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CIS- AND *TRANS*-DIHYDROQUERCETIN GLUCOSIDES FROM NEEDLES OF *PINUS SYLVESTRIS**

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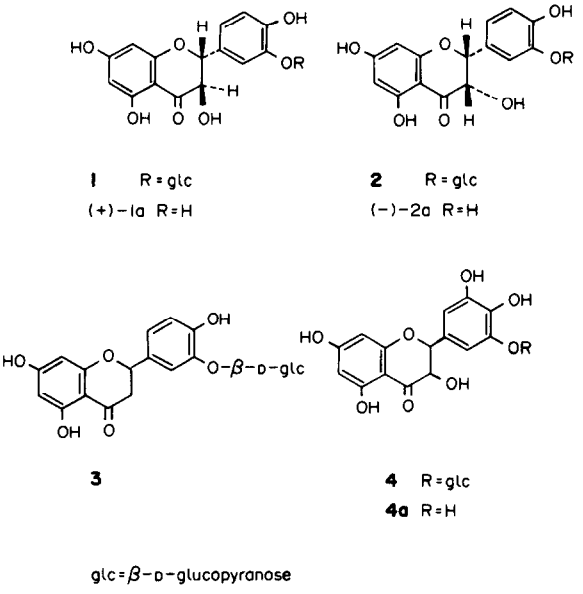
Key Word Index—*Pinus sylvestris*; Pinaceae; *cis*- and *trans*-dihydroflavonol glycosides; flavanone glucoside; dihydroquercetin; dihydromyricetin; eriodictyol *cis-trans* isomerism; chemotypes.

Abstract—(−)-*cis*-2,3-Dihydroquercetin (presumably as the 3′-*O*-β-D-glucopyranoside); the 3′-*O*-D-glucopyranosides of (+)-*trans*-2,3-dihydroquercetin, dihydromyricetin and eriodictyol; (+)-catechin and (+)-gallocatechin have been isolated from the needles of *Pinus sylvestris*. The dihydroquercetin aglycones interconvert in methanolic solution. Two chemotypes of *Pinus sylvestris* can be distinguished on the basis of their dihydroquercetin, dihydromyricetin and eriodictyol contents.

INTRODUCTION

Recently, four monoaryl and two cyclohexenone glucosides were identified from *Pinus sylvestris* L. needles [1]. To the best of our knowledge, three were new natural products, and the others had not been reported as constituents of *P. sylvestris* previously. This paper deals with the isolation and identification of flavan-3-ol, dihydroflavonol and flavanone compounds from the same needles. The dihydroflavonols occurring in Nature are known to possess the 2,3-*trans* configuration and the natural occurrence of 2,3-*cis* isomers has long been questioned. We now report the isolation of optically active *cis*- and *trans*-dihydroquercetin. One reason for our investigation was to identify those compounds, which, from recent HPLC screenings, occur in markedly different concentrations in individual trees from different clones of *P. sylvestris*. In this paper, we postulate the existence of two chemotypes of *P. sylvestris* on the basis of the isolated compounds. A presentation of isolated flavonols and hydroxystilbenes will be published elsewhere.



RESULTS AND DISCUSSION

From the aqueous ethanol extract of the needles, (+)-catechin, (+)-gallocatechin and flavonoids **1**–**4** were isolated. Among them (+)-catechin, (+)-gallocatechin, (+)-dihydroquercetin-3′-*O*-β-D-glucopyranoside (**1**) and eriodictyol-3′-*O*-β-D-glucopyranoside (**3**) were identified by direct comparison (TLC, NMR) with authentic samples. These compounds have previously been isolated in our laboratory from needles of *P. sylvestris* [2] and *P. massoniana* Lamb. [3] but **3** has not been found in *P. sylvestris* before.

Compound **4**, $[\alpha]_D$ −22.1°, was characterized as a dihydroflavonol glucoside from its ^{1}H NMR spectrum which differed considerably from that of **1** only with respect to the signals from the B-ring protons. In **4**, these gave rise to a pair of doublets at δ6.74 and 6.92 with *J* 2.0 Hz, consistent with a pair of non-equivalent *meta*-related protons. On acetylation, **4** produced a nonaacetate with four aromatic and five aliphatic acetoxy groups. Enzymatic hydrolysis yielded D-glucose and (+)-dihydromyricetin (**4a**). The structure of **4a** was deduced from mass spectra and ^{1}H NMR spectra and by comparison with literature data [4, 5]. The ^{1}H NMR signals from the B-ring protons in **4** exhibited considerable upfield shifts (0.21 and 0.39 ppm) upon hydrolysis and appeared in **4a** as a split singlet at δ6.53 with *J* 0.4 Hz. The small split is due to a four bond coupling between H-2 and the equivalent H-2′ and H-6′. In **4** this coupling only caused peak broadening. From these results the structure of **4** was

*Part 14 in the series 'The Constituents of Conifer Needles'. Part 13, see Ref. [1].

established as (+)-dihydromyricetin-3′-*O*-β-D-glucopyranoside. As far as we know, **4** has not been reported previously, and only one other glycoside of **4a** has been observed [4]. The aglycone **4a** has previously been reported from bark of *P. contorta* [5] and, along with the 6-methyl derivative of **4**, from cedar wood [6].

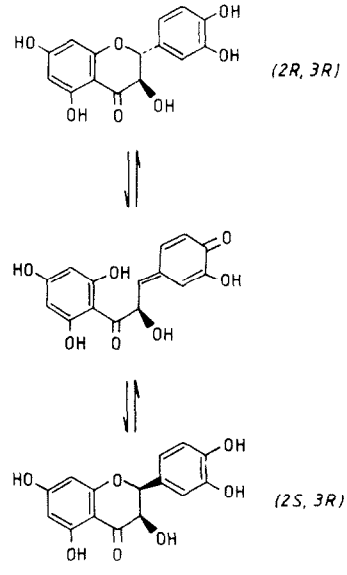
cis- and *trans*-Dihydroquercetin

Dihydroflavonols can occur in four stereoisomeric forms, owing to the asymmetric carbons C-2 and C-3, but, in Nature, they occur predominantly as the 2,3-*trans* isomers with the C-2 phenyl and C-3 hydroxyl group in equatorial positions [7]. The majority have the absolute configuration (2*R*,3*R*). Reports of 2,3-*cis* isomers are rare. Clark-Lewis *et al.* [8] discussed the relative thermodynamic stability of *cis*- and *trans*-dihydroflavonols and suggested that, owing to the hydrogen bonding between the carbonyl group and the equatorial 3-hydroxyl group, the 2,3-*trans* isomers should be favoured. They also suggested that the *cis*-isomers, which had been claimed earlier, were actually structural isomers of the dihydroflavonols e.g. 2-benzyl-2-hydroxycoumaranones or 2-(α-hydroxybenzyl)coumaran-3-ones. Furthermore, lack of reliable evidence for the existence of natural *cis*-isomers [7] and also of *cis–trans* isomerism among the dihydroflavonols [9], places the existence of *cis*-isomers in considerable doubt. Quite recently, however, a 7-*O*-glycoside of (−)-*cis*-5,7-dihydroxy-3′-methoxy-2,3-dihydroflavonol was isolated from peelings of *Citrus junos* [10] and (−)-*cis*-7,8-3′,4′-tetrahydroxy-2,3-dihydroflavonol was reported [11, 12] as a constituent of the heartwood of *Acacia melanoxylon*. The latter compound was suggested to be the precursor of proanthocyanidins with 2,3-cis flavanol units, previously found in the same plant. The racemic *cis*-dihydroflavonol has recently been reported [13] as a synthetic product from the oxidation of flavanone by hypervalent iodine.

Compound **1** was isolated, chromatographically pure, in a yield of 2% of the needle dry weight and was by far the most abundant low M_r phenolic in the extract. The aglycone (+)-dihydroquercetin, (+)-**1a**, has been shown [14] to possess (2*R*,3*R*) configuration with H-2 and H-3 in *trans*-diaxial positions. The ^{1}H NMR signals for these protons in **1** appeared as doublets at δ4.98 and 4.57 with *J* 11.7 Hz. Careful inspection of the spectra revealed two more doublets at δ5.36 and 4.23 with *J* 2.8 Hz. The latter shifts and coupling constant are well in accord with those reported [11] for the *cis*-isomer from *A. melanoxylon* and with signals from related protons in 3-substituted *cis*-dihydroflavonols [15, 16]. For the synthetic *cis*-dihydroflavonol, however, a coupling constant of 6.0 Hz was reported. Also, in the aromatic region of **1**, the signals from all protons except H-6′ (obscured by overlap) were accompanied by low-intensity signals with similar coupling constant patterns. Thus, **1** seemed to consist of both the *trans*- and *cis*-dihydroquercetin glycoside. The estimated amount of *cis*-isomer was 1–2%. Attempts to separate the two isomers by TLC or reversed-phase HPLC were not successful. Enzymatic hydrolysis yielded D-glucose and (from HPLC analysis) a mixture of two aglycones. Compound (+)-**1a**, $[\alpha]_D$ + 19.4°, was crystallized from water. The second aglycone, (−)-**2a**, $[\alpha]_D$ -20°, which was isolated from the mother liquor by semi-preparative HPLC, showed mass, UV, and ^{1}H NMR spectra closely similar to those of (+)-1a. In (+)-**1a** the signals for H-2 and H-3 appeared as doublets at δ4.92 and 4.49 with *J* 11.3 Hz whereas for (−)-**2a** they appeared at δ5.29 and 4.17 with *J* 2.8 Hz. This suggests that (−)-**2a** is (−)-2,3-*cis*-dihydroquercetin. Upon hydrolysis, the ^{1}H NMR signals from H-2′ and H-5′ in **2** showed the same upfield shifts as the corresponding protons in **1**. Compound **2** is therefore suggested to be the 3′-*O*-β-D-glucopyranoside of (−)-**2a**.

Optically active *trans*-dihydroflavonols are known [17] to racemize readily under acidic or alkaline conditions, presumably by way of a chalcone-like intermediate. In view of their lesser stability, the *cis*-isomers can be expected to racemize more easily. Foo [11] reported the quantitative conversion of *cis*-7,8,3′,4′-tetrahydroxy-2,3-dihydroflavonol into the racemic *trans*-isomer in ethanol–hydrochloric acid. On isomerization of (2*R*,3*R*) *trans*-dihydroquercetin-3-*O*-rhamnoside in D_2O–EtOD–sodium acetate, a mixture of all four stereoisomers was formed [15]. In this reaction, deuterium was incorporated at C-3, and a mechanism involving both ring opening at C-2 and proton abstraction with formation of an enolate anion at C-3 was proposed. It has also been claimed [18] that hydroxylation of flavanones with hydrogen peroxide results in *cis*-dihydroflavonols, which easily epimerize to *trans*-isomers via 3-flavene-3,4-diol intermediates. This reaction was later questioned [9]. It was suggested that 2-hydroxycoumarone had been mistaken for *cis*-dihydroflavonol. On the other hand, flavan-3-ols are known to epimerize with relative ease at the position 2 in aqueous solutions [19], and the reaction presumably involves opening of the heterocyclic ring and formation of an intermediate quinone methide (Scheme 1) [20].

We found that *cis* (−)-**2a** slowly epimerized to the *trans* (−)-**1a** in methanolic solution at room temp. The *cis*:*trans* ratio, estimated at intervals by ^{1}H NMR, attained a 1:10 equilibrium limit value after more than one month. The CD spectra of (+)- and (−)-**1a** were symmetrically opposed and, hence, (−)-**1a** was (2*S*,3*S*)-



Scheme 1. Proposed mechanism for *cis–trans* epimerization of (+)-dihydroquercetin.

dihydroquercetin. The amplitude of the CD-spectrum was somewhat smaller for (−)-**1a** than for the (+)-isomer indicating that the former was not optically pure. Moreover, (+)-**1a** was found to epimerize similarly to (+)-**2a**, $[\alpha]_D$ + 30.5°, in methanol. Since this reaction will proceed during the purification, the isolated *cis*-isomer can be expected to be a mixture of the enantiomers. Hence, in our opinon (−)-**2a**, presumably as the 3′-*O*-β-D-glucopyranoside, is a natural constituent in the needles, whereas (+)-**2a** is an artefact. The *cis–trans* rearrangement proceeds more rapidly in the presence of needle extract, indicating that the reaction is catalysed by some constituent or is promoted by a pH decrease in the solution. Considering the relative ease of the epimerization, a mild and rapid extraction procedure is essential.

The absolute configuration of (−)-**2a** is (2*R*,3*S*). The CD spectra of (−)-**2a** agreed with published [15] CD data for (2*R*,3*S*)-*cis*-dihydroquercetin-3-*O*-rhamnoside and, furthermore, there was no deuterium exchange at C-3 during the interconversions of the aglycones in CD_3OD or in D_2O–CD_3OD (1:1). This excludes formation of an intermediate enolate anion at C-3 and supports a reaction mechanism, involving rearrangement at C-2 (Scheme 1), analogous to the mechanism proposed for epimerization of flavan-3-ols [19]. The natural occurrence in the needles of *cis*-dihydroquercetin, with the same absolute configuration at C-2 and C-3 as (2*R*,3*R*)-(−)-epicatechin, supports previous suggestions [11, 21] that *cis*-dihydroquercetin is a precursor of (−)-epicatechin or proanthocyanidins containing (−)-epicatechin units.

Clearly, the glycosides **1**, **3** and **4** (and tentatively **2**) which all have glucose linked in the 3′-position, are biosynthetically related. With regard to **1**–**4**, our investigations have revealed two chemotypes within *P. sylvestris*. Needle extracts from trees of different clones have been hydrolysed and analysed (reversed-phase HPLC/UV detection) for neutral low M_r phenols including phenolic aglycones. The experimental procedures and results have recently been presented briefly [22]. Compound **1** is predominant in the first chemotype and constitutes 2–3% of the needle dry weight. It is always accompanied by the glycosides **2**–**4** (0.01–0.1%). Needles of trees from the second chemotype, however, contain only small amounts (about 0.1%) of **1** and only traces of the three other compounds. Flavanones and dihydroflavonols are precursors of flavan-3-ols, but catechin and gallocatechin did not show clone dependence. All analysed trees were grouped within the two chemotypes. A detailed presentation of these clone studies will be published separately. For the present investigation, a tree of the first chemotype was used.

EXPERIMENTAL

The general procedures and the instruments used were as described in the previous paper [1]. For analytical and semi-prep. HPLC a NOVA-PAK C-18 Radial-PAK column (Waters Associates) was used. The LH-20 fractions I–K (eluted with 50% aq. EtOH) were fractionated by CC on silica gel (230–400 mesh) using $CHCl_3$–MeOH–H_2O in different proportions as eluent. From fraction I, a 100:1 mixture (9.3 g) of **1** and **2** together with **4** (320 mg) were obtained; from fraction J, (+)-catechin (157 mg) and crude **3** (282 mg) were obtained; from fraction K, (+)-gallocatechin (131 mg) was obtained. Pure **3** (10 mg) was isolated from a sample of crude **3** by semi-prep. HPLC (30% aq. MeOH as eluent).

Mixture of **1** *and* **2**:**1** (99%). ^{1}H NMR (CD_3OD): δ 3.3–4.0 (6H, *m*, H-2″–H-6″), 4.57 (1H, *d*, *J* = 11.7 Hz, H-3), 4.84 (1H, *d*, *J* = 7.5 Hz, H-1″), 4.98 (1H, *d*, *J* = 11.7 Hz, H-2), 5.89 (1H, *d*, *J* = 2.1 Hz, H-6), 5.92 (1H, *d*, *J* = 2.1 Hz, H-8), 6.90 (1H, *d*, *J* = 8.3 Hz, H-5′), 7.10 (1H, *dd*, $J_{2',6'}$ = 2.1 Hz, $J_{5',6'}$ = 8.3 Hz, H-6′), 7.39 (1H, *d*, *J* = 2.1 Hz, H-2′).

2 (1%). ^{1}H NMR (CD_3OD): δ 4.23 (1H, *d*, *J* = 2.8 Hz, H-3), 5.36 (1H, *d*, *J* = 2.8 Hz, H-2), 5.91 (1H, *d*, *J* = 2.2 Hz, H-6), 5.96 (1H, *d*, *J* = 2.2 Hz, H-8), 6.86 (1H, *d*, *J* = 8.3 Hz, H-5′), 7.40 (1H, *d*, *J* = 1.7 Hz, H-2′). The signals for H,6′ and H-1″–H-6″ were not recognized due to overlap by signals from compound **1**.

Enzymatic hydrolysis of the mixture (6 g) of **1** and **2** was performed in aq. solution with crude pectinase from *Aspergillus niger* (100 mg) at room temp. overnight. The aglycones were extracted with EtOAc. Compound (+)-**1a** (3 g) was obtained by crystallization from an aq. solution of the aglycone mixture. Compound (−)-**2a** (20 mg) was obtained from the mother liquor by semi-prep. HPLC (25% aq. MeOH as eluent). D-Glucose was isolated from the aq. phase.

(+)-**1a**. $[\alpha]_D^{20}$ + 19.4° (MeOH; *c* 0.5). λ_{max}^{MeOH} nm: 290, 332 sh; MeOH–$AlCl_3$: 315, 373; MeOH–NaOMe: 247, 326. ^{1}H NMR (CD_3OD): δ 4.49 (1H, *d*, *J* = 11.3 Hz, H-3), 4.92 (1H, *d*, *J* = 11.3 Hz, H-2), 5.89 (1H, *d*, *J* = 2.2 Hz, H-6), 5.93 (1H, *d*, *J* = 2.2 Hz, H-8), 6.81 (1H, *d*, *J* = 8.2 Hz, H-5′), 6.85 (1H, *dd*, $J_{2',6'}$ = 2.0 Hz, $J_{5',6'}$ = 8.2 Hz, H-6′), 6.97 (1H, *d*, *J* = 2.0 Hz, H-2′). CD: $[\theta]_{330}$ + 9100, $[\theta]_{296}$ -35700 (MeOH; *c* 0.17). The MS data agreed well with the literature [5].

(−)-**2a**. $[\alpha]_D^{20}$ − 20° (MeOH; *c* 0.5). λ_{max}^{MeOH} nm: 290,332 sh; MeOH–$AlCl_3$: 313, 383; MeOH–NaOMe: 244, 329. ^{1}H NMR (CD_3OD): δ 4.17 (1H, *d*, *J* = 2.8 Hz, H-3), 5.29 (1H, *d*, *J* = 2.8 Hz, H-2), 5.90 (1H, *d*, *J* = 2.2 Hz, H-6), 5.95 (1H, *d*, *J* = 2.2 Hz, H-8), 6.76 (1H, *d*, *J* = 8.1 Hz, H-5′), 6.83 (1H, *ddd*, $J_{2',6'}$ = 2.0 Hz, $J_{5',6'}$ = 8.1 Hz, $J_{2,6'}$ = 0.7 Hz, H-6′), 7.0 (1H, *d*, *J* = 2.0 Hz, H-2′). CD: $[\theta]_{340}$ + 9053, $[\theta]_{295}$ − 18216 (MeOH; *c* 0.11). The MS data were identical with those for (+)-**1a**.

Compound (−)-**2a** (5 mg) was allowed to rearrange in CD_3OD at room temp. in the dark for two months. The reaction was followed by ^{1}H NMR, and the *cis–trans* ratio was determined from the heights of the peaks (H-3) in the substrate and the product. At equilibrium, compound (−)-**1a** was isolated from the reaction mixture by semi-preparative HPLC (25% aq. MeOH as eluent). The reaction was repeated in MeOH solution and followed by HPLC analysis and polarimetry.

(−)-**1a**. $[\alpha]_D^{20}$ − 15° (MeOH; *c* 0.1). CD: $[\theta]_{330}$ − 5200, $[\theta]_{296}$ + 18 500 (MeOH; *c* 0.04). λ_{max}, MS and ^{1}H NMR data were identical with those for (+)-**1a**.

Compound (+)-**1a** (1 g) was allowed to rearrange in MeOH for one month in the dark at room temp. and compound (+)-**2a** was isolated from the reaction mixture in the same way as described for (−)-**2a**.

(+)-**2a**. $[\alpha]_D^{20}$ + 30.5° (MeOH; *c* 0.4). CD: $[\theta]_{341}$ − 10 582, $[\theta]_{293}$ + 20 020 (MeOH; *c* 0.04). λ_{max}, MS and ^{1}H NMR data were identical with those for (−)-**2a**.

In a similar run (+)-**1a** was allowed to rearrange in D_2O–CD_3OD (50:50) at room temp. for four months. The *cis–trans* composition (1:10; from ^{1}H NMR) were determined at the end of that time.

4. $[\alpha]_D^{20}$ − 22.1° (MeOH; *c* 1.4). λ_{max}^{MeOH} nm: 291, 335 sh; MeOH–$AlCl_3$: 315, 377; MeOH–NaOMe: 249, 326. ^{1}H NMR (CD_3OD): δ 3.2–4.0 (6H, *m*, H-2″–H-6″), 4.52 (1H, *d*, *J* = 11.5 Hz, H-3), 5.89 (1H, *d*, *J* = 2.1 Hz, H-6), 5.92 (1H, *d*, *J* = 2.1 Hz, H-8), 6.74 (1H, *d*, *J* = 2.0 Hz, H-6′), 6.92 (1H, *d*, *J* = 2.0 Hz, H-2′). The signals from H-2 and H-1″, hidden under the broad hydroxyl peak, were visualized by warming the sample; δ 4.81 (1H, *d*, *J* = 7.6 Hz, H-1″), 4.91 (1H, *d*, *J* = 11.5 Hz, H-2). Acetylation (Ac_2O–pyridine) of **4** (35 mg) and CC on silica gel (EtOAc–petrol

3:2) produced the nona-acetate (21 mg). $[\alpha]_D^{20}$ + 30.0° ($CHCl_3$; *c* 1.1). ^{1}H NMR ($CDCl_3$): δ 1.99, 2.03, 2.04, 2.077, 2.082 (5 *s*, 50Ac), 2.28, 2.29, 2.32, 2.38 (4s, 40Ac), 3.90–5.35 (7H, *m*, H-1″–H-6″), 5.40 (1H, *d*, *J* = 12.0 Hz, H-2), 5.66 (1H, *d*, *J* = 12.0 Hz, H-3), 6.61 (1H, *d*, *J* = 2.2 Hz, H-6), 6.79 (1H, *d*, *J* = 2.2 Hz, H-8), 6.96 (1H, *d*, *J* = 1.9 Hz, H-6′), 7.07 (1H, *d*, *J* = 1.9 Hz, H-2′).

Hydrolysis of **4** (40 mg) yielded **4a** (27 mg). $[\alpha]_D^{20}$ + 15.5° (MeOH; *c* 2.7). ^{1}H NMR (CD_3OD): δ 4.45 (1H, *d*, *J* = 11.4 Hz, H-3), 4.85 (1H, *d*, *J* = 11.4 Hz, H-2), 5.88 (1H, *d*, *J* = 2.2 Hz, H-6), 5.92 (1H, *d*, *J* = 2.2 Hz, H-8), 6.53 (2H, *d*, *J* = 0.4 Hz, H-2′, H-6′). λ_{max} and MS data agreed well with the literature [4, 5]. D-Glucose was isolated from the aq. phase.

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