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6-C-GLUCOSYLNARINGENIN FROM *TULIPA GESNERIANA*

JAROMIR BUDZIANOWSKI and LUTOSŁAWA SKRZYPCZAKOWA

Department of Pharmacognosy, Institute of Biology and Pharmacy, Medical Academy, Poznań, Poland

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Key Word Index—*Tulipa gesneriana*; Liliaceae; *C*-glucosylflavanone; hemiphloin.

Abstract—6-*C*-glucosylnaringenin, the first flavanone derivative found in Liliaceae, was isolated from the perianths of *Tulipa gesneriana* cv 'Paradae'.

INTRODUCTION

Harborne [1] showed that kaempherol and quercetin 7-*O*-glucuronide-3-*O*-rutinoside are characteristic constitutuents of the genera *Tulipa*, *C*-glycosylflavones have been previously reported to occur in *Urginea maritima* Baker [2], *Polygonatum multiflorum* (L.) All. [3, 4] and *P. odoratum* Mill [5]. This is the first report of *C*-glucosylflavanone in the Liliaceae.

RESULTS AND DISCUSSION

The isolated compound **1** gave colour reactions characteristic for a flavanone [Mg + HCl; Mg acetate; $AlCl_3$] and the high R_f values in polar solvents suggested its glycosidic nature. However, neither sugar nor aglycone were obtained on acid hydrolysis. The compound had a UV spectrum [6] and diagnostic shifts typical for a flavanone containing free hydroxyls in C-7 and C-5 positions. The NMR spectrum in DMSO-d_6 showed signals like naringenin and additionally those attributable to a hexosyl moiety at 3.35 ppm and its anomeric proton at 4.55 ppm. The singlet at 6.00 ppm integrated for one proton. These observations indicated that the sugar was attached to the flavonoid nucleus by a C—C linkage. The MS spectrum of the underivatized compound showed three strong peaks due to the sequential loss of three molecules of water. The intensity of M-148 peak relative to M-149 peak was 42% thus indicating that the sugar moiety must be attached to the C_6-position of the flavonoid nucleus [7]. The CD curve was similar to that observed in the case of naringenin [8].

The structural determination of **1**, as 6-*C*-β-D-glucopyranosyl-naringenin, was provided by direct IR, TLC, mmp comparison with natural [9, 10] and synthetic [11] hemiphloin which was isolated by Hillis and Carle [9] from *Eucalyptus hemiphloia* F. Muell. (Myrtaceae).

EXPERIMENTAL

The mps are uncorr. UV spectrum was determined in MeOH; ^{1}H NMR on EM-360 with TMS as internal standard; MS on JMS-D100; CD on Dichrographe III; MeOH c = 1.047 mg/10 cm^3. The perianths of *Tulipa gesneriana* L. cv. 'Paradae', cultivated at the Experimental Department of Agricultural Academy, Poznań, were collected in May 1975 and dried at 100°.

Isolation. Plant material (2 kg) was exhaustively extracted with MeOH under reflux. The extract, after concn at red. pres. (490 g) was taken up in H_2O and sequentially extracted with $CHCl_3$, Et_2O and EtOAc. The last fraction was dissolved in H_2O (36 g) and passed through a cellulose column. The eluates were concd and kept at 4°. The precipitate was filtered off and the remaining soln chromatographed over polyamide using H_2O and 20% MeOH. The latter fraction gave a solid which was chromatographed over cellulose powder in H_2O. The first eluates gave **1**.

Compound **1**. After crystallization from MeOH and H_2O yielded long white needles (60 mg) mp 208–210°, $[\alpha]_D^{24.7°}$ +45.8° (c = 0.5, Me_2CO–H_2O, 1:1). Colour reaction: Mg + HCl—violet, Mg acetate—blue, $AlCl_3$—yellow-blue. *PC*: H_2O (R_f 0.61), 30% AcOH (0.76), 5% AcOH (0.71) BAW 4:1:5 (0.53). *TLC* polyamide (Woelm): H_2O–EtOH–Ac_2CH_2 4:2:1 (0.41), $CHCl_3$–MeOH–EtCOMe 9:4:2 (0.21). *UV* λ_{max}^{MeOH} nm: 291, 334 (sh); + NaOMe 329, + NaOAc 330; + NaOAc + H_3BO_3 295, 332 (sh); + $AlCl_3$ 325, 390; + $AlCl_3$ + HCl 312, 385. *NMR* (DMSO-d_6, 60 MHz): δ2.90 (2H, *q*, overlapped, H_{cis}-3,H_{trans}-3), 3.35 (6H, *m*, glucosyl), 4.55 (1H, *d*, J = 9 Hz, H-1 of glucose), 5.50 (1H, *q*, J_{cis} = 5 Hz, J_{trans} = 10 Hz, H-2), 6.00 (1H, *s*, H-8), 6.84 (2H, *d*, J = 8.5 Hz, H-3', H-5'), 7.39 (2H, *d*, J = 8.5 Hz, H-2', H-5'). *MS* (probe) 70 eV, 250° (*m/e*, rel. int. %): M^+ 434 (0), 416 (M-1H_2O; 44), 398 (M-2H_2O; 36), 380 (M-3H_2O; 18), 286 (M-148; 17), 285 (M-149; 40), 272 (A, 31), 165 (100%), 153 (18), 152 (15), 120 (100), 69 (31), 55 (28); 20 eV (*m/e*, rel. int. %): 434 (0), 416 (100), 398 (58), 380 (29), 286 (21), 285 (42), 272 (18), 165 (41), 153 (13), 152 (14), 120 (34), 69 (1), 55 (2). *CD* (MeOH): $[\theta]_{329}$ +10270, $[\theta]_{290}$ −36971, $[\theta]_{252}$ +4792, $[\theta]_{217}$ +39710. IR (KBr) spectra, R_f values in APWM, mp and mmp of natural with synthetic hemiphloin were identical

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