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A PYRAN-TYPE GLYCOSIDE FROM *DIANTHUS SUPERBUS* VAR. *LONGICALYCINUS**

MINEO SHIMIZU, TOSHIMITSU HAYASHI, KATSUMI SHIMIZU and NAOKATA MORITA

Faculty of Pharmaceutical Sciences, Toyama Medical and Pharmaceutical University, Toyama 930-01, Japan

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Key Word Index—*Dianthus superbus* var. *longicalycinus*; Caryophyllaceae; young leaves; dihydropyrans; 2-methyl-3,4-dihydroxydihydropyran; 2-methyl-3,4-dihydroxy-4-*O*-β-D-glucoside.

Abstract—From the young fresh leaves of *Dianthus superbus* var. *longicalycinus* 2-methyl 3,4-dihydropyran and its monoglucoside have been isolated.

INTRODUCTION

Continuing our investigation on constituents of *Dianthus superbus* var. *longicalycinus* [1], we have now isolated a dihydropyran derivative and its glycoside from aqueous MeOH extracts of the young fresh leaves. These compounds do not occur in more mature parts of the plant. This paper deals with their structure elucidation.

RESULTS AND DISCUSSION

70% MeOH–H_2O extracts of the young fresh leaves of *Dianthus superbus* were extracted successively with Et_2O, EtOAc and *n*-BuOH. Purification of the EtOAc-soluble part by Si gel column using petrol–EtOAc (17:3) as eluting solvent gave **1**, white needles, mp 64–65°, $C_6H_{10}O_3$. The IR spectrum of **1** showed the presence of hydroxyl groups (3200–3580 cm^{-1}) and double bonds (1640 cm^{-1}). In the mass spectrum, **1** gave fragment ion peaks at *m/z* 130 (M^+), and *m/z* 58 and 71 derived from retro-Diels–Alder rearrangement [2]. In the ^1H NMR spectrum of **1**, a signal due to a methyl group appeared at δ 1.38 as a doublet (J = 6 Hz), double bond protons at 4.67 (1 H, *q*, J_1 = 6 Hz, J_2 = 2 Hz) and 6.29 (1 H, *d*, J = 6 Hz) and broad signals at 3.10–4.56 ppm (5 H). Catalytic hydrogenation of **1** yielded a dihydro derivative (**3**), $C_6H_{12}O_3$, not giving signals due to double bond protons in the ^1H NMR. The ^1H NMR data of **1** and **3** demonstrated the partial structure –O–CH=CH–CH< taking into consideration the large differences in the chemical shift between the two double bond protons. By the usual acetylation, **1** gave a diacetate (**4**) (oil). In the ^1H NMR spectrum of **4** (Table 1) three proton signals overlapped with the hydroxyls in **1** (3.10–4.56 ppm) and were shifted to 4.07 (1 H, *m*), 5.0 (1 H, *t*) and 5.3 ppm (1 H, *m*). On irradiation of the methyl signal at δ 1.3, the multiplet at 4.07 changed into doublet. By additional decoupling examination, the signal at δ 4.75 was assigned to the double bond proton, that at δ 5.0 to the proton attached to the acetoxyl group adjacent to the methyl-bearing methine while the multiplet at δ 5.3 was found to couple with the double bond proton (4.75). Hence, the structure of **1** was concluded to be 2-methyl-3,4-dihydroxydihydropyran.

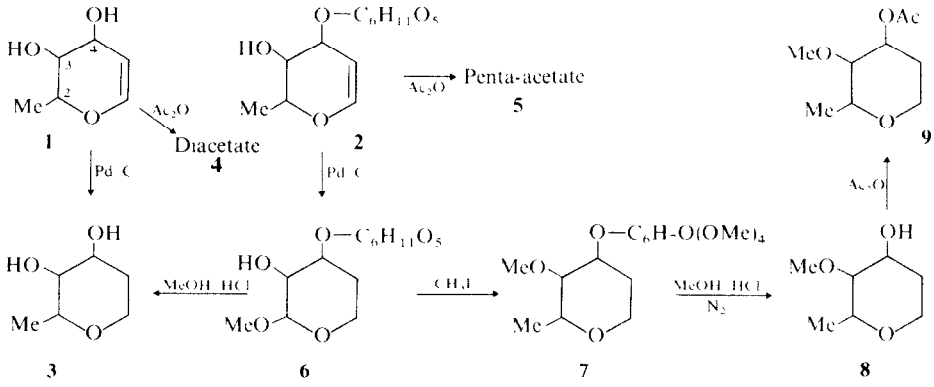
Purification of the BuOH-soluble fraction afforded white needles (2) ($CHCl_3$–MeOH), mp 179°, $C_{12}H_{20}O_8$. The IR spectrum of **2** is similar to that of **1** except in the absorption region of the hydroxyl group. Acetylation of **2** gave a pentaacetate (**5**), mp 133–135°, MS *m/z* 442 (M^+ −60), 331. Hydrolysis of **2** with MeOH–HCl, did not yield the corresponding aglycone but glucose was confirmed by PPC. The dihydro derivative (**6**) obtained by

Table 1. ^1H NMR chemical shifts of compound **4** and **9**.* Values of δ (from TMS) for $CDCl_3$

Compound	Assignment							
	2	3	4	5	6	–Me	–OAc	–OMe
4	4.07 (*m*)	5.00 (*t*) (J = 7 Hz)	5.30 (*m*)	4.75 (*q*) (J = 6.2 Hz)	6.38 (*d*) (J = 6 Hz)	1.30 (*d*) (J = 6 Hz)	2.01, 2.06	
9	3.06–4.03 (overlapped)	2.83 (*t*) (J = 7)	4.83 (*m*)	1.65 (2 H, *m*)	3.06–4.03 (overlapped)	1.27 (*d*) (J = 6 Hz)	2.06	3.49

* Numbering as formulae **1**.

* Part II in the series "The Constituents of Caryophyllaceous Plants". For Part I, see ref. [1].



catalytic hydrogenation of **2**, however, gave **3** on hydrolysis with MeOH–HCl in N_2. These assignments are in accord with the fact that **1** is labile to heat, acid and light while **3** is relatively stable. The location of the glucose moiety in **2** was decided as follows. The permethylether (**7**) of **6** prepared by Hakomori's method [3] was hydrolysed to afford the corresponding aglycone (**8**). In the ^{1}H NMR spectrum (Table 1) of the acetate (**9**) of **8**, the decoupling experiments indicated that a proton at δ 2.83 (1 H, *t*) (CHOMe) does not couple but a proton at δ 4.83 (1 H, *m*) (CHOAc) does couple with the C-5 methylene protons (1.65, 2 H, *m*). The glucose moiety would be thus linked to the C-4 hydroxyl group of **1**. The ^{1}H NMR spectrum of **7** showed a broad doublet at δ 4.4 (1 H, J = 7 Hz) assigned to the anomeric proton indicating β-linked glucose. Finally, C-2 methyl, C-3 and C-4 hydroxyl groups in **1** are considered to be equatorially orientated based on the fact that a signal due to a proton attached to the methoxyl group in **9** appeared as triplet (J = 7 Hz) and that **1** gave no acetonide by the usual method [4]. **1** is considered to be 2-methyl 3,4-dihydroxydihydropyran and **2** is therefore the corresponding 4-β-D-monoglucoside.

EXPERIMENTAL

Mps are uncorr. ^{1}H NMR spectra were measured at 60 MHz in $CDCl_3$ soln and chemical shifts are given in δ (ppm) scale. Optical rotations were measured in MeOH as solvent.

Extraction and isolation of **1** *and* **2**. Young fresh leaves of *D. superbus* collected in Toyama, Japan, in May (4.5 kg) were extrd with 70% MeOH (H_2O) at room temp. The extracts were concd *in vacuo* to leave a residue which was extrd successively with Et_2O, EtOAc and *n*-BuOH. EtOAc extracts (5 g) were chromatographed on Si gel (petrol–EtOAc, 17:3) to yield 2-methyl 3,4-dihydroxydihydropyran (**1**) (300 mg), mp 64–66° (petrol–EtOAc), $[\alpha]_D^{25}$ −30.9° (*c* 0.84), IR ν_{max} 3200–3580, 1640 cm^{-1}. MS (*m/z*): M$^+$ 130, 58 and 71. ($C_6H_{11}O_3$, anal. calc.: C, 55.38; H, 7.69. Found: C, 55.38; H, 7.59.) *n*-BuOH extracts were purified by repeated recrystallization from MeOH–$CHCl_3$ to yield **2** (4 g), mp 179°, $[\alpha]_D^{25}$ −60.4° (*c* 1.00). IR ν_{max}^{KBr} 3300–3500, 1655 cm^{-1}. ($C_{12}H_{22}O_8$. 1/2 H_2O, anal. calc.: C, 47.83; H, 7.02. Found: C, 48.31; H, 7.14.)

2-Methyl-3,4-dihydroxydihydropyran diacetate (**4**). To a pyridine soln (1 ml) of **1** (50 mg) was added Ac_2O (1 ml) and the reaction mixture after allowing to stand for 2 hr, poured into ice H_2O and extrd with Et_2O. The solvent was evapd and the residue purified on a Si gel column giving an oil (**4**). IR ν_{max} 1745, 1645. MS (*m/z*): 154 (M$^+$ −60).

2-Methyl-3,4-dihydroxy tetrahydropyran (**3**). A MeOH soln (6 ml) of **1** (100 mg) was hydrogenated with Pd–C (100 mg) at room temp. and treated as usual giving an oil **3**. IR ν_{max} 3400–3600, no double bond.

Hydrolysis of **2**. **2** was refluxed with 5% MeOH–HCl in N_2. The reaction mixture turned brown and no aglycone could be isolated. Glucose was determined by PPC.

Acetate of **2** (**5**). **2** (100 mg) in Ac_2O (0.5 ml) and pyridine (0.5 ml) was allowed to stand overnight and then poured into ice–H_2O, giving a pentaacetate (**5**) (100 mg) mp 134–135° (MeOH–H_2O). MS (*m/z*): 442 (M$^+$), 331 (terminal acetylated hexose residue).

Catalytic hydrogenation of **2** (**6**). H_2 gas was passed through a MeOH soln (50 ml) of **2** (1 g) with Pd–C (1 g) for 30 min. The reaction mixture was concd to yield crude solid which was column chromatographed over Si gel (eluant EtOAc–MeOH, 10:1), subsequent recrystallization from $CHCl_3$–MeOH yielded **6** (700 mg), mp 162–163°. IR ν_{max} no double bond.

Hydrolysis of **6** (*formation of* **3**). **6** (500 mg) was refluxed with 10% MeOH–HCl (15 ml) in N_2 for 3 hr, and concd *in vacuo* to leave a residue which after CC on Si gel (eluant EtOAc) yielded **3** identical with that obtained by hydrogenation of **1** (TLC, IR).

Permethylether of **6** (**7**). According to Hakomori's method [3], 50% NaH (5 g) washed with *n*-hexane was added to DMSO (50 ml) and heated for 1 hr at 60–65°. The mixture was added to a stirred soln of **6** (800 mg) in DMSO (7 ml) and stirred at room temp. for 1 hr. MeI (7 ml) was added under cooling and the reaction was continued overnight at room temp. The reaction mixture was poured into H_2O and extrd with Et_2O. The organic layer was washed with H_2O and evapd to dryness. The residue was chromatographed over Si gel (petrol–EtOAc, 9:1) to give an oil **7** (100 mg). IR ν_{max} no hydroxyl group. ^{1}H NMR (δ): 1.35 (3 H, *d*, J = 7 Hz, C-2 Me), 3.4–3.7 (15 H, –OMe × 5), 4.4 (1 H, *br d*, J = 7 Hz, anom.) and 4.8 (3 H, *br*, H-2, H-6).

Hydrolysis of **7** (**8**). **7** (470 mg) was hydrolysed with 10% MeOH–HCl (14 ml) in N_2 to give crude aglycone which was chromatographed over Si gel (eluant $CHCl_3$) to afford **8** as an oil (46 mg). PMR (δ): 1.30 (3 H, *d*, C-2 Me), 1.87 (2 H, *m*, H-5), 2.65 (1 H, *t*, J = 7 Hz, H-3), 3.58 (3 H, *s*, OMe), 2.90–4.15 (5 H, *m*, H-2, H-6).

Acetate (**9**) *of* **8**. A mixture of **8** (46 mg), Ac_2O (0.5 ml) and pyridine (0.5 ml) was allowed to stand overnight at room temp., poured into H_2O and extrd with Et_2O. The Et_2O soln was evapd to give an oil (**9**) (36 mg). IR ν_{max} 1730 cm^{-1}. ^{1}H NMR data shown in Table 1.

Acetonide of **1**. **1** was treated using the method of ref. [4] with Me_2CO–TsOH but gave no acetonide.

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A CHALCONE GLYCOSIDE FROM THE FLOWERS OF *ADHATODA VASICA*

H. P. BHARTIYA and P. C. GUPTA

Department of Chemistry, University of Allahabad, Allahabad, India

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Key Word Index—*Adhatoda vasica*; Acanthaceae; 2′,4-dihydroxychalcone 4-*O*-β-D-glucopyranoside.

Abstract—2′,4-Dihydroxychalcone 4-glucoside has been identified in the flowers of *Adhatoda vasica*.

In the flowers of this plant, we have found a new glucoside, $C_{21}H_{22}O_8$, mp 195–197°, which gave the characteristic colour reactions of a chalcone [1] and gave 2′,4-dihydroxychalcone, $C_{15}H_{12}O_3$ [2] and glucose on acid hydrolysis (8% ethanolic solution for 14 hr). The identity of the sugar was confirmed by co-chromatography with an authentic sample and by the preparation of the osazone.

The pale yellow aglycone, $C_{15}H_{12}O_3$, mp 145–146°, was identified as 2′,4-dihydroxychalcone from its R_f values (0.93 in *t*-BuOH–HOAc–H_2O (3:1:1) and 0.11 in 15% HOAc and by alkaline cleavage [3] to give the *o*-hydroxyacetophenone, oxime (mp 115°, lit. 117°), phenylhydrazone (mp 107°, lit. 109°), *p*-hydroxybenzoic acid (mp 210°, lit. 213°) and amide (mp 160°, lit. 162°).

These results indicate the presence of 2′,4-dihydroxychalcone having one hydroxyl group in each ring which was further confirmed by spectral studies. UV λ_{max}^{MeOH} were 369 and 278 nm and a bathochromic shift of 58 nm was obtained on the addition of $AlCl_3$ + HCl showing the presence of a free hydroxyl group at position 2′. The aglucone also gave a bathochromic shift of 60 nm with NaOMe, the glucoside did not give this shift, indicating that the glucose is attached at position 4.

Periodate oxidation of the glucoside indicated the pyranose configuration: 2 mol of periodate were consumed with the liberation of 1 mol of formic acid. On methylation of the glucoside followed by hydrolysis with the Kiliani reagent (HCl–HOAc–H_2O) (7.1:3:1) 2,3,4,6-tetra-*O*-methyl-D-glucose [4] was identified. The identity of the methylated sugar was confirmed by comparison of R_G value with 2,3,4,6-tetra-*O*-methyl-D-glucose (TMG); R_G, 0.99 (lit. 1.00) in butanone–H_2O–NH_4OH (100:50:3) and 0.99 (lit. 1.00) in *n*-BuOH–EtOH–H_2O (5:1:4). This result indicates that C_1 of the glucose is linked with the aglucone at position 4. The methylated aglucone was identified as 4-hydroxy-2′-*O*-methoxychalcone. Complete enzymic hydrolysis with emulsin indicates that the sugar is β-linked. Thus, the new compound is 2′-hydroxy-4-glucosyloxychalcone.

Flowers were collected from the Vindh area of Mirzapur (U.P.) and identified by the Botanical Survey of India, Allahabad.

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