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A STILBENE XYLOSIDE FROM *HOLODISCUS DISCOLOR* BARK

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Key Word Index—*Holodiscus discolor*; Rosaceae; bark; stilbene xyloside; ocean spray; resveratrol.

Abstract—(*E*)-Resveratrol-3-0-β-D-xylopyranoside was isolated from the stem bark of *Holodiscus discolor*. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Holodiscus discolor is a common shrub in the coastal forests of the Pacific Northwest. Called ocean spray or sometimes creambush, this plant was used for both materials and medicines by indigenous peoples from British Columbia southward into Washington state [1–3]. The hard, dense wood from the stem was utilized for spear and arrow shafts, digging sticks, and fishing hooks. Leaves, stems, bark, roots, and seeds were all used for a variety of medicines that ranged from those for treating viral diseases to general tonics. In an investigation of phenolic constituents of the bark, the novel stilbene glycoside (*E*)-resveratrol-3-0-β-D-xylopyranoside **1** was isolated and characterized by spectral techniques.

RESULTS AND DISCUSSION

Compound **1**, $[\alpha]_D^{29} = -7.4$ (MeOH,*c* 2.15), was detected as an intense blue spot on 2-D cellulose TLC when visualized with vanillin-HCl spray reagent [4]. Isolation was achieved by column chromatography over Sephadex LH-20 and Toyopearl HW-40S using ethanol–water gradients.

^{1}H and ^{13}C NMR spectra (Table 1) indicated **1** had an (*E*)-resveratrol aglycone moiety by showing signals consistent with those published for (*E*)-resveratrol glucoside [5, 6]. The assignments in Table 1 were confirmed by HETCOR and HMBC spectra. The ^{1}H NMR spectrum showed signals for two *trans* olefinic protons at δ 6.93 (Hα, *d*, *J* = 16.4 Hz) and δ 7.07 (Hβ, *d*, *J* = 16.4 Hz). In the HMBC spectrum, the Hα proton signal was connected to the C2 (106.7 ppm) and C6 (107.9 ppm) carbon signals of the A ring. The Hβ proton signal in turn showed connectivity to the carbon signal (2 ×) for C2′ and C6′ at 128.7 ppm, thus confirming the positions of the A and B aromatic

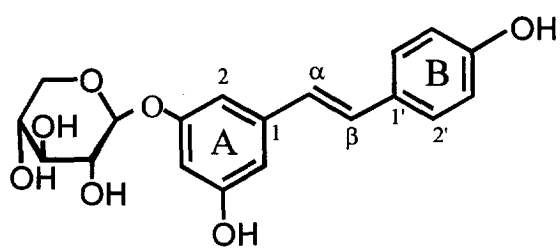

Table 1. ^{1}H and ^{13}C NMR data for **1**

Position	^{13}C NMR, ppm	^{1}H NMR, δ (*J* Hz)
1	140.7	
2	106.7	6.75, *bs*
3	159.9	
4	103.8	6.48, *t*, *J* = 2.1
5	159.2	
6	107.9	6.71, *t*, *J* = 1.7
α	126.3	6.93, *d*, *J* = 16.4
β	129.5	7.07, *d*, *J* = 16.4
1′	129.7	
2′,6′	128.7 (2×)	7.42, *d*, *J* = 8.6 (2H)
3′,5′	116.3 (2×)	6.84, *d*, *J* = 8.6 (2H)
4′	158.1	
Xylose		
1	102.2	4.97, *d*, *J* = 6.9
2	74.2	3.50, *m*
3	77.3	3.53, *m*
4	70.5	3.65, *m*
5	66.3	3.94, *dd*, *J* = 5.0, 11.2
		3.43, *dd*, *J* = 9.7, 11.2

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rings. The xylopyranoside moiety was shown to be attached to the resveratrol A ring by the connectivity of the C3 oxygen bearing carbon signal at 159.9 ppm to the xylosyl anomeric proton signal at δ 4.97 in the HMBC spectrum. The carbon signal at 159.9 ppm also showed a 2 bond connectivity to the A ring proton signals at δ 6.75 (H-2) and δ 6.48 (H-4). The carbon signal at 159.2 ppm was shown to have connectivity to the A ring proton signals at δ 6.71 (H-6) and δ 6.48 (H-4). The carbon signal at 158.1 ppm was confirmed as the C4′ signal by its 3 bond connectivity to the 2 proton doublet at δ 7.42 which is due to H2′ and H6′ protons of the phenolic B ring. It seems that in contrast to glycosylation of flavonoids which causes an upfield shift of the *ipso* carbon, glycosylation in this stilbene has caused a downfield shift relative to the unsubstituted C5 hydroxyl bearing carbon [7, 8].

A β-D-xylopyranosyl moiety was evident from the five carbon signals from 102.2 ppm to 66.3 ppm which are in agreement with literature values [7, 8]. The anomeric proton signal at δ 4.97 exhibited connectivity to the carbon signal at 102.2 ppm in a HETCOR spectrum confirming this proton's attachment to the anomeric carbon. The doublet with $J = 6.9$ Hz for the anomeric proton signal also gave confirmation of the β-anomeric configuration of **1**. A negative ion FAB mass spectrum of **1** gave an intense $[M-H]^-$ ion peak at m/z 359 and a fragment ion peak at m/z 227 corresponding to loss of the anhydroxylose moiety from the $[M-H]^-$ ion confirming the M_r of **1** and its aglycone moiety. Acid-catalysed hydrolysis of **1** gave D-xylose as confirmed by TLC.

While resveratrol and its glucosides are widely distributed in a number of plant genera, [5, 9], **1** appears to be the first known xyloside. Stilbenes and their glycosides have been associated with varied biological and medicinal activities [5, 9–11]. The role of **1** in the herbal use of ocean spray has yet to be determined.

EXPERIMENTAL

Plant material. Ocean spray (*Holodiscus discolor*) bark was collected in the Oregon Coast Range, 6 miles west of Philomath, Oregon in June 1995. A voucher specimen is deposited at the Oregon State University Herbarium.

General. NMR spectra were recorded on samples dissolved in Me_2CO-d_6 (OH groups exchanged with D prior to analysis) using a Bruker AM 300 spectrometer. FABMS was done on a Kratos MS-50TC instrument using a *m*-nitrobenzyl alcohol matrix. Optical rotation was measured on a JASCO DIP-370 instrument. TLC used to monitor isolation: 2-D cellulose, (a) *t*-BuOH–HOAc–H_2O (3:1:1), (b) 6% HOAc. Detection with vanillin-HCl, $R_{f_a} = 0.4$, $R_{f_b} = 0.15$: Silica TLC, C_6H_6–Me_2CO–MeOH (6:3:1), $R_f = 0.25$. EtOAc–Pyr–H_2O (8:2:1) was used on cellulose TLC with an authentic standard to confirm D-xylose ($R_f = 0.22$) after visualization with aniline hydrogen phthalate reagent.

Extraction and isolation. The bark (500 g) was exhaustively extracted with Me_2CO–H_2O (7:3) at room temp. The Me_2CO was evapd and the aq. residue extracted sequentially $\times 3$ with equal vols of the following solvents, which on evapn gave the following yields: hexane (10.5 g), Et_2O (7.8 g), EtOAc (47.9 g), and *n*-BuOH (15.9 g).

Chromatography of the EtOAc extract (25 g) over a Sephadex LH-20 column (10×60 cm) and elution with EtOH (95%) gave 45 frs of 500 ml each. Frs 7 and 8 were combined (6.42 g) and rechromatographed over columns of Toyopearl HW-40S and Sephadex LH-20 using EtOH–H_2O gradients to give 75 mg of **1** as freeze-dried powder.

REFERENCES

1. Pojar, J. and MacKinnon, A., eds., in *Plants of the Pacific Northwest Coast*. Lone Pine Publishing, Vancouver, 1994, p. 71.
2. Gunther, E., in *Ethnobotany of Western Washington*, Revised edn. University of Washington Press, Seattle, 1973, p. 33.
3. Forlines, D. R., Tavenner, T., Malan, J. C. S. and Karchesy, J. J., in *Plant Polyphenols*, ed. R. W. Hemingway and P. E. Laks. Plenum Press, New York, 1992, p. 767.
4. Karchesy, J. J., Bae, Y., Chalker-Scott, L., Helm, R. F. and Foo, L. Y., in *Chemistry and Significance of Condensed Tannins*, ed. R. W. Hemingway and J. J. Karchesy. Plenum Press, New York, 1989, p. 139.
5. Mattivi, F., Reniero, F. and Korhammer, S., *Journal of Agriculture and Food Chemistry*, 1995, **43**, 1820.
6. Nyemba, A. M., Ngando Mpondo, T., Kimbu, S. F. and Connolly, J. D., *Phytochemistry*, 1995, **39**, 895.
7. Agrawal, P. K., *Phytochemistry*, 1992, **31**, 3307.
8. Markham, K. R. and Chari, V. M., in *The Flavonoids: Advances in Research*, ed. J. B. Harborne and T. J. Mabry. Chapman and Hall, London, 1982, p. 19.
9. Jayatilake, G. S., Jayasuriya, H., Lee, E.-S., Koonchanok, N. M., Geahlen, R. L., Ashendel, C. L., McLaughlin, J. L. and Chang, C.-J., *Journal of Natural Products*, 1993, **56**, 1805.
10. Kubo, I. and Murai, Y., *Journal of Natural Products*, 1991, **54**, 1115.
11. Schultz, T. P., Harms, W. B., Fisher, T. H., McMurtrey, K. D., Minn, J. and Nicholas, D. D., *Holzforschung*, 1995, **49**, 29.