Pergamon

0031-9422(95)00057-7

Phytochemistry, Vol. 40, No. 1, pp. 341–343, 1995

0031-9422/95 $9.50 + 0.00

LIGNAN GLYCOSIDES FROM INNER BARK OF *BETULA PENDULA*

ELITA ŠMITE,* HEFENG PAN and LENNART N. LUNDGREN†

Department of Chemistry, Swedish University of Agricultural Sciences, P.O. Box 7015, S-750 07, Uppsala, Sweden; *Latvia State Institute of Forestry Science, Rigas Street 111, Salaspils, LV-2169, Latvia

(*Received* 11 *November* 1994)

Key Word Index—*Betula pendula*; Betulaceae; inner bark; lignan; monoaryl glycoside.

Abstract—Four lignan glycosides [lyoniside, nudiposide, (−)-isolariciresinol 3α-*O*-β-D-xylopyranoside and (2*R*,3*R*)-2,3-dihydro-3-hydroxymethyl-7-methoxy-2-(3′-methoxy-4′-α-L-rhamnopyranosyloxyphenyl)-5-benzofuranpropanol] were isolated from the inner bark of *Betula pendula*, in addition to (+)-catechin, (+)-catechin 7-*O*-β-D-xylopyranoside, salidroside, tachioside and isotachioside.

INTRODUCTION

In a previous paper [1], we reported on structural studies of a series of arylbutanoid and diarylheptanoid glycosides from the inner bark of *Betula pendula*. The present communication describes the isolation and identification of other phenolic constituents from the same material.

RESULTS AND DISCUSSION

From the aqueous ethanol extract of the inner bark, **1**–**7**, (+)-catechin and (+)-catechin 7-*O*-β-D-xylopyranoside were isolated. (+)-Catechin and (+)-catechin 7-*O*-β-D-xylopyranoside were identified by direct comparison ($[\alpha]_D$, TLC, ^{1}H NMR) with authentic samples [2]; **3** (salidroside) was identified by comparison ($[\alpha]_D$, and ^{1}H NMR) with literature data [3, 4].

Compounds **1** and **2**, which were isolated as a mixture in a ratio of 5:3, were identified as tachioside (4-hydroxy-3-methoxyphenyl β-D-glucopyranoside) and isotachioside (4-hydroxy-2-methoxyphenyl β-D-glucopyranoside), respectively; enzymatic hydrolysis of the mixture afforded glucose and an aglycone characterized by ^{1}H NMR and mass spectrometry as methoxyhydroquinone. The ^{1}H NMR spectrum of the **1**/**2** mixture was in accordance with published spectra [5] of tachioside and isotachioside.

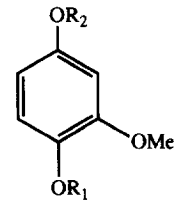
Compounds **4** ($[\alpha]_D$ + 25.4°) and **5** ($[\alpha]_D$ −60.0°) were isolated in low amounts (8 and 6 mg, respectively) by reverse-phase HPLC and identified as lyoniside [(+)-lyoniresinol 3α-*O*-β-D-xylopyranoside] and nudiposide [(−)-lyoniresinol 3α-*O*-β-D-xylopyranoside], respectively. Their ^{13}C NMR spectra and optical rotations were in excellent accordance with literature data [5]. Acetylation (Ac_2O–pyridine) yielded the hexaacetates and enzymatic hydrolysis of **4** and **5** afforded xylose and the aglycones. The latter were not separated by TLC or HPLC, and showed specific rotations (+ 20° and − 44°) of opposite signs. The deviation from known [5, 6] optical rotation values of (+)- and (−)-lyoniresinol (+ 53° and −53°) is accounted for by the small amounts of the aglycones available. The ^{1}H NMR spectra of **4** and **5** differed only with respect to the signal from the anomeric proton and for some alicyclic protons (Table 1). Complete assignments of the spectra were made with ^{1}H–^{1}H COSY techniques, apparently for the first time. Compounds **4** and **5** have been found in several species [5, 7–9] previously, but just once [10] in the same species. The corresponding 3α-glucosides were recently reported [11].

Compound **6** was identified as (−)-isolariciresinol 3α-*O*-β-D-xylopyranoside and **7** as (2*R*,3*R*)-2,3-dihydro-3-hydroxymethyl-7-methoxy-2-(3′-methoxy-4′-α-L-rhamnopyranosyloxyphenyl)-5-benzofuranpropanol by comparison ($[\alpha]_D$, TLC, ^{1}H NMR) with authentic samples. These compounds have been isolated previously from needles of *Picea abies* and *Pinus massoniana* [12, 13]. To the best of our knowledge, **1**, **2** and **4**–**7** have not been reported from *Betula* species previously.

EXPERIMENTAL

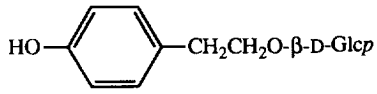
Extraction of plant material, fractionation of extractives on SephadexLH-20, general procedures and the instruments used were as described in a previous paper [1]. Silica gel CC of LH-20 frs C-H [1] with EtOAc–MeOH–H_2O (50:6:5) and $CHCl_3$–MeOH–H_2O in different proportions yielded **1** and **2** (5:3 mixt. 2 mg), and **3** (3 mg) from fr. *C*, **7** (20 mg) and a mixt. of **4** and **5** from fr. D, **6** (7 mg) from fr. F, (+)-catechin

†Author to whom correspondence should be addressed.

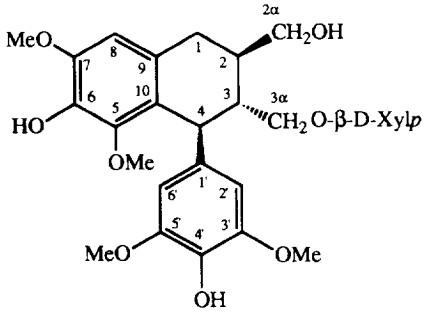


1 R_1 = H; R_2 = β-D-Glc*p*

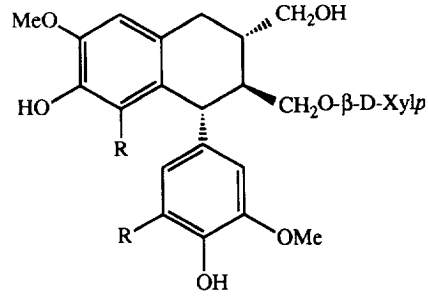
2 R_1 = β-D-Glc*p*; R_2 = H



3

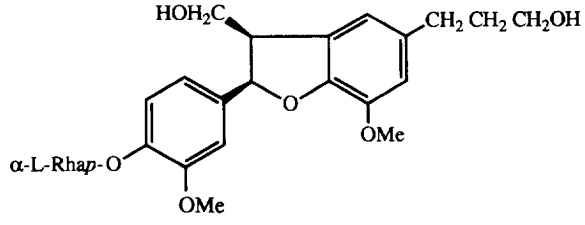


4



5 R = OMe

6 R = H



7

Table 1. ^{1}H NMR spectral data of **4** and **5** (in CD_3OD)

H	4	5	H	4	5
1a	2.71	2.68	5-OMe	3.32	3.30
1b	2.63	2.68	7-OMe	3.85	3.85
2	1.70	1.71	3',5'-OMe	3.74	3.75
2αa	3.65	3.62	D-xylose moiety		
2αb	3.55	3.62	1''	4.21	4.10
3	2.04	2.03	2''	3.21	3.19
3αa	3.84	3.81	3''	3.30	3.27
3αb	3.41	3.58	4''	3.47	3.49
4	4.38	4.23	5''a	3.82	3.86
8	6.56	6.57	5''b	3.16	3.13
2',6'	6.42	6.41			

J[Hz]: **4**: 1a,1b = 15.1; 1a,2 = 4.9; 1b,2 = 11.2; 2,2αa = 4.2; 2,2αb = 6.5; 2αa, 2αb = 10.8; 3,4 = 6.6; 3,3αa = 5.3; 3,3αb = 4.0; 3αa, 3αb = 9.8; 1'',2'' = 7.5; 2'',3'' = 9.1; 3'',4'' = 8.7; 4'',5''a = 5.5; 4'',5''b = 10.4; 5''a,5''b = 11.4; **5**: 3,4 = 7.0; 3,3αa = 4.6; 3,3αb = 4.9; 3αa,3αb = 10.1; 1'',2'' = 7.3; 2'',3'' = 9.1; 3'',4'' = 8.9; 4'',5''a = 5.5; 4'',5''b = 10.4; 5''a,5''b = 11.6.

7-*O*-β-D-xylopyranoside (80 mg) from fr. G and (+)-catechin (2.8 g) from fr. H. Refractionation by reverse-phase HPLC of the **4**/**5** pair using aq. MeOH as mobile phase yielded **4** (8 mg) and **5** (6 mg).

Hexaacetate of **4**. ^{1}H NMR (CD_3OD): δ1.60–5.19 (*m*, 15H), 2.02, 2.04, 2 × 2.05, 2.28, 2.31 (6*s*, 6OAc), 3.17 (*s*, 5-OMe), 2 × 3.74 (2*s*, 3'-OMe and 5'-OMe), 3.82 (*s*, 7-OMe), 6.32 (2H, *s*, H-2' and H-6'), 6.52 (1H, *s*, H-8).

Hexaacetate of **5**. ^{1}H NMR (CD_3OD): δ1.60–5.21 (*m*, 15H), 2.00, 2.02, 2.03, 2.05, 2.29, 2.31 (6*s*, 6OAc), 3.23 (*s*, 5-OMe), 2 × 3.72 (2*s*, 3'-OMe and 5'-OMe), 3.82 (*s*, 7-OMe), 6.33 (2H, *s*, H-2' and H-6'), 6.52 (1H, *s*, H-8).

Acid hydrolysis of **7** gave rhamnose and (2*R*,3*R*)-2,3-dihydro-7-hydroxy-2-(4'-hydroxy-3'-methoxyphenyl)-3-(hydroxymethyl)-5-benzofuranpropanol, identical ($[\alpha]_D$ and ^{1}H NMR) with an authentic sample [12].

Acknowledgements—This work was supported financially by the Royal Swedish Academy of Agriculture and Forestry.

REFERENCES

1. Šmite, E., Lundgren, L. N. and Andersson, R. (1993) *Phytochemistry* **27**, 365.
2. Pan, H. and Lundgren, L. N. (1994) *Phytochemistry* **36**, 79.
3. Thieme, H. (1964) *Naturwissenschaften* **51**, 360.
4. LaLonde, R. T., Wong, C. and Tsai, A. I. M. (1976) *J. Am. Chem. Soc.* **98**, 3007.
5. Inoshiri, S., Sasaki, M., Kohda, H., Otsuka, H. and Yamasaki, K. (1987) *Phytochemistry* **26**, 2811.
6. Freudenberg, K. and Weinges, K. (1959) *Tetrahedron Letters* 19.
7. Ogawa, M. and Ogihara, Y. (1976) *Chem. Pharm. Bull.* **24**, 2102.
8. Dada, G., Corbani, A., Manitto, P., Speranza, G. and Lunazzi, L. (1989) *J. Nat. Prod.* **52**, 1327.
9. Yoshinari, K., Sashida, Y. and Shimomura, H. (1989) *Chem. Pharm. Bull.* **37**, 3301.
10. Miyase, T., Ueno, A., Takizawa, N., Kobayashi, H. and Oguchi, H. (1989) *Phytochemistry* **28**, 3483.
11. Achenbach, H., Löwel, M., Waibel, R., Gupta, M. and Solis, P. (1992) *Planta Med.* **58**, 270.
12. Lundgren, L. N., Popoff, T. and Theander, O. (1981) *Phytochemistry* **20**, 1967.
13. Lundgren, L. N., Shen, Z. and Theander, O. (1985) *Acta Chem. Scand.* **B 39**, 241.