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Arylglycerol Glucosides from *Pinus sylvestris**

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The 2- and 3-*O*-β-D-glucopyranosides of 1-(4-hydroxyphenyl)-1,2,3-propanetriol [1-*C*-(*p*-hydroxyphenyl)glycerol] and 1-(4-hydroxy-3-methoxyphenyl)-1,2,3-propanetriol [1-*C*-guaiacylglycerol] have been isolated from needles of *Pinus sylvestris* L. and identified. Syntheses of the (1*S*, 2*R*)- and (1*R*, 2*R*)-forms (D-*erythro*- and D-*threo*, respectively) of the above aglycones are reported. The results indicate the presence of both D- and L-forms of the respective aglycones in the plant material.

Using chromatography on Sephadex LH-20 and silicic acid, a series of dilignol and flavonoid glycosides have previously been isolated from needles of *Pinus sylvestris* L. and *Picea abies*, respectively, and identified.[1,2] The isolation of the 1- and 2-*O*-β-D-glucopyranosides of 1-*C*-guaiacylglycerol[3] is also reported. By treating heartwood of *Pinus resinosa* with *p*-dioxane under acetylating conditions, acetates of D,L-*threo*- and D,L-*erythro*-1-*C*-guaiacylglycerol have been isolated in trace amounts.[4] These were suggested to be lignin degradation products. The compounds were subsequently isolated from the cambium of *Tsuga heterophylla*[5] and, after mild hydrolytic treatment, from wood of *Picea excelsa*[6] and *Picea jezoenesis*.[7] In the latter publication, the isolation of 1-*C*-(*p*-hydroxyphenyl)glycerol was also reported. It has also been shown that arylglycerols, obtained in the form of *threo*- and *erythro*-isomers, can be formed enzymatically from cinnamyl alcohols,[8] which are proposed to be lignin precursors. A dimer of guaiacylglycerol and a series of lignans in which guaiacylglycerol is linked by ether bonds were recently isolated[9,10] from *Larix leptolepis*. The present publication reports the isolation of 1-*C*-(*p*-hydroxyphenyl) glycerol (*6*), 1-*C*-guaiacylglycerol (*5*) and their 2- and 3-*O*-β-D-glucopyranosides *1* – *4* from needles of *Pinus sylvestris* L. and their identification, and the synthesis of the D-*erythro*- and D-*threo*-forms of *5* and *6*. The configuration of the isolated compounds is discussed.

* Part 9 in the series *The Constituents of Conifer Needles*. Part 8, see Ref. 2.

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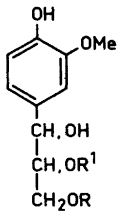
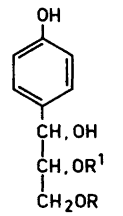


1 R = β-D-glucopyranoside; R¹ = H
2 R = H; R¹ = β-D-glucopyranoside
5 R = R¹ = H



3 R = β-D-glucopyranoside; R¹ = H
4 R = H; R¹ = β-D-glucopyranoside
6 R = R¹ = H

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RESULTS AND DISCUSSION

The compounds *1*–*6* were all obtained amorphous but chromatographically homogeneous after subfractionation on anion-exchange resins and silicic acid columns. The positive colour reactions towards spray *a* – orange for compounds *1*, *2*, and *5* and yellow for *3*, *4*, and *6* – indicating free phenolic hydroxyl group (s), were in accordance with those previously reported [7] for guaiacylglycerol and *p*-hydroxyphenylglycerol, respectively. Enzymatic hydrolysis (β-glucosidase) of compounds *1* and *2* yielded D-glucose and a mixture of *erythro*- and *threo*-1-*C*-guaiacylglycerol (*5*) (shown by borate buffer paper electrophoresis [11] and ^{1}H NMR of their acetates [12,13]; identical with those of authentic samples). Periodate oxidation [14] of compound *1* gave vanillin, indicating that the glucose was linked to the 3-hydroxyl group in the glycerol chain. Compound *2* was chromatographically and electrophoretically identical with the previously isolated β-glucoside [3] and, since periodate oxidation of compound *2* did not give vanillin, the glucose must be linked to either the 1- or the 2-hydroxyl group in the glycerol chain. In the ^{1}H NMR comparison of compound *2* with that of its acetate, a downfield shift for the benzylic proton was noted, indicating an acetyl on the 1-position. Glucose must hence be linked to the 2-hydroxyl group. The sugars in compounds *1* and *2* are linked as β-glucopyranosides, which was shown by ^{1}H NMR ($J_{1,2}$ 7 Hz) and by hydrolysis with β-glucosidase.

In the same way, compounds *3* and *4* were identified as 3-*O*- and 2-*O*-β-D-glucopyranosides, respectively, of 1-*C*-(*p*-hydroxyphenyl)glycerol (*6*). By ^{1}H NMR and electrophoresis, compound *3* was found to be a mixture of *erythro*- and *threo*-isomers while compound *4* was found, by ^{1}H NMR, to be a pure *threo*-isomer ($[\alpha]_D$ +18.7°).

Small amounts of pure *threo-5* and *-6* ($[\alpha]_D$ +12.8 and $[\alpha]_D$ +19.5°) were isolated by preparative electrophoresis. The optical rotations for these *threo* compounds differ markedly from those for the synthetic D-*threo-5* and *-6* ($[\alpha]_D$ −26.1 and $[\alpha]_D$ −33.8°) and that previously [3] found for *threo-5* ($[\alpha]_D$ −18°). To check these results, pure *erythro*- and *threo-5* and *-6* were isolated from a larger batch of an enzymatically hydrolyzed glucoside mixture by LC on Sephadex LH-20 and silicic acid and by preparative HPLC. Before hydrolysis, only traces of the free aglycones *5* and *6* could be detected in the aqueous extract remaining after extraction with chloroform and ethyl acetate, respectively. The isolated aglycones released by hydrolysis showed almost no optical rotation ($[\alpha]_D < |2°|$). A check was also made on pure *erythro-6* that the mild conditions used during the isolation experiment B had no influence on its optical rotation. These results support the notable existence of both D- and L-forms of compounds *5* and *6*, glycosidically linked in the plant. Enantiomeric mixtures of procyanidin polymers in Palmae species were also reported recently. [15]

The D-*erythro*- and D-*threo-5* and *-6* were prepared by addition of 2,3-*O*-isopropylidene-D-glyceraldehyde to (4-benzyloxy-3-methoxyphenyl)magnesium bromide and (4-benzyloxyphenyl)magnesium bromide, respectively. All isomers were crystalline, as previously reported for D,L-mixtures of *erythro-* [16] and *threo-5* [6] and *erythro-6*. [17]

EXPERIMENTAL

General. ^{1}H NMR spectra were determined at 89.60 MHz (TMs as internal reference); s, d, m and q denote singlet, doublet, multiplet and quartet, respectively. Data for the strongly coupled protons in *threo-5* and *-6* were obtained by ABX analysis, checked by computer simulation, and adjusted if necessary. [20] TLC studies were performed on silica gel HF_{254} plates with (*a*) 2-butanone – MeOH – H_2O, (9:0.5:1) as solvent, and for further deter-

Table 1. Mobilities on paper electrophoresis in borate buffer and retention on HPLC on a RAD-PAK C_{18} column.

Compound[a]	*1*t	*1*e	*2*t,*2*e	*3*t	*3*e	*4*t	*5*t	*5*e	*6*t	*6*e
Mg-value[b]	0.50	0.27	0.18	0.52	0.28	0.20	0.59	0.43	0.65	0.46
HPLC[c]	–	–	–	–	–	–	3.0	2.4	3.7	2.8

[a] t = *threo* and e = *erythro*. [b] Mobilities compared with glucose (1.0) and 5-hydroxymethylfurfural (0). [c] Retention times in min. Mobile phase: H_2O – MeOH – HOAc, 100:10:1 for *5* and H_2O – HOAc, 100:1, for *6*, respectively. Flow rate for both: 1 ml/min.

mination of the purities of the compounds, also with (*b*), $CHCl_3$ – MeOH – H_2O, (7:3:0.5). TLC plates (after inspection in UV light) were sprayed with (*a*) 0.1 % diazotized sulfanilic acid in 10 % Na_2CO_3, followed by 50 % H_2SO_4 or (*b*) anisaldehyde – H_2SO_4 – EtOH (1:1:18). Electrophoresis was performed on Whatman 1 paper with 0.05 M borate buffer, pH 9.2, as electrolyte, for 1.5 h at 1500 V. The mobilities are given in Table 1. The visualizing agents used were spray *a* (without subtreatment with 50 % H_2SO) and (*c*) $AgNO_3$ [1.5 % in aq. $(CH_3)_2CO$], followed by 2 N NaOH. HPLC was performed on a RAD-PAK C_{18} high-sensitivity column (Waters) and the UV-absorbance at 254 nm was measured. The mobile phase consisted of H_2O – MeOH – HOAc, 100:10:1 for compound 5 and H_2O – HOAc, 100:1 for compound 6. The retention times are given in Table 1. All reagents were commercial samples of good grade. 1-Hydroxy-2-methoxybenzene was brominated as described for hydroxybenzene.[18] The benzyl derivatives of 1-bromo-4-hydroxy-3-methoxybenzene and 1-bromo-4-hydroxybenzene were prepared by reaction with benzylbromide in the presence of tetrabutylammonium hydrogen sulfate.[19] Melting points are corrected.

Syntheses

(1S, 2R)- and (1R, 2R)-1-(4-hydroxy-3-methoxyphenyl)-1,2,3-propanetriol [D-erythro-5 *and* D-threo-5]. 1-Benzyloxy-4-bromo-2-methoxybenzene (6.9 g, 25 mmol) was allowed to react with magnesium metal (0.52 g, 21.3 g-atom) and 2,3-*O*-isopropylidene-D-glyceraldehyde (1.8 g, 16 mmol) was added to the Grignard reagent as described for bromobenzene in the synthesis of D-*erythro*- and D-*threo*-1-phenyl glycerol ($[\alpha]_D$ +19.6 and $[\alpha]_D$ −38.6°),[21] but with tetrahydrofuran as solvent. The reaction mixture was poured onto ice-water, neutralized with dilute hydrochloric acid and extracted with ether. LC of the evaporation residue on silica acid [light petroleum (60 – 70 °C) – EtOAc, 4:1] yielded a mixture of (1*S*, 2*R*)- and (1*R*, 2*R*)-1-(4-benzyloxy-3-methoxyphenyl)-2,3-*O*-isopropylidene-1,2,3-propanetriol. The mixture was debenzylated by catalytic hydrogenation on 5 % Pd/C in methanol for 1 h. After filtration and evaporation, it was hydrolyzed in 0.05 M sulfuric acid for 1 h at room temperature. The solution was neutralized with barium carbonate, centrifuged and evaporated. By LC of the residue on Sephadex LH-20 (elution with water) and preparative HPLC, D-*erythro*-5 and D-*threo*-5 were separated. Recrystallization was performed from acetone – dichloromethane. D-*erythro*-5 contained 1 mol water as previously reported.[16] It was not intended to optimize the preparations for yield, but rather to obtain pure reference specimens.

Compound 5. D-*erythro*-Isomer. (96 mg, 2.8 %), m.p. 82 – 84 °C (Lit.[16] D,L-mixture 83 – 84 °C), $[\alpha]_D^{23}$ +9.4° (*c* 3.0, EtOH). Anal. $C_{10}H_{14}O_5$, H_2O; C, H, O. MS, m/e (rel. int.): 214 (7, M), 197 (4), 154 (13), 153 (100), 152 (36), 151 (19), 137 (17), 125 (31), 110 (13), 93 (82), 65 (51). ^{1}H NMR (CD_3OD): δ 3.4 – 3.9 m (3 H), 3.85 s (3 H), 4.52 d, J 5.9 Hz (1 H), 6.7 – 7.0 m (3 H). Tetraacetate of D-*erythro*-5 (Ac_2O-Pyr): ^{1}H NMR ($CDCl_3$): δ 2.00 s (3 H), 2.03 s (3 H), 2.13 s (3 H), 2.30 s (3 H), 3.84 s (3 H), 4.24 d, *J* 5.0 Hz (2 H), 5.39 q (1 H), 6.01 d, *J* 5,6 Hz (1 H), 6.8 – 7.1 m (3 H).

Compound 5. D-*threo*-Isomer. (60 mg, 1.7 %), m.p. 133 – 134 °C (Lit.[6] D,L-mixture, 133 – 134 °C), $[\alpha]_D^{23}$ −26.1° (*c* 1.4, EtOH). Anal. $C_{10}H_{14}O_5$; C, H, O. MS was identical with MS for the D-*erythro*-isomer. ^{1}H NMR ($CDCl_3$): δ 3.32 dd, *J* 11.2 and 6.3 Hz (1 H), 3.45 dd, *J* 11.2 and 3.4 Hz (1 H), 3.65 m (1 H), 3.85 s (3 H), 4.51 d, *J* 6.2 Hz (1 H), 6.7 – 7.0 m (3 H). Tetraacetate of D-*threo*-5 (Ac_2O-Pyr): ^{1}H NMR ($CDCl_3$): 2.05 s (3 H), 2.07 s (3 H), 2.09 s (3 H), 2.30 s (3 H), 3.81 dd, *J* 5.6 Hz and 12.0 Hz (1 H), 3.84 s (3 H), 4.29 dd, *J* 3.7 Hz and 12.0 Hz (1 H), 5.3 – 5.6 m (1 H), 5.96 d, *J* 7.5 Hz (1 H), 6.8 – 7.1 m (3 H).

(1S, 2R)- and (1R, 2R)-1-(4-hydroxyphenyl)-1,2,3-propanetriol [D-erythro-6 *and* D-threo-6] were prepared from 1-benzyloxy-4-bromobenzene (8.9 g, 34 mmol) in the same way as the isomers of 5. The compounds were recrystallized from acetone – dichloromethane.

Compound 6. D-*erythro*-Isomer. (320 mg, 9.7 %, m.p. 140 – 141 °C (Lit.[17] D,L-mixture, 149 – 151 °C), $[\alpha]_D^{23}$ +21.3° (*c* 0.6, EtOH). Anal. $C_9H_{12}O_4$; C, H, O. MS, *m/e* (rel. int.): 166 (4, M − 18), 124 (13), 123 (100), 122 (12), 121 (25), 107 (26), 95 (58), 77 (58), 65 (14). ^{1}H NMR (CD_3OD): δ 3.4 – 3.9 m (3 H), 4.51 d, *J* 5.7 Hz (1 H), 6.74 d, *J* 8.5 Hz (2 H), 7.21 d, *J* 8.5 Hz (2 H). Tetraacetate of D-*erythro*-6 (Ac_2O – Pyr): ^{1}H NMR ($CDCl_3$): δ 2.00 s (3 H), 2.03 s (3 H), 2.12 s (3 H), 2.30 s (3 H), 4.23 d, *J* 5.0 Hz (2 H), 5.38 q (1 H), 6.02 d, *J* 5.5 Hz (1 H), 7.08 d, *J* 8.5 Hz (2 H), 7.39 d, *J* 8.5 Hz (2 H).

Compound 6. D-*threo*-Isomer. (570 mg, 17.2 %), m.p. 144 – 146 °C, $[\alpha]_D^{23}$ −33.8° (*c* 1.2, EtOH). Anal. $C_9H_{12}O_4$; C, H, O. MS was identical with MS for the D-*erythro*-isomer. ^{1}H NMR (CD_3OD): δ 3.32 dd, *J* 11.2 and 6.3 Hz (1 H), 3.45 dd, *J* 11.2 and 3.4 Hz (1 H), 3.65 m (1 H), 4.50 d, *J* 6.6 Hz (1 H), 6.74 d, *J* 8.5 Hz (2 H). 7.19 d, *J* 8.5 Hz (2 H). Tetraacetate of D-*threo*-6 (Ac_2O – Pyr): ^{1}H NMR ($CDCl_3$): δ 2.05 s (3 H), 2.06 s (3 H), 2.08 s (3 H), 2.29 s (3 H), 3.79 dd, *J* 5.6 Hz and *J* 12.2 Hz (1 H), 4.29 dd, *J* 4.0 Hz and 12.2 Hz (1 H), 5.3 – 5.6 m (1 H), 5.98 d, *J* 7.2 Hz (1 H), 7.10 d, *J* 8.5 Hz (2 H), 7.39 d, *J* 8.5 Hz (2 H).

Isolation

Experiment A. Needles of *Pinus sylvestris* L. (190 g dry weight), collected in spring, were extracted without drying for 1 h with boiling Me_2CO. After filtration, the needles were dried, milled and extracted on a boiling water bath, 2 × 30 min with Me_2CO and 2 × 30 min with Me_2CO-H_2O (1:1). The extracts were combined, the Me_2CO was evaporated, and the suspension obtained was extracted several times with $CHCl_3$. The remaining H_2O fraction (24 g) was fractionated on a Sephadex LH-20 column (elution with H_2O). Twelve main fractions were collected. From fraction 1 (10.6 g), by repeated subfractionation on anion-exchange resin (Dowex 1-x8 in its acetate form), *1*, *3*, *2*, *4*, *5* and *6* were eluted with water in the order given; and on a silicic acid column (elution with $CHCl_3-MeOH-H_2O$, 7:3:0.5) compounds *1*–*6* were obtained in chromatographically pure form. The yields corresponded to 0.01 (compounds *3*, *5* and *6*), 0.02 (compounds *1* and *4*) and 0.03 % (compound *2*), respectively, of the dry weight of the needles.

Experiment B. Needles of *Pinus sylvestris* L. (360 g dry weight) collected in November, were treated as in Exp. A. The remaining H_2O fraction (48 g) was extracted with EtOAc and the aqueous residue was treated with a commercial crude enzyme (cellulase C 36, Rohm and Haas Co.) for 48 h at room temperature and then evaporated. LC of the residue on Sephadex LH-20 (elution with H_2O) and silicic acid (elution with $CHCl_3-MeOH-H_2O$, 60:15:1) separated the *erythro-threo-5* from *erythro-threo-6*. By preparative HPLC pure *erythro-5* (5 mg), *threo-5* (28 mg), *erythro-6* (6 mg) and *threo-6* (31 mg) were obtained.

Experiment C. In order to check if any isomerization could occur during the preparation and isolation under the conditions used in Exp. B, a pure sample of *erythro-6* was treated as in Exp. B. No change in the optical rotation of the compound could be observed during these treatments.

Compound 1. Mixture of the *erythro-* and *threo-*isomers in ratio 1:3. NMR (CD_3OD): δ 3.2–4.0 m (9 H), 3.84 s (3 H), 4.21 d, *J* 7.0 Hz (1 H), 4.57 d, J 6.0 Hz (1 H), 6.7–7.1 m (3 H). Heptaacetate of *1* (Ac_2O-Pyr): NMR ($CDCl_3$): δ 2.0–2.2 m (18 H), 2.29 s, (3 H), 3.48 dd, *J* 6.0 and 11.5 Hz (1 H), 3.5–3.8 m, (1 H), 3.85 s, (3 H), 3.88 dd, *J* 4.0 and 11.5 Hz (1 H), 4.08 dd, *J* 2.5 and 11.0 Hz (1 H), 4.24 dd, J 5.0 and 11.0 Hz (1 H), 4.40 d, *J* 7.5 Hz (3/4 H), 4.52 d, *J* 7.5 Hz (1/4H), 4.8–5.2 m, (3 H), 5.2–5.4 m, (1 H), 5.93 d, *J* 7.5 Hz (3/4 H), 5.95 d, *J* 5.5 Hz (1/4 H), 6.8–7.1 m, (3 H).

Compound 2. Mixture of the *erythro-* and *threo-*isomers in ratio 1:4. NMR (CD_3OD): δ 3.3–4.0 m, (9 H), 3.85 s, (3 H), 4.43 d, *J* 7.0 Hz (4/5 H), 4.45 d, *J* 7.0 Hz (1/5 H), 4.64 d, *J* 8.0 Hz (1/5 H), 4.67 d, *J* 7.5 Hz (4/5 H), 6.7–7.1 m, (3 H). Heptaacetate of *2* (Ac_2O-Pyr): NMR ($CDCl_3$): δ 1.98–2.10 m, (15 H), 2.13 s, (3 H), 2.29 s, (3 H), 3.6–4.0 m, (2 H), 3.84 s, (3 H), 4.0–4.3 m, (1 H), 4.10 dd, J 4.0 and 12.5 Hz (1 H), 4.18 dd, *J* 5.0 and 12.5 Hz (1 H), 4.68 d, *J* 7.0 Hz (1/5 H), 4.72 d, *J* 7.0 (4/5 H), 5.85 d, *J* 7.8 Hz (4/5 H), 6.00 d, *J* 5.5 Hz (1/5 H), 6.8–6.1 m, (3 H).

Compound 3. Mixture of the *erythro-* and *threo-*isomers in ratio 1:9. NMR (CD_3OD): δ 4.2–4.0 m, (9H), 4.20 d, *J* 7.0 Hz (1 H), 4.55 d, 6.5 Hz (1 H), 6.75 d, *J* 8.5 Hz (2 H), 7.21 d, *J* 8.5 Hz (2 H). Heptaacetate of *3* (Ac_2O-Pyr): NMR ($CDCl_3$): δ 2.00 s (3 H), 2.01 s (3 H), 2.05 s (3 H), 2.06 s (3 H), 2.07 s (3 H), 2.09 s (3 H), 2.29 s (3 H), 3.38 dd, *J* 5.5 and 12.0 Hz (1 H), 3.55–3.75 m (1 H), 3.88 dd, *J* 4.0 and 12.0 Hz (1 H), 4.08 dd, *J* 3.0 and 12.0 Hz (1 H), 4.25 dd, *J* 4.0 and 12.0 Hz (1 H), 4.40 d, *J* 7.0 Hz (1 H), 4.9–5.2 m (3 H), 5.2–5.4 m (1 H), 5.94 d, *J* 7.5 Hz (1 H), 7.09 d, *J* 8.5 Hz (2 H), 7.37 d, J 8.5 Hz (2 H).

*Compound 4. threo-*Isomer $[\alpha]_D^{23}$ +18.7° (*c* 0.5, EtOH). NMR (CD_3OD): δ 3.2–4.0 m (9 H), 4.45 d, *J* 7.5 Hz (1 H), 4.64 d, *J* 7.5 Hz (1 H), 6.76 d, *J* 8.7 Hz (2 H), 7.22 d, *J* 8.7 (2 H). Heptaacetate of *4* (Ac_2O-Pyr): NMR ($CDCl_3$): δ 1.99 s (6 H), 2.00 s (3 H), 2.01 s (3 H), 2.08 s (3 H), 2.11 s (3 H), 2.28 s (3 H), 3.65–3.85 m (1 H), 3.7–4.2 m (2 H), 4.11 dd, *J* 3.5 and 12.5 Hz (1 H), 4.28 dd, *J* 4.0 and 12.5 Hz (1 H), 4.71 d, *J* 7.5 Hz (1 H), 4.8–5.2 m (4 H), 5.88 d, *J* 7.5 Hz (1 H), 7.08 d, *J* 8.5 Hz (2 H), 7.34 d, *J* 8.5 Hz (2 H).

*Compound 5. erythro-*Isomer from Exp. B. $[\alpha]_D^{23}$ 0° (0.5, EtOH).

*Compound 5. threo-*Isomer from Exp. A. $[\alpha]_D^{23}$ +12.8° (*c* 1, EtOH). *threo-*Isomer from Exp. B. $[\alpha]_D^{23}$ −1.4° (*c* 2.8 EtOH).

*Compound 6. erythro-*Isomer from Exp. B. $[\alpha]_D^{23}$ −1.5° (*c* 0.6, EtOH).

*Compound 6. threo-*Isomer from Exp. A. $[\alpha]_D^{23}$ +19.5° (*c* 0.6, EtOH). *threo-*Isomer from Exp. B. $[\alpha]_D^{23}$ +1.2° (*c* 3.1, EtOH).

TLC, HPLC, paper electrophoresis, ^1H NMR and MS for compounds *5* and *6* were identical with those for the synthetic samples.

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