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MONOARYL AND CYCLOHEXENONE GLYCOSIDES FROM NEEDLES OF *PINUS SYLVESTRIS**

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Key Word Index—*Pinus sylvestris*; Pinaceae; needles; monoaryl glycoside; cyclohexenone glycoside; β-hydroxypropiovanillone; coniferyl alcohol; dihydrovomifoliol; vomifoliol.

Abstract—The 4′-*O*-β-D-glucopyranosides of 4-(4′-hydroxyphenyl)-2-butanone [rheosmin] and its 3′-methoxy derivative [zingerone]; the 3-*O*-β-D-glucopyranosides of 3-hydroxy-1-(4′-hydroxy-3′-methoxyphenyl)-1-propanone [β-hydroxypropiovanillone] and *trans*-3-hydroxy-1-(4′-hydroxy-3′-methoxyphenyl) propene [*trans*-coniferyl alcohol]; and the 3′-*O*-β-D-glucopyranosides of (4*S*,3′*R*)-4-hydroxy-4-(3′-hydroxybutyl)-3,5,5-trimethyl-2-cyclohexenone [dihydrovomifoliol] and (4*S*,3′*R*)-4-hydroxy-4-(3′-hydroxy-*trans*-1′-butenyl-3,5,5-trimethyl-2-cyclohexenone [vomifoliol] have been isolated from the needles of *Pinus sylvestris* and identified.

INTRODUCTION

Low M_r phenolic compounds in needles of *Pinus sylvestris* and *Picea abies* have been the subject of considerable attention in our laboratory for many years. Up to now, a series of monoaryls, flavonoids, lignans and stilbenes, mainly present as glycosides, have been isolated and identified. The results obtained up to 1982 have been reviewed [1]. In addition, the phenolics present in the needles of the Chinese pine *Pinus massoniana* have recently been investigated [2–4].

In our current screenings for biochemical markers among the phenolics, for use in chemosystematic and genetic studies, a comprehensive HPLC analysis of extracts from various clones of *P. Sylvestris* and *P. abies* were carried out. Several compounds were detected from both species, differing significantly in concentration between clones. The results have recently been presented briefly [5]. However, among the detected compounds, we observed several, that were unknown judging from their HPLC retention. Accordingly, we decided to make complementary isolation and characterization studies of the phenolics and other constituents that absorb UV light. The present paper deals with the isolation and identification of monoaryl and cyclohexenone glucosides from *P sylvestris.* The latter are structurally related to abscisic acid. A presentation of isolated flavonoids and stilbenes will be published elsewhere.

RESULTS AND DISCUSSION

Four monoaryl (**1–4**) and two cyclohexenone (**5, 6**) glucosides were isolated from the aqueous ethanol extract of the needles by successive CC on Sephadex LH-20 (H_2O as eluent) and silica gel and (**1–3, 5, 6** by) semipreparative HPLC. Compounds **1** and **2** were identified as the *O*-β-D-glucopyranosides of the C_6–C_4 compounds rheosmin and zingerone. The ^{1}H NMR spectra and $[\alpha]_D$ for **1, 2** and their tetraacetates agreed well with data reported previously for needles of *P. contorta* [6]. Moreover, enzymatic hydrolysis of **1** or **2** yielded equimolar amounts of D-glucose and rheosmin or zingerone, respectively, identified by comparison with synthetic samples. [7].

Compound **3** was characterized by ^{1}H NMR as a glycoside containing a 1,2,4-trisubstituted benzene ring and a methoxyl group. The aromatic pattern showed close resemblance to the spectrum of authentic acetovanillone available in our laboratory. The anomeric proton gave rise to a doublet at δ4.32 with $J = 7.8$ Hz. Enzymatic hydrolysis yielded D-glucose and the aglycone **3b**, $[M]^+$ m/z 196, identified by ^{1}H NMR as β-hydroxypropiovanillone by comparison with literature data [8]. The C-2 and C-3 protons of **3b** gave rise to triplets at δ3.19 and 4.02 with $J = 5.3$ Hz. However, those of the pentaacetate **3a** showed an ABCD system at 400 MHz, which indicating linkage of the C-3 hydroxyl group to glucose. The anomeric doublet at δ4.59 with $J = 7.8$ Hz, consistent with an aliphatic β-glucopyranoside, and the occurrence of an aromatic acetoxy signal at δ2.34 confirmed this linkage. Thus, compound **3** is β-hydroxypropiovanillone 3-*O*-β-D-glucopyranoside. To our knowledge, this glucoside has not been reported previously.

Compound **4** was isolated as an amorphous powder and, notably, gave a bright red colour on TLC with 50% sulphuric acid. ^{1}H NMR suggested a guaiacylpropene glycoside. The olefinic protons in the side-chain were represented by further split doublets at δ6.19 and 6.58 with $J = 15.8$ Hz consistent with the *trans*-configuration. Enzymatic hydrolysis resulted in equimolar amounts of D-glucose and the aglycone **4b**, identified as *trans*-coniferyl alcohol by comparison (^{1}H NMR, mass spectrum, TLC) with an authentic sample. On the other hand **4** was found to differ from authentic coniferin available in our laboratory. The ^{1}H NMR spectrum of the pentaacetate **4a** showed one aromatic acetoxy signal and shifts for the acetylated glucose moiety in close agreement with those

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*Part 13 in the series 'The Constituents of Conifer Needles'. For part 12, see ref. [4].

for **3a**. On the basis of this evidence, **4** was formulated as *trans*-coniferyl alcohol 3-*O*-β-D-glucopyranoside. The analogous *cis*-compound has previously been isolated from the bark of *Fagus silvatica* [9]. To our knowledge the *trans*-isomer has not been reported as a plant constituent. However, 4 has been tentatively identified as a product from a reaction of coniferyl alcohol and UDP-glucose catalysed by a glucosyltransferase [10]. The isomeric glucoside coniferin, which seems to be ubiquitous in the cambium of conifers and essential in lignin biosynthesis [11], was not found in the needle extract. The aglycones **3b** and **4b** have been isolated after microbial degradation of guaiacylglycerol-β-coniferyl ether [8]. Dilignol glycosides, structurally related to the latter compound, occur frequently in pine needles [1, 4], and it seems reasonable that **3** and **4** might be involved in their biosynthesis. Compound **3** could also be a biosynthetic product of guaiacylglycerol 3-*O*-β-D-glucoside, previously isolated in our laboratory from needles of *P. sylvestris* as a mixture of *erythro*- and *threo*-isomers [12]. Essentially, this requires only a dehydration of the latter glucosides.

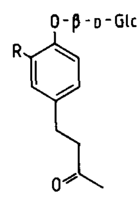
Compound **5** was isolated as a colourless oil. Enzymatic hydrolysis yielded equimolar amounts of D-glucose and the aglycone **5b**, which was identified (^{1}H and ^{13}C NMR) as the known compound dihydrovomifoliol by comparison with literature data [13, 14]. On hydrolysis, the ^{13}C signal for C-3′ moved upfield by 7.5 ppm and C-2′ downfield by 0.2–1.7 ppm (the assignments for C-1′ and C-2′ may be reversed), which fully confirmed the 3′-*O* position of the glucose [15]. Acetylation produced the tetraacetate **5a**. The sterically hindered hydroxyl group at C-4 remained intact. In the ^{1}H NMR spectrum of **5a** the anomeric proton appeared as a doublet at δ4.50 with J = 8.0 Hz. Thus, **5** was identified as dihydrovomifoliol-*O*-β-D-glucopyranoside, which to our knowledge, has not been reported previously. The aglycone **5b** has, however, been found in *Podocarpus blumei* [13] and *Cannabis sativa* [14].

Compound **6** was identified as vomifoliol 3′-*O*-β-D-glucopyranoside or roseoside, which has previously been found in *Vinca rosea* [16], *Nicotiana tabacum* [17], *Cydonia oblonga* and *Betula alba* [18]. The unsaturated part of the side-chain was documented by ^{13}C NMR resonances at δ135.4 and 131.7 and a ^{1}H NMR singlet (two protons) at δ5.85. Enzymatic hydrolysis yielded D-glucose and the aglycone vomifoliol **6b**. This compound was first isolated from *Rauwolfia vomitoria* [19].

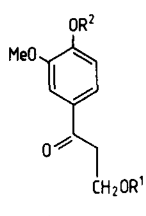
Compounds **5b** and **6b** are structurally related to the plant growth regulator *S*-(+)-abscisic acid. As shown [20, 21] all the three compounds have the same absolute configuration at C-4. The stereochemistry of the second asymmetrical centre in **5b** and **6b** has been established to 3′*R* [20]. Compound **6b** has been reported to exhibit properties similar to those of (±)-abscisic acid on the stomatal aperture in epidermal strips from *Eichhornia crassipes* [22] and is believed to play an important role as an endogenous regulator of the stomatal aperture.

EXPERIMENTAL

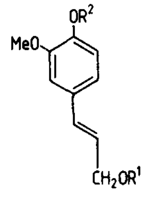
General. NMR spectra were measured at 400 (^{1}H) or 22.5 MHz (^{13}C). Chemical shifts are given on the δ(ppm) scale with TMS as int. std. ^{13}C NMR assignments were made partly through comparison of the chemical shifts with the data published for similar compounds [2, 23] and partly using the DEPT technique.



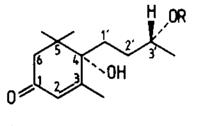
1 R=H
2 R=OMe



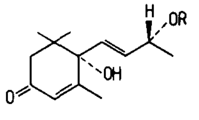
3 R¹=β-D-glucopyranoside; R²=H
3a R¹=β-D-glucopyranoside (Ac₄); R²=Ac
3b R¹=R²=H



4 R¹=β-D-glucopyranoside; R²=H
4a R¹=β-D-glucopyranoside (Ac₄); R²=Ac
4b R¹=R²=H



5 R=β-D-glucopyranoside
5a R=β-D-glucopyranoside (Ac₄)
5b R=H



6 R=β-D-glucopyranoside
6a R=β-D-glucopyranoside (Ac₄)
6b R=H

The ^{1}H NMR data for the individual protons H-1″–H-6″in the glucose moiety are not listed for compounds **4a**–**6a**. They were identical, or very close to, the values listed for the same protons in **3a**, except for $J_{5'',6''b}$ = 2.6 and $J_{5'',6''b}$ = 4.4 Hz for compounds **5a** and **6a**. The data for the strongly coupled protons in **3**, **5b** and **6a** were checked by computer spin-simulation and adjusted if necessary. MS were recorded on a quadrupole instrument at 70 eV. TLC was performed on silica gel HF_{250} plates.

Plant material. Needles from a 15-year-old specimen of *P. sylvestris* were collected in March 1986, near Uppsala, Sweden and immediately deep-frozen.

Extraction and isolation. Needles (dry wt 0.5 kg) were homogenized in 96% EtOH (3 × 2l) and aq. 80% EtOH (3 × 2l) for 6 × 5min at room temp. The combined ext. was concd *in vacuo* at 30°, dil. with H_2O (1 l) and extracted with petrol (2 × 0.5 l). After evapn of the aq. phase at 30°, the residue (101 g) was chromatographed over Sephadex LH-20, with H_2O and aq. EtOH as eluents, with stepwise increasing EtOH content. Twelve fractions (A–M) were collected. Fractions B–D (H_2O as eluent) were fractionated by CC on silica gel (230–400 mesh), using $CHCl_3$-MeOH-H_2O in different proportions and MeCOEt–H_2O (10:1) as eluents. From fractions B, crude **1** (120 mg), **2** (150 mg), **5** (125 mg) and **6** (125 mg); from fraction C, crude **3** (176 mg); and from fraction D, pure **4** (373 mg) were obtained. Parts of the crude fractions were subfractionated by HPLC on a NOVA-PAK C18 Radial-PAK column (Waters Associates). Pure compounds **1** (33 mg), **2** (18 mg) and **3** (12 mg) (35% aq. MeOH as eluent), **5** (10 mg) and **6** (15 mg) (MeOH–HCO_2H–H_2O 25:1:75 as eluent) were obtained.

Enzymatic hydrolysis of compounds **1**–**6** was performed in aq. solns with crude pectinase from *Aspergillus niger* (Sigma Chemical Co.) at room temp. overnight. The aglycone was extracted with EtOAc. The sugar in the aq. phase was purified on a SEP-PAK C18 cartridge (Waters Associates), with H_2O as eluent and was identified by its optical rotation and the GC-R_t of the corresponding alditol acetate.

3. $[\alpha]_D^{20} = -9.5°$ (MeOH; *c* 1.2). λ_{max}^{MeOH} nm: 228, 275, 306. ^{1}H NMR (CD_3OD): δ3.1–3.9 (*m*, H-2, H-2″–H-6″), 3.90 (*s*, OMe), 3.99 (*dt*, H-3b), 4.26 (*dt*, H-3a), 4.32 (*d*, H-1″), 6.86 (*d*, H-5′), 7.54 (*d*, H-2′), 7.60 (*dd*, H-6′); *J*: 2a,3a = 2a,3b = 2b,3a = 2b,3b = 6.4; 3a,3b = 10.1; 2′,6′ = 2.0; 5′,6′ = 8.3; 1″,2″ = 7.8 Hz. The signals from the methylene protons at C-2 were overlapped by those from the solvent CD_3OD.

Acetylation (Ac_2O–pyridine) of **3** (3 mg) gave the pentaacetate **3a** (4 mg). $[\alpha]_D^{20} = -14.5°$ ($CHCl_3$; *c*0.4). ^{1}H NMR ($CDCl_3$): δ1.91, 1.99. 2.03, 2.08 (4*s*, 4OAc), 2.34 (*s*, OAc), 3.12 (*ddd*, H-2b), 3.36 (*ddd*, H-2a), 3.71 (*ddd*, H-5″), 3.89 (*s*, OMe), 4.04 (*ddd*, H-3b), 4.12 (*dd*, H-6″b), 4.24 (*ddd*, H-3a), 4.27 (*dd*, H-6″a), 4.59 (*d*, H-1″), 4.96 (*dd*, H-2″), 5.08 (*dd*, H-4″), 5.20 (*dd*, H-3″), 7.13 (*d*, H-5′), 7.55 (*dd*, H-6′), 7.56 (*br s* H-2′); *J*: 2a,2b = 17.4; 2a,3a = 6.5; 2a,3b = 7.8; 2b,3a = 5.4; 2b,3b = 6.0; 3a,3b = 9.8; 2′,6′ = 2.0; 5′,6′ = 8.4; 1″,2″ = 7.8; 2″,3″ = 3″,4″ = 9.4; 4″,5″ = 9.9; 5″,6″a = 4.9; 5″,6″b = 2.3; 6″a,6″b = 12.3 Hz.

Hydrolysis of **3** (5 mg) yielded **3b** (2 mg). MS (probe) *m/z* (rel. int.): 196 $[M]^+$ (23), 178 (4), 166 (3), 151 (100), 137 (4), 123 (20), 108 (9). D-glucose (2 mg) was isolated from the aq. phase.

4. $[\alpha]_D^{20} = -16.9°$ (MeOH; *c* 4.1). λ_{max}^{MeOH} nm: 267, 304 sh. ^{1}H NMR (CD_3OD): δ3.15–3.90 (*m*, H-2″–H-6″), 3.86 (*s*, OMe), 4.29 (*ddd*, H-3b), 4.36 (*d*, H-1″), 4.49 (*ddd*, H-3a), 6.19 (*ddd*, H-2), 6.58 (*ddd*, H-1), 6.73 (*d*, H-5′), 6.85 (*dd*, H-6′), 7.01 (*d*, H-2′); *J*: 1,2 = 15.8; 1,3a = 1.5; 1,3b = 1.3; 2,3a = 5.9; 2,3b = 6.9; 3a,3b = 12.4; 2′,6′ = 2.0; 5′,6′ = 8.1; 1″,2″ = 7.8 Hz. Acetylation (Ac_2O–pyridine) of **4** (5 mg) yielded the pentaacetate **4a** (8 mg). ^{1}H NMR ($CDCl_3$): δ2.02, 2.03, 2.06, 2.09 (4*s*, 4 OAc), 2.32 (*s*, OAc), 3.70–5.25 (*m*, H1″–H6″), 3.85 (*s*, OMe), 4.27 (*ddd*, H-3b), 4.50 (*ddd*, 3a), 6.17 (*ddd*, H-2), 6.56 (*ddd*, H-1), 6.94 (*dd*, H-6′), 6.98 (*d*, H-2′), 6.99 (*d*, H-5′); *J*: 1,2 = 15.9; 1,3a = 1.5; 1,3b = 1.4; 2,3a = 5.4; 2,3b = 6.4; 3a,3b = 13.0; 2′,6′ = 1.8; 5′,6′ = 8.1 Hz. Hydrolysis of **4** (30 mg) yielded **4b** (12 mg) and D-glucose (12 mg).

5. $[\alpha]_D^{20} = -4.4°$ (MeOH; *c*0.8). λ_{max}^{MeOH} nm: 242. ^{1}H NMR (CD_3OD): δ1.01 (*s*, 5-Me_b), 1.09 (*s*, 5-Me_a), 1.17 (*d*, 3′-Me), 1.48 (*m*, H-2′b), 1.78 (*m*, H-2′a), 1.82 (*m*, H-1′b), 1.98–2.08 (*m*, H-1′a), 2.03 (*d*, 3-Me), 2.14 (*dd*, H-6b), 2.62 (*d*, H-6a), 3.10–3.90 (*m*, H-2″–H-6″), 3.81 (*m*, H-3′), 4.30 (*d*, H-1″), 5.83 (*dq*, H-2); *J*: 2,3-Me = 1.3; 2,6b = 1.1; 6a,6b = 18.1; 3′,3′-Me = 6.2; 1″,2″ = 7.8 Hz. ^{13}C NMR (CD_3OD): δ201.0 (C-1), 171.6 (C-3), 126.7 (C-2), 102.4 (C-1″), 79.3 (C-4), 78.2 (C-5″), 77.9 (C-3″), 76.3 (C-3′), 75.2 (C-2″), 71.9 (C-4″), 63.0 (C-6″), 51.2 (C-6), 42.9 (C-5), 34.9, 33.6 (2 CH_2), 24.7, 24.1, 21.6, 20.1 (4 Me).

Acetylation (Ac_2O–pyridine) of crude **5** (10 mg) and CC on silica gel using $CHCl_3$–MeOH (50:1) produced the tetraacetate **5a** (7 mg). $[\alpha]_D^{20} = -4.7°$ ($CHCl_3$; *c*0.7). $\lambda_{max}^{CHCl_3}$ nm: 241. ^{1}H NMR ($CDCl_3$): δ1.06 (*s*, 5-Me_b), 1.08 (*s*, 5-Me_a), 1.12 (*d*, 3′-Me), 1.4–2.1 (*m*, H-1′, H-2′), 2.00 (*d*, 3-Me), 2.01 (*s*, OAc), 2.04 (2*s*, 2OAc), 2.09 (*s*, OAc), 2.22 (*dd*, H-6b), 2.47 (*d*, H-6a), 3.65 (*m*, H-3′), 3.60-5.25 (*m*, H-1″ – H-6″), 5.85 (*dq*, H-2); *J*: 2,3-Me = 1.3; 2,6b = 0.8; 6a,6b = 18.0; 3′,3′-Me = 6.2 Hz.

Hydrolysis of crude **5** (25 mg) and CC of the EtOAc extract on silica gel using $CHCl_3$–MeOH (15:1) yielded the aglycone **5b** (6 mg). $[\alpha]_D^{20} = -17°$ (MeOH; *c*0.6). λ_{max}^{MeOH}nm: 243. ^{1}H NMR ($CDCl_3$): δ1.06 (*s*, 5-Me_b), 1.10 (*s*, 5-Me_a), 1.24 (*d*, 3′-Me), 1.54 (*dddd*, H-2′b), 1.64 (*dddd*, H-2′a), 1.84 (*ddd*, H-1′b), 1.99 (*ddd*, H-1′a), 2.06 (*d*, 3-Me), 2.25 (*dd*, H-6b), 2.50 (*d*, H-6a), 3.80 (*ddq*, H-3′), 5.86 (*dq*, H-2); *J*: 2,3-Me = 1.4; 2,6b = 1.1; 6a,6b = 18.2; 1′a,1′b = 14.0; 1′a,2′a = 5.7; 1′a,2′b = 9.2; 1′b,2′a = 8.6; 1′b,2′b = 6.7; 2′a,2′b = 14,0; 2′a,3′ = 8.6; 2′b,3′ = 3.8; 3′,3′ -Me = 6.2 Hz. ^{13}C NMR (CD_3OD): δ200.4 (C-1), 171.3 (C-3), 126.4 (C-2), 78.9 (C-4), 68.8 (C-3′), 51.0 (C-6), 42.8 (C-5), 35.3, 35.1 (2 CH_2), 24.6, 24.0, 23.5, 21.8 (4 Me). MS agreed well with lit. [14]. D-Glucose (10 mg) was isolated from the aq. phase.

6. ^{1}H NMR (CD_3OD): δ1.028 (*s*, 5-Me_b), 1.032 (*s*, 5-Me_a), 1.28 (*d*, 3′-Me), 1.92 (*d*, 3-Me), 2.14 (*dd*, H-6b), 2.52 (*d*, H-6a), 3.10–3.90 (*m*, H-2″–H6″), 4.34 (*d*, H-1″), 4.42 (*m*, H-3′), 5.85 (*br s* H-1′, H-2′), 5.86 (*dq*, H-2), *J*: 2,3-Me = 1.4; 2,6b = 1.0; 6a,6b = 17.0; 3′,3′-Me = 6.4; 1″,2″ = 7.8 Hz. ^{13}C NMR (CD_3OD): δ201.2 (C-1), 167.2 (C-3), 135.4 (C-2′), 131.7 (C-1′), 127.3 (C-2), 102.9 (C-1″), 80.1 (C-4), 78.3, 78.1 (C-3″, C-5″), 77.3 (C-3′), 75.4 (C-2″), 71.8 (C-4″), 63.0 (C-6″), 50.8 (C-6), 42.5 (C-5), 24.8, 23.5, 21.2, 19.6 (4 Me). λ_{max} and $[\alpha]_D$ showed good agreement with lit. [19]. Acetylation (Ac_2O–pyridine) of crude **6** (10 mg) and CC on silica gel using $CHCl_3$–MeOH (50:1) produced the tetraacetate **6a** (6 mg). ^{1}H NMR ($CDCl_3$): δ1.02 (*s*, 5-Me_b), 1.09 (*s*, 5-Me_a), 1.24 (*d*, 3′-Me), 1.89 (*d*, 3-Me), 2.01, 2.04, 2.05, 2.10 (4*s*, 4 OAc), 2.24 (*dd*, H-6b), 2.43 (*d*, H-6a), 3.60–5.20 (*m*, H-1″–H-6″), 4.25 (*m*, H-3′), 5.77 (*d*, H-1′), 5.82 (*dd*, H-2′), 5.90 (*dq*, H-2); *J*: 2,3-Me = 1.4; 2,6b = 0.8; 6a,6b = 17.1; 1′,2′ = 15.7; 2′,3′ = 5.6; 3′,3′-Me = 6.5 Hz.

Hydrolysis of crude **6** (25 mg) and CC of the EtOAc extract on silica gel using $CHCl_3$–MeOH (15:1) yielded the aglycone **6b** (8 mg). ^{13}C NMR (CD_3OD): δ201.2 (C-1), 167.4 (C-3), 137.1 (C-2′), 130.1 (C-1′), 127.2 (C-2), 80.0 (C-4), 68.7 (C-3′), 50.8 (C-6), 42.5 (C-5), 24.6, 23.9, 23.5, 19.6 (4 Me). ^{1}H NMR, MS, $[\alpha]_D$ and mp agreed well with lit. values [23, 24]. D-Glucose (10 mg) was isolated from the aq. phase.

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