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A SPIRO-*BIS*-γ-LACTONE GLUCOSIDE FROM *VIBURNUM DILATATUM*

TETSUO IWAGAWA and TSUNAO HASE

Department of Chemistry, Faculty of Science, Kagoshima University, Korimoto 1-21-35, Kagoshima 890, Japan

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Key Word Index—*Viburnum dilatatum*, Caprifoliaceae, spiro-*bis*-γ-lactone glucoside dilaspirolactone

Abstract—A new spiro-*bis*-γ-lactone glucoside was isolated from the leaves of *Viburnum dilatatum* and its structure was elucidated on the basis of spectral and chemical evidence

INTRODUCTION

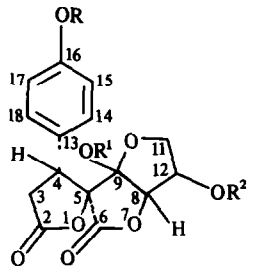
The deciduous shrub *Viburnum dilatatum* is widely distributed in Japan The fruits are used as a spice in wine and pickles Previous work on the plant has yielded a number of known compounds from the flowers and fruits [1, 2] We have now examined the methanolic extract of the leaves As a result a new glucoside (1), which is named dilaspirolactone, as well as sitosterol, ursolic acid, sitosteryl β-D-glucoside, isoquercitrin and *p*-hydroxyphenyl β-D-alloside [3] have been isolated

RESULTS AND DISCUSSION

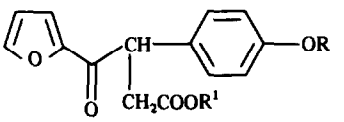
Compound **1** was crystallized as prisms, mp 165–167° with a molecular formula $C_{21}H_{24}O_{13}$ H_2O It exhibited typical IR absorption bands of γ-lactones at 1810 and 1780 cm^{-1}, the former band indicating an electronegative substituent in the γ-position Further absorption bands at 3300 cm^{-1}, and 1610, 1600, 1515 and 840 cm^{-1} showed a hydroxyl group and a *p*-substituted phenyl group, respectively The ^1H NMR spectrum indicated an ABX system at δ3 35, 3 51 and 5 47 (J = 9, 12 and 17 Hz) arising from a $-CH_2CH-$ group in addition to signals of the *p*-substituted phenyl group at δ7 02 and 7 52 (A_2B_2, J = 10 Hz) Acetylation of **1** with acetic anhydride in pyridine gave a hexa-acetate (**2**), $C_{33}H_{36}O_{19}$ and a penta-acetate (**3**), $C_{31}H_{34}O_{18}$ The IR spectrum of **3** showed an absorption band typical of a tertiary hydroxyl group at 3480 cm^{-1}

On hydrolysis with 2 N HCl, compound **1** afforded a carboxylic acid (**4**), mp 133° with a molecular formula $C_{14}H_{12}O_5$ and D-glucose The IR spectrum of **4** showed absorption bands for hydroxyl (3400 cm^{-1}), carboxylic (2750–2400 and 1710 cm^{-1}) and conjugated carbonyl (1670 cm^{-1}) functionalities together with a *p*-substituted phenyl group (1620, 1600, 1515 and 820 cm^{-1}) An absorption band at 1570 cm^{-1} suggested that a furan ring was newly produced The ^1H NMR spectrum also indicated the presence of the furan group Signals at δ6 52 (1H, *dd*, J = 2 and 3 Hz), 7 22 (1H, *d*, J = 3 Hz) and 7 67 (1H, *d*-like, J = 2 Hz) were in good agreement with those observed in the α-furoyl group of furoin [4] An ABX system at δ2 59, 3 24 and 4 78 (J = 5, 10 and 17 Hz) was due to a $-CH_2CH-$ group The presence of the *p*-substituted phenyl group was confirmed by signals at δ6 74 and 7 15 (2H each, A_2B_2, J = 8 Hz) The above results suggested that compound **4** was 3-(α-furoyl)-3-(*p*-hydroxyphenyl)-propionic acid, which was also supported by the ^{13}C NMR spectrum of **4**.

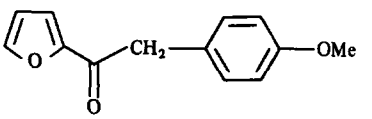
Acid methanolysis of **1** yielded a methyl ester (**5**), $C_{15}H_{14}O_5$ and a methyl ether (**6**), mp 261–262°, $C_{16}H_{16}O_8$ The ^1H NMR spectrum of **5** was very similar to that of **4** except for an additional three-proton singlet at δ3 72 due to a carbomethoxyl group Therefore, compound **5** could be deduced to be methyl 3-(α-furoyl)-3-(*p*-



1 R = R^1 = H, R^2 = Glu
2 R = R^1 = Ac, R^2 = $GluAc_4$
3 R = Ac, R^1 = H, R^2 = $GluAc_4$
6 R = R^2 = H, R^1 = Me



4 R = R^1 = H
5 R = H, R^1 = Me
7 R = R^1 = Me
9 R = Me, R^1 = Et



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hydroxyphenyl)-propionate, which was confirmed as the corresponding methyl ether (7) by preparing it from furan Acylation of furan with *p*-methoxyphenylacetic acid in the presence of phosphorus pentoxide gave 2-(*p*-methoxyphenyl)-acetylfuran (**8**) Condensation of **8** with ethyl bromoacetate in benzene containing sodium resulted in formation of an ethyl ester (**9**) The ethyl ester **9** was subjected to hydrolysis with 1 N NaOH followed by treatment with diazomethane to give a methyl ester, whose IR and ^{1}H NMR spectra were identical with those of **7** obtained by methylation of **5** with diazomethane On the other hand, an absorption band at 1800 cm^{-1} in the IR spectrum of **6** showed that the γ-lactone in **1** remained intact The IR spectrum also indicated absorption bands 3590 (OH), 3350 (phenolic OH), 1610, 1590, 840 and 815 cm^{-1} (*p*-substituted phenyl group) The structure of the aglycone **6** could be established from the ^{1}H NMR data A three-proton singlet assignable to a methoxyl group appeared at δ3 71

Thus, one oxygen atom remained to be accounted for, and the molecular formula suggested that compound **6** had a furanose moiety (C-ring) as a third ring This was reminiscent of piptoside having two spiro-joined γ-lactone rings, one of which was fused to a ketofuranose ring [5] The methoxyl group was therefore formed by methylation of a hemiacetal hydroxyl group at C-9 An ABX system at δ4 27, 4 47 and 4 65 (J = 4, 6 4 and 10 Hz) was assigned to the three proton on C-ring (H-11 × 2 and H-12) Thus, the remaining one aliphatic hydroxyl group to be assigned could be placed at C-12, and its β-configuration was assumed from the coupling constant (J = 0 Hz) between the C-12 and C-13 protons Another ABX system at δ3 15, 3 59 and 4 46 (J = 8 6, 13 and 17 Hz) was very close to that of the A-ring in leucodrin [6], suggesting that the *p*-hydroxyphenyl group was located at C-4 and had a α-configuration

The glucose was attached to the hydroxyl group at C-12 and the $W_{1/2}$ value (10 Hz) of the anomeric proton at δ5 71 in the ^{1}H NMR spectrum of **1** suggested that the glycosidic linkage must be β in **1**

To establish the absolute structure of **1**, it was methylated with diazomethane followed by oxidation with sodium periodate yielding fairly racemized (−)-*p*-methoxyphenylsuccinic acid, mp 198–200°, $[\alpha]_D$ −15° [6] Therefore, dilaspirolactone was shown to have the absolute structure **1**

A series of natural products containing the 1,7-dioxa-2,6-dioxospiro [4, 4] nona skeleton has so far been isolated, leucodrin, leudrin and leucoglycodrin from *Leucadedron* sp (Proteaceae) [6, 7], conocarpin and two closely related ring-A-opened lactones, conocapric acid and reflexin from *Luecospermum* sp (Proteaceae) [8, 9], and piptoside from *Piptocalys moorei* (Trimeniaceae) [5] This is the first example of the spiro-*bis*-γ-lactone isolated from the Caprifoliaceae

EXPERIMENTAL

Extraction and isolation Plant material was collected in Kagoshima city and identified by Dr S Sako (Herbarium sample No 6) Fresh leaves of *V dilatatum* (2 9 kg) were extracted with MeOH (13 *l* × 2) After concentration of the combined MeOH solns, H_2O was added and the insoluble material filtered off The filtrate was extracted with Et_2O and then EtOAc The Et_2O extract was evapd to give a dark green residue (25 g), which was chromatographed on a column of silica gel, eluting with $CHCl_3$–MeOH with increasing proportions of MeOH From the fractions eluted with $CHCl_3$, sitosterol (326 mg) and ursolic acid (87 mg) were obtained The fractions eluted with $CHCl_3$–MeOH (9 1) gave sitosteryl β-D-glucoside (98 mg) The EtOAc extract was evapd to give a reddish brown residue (31 g), which was subjected to CC on silica gel with $CHCl_3$–MeOH with increasing proportions of MeOH Elution with $CHCl_3$–MeOH (17 3) gave isoquercitrin (70 mg) and *p*-hydroxyphenyl β-D-alloside (110 mg) successively Dilaspirolactone **1** (941 mg) was obtained from the fractions eluted with $CHCl_3$–MeOH (5 1)

Dilaspirolactone **1** Prisms from Me_2CO–MeOH, mp 165–167°, $[\alpha]_D$ −17 6° (MeOH, *c* 0 5), UV λ_{max}^{MeOH} nm (ε) 202 (7000), 227 (6800), 276 (1100), 284 (8700), IR ν_{max}^{Nujol} cm^{-1} 3300, 1810, 1780, 1610, 1600, 1515, 900, 840, ^{1}H NMR (200 MHz, C_5D_5N) δ3 35, 3 51 and 5 47 (ABX, $J_{A,B}$ = 17, $J_{A,X}$ = 9 and $J_{B,X}$ = 12 Hz, H-3 × 2, and H-4), 4 20–4 80 (10H, *m*), 5 72 (1H, $W_{1/2}$ 10 Hz, sugar H-1), 7 02 and 7 32 (A_2B_2, J = 8 Hz), ^{13}C NMR (22 6 MHz, C_5D_5N) δ34 0 (C-3), 44 3 (C-4), 61 8 (C'-6), 71 0 (C'-4), 74 2* (C'-2), 74 7* (C'-3), 77 1 (C-11), 78 3† (C'-5), 78 6† (C-8), 88 6 (C-12), 90 5 (C-5), 97 5 (C'-1), 108 7 (C-9), 116 (C-15 and C-17), 123 6 (C-13), 130 8 (C-14 and C-18), 159 2 (C-16), 171 8 (C-6), 174 8 (C-2), MS *m/z* (rel int) no [M]$^+$, 322 (3), 304 (8), 147 (63), 120 (91), 73 (50), 61 (100) (Found C, 51 23, H, 5 61% Calc for $C_{21}H_{24}O_{13}$ H_2O C, 51 20, H, 5 22%) Compound **1** (40 mg) was acetylated with Ac_2O in pyridine at 5° CC of the crude product gave **2** (24 mg) and **3** (10 mg) Compound **2**, an amorphous powder, IR ν_{max}^{film} cm^{-1} 1820, 1760, 1615, 1515, 1220, ^{1}H NMR (100 MHz, $CDCl_3$) δ2 00 and 2 04 (3H × 4, *s*, OAc), 2 32 (3H, *s*, OAc), 2 88–3 52 (2H, *m*), 3 84–4 20 (2H, *m*), 4 20–4 90 (2H, *m*), 5 10–5 48 (5H, *m*), 7 24 and 7 40 (A_2B_2, J = 8 Hz), MS *m/z* 736 [M]$^+$ (Found C, 54 27, H, 5 32% Calc for $C_{33}H_{36}O_{14}$ C, 53 80, H, 4 93%) Compound **3**, an amorphous powder, IR ν_{max}^{film} cm^{-1} 3480, 1810, 1750, 1605, 1510, 1225, ^{1}H NMR (200 MHz, $CDCl_3$) δ2 06, 2 07, 2 12, 2 14, 2 30 (3H each, *s*), 2 94 and 3 51 (AB of ABX, J_{AB} = 17 Hz, J_{AX} = 9 Hz, J_{BX} = 13 Hz, H-3 × 2), 3 52–3 84 (2H, *m*), 3 88–3 94 (1H, *m*), 4 01 (1H, *s*, OH), 4 20 (1H, *dd*, J = 3 and 13 Hz, H'-6), 4 30 (1H, *dd*, J = 2 and 13 Hz, H'-6), 4 56–4 66 (2H, *m*), 4 92–5 04 (1H, *m*), 5 04–5 28 (3H, *m*), 7 14 and 7 36 (A_2B_2, J = 9 Hz), MS *m/z* 694 [M]$^+$

Hydrolysis of **1** A soln of **1** (21 mg) in 2 N HCl (1 ml) was refluxed for 2 hr The reaction soln was extracted with Et_2O The Et_2O extract was evapd and recrystallized from $CHCl_3$–MeOH to give pale yellow needles of **4** (7 mg), mp 133°, UV λ_{max}^{MeOH} nm (ε) 220 (15 000), 270 (21 000), IR ν_{max}^{Nujol} cm^{-1} 3450, 2750–2400, 1710, 1670, 1620, 1600, 1570, 1515, 980, 840, 820 ^{1}H NMR [90 MHz, $(CD_3)_2CO$] δ2 59, 3 24 and 4 78 (ABX, J_{AB} = 17 Hz, J_{AX} = 5 Hz and J_{BX} = 10 Hz, H-2 × 2 and H-3), 6 52 (1H, *dd*, J = 2 and 3 Hz, furan H-4), 6 74 and 7 15 (A_2B_2, J = 8 Hz, Ar–H), 7 22 (1H, *d*, J = 3 Hz, furan H-3), 7 67 (1H, *br d*, J = 2 Hz, furan H-5), ^{13}C NMR [22 6 MHz, $(CD_3)_2CO$] δ37 7 (CH_2), 49 2 (CH), 112 9 (furan C-4), 116 4 (Ar C-3 and C-5), 118 5 (furan C-3), 130 1 (Ar C-1, C-2 and C-6), 147 5 (furan C-5), 153 1 (Ar C-4), 157 5 (furan C-2), 172 9 (COOH), 187 9 (CO), MS *m/z* (rel int) 260 [M]$^+$ (43), 165 (67), 123 (100), 120 (37), 95 (44) (Found *m/z* 260 0776 Calc for $C_{14}H_{12}O_5$ *m/z* 260 0685)

Methanolysis of **1** To a soln of **1** (130 mg) in dry MeOH (3 ml), was added three drops of conc HCl and the mixture refluxed for 6 days The reaction mixture was diluted with H_2O and extracted with Et_2O The extract was washed with H_2O and dried (Na_2SO_4) The crude product was recrystallized from $CHCl_3$–MeOH to afford **6** (12 mg), prisms, mp 261–262°, $[\alpha]_D$ −33 3° (MeOH, *c* 0 33), IR ν_{max}^{KBr} cm^{-1} 3590, 3350, 1800, 1610,

*,† Assignments may be interchanged

1590, 895, 840, 815, ^{1}H NMR (400 MHz, C_5D_5N) δ3 15, 3 59 and 4 49 (ABX, J_{AB} = 17 Hz, J_{AX} = 8 6 Hz, and J_{BX} = 13 Hz, H-2 × 2 and H-3), 3 62 (1H, *s*, OH), 3 71 (3H, *s*, OMe), 4 27, 4 47 and 4 67 (ABX, J_{AB} = 10 Hz, J_{AX} = 6 4 Hz and J_{BX} = 4 Hz, H-11 × 2 and H-10), 7 15 and 7 53 (A_2B_2, J = 8 5 Hz, Ar–H), MS *m/z* (rel int) 336 $[M]^+$ (15), 318 (13), 203 (13), 147 (15), 120 (100), 99 (79), 91 (31) (Found *m/z* 336 0846 Calc for $C_{16}H_{16}O_8$ *m/z* 336 0845) The mother soln was evapd and subjected to CC on silica gel Elution with $CHCl_3$–MeOH (99 1) gave a solid 5 (11 mg), $[\alpha]_D$ −4° (MeOH, *c* 0 75), UV λ_{max}^{MeOH} nm (ε), 222 (8700), 272 (12 900), IR ν_{max}^{film} cm^{-1} 3400, 1730, 1665, 1610, 1590, 1560, 1510, 960, 900, 880, 835, 810, ^{1}H NMR (100 MHz, $CDCl_3$) δ 2 77, 3 40 and 4 94 (ABX, J_{AB} = 20 Hz, J_{AX} = 6 Hz and J_{BX} = 10 Hz, H-2 × 2 and H-3), 3 72 (3H, *s*, COOMe), 6 63 (1H, *dd*, *J* = 2 and 4 Hz, furan H-4), 6 96 and 7 39 (A_2B_2, *J* = 9 Hz), 7 40 (1H, *d*, *J* = 4 Hz, furan H-3), 7 76 (1H, *m*, furan H-3), MS *m/z* 274 $[M]^+$ (Found *m/z* 274 0843 Calc for $C_{15}H_{14}O_5$ *m/z* 274 0841)

2-(p-*Methoxyphenyl*)-*acetylfuran* (**8**) P_2O_5 (4 2 g) was weighed into benzene (16 ml) containing furan (2 g) and the soln was slowly added to *p*-methoxyphenylacetic acid (4 88 g) The reaction mixture was refluxed for 4 hr and the benzene layer washed with dil NaOH and H_2O CC of the crude product on silica gel with $CHCl_3$–hexane (1 1) gave the acetate **8** (200 mg), an oil, IR ν_{max}^{film} cm^{-1} 3125, 2850, 1670, 1610, 1565, 1510, 880, 820, ^{1}H NMR (60 MHz, $CDCl_3$) δ 3 77 (3H, *s*), 4 05 (2H, *s*), 6 50 (1H, *dd*, *J* = 1 5 and 4 Hz), 6 72 and 7 20 (A_2B_2, *J* = 8 Hz), MS *m/z* 216 $[M]^+$

Ethyl 3-(α-*furoyl*)-3-(p-*methoxyphenyl*)-*propionate* (**9**) To a suspension of powdered Na (40 mg) in dry toluene (0 5 ml) and dry benzene (3 ml), compound **8** (262 mg) was added and the mixture refluxed for 6 hr Ethyl bromoacetate (200 mg) was slowly added to the stirred mixture and the whole refluxed with stirring for 9 hr After cooling, H_2O was added and the benzene soln seperated, dried and evapd CC of the residue on silica gel with $CHCl_3$–hexane (1 1) afforded **9** (71 mg), an oil, IR ν_{max}^{film} cm^{-1} 1725, 1670, 1605, 1560, 1510, 1250, 880, 830, ^{1}H NMR (60 MHz, $CDCl_3$) δ1 13 (3H, *t*, *J* = 7 Hz), 2 78, 3 24 and 4 97 (ABX, J_{AB} = 17 Hz, J_{AX} = 6 Hz and J_{BX} = 9 Hz), 3 85 (3H, *s*), 4 18 (2H, *q*, *J* = 7 Hz), 6 52 (1H, *dd*, *J* = 1 5 and 4 Hz), 6 89 and 7 31 (A_2B_2, *J* = 8 Hz), 7 25 (1H, *m*), 7 60 (1H, *m*), MS *m/z* 302 $[M]^+$

Methyl 3-(α-*furoyl*)-3-(p-*methoxyphenyl*)-*propionate* (**7**) Compound **5** (8 mg) was treated with CH_2N_2 to give a residue, which was subjected to CC on silica gel with $CHCl_3$, yielding the Me ether **7** (4 8 mg), an oil, $[\alpha]_D$ −35 4° (MeOH, *c* 0 24), IR ν_{max}^{film} cm^{-1} 1735, 1670, 1605, 1560, 1510, 1250, 880, 830, ^{1}H NMR (60 MHz, $CDCl_3$) δ2 80, 3 40 and 4 90 (ABX, J_{AB} = 17 Hz, J_{AX} = 6 Hz and J_{BX} = 9 Hz, H-2 × 2 and H-3), 3 72 (3H, *s*, COOMe), 3 83 (3H, *s*, OMe), 6 50 (1H, *dd*, *J* = 1 5 and 4 Hz, furan H-4), 6 86 and 7 27 (A_2B_2, *J* = 8 Hz, Ar–H), 7 23 (1H, *m*, furan H-3), 7 57 (1H, *m*, furan H-5), MS *m/z* 288 $[M]^+$ A soln of **9** (60 mg) was added to 1 N NaOH (0 5 ml) and the soln stirred at 85° for 1 hr The reaction mixture was diluted with H_2O and extracted with Et_2O to remove neutral material The aq layer was acidified with dil HCl, extracted with Et_2O, washed with H_2O and dried (Na_2SO_4) The crude product was methylated with CH_2N_2 to give a residue CC of the residue on silica gel with $CHCl_3$ afforded the Me ester **7** (10 mg), an oil, IR ν_{max}^{film} cm^{-1} 1735, 1670, 1605, 1565, 1510, 1250, 880, 830, ^{1}H NMR (60 MHz, $CDCl_3$) δ2 80, 3 40 and 4 90 (ABX, J_{AB} = 17 Hz, J_{AX} = 6 Hz and J_{BX} = 9 Hz), 3 72 and 3 83 (3H each, *s*), 6 38 (1H, *dd*, *J* = 1 5 and 4 Hz), 6 91 and 7 32 (A_2B_2, *J* = 8 Hz), 7 23 (1H, *m*), 7 60 (1H, *m*), MS *m/z* 288 $[M]^+$

Methylation of **1** *with* CH_2N_2 *followed by oxidation with* $NaIO_4$ A soln of **1** (160 mg) in MeOH (1 ml) was treated with excess CH_2N_2 The crude product (82 mg) was boiled for 3 min in 1 N KOH (1 5 ml) and diluted with H_2O (8 3 ml) The soln was treated with $NaIO_4$ (480 mg) in H_2O (8 3 ml) and stirred at room temp for 4 hr The reaction mixture (pH 6 86) was acidified with dil H_2SO_4, continuously extracted with Et_2O and washed with $Na_2S_2O_3$ and H_2O The crude product was recrystallized from HOAc to yield *p*-methoxyphenylsuccinic acid (2 2 mg), needles, mp 198–200°, $[\alpha]_D$ −15° (MeOH, *c* 0 05), IR ν_{max}^{KBr} cm^{-1} 2740–2600, 1700, 1610, 1580, 1512, 930, 735 The IR spectrum was identical with that of an authentic sample of *p*-methoxyphenylsuccinic acid

Sitosterol Plates from MeOH, mp 139–140°, IR ν_{max}^{Nujol} cm^{-1} 3300, 1640, ^{1}H NMR (60 MHz, $CDCl_3$) δ0 68–2 36 (*m*), *ca* 3 40 (1H, *m*), 5 36 (1H, *m*), MS *m/z* 414 $[M]^+$ (Found C, 83 78, H, 12 52% Calc for $C_{29}H_{50}O$ C, 83 99, H, 12 15%) The spectral data were identical with those of an authentic sample

Ursolic acid A white powder from MeOH, mp 270–288°, IR ν_{max}^{Nujol} cm^{-1} 3400, 1690, ^{1}H NMR (60 MHz, C_5D_5N) δ0 93–2 76 (*m*), 3 50 (1H, *m*), 5 67 (1H, *m*) The spectral data were identical with those of an authentic sample

Sitosteryl β-D-*glucoside* A white powder from MeOH, mp 263–265°, IR ν_{max}^{Nujol} cm^{-1} 3400, 1650, ^{1}H NMR (60 MHz, C_5D_5N) δ0 65–2 63 (*m*), 3 8–4 57 (6H, *m*), 5 08 (1H, *d*, *J* = 8 Hz), 5 43 (1H, *m*) (Found C, 71 98, H, 10 90% Calc for $C_{35}H_{60}O_6 \cdot \frac{1}{2}H_2O$ C, 72 06, H, 10 54%) The spectral data were identical with those of an authentic sample

Isoquercitrin Needles from MeOH, mp 209–210°, IR ν_{max}^{Nujol} cm^{-1} 3250, 1650, 1600, 1550, 1505, ^{1}H NMR (60 MHz, C_5D_5N) δ3 92–4 42 (6H, *m*), 6 08 (1H, *d*, *J* = 8 Hz), 6 62 (2H, *m*), 7 22 (1H, *d*, *J* = 8 Hz), 7 93 (1H, *dd*, *J* = 2 and 8 Hz), 8 37 (1H, *d*, *J* = 2 Hz) The spectral data were identical with those of an authentic sample

p-*Hydroxyphenyl* β-D-*alloside* Prisms from MeOH, mp 188–191° and mp 201–202°, IR ν_{max}^{Nujol} cm^{-1} 3200, 1600, 1510, 1210, 1090, 1040, 870, 850, 830, 790, ^{1}H NMR (60 MHz, C_5D_5N) δ4 10–4 73 (5H, *m*), 4 83 (1H, *t*-like, *J* = 3 Hz), 5 97 (1H, *d*, *J* = 8 Hz), 7 06 and 7 32 (A_2B_2, *J* = 9 Hz) The spectral data were identical with those of an authentic sample

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