H) and six alcoholic acetoxyls at $\delta 2.05$ (15H, *s*, OAc) and $\delta 1.78$ (3H, *s*, OAc). The positions of the H-1 protons of the rhamnosyl $\delta 4.68$ (*d*) and glucosyl $\delta 5.12$ (*d*) moieties and of the rhamnosyl methyl $\delta 1.20$ (*d*) along with the integration of the region $\delta 4.55$–5.60 and $\delta 3.52$–4.50 (ratio 7:5) of **1b** fully supported the 7-*O*-neohesperidosyl group [5, 6].

Hydrolysis of permethylated **1** yielded 3,4,6-tri-*O*-methyl-D-glucose, 2,3,4-tri-*O*-methyl-L-rhamnose and an aglycone (7-hydroxy 4′,5,8-trimethoxyflavone) which showed a bathochromic shift of 10 nm in band II with NaOAc, thus finally confirming the inter-sugar linkage as (1 → 2) as in neohesperidose [7, 8] and that the sugars are linked to position 7. Hydrolysis of **1** with diastase liberated free rhamnose indicating the α-nature of the inter-sugar linkage. Quantitative estimation of the sugar [9] showed the presence of 2 moles of sugar/mole of aglycone. Compound **1** is thus characterized as 4′-hydroxywogonin 7-*O*-neohesperidoside. To our knowledge this constitutes the first report of a glycoside of this aglycone.

EXPERIMENTAL

All mps are uncorr. The MeOH extract after fractionation on the basis of differential basicity was subjected to CC over silica gel. The EtOAc–MeOH (7:3) eluate was rechromatographed on a silica gel column with EtOAc–Me_2CO (1:1) as eluating solvent to afford **1** mp 320° (*d*), which crystallized from MeOH as yellow needles. Found C, 55.36; H, 5.28; $C_{28}H_{32}O_{15}$ requires C, 55.31; H, 5.24%; UV λ_{max}^{MeOH} nm: 272, 290 (sh) 330; + $AlCl_3$ 280, 295 (sh) 350; + $AlCl_3$–HCl 280, 300 (sh) 345; + NaOAc–H_3BO_3 272, 330; + NaOAc 272, 330; + NaOMe 270, 380.

Acetylation of **1**. Compound **1** was acetylated (Ac_2O–pyridine 24 hr, room temp.) and worked up in the usual way to afford an octaacetate derivative as cream needles, mp 121–122°. ^1H NMR (90 MHz, $CDCl_3$, TMS as internal standard) $\delta 7.80$ (2H, *d*, $J = 9$ Hz, H-2′,6′), 7.19 (2H, *d*, $J = 9$ Hz, H-3′,5′), 6.80 (1H, *s*, H-6), 6.51 (1H, *s*, H-3), 4.01 (3H, *s*, OMe), 2.31, 2.48 (3H each, *s*, OAc-4′,5), 2.05 (15H, *d*, 5 × OAc), 1.78 (3H, *s*, OAc) rhamnoglucosyl protons: 4.55–5.60 (glucose H-1,3,4 and rhamnose H-1,2,3,4), 3.52–4.50 (glucose H-2,5,6,6 and rhamnose H-5), 1.20 (3H, *d*, $J = 6$ Hz, rhamnosyl-Me). MS EIMS (70 eV) of PM ether: 328 $[M - gly]^+$ (16); 189 $[T_1]^+$ (43); 157 $[T_1 - MeOH]^+$ (18); 125 $[T_1 - 2\,MeOH]^+$ (10); 196 $[A_1]^+$ (1.5); 132 $[B_1]^+$ (2.0).

Acid hydrolysis of **1**. Compound **1** on acid hydrolysis with 7% aq. H_2SO_4 gave an aglycone (**1a**) mp 300°, characterized as 4′-hydroxywogonin by spectral and chromatographic comparison with an authentic sample [4]. Found C, 63.96; H, 3.98; $C_{16}H_{12}O_6$ requires C, 64.00; H, 4.00%. PC of aq. hydrolysate in EtOAc–pyridine–H_2O (12:5:4) and EtOAc–*i*-PrOH–H_2O (3:1:1) gave glucose and rhamnose as sugar moieties. The sugars were confirmed by GLC of the carbohydrate mixture after prep. of their alditol acetates [10].

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LILALINE—A FLAVONOID ALKALOID FROM *LILIUM CANDIDUM*

IRENA MAŠTEROVÁ, DUŠAN UHRÍN* and JOZEF TOMKO

Department of Pharmacognosy and Botanics, Pharmaceutical Faculty, Odbojárov 10, 83232 Bratislava, Czechoslovakia; *Chemical Institute of the Chemical Research Centre of the Slovak Academy of Sciences, 81238 Bratislava, Czechoslovakia

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Key Word Index—*Lilium candidum;* Liliaceae; flavonoid; alkaloid; 3,5,7,4′-tetrahydroxy-8-(3-methyl-2-oxo-5-pyrrolidinyl)flavone; structure determination.

Abstract—A new flavonoid alkaloid, lilaline, was isolated from the aerial part of *Lilium candidum.* Its structure has been elucidated as 3,5,7,4′-tetrahydroxy-8-(3-methyl-2-oxo-pyrrolidinyl)flavone.

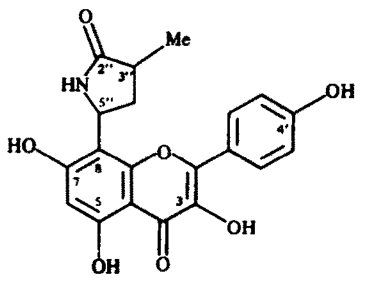
INTRODUCTION

During our search for new medicinal plant components, we investigated the aerial part of *Lilium candidum* L. growing in Czechoslovakia. In a previous publication [1] we described the isolation of a substance with the composition $C_{20}H_{17}NO_7$, while in this paper we describe its structure determination.

RESULTS AND DISCUSSION

A floral extract of white lily afforded an alkaloid which crystallizes from acetone in the form of yellow prisms, $C_{20}H_{17}NO_7$. The substance does not react with Dragendorff's reagent, but it gives a positive reaction with ferric chloride and aluminium chloride. In UV light the compound displays a yellow fluorescence, which becomes more intensive after exposure to ammonia. In the UV spectrum the absorption maxima at 272, 322 and 371 nm are characteristic of flavonols with a free 3-OH and spectral shift reagents [2] indicated free hydroxyl groups at the 5-, 7- and 4′-positions. The IR spectrum shows bands at 3300 cm^{-1} (OH), 1690 cm^{-1} (C=O in a five-membered lactam), 1640 cm^{-1} (C=O of benzopyrone) and 800 and 840 cm^{-1} (aromatic nucleus). The mass spectrum displays peaks at M^+ 383 for $C_{20}H_{17}NO_7$, calculated 383.3610, and further important fragment ion peaks at m/z 339 ($C_{19}H_{15}O_6$), 286 ($C_{15}H_{10}O_6$) and 176 ($C_{10}H_{10}NO_2$). The presence of the fragment ion 286 may be due to kaempferol while that at m/z 97 (C_5H_7NO) corresponds to the alkaloidal moiety.

It is evident from the ^{1}H NMR spectrum of lilaline that the alkaloidal moiety contains the fragment CH_3-/-CH–CH_2–CH-/-heteroatom. This fact and the IR and MS data indicate the presence of a 3-methyl-2-oxo-5-pyrrolidinyl group. The remaining signals in the ^{1}H NMR spectrum belong to the flavonoid moiety and characteristic for kaempferol substituted in position C-8 or C-6 (singlet at δ6.24). A comparison of the corresponding signals in the ^{13}C NMR spectra of lilaline at δ99.3 (C-6) resp. δ106.9 (C-8) and kaempferol [3] at δ98.2 (C-6) resp. δ93.5 (C-8) favour C-8 substitution. The signal at δ183.9 (C-2′) confirms the presence of pyrrolidinone in the molecule of lilaline. Thus lilaline is 3,5,7,4′-tetrahydroxy-8-(3-methyl-2-oxo-5-pyrrolidinyl)flavone (1).



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