into a doublet (J = 8 Hz). A C'-4 proton appeared at δ3.88 as a double doublet (J = 8 and 9 Hz) coupled with a C'-3 proton and a C'-5 proton at δ4.10 (1H, *ddd*, J = 1.8, 6 and 9 Hz). Two methylene protons of C'-6 occurred at δ4.52 (1H, *dd*, J = 6 and 12 Hz) and 4.86 (1H, *dd*, J = 1.8 and 12 Hz). The above results showed that the hydroxyl groups at C'-2 and C'-6 in **1** were acetylated because their chemical shifts were in low fields. The new compound is thus the 2',6'-diacetate of scopolin.

EXPERIMENTAL

All Mps are uncorr. The chemical shifts of ^{1}H NMR spectra are given in δ-values with respect to TMS as the internal standard.

Extraction and isolation. The plants were collected in Kagoshima city and identified by Dr. Sako (Herbarium sample No. 1.). The fresh leaves of *V. suspensum* (1.5 kg) were extracted with MeOH (11 l. × 2). The extracts were evaporated to dryness to afford a dark green material. The material was diluted with H_2O, and extracted with Et_2O and then EtOAc. The EtOAc extract was further extracted with MeOH–$CHCl_3$ (1:19) to give a dark brown residue (17 g). The residue was subjected to column chromatography on silica gel with MeOH–$CHCl_3$ (1:19) and recrystallized from MeOH to give needles of **1** (11 mg), mp 178–179.5°; $[\alpha]_D^{25}$ −100° (MeOH; *c* 0.025); UV λ_{max}^{MeOH} nm (ε): 227 (10800), 286 (5600) and 328 (7600); IR ν_{max}^{nujol} cm^{-1}: 3550, 3250, 1740, 1620, 1570 and 1510; ^{1}H NMR (C_5D_5N): δ2.07 (3H × 2, *s*, COMe), 3.70 (3H, *s*, OMe), 3.88 (1H, *dd*, J = 8 and 9 Hz, C'-4 H), 4.10 (1H, *ddd*, J = 1.8, 6 and 9 Hz, C'-5 H), 4.23 (1H, *dd*, J = 8 and 8.5 Hz, C'-3H), 4.52 (1H, *dd*, J = 6 and 12 Hz, C'-6H), 4.86 (1H, *dd*, J = 1.8 and 12 Hz, C'-6H), 5.43 (1H, *d*, J = 8.5 Hz, C'-1H), 5.68 (1H, *dd*, J = 8.5 and 8.5 Hz, C'-2H), 6.30 (1H, *d*, J = 9.8 Hz, C-3H), 7.00 (1H, *s*, C-8H), 7.38 (1H, *s*, C-5H) and 7.63 (1H, *d*, J = 9.8 Hz, C-4H); MS *m/z*: 438 $[M]^+$. (Found: C, 52.75; H, 5.07%. Calc. for $C_{20}H_{22}O_{11} \cdot 1/2\ H_2O$: C, 52.61; H, 5.30%.)

Acetylation of **1**. Compound **1** was acetylated with Ac_2O–pyridine. The product was recrystallized from EtOH to give **2**, needles, mp 168–169°; IR ν_{max}^{nujol} cm^{-1}: 1770–1730, 1620, 1570, 1505, 920, 890 and 825; ^{1}H NMR ($CDCl_3$): δ2.10 (3H × 3, *s*, COMe), 2.17 (3H, *s*, COMe), 3.95 (3H, *s*, OMe), 6.38 (1H, *d*, J = 10 Hz, C-3H), 7.20 (1H, *s*, C-8H), 7.40 (1H, *s*, C-5H) and 7.95 (1H, *d*, J = 10 Hz, C-4H). (Found: C, 55.12; H, 5.08%. Calc. for $C_{24}H_{26}O_{13}$: C, 55.17; H, 5.02%.) The IR and ^{1}H NMR spectra were identical with those of scopolin acetate.

Acknowledgement—The authors are grateful to Dr. Y. Uchio, Hiroshima University, for measurement of ^{1}H NMR spectra and valuable discussions.

REFERENCES

1. Hase, T. and Nakatani, M. (1976) *Rep. Fac. Sci. Kagoshima Univ.* **9**, 59.
2. Hase, T. and Iwagawa, T. (1982) *Chem. Letters* 13.
3. Kasymov, Sh. Z. and Sidyakin, G. P. (1969) *Khim. Prir. Soedin.* **5**, 319.

Phytochemistry, Vol. 23, No. 2, pp. 468–469, 1984.
Printed in Great Britain.

0031-9422/84 $3.00 + 0.00

A PHENOL ALLOSIDE FROM *VIBURNUM WRIGHTII*

TETSUO IWAGAWA, HIDEO TAKAHASHI, KIYOTAKA MUNESADA and TSUNAO HASE

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

(*Received* 30 *June* 1983)

Key Word Index—*Viburnum wrightii*; Caprifoliaceae; phenol alloside.

Abstract—A new phenol alloside, *p*-hydroxyphenyl β-D-alloside, has been isolated from the leaves of *Viburnum wrightii* in addition to several known compounds. The structures were elucidated by spectroscopic and chemical methods.

INTRODUCTION

In continuation of our studies of the glycosides in *Viburnum* species, especially bitter components [1–4], we have now investigated *V. wrightii* Miq. From this plant a new non-bitter phenol alloside (**1**) has been isolated together with seven known compounds, α-amyrin palmitate, sitosterol, ursolic acid, *p*-coumaric acid, cosmosiin, 6-*O*-acetylarbutin and arbutin.

RESULTS AND DISCUSSION

The glycoside (**1**) had the molecular formula $C_{12}H_{16}O_7$. The IR spectrum showed absorption bands for a hydroxyl group at 3300 cm^{-1} and a *p*-substituted phenyl group at 1600, 1500 and 830 cm^{-1}. The presence of the *p*-substituted phenyl group was also apparent from the signals at δ 6.95–7.32 (4H, A_2B_2, J = 10 Hz) in the ^{1}H NMR spectrum. Four singlets at δ 1.98–2.14 (3H × 4)

due to alcoholic acetoxyl protons and one singlet at δ 2.22 (3H × 1) assignable to phenolic acetoxyl protons were observed in the ^{1}H NMR spectrum of the acetate of **1**.

Hydrolysis of **1** with 2 M hydrochloric acid gave hydroquinone whose IR spectrum was identical with that of an authentic sample. D-Allose as sugar was confirmed by paper chromatography. In addition, the IR spectrum of the sugar acetate obtained by acetylation with acetic anhydride–pyridine was in good agreement with that of D-allose pentaacetate. The β-configuration of the anomeric proton was deduced from the coupling constant (J = 8 Hz) at δ 5.87 in the ^{1}H NMR spectrum of **1**. Thus the new glycoside **1** should be *p*-hydroxylphenyl β-D-alloside, which was further supported by the ^{13}C NMR spectrum (see Experimental). This is the second alloside from *Viburnum* species [5].

EXPERIMENTAL

Extraction and isolation. The plants were collected in the northern highlands of Miyazaki prefecture and identified by Dr. S. Sako (Herbarium sample No. 5). The fresh leaves of *Viburnum wrightii* Miq. (4.3 kg) were extracted with MeOH (8 l. × 2). The extracts were evapd to dryness *in vacuo* to give a dark residue. The residue was diluted with H_2O, extracted with Et_2O and then EtOAc, yielding an Et_2O-soluble portion (10 g) and an EtOAc-soluble portion (6 g). Known compounds were identified by their IR and ^{1}H NMR (100 MHz) spectra.

The Et_2O extract was chromatographed on silica gel. Elution with $CHCl_3$–hexane (1:9) gave α-amyrin palmitate (200 mg), a waxy substance, IR ν_{max}^{film} cm^{-1}: 1740, 1650 and 720; ^{1}H NMR ($CDCl_3$): δ 0.79, 0.84, 0.87, 0.97, 1.01 (Me × 7), 1.29 (*s*), 4.50 (1H, *m*) and 5.13 (1H, *m*); MS *m/z*: 665 $[M+1]^+$. Elution with $CHCl_3$–hexane (4:1) was evapd to give sitosterol (150 mg), plates from Me_2CO, mp 131–134°, IR ν_{max}^{Nujol} cm^{-1}: 3300 and 1640; ^{1}H NMR ($CDCl_3$): δ 0.67–1.27 (3H × 6), 3.50 (1H, *m*) and 5.37 (1H, *m*). Elution with $CHCl_3$ afforded crude ursolic acid (420 mg), mp 255°, IR ν_{max}^{Nujol} cm^{-1}: 3400, 2600–2300 and 1685; ^{1}H NMR (C_5D_5N): δ 0.97, 1.00, 1.02, 1.06, 1.24 (3H × 7), 3.47 (1H, *m*) and 5.48 (1H, *m*). Elution with MeOH–$CHCl_3$, (1:19) gave *p*-coumaric acid (10 mg), needles from MeOH–$CHCl_3$, mp 202–204°, IR ν_{max}^{Nujol} cm^{-1}: 3400, 2750–2350, 1680, 1630, 1610, 1510 and 840; ^{1}H NMR (Me_2CO-d_6): δ 6.47, 7.87 (1H each, *d*, J = 16 Hz), 7.07 and 7.68 (2H each, *d*, J = 8 Hz); MS *m/z*: 164 $[M]^+$.

The EtOAc extract was further extracted with MeOH–$CHCl_3$ (3:17) to give a dark brown residue (4 g) and an insoluble ppt. The ppt. was recrystallized to give cosmosiin (apigenin 7-glucoside) (200 mg), yellow needles from MeOH, mp 227.8–228.8°, IR ν_{max}^{Nujol} cm^{-1}: 3300, 1660, 1610, 1590, 1500 and 830; ^{1}H NMR (C_5D_5N): δ 6.97, 7.18 (1H each, *d*, J = 2 Hz), 7.02 (1H, *s*), 7.35 and 8.08 (2H each, *d*, J = 10 Hz); UV λ_{max}^{MeOH} nm (ε): 268 (20400) and 335 (24100); $\lambda_{max}^{MeOH-NaOAc}$: no shift. The dark brown residue was chromatographed on silica gel. Elution with MeOH–$CHCl_3$ (3:17) gave 6-*O*-acetylarbutin (30 mg), needles from MeOH, mp 198.5–199.5°, IR ν_{max}^{Nujol} cm^{-1}: 3500–3000, 1750, 1520, 1220 and 830; ^{1}H NMR (C_5D_5N): δ 1.90 (3H, *s*), 4.12–4.96 (6H, *m*), 5.36 (1H, *m*, $W_{1/2}$ = 8 Hz), 7.09 and 7.29 (2H each, A_2B_2, J = 8 Hz); MS *m/z*: 314 $[M]^+$. Further elution with MeOH–$CHCl_3$ (3:17) afforded arbutin (28 mg) and compound **1** (43 mg). Arbutin, needles from MeOH–$CHCl_3$, mp 198–199°, IR ν_{max}^{Nujol} cm^{-1}: 3300, 1610, 1510 and 830. Compound **1**, prisms from MeOH–$CHCl_3$, mp 189–191° and 201–202°, $[\alpha]_D^{25}$ −154° (MeOH; *c* 0.48); UV λ_{max}^{MeOH} nm (ε): 225 (5000) and 286 (2200); IR ν_{max}^{Nujol} cm^{-1}: 3300, 1650 and 1510; ^{1}H NMR (C_5D_5N): δ 3.84–4.82 (6H, *m*), 5.87 (1H, *d*, J = 8 Hz, allose H-1) and 6.95–7.32 (4H, A_2B_2, J = 10 Hz, aromatic H); ^{13}C NMR (25.1 MHz, C_5D_5N): δ 62.6 (C-6'), 68.7 (C-4'), 72.2 (C-3'), 73.1 (C-2'), 76.1 (C-5'), 101.2 (C-1'), 116.7* (C-3 and C-6), 118.7* (C-2 and C-5), 151.9† (C-1) and 153.9† (C-4) [*, †: Assignments may be interchanged]; MS *m/z*: 272 $[M]^+$. (Found: C, 52.78; H, 6.06. Calc. for $C_{12}H_{16}O_7$: C, 52.94; H, 5.92%.)

Acetylation of **1**. Compound **1** (40 mg) was treated with Ac_2O–pyridine at room temp. overnight. The crude product was recrystallized from EtOH to give needles, **2** (40 mg), mp 146.5–147.5°, IR ν_{max}^{Nujol} cm^{-1}: 1750, 1500 and 1225; ^{1}H NMR ($CDCl_3$): δ 1.98, 2.02, 2.06, 2.14, 2.26 (3H × 5, *s*, COMe), 4.06–4.32 (3H, *m*), 5.68 (1H, *t*-like, J = 2 Hz, H-3') and 6.98 (4H, *s*, aromatic H). (Found: C, 54.65; H, 5.40. Calc. for $C_{22}H_{26}O_{12}$: C, 54.71; H, 5.43%.)

Hydrolysis of **1**. Compound **1** (20 mg) was refluxed with 2 M HCl (1 ml) for 2 hr. The soln was diluted with H_2O, extracted with Et_2O, washed and dried. The extract was evapd to give hydroquinone (13 mg), IR ν_{max}^{film} cm^{-1}: 3200, 1520, and 840. The IR spectrum wad identical with that of hydroquinone. The aq. soln was neutralized with Amberlite IRA-45 and evapd to dryness *in vacuo*. The presence of D-allose in the residue was confirmed by co-PC with an authentic sample (solvent system, EtOAc–pyridine–H_2O–HOAc, 5:5:3:1). Acetylation of the residue with Ac_2O–pyridine gave an acetate, IR ν_{max}^{film} cm^{-1}: 1750, 1220, 1070, 1020 and 950. The IR spectrum was identical with that of D-allose pentaacetate.

Acknowledgements—We are grateful to Dr. Y. Uchio, Hiroshima University, for measurement of ^{13}C NMR and Misses M. Tanisako and M. Imakiire for the preliminary experiment.

REFERENCES

1. Hase, T. and Iwagawa, T. (1982) *Chem. Letters* 13.
2. Hase, T., Iwagawa, T. and Munesada, K. (1982) *Phytochemistry* **21**, 1435.
3. Iwagawa, T. and Hase, T. (1983) *Phytochemistry* **22**, 255.
4. Hase, T., Takao, H. and Iwagawa, T. (1983) *Phytochemistry* **22**, 1977.
5. Bock, K. Jensen, S. R., Nielsen, B. J. and Norn, V. (1978 *Phytochemistry* **17**, 753.