of *Teucrium belion* (aerial parts) were extracted with EtOH–H_2O (7:3) (3 ×) at room temp. The extracts were combined and the EtOH was eliminated by concn. The aq. soln was then extracted with EtOAc to give a pale-beige powder. 200 mg of this residue was passed through a polyamide column (40 g) and elution with H_2O–MeOH (13:7) yielded 30 mg pure poliumoside, R_f 0.32, $[\alpha]_D^{22}$ −80° (MeOH).

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(−)-MASSONIRESINOL, A LIGNAN FROM *PINUS MASSONIANA**

ZHAOBANG SHEN† and OLOF THEANDER

Department of Chemistry and Molecular Biology, Swedish University of Agricultural Sciences, S-750 07 Uppsala, Sweden

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Key Word Index—*Pinus massoniana*; Pinaceae; needles; lignan; massoniresinol; olivil.

Abstract—A new lignan, named (−)-massoniresinol, has been isolated from *Pinus massoniana* needles. Its structure has been proved to be (2*R*,3*S*,4*R*)-3,4-dihydroxy-2-(4-hydroxy-3-methoxyphenyl)-4-(4-hydroxy-3-methoxybenzyl)-3-tetrahydrofuranmethanol by ^{1}H NMR, ^{13}C NMR, mass and CD spectroscopy.

INTRODUCTION

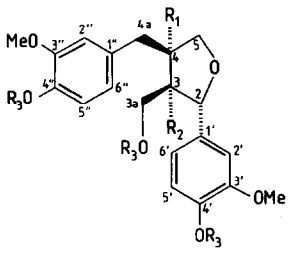
We recently isolated and identified seven flavonoids, including three, to our knowledge, new natural compounds, 6-*C*-methylaromadendrin 7-*O*-β-D-glucopyranoside, taxifolin 3′-*O*-β-D-(6″-phenylacetyl)-glucopyranoside and eriodictyol 3′-*O*-β-D-glucoside, from *Pinus massoniana* L. needles [1]. This paper describes the isolation and structural elucidation of a new lignan, named (−)-massoniresinol, from the same needles. The other hydrophilic phenolic compounds of the acetone and aqueous acetone extracts, mainly dilignol glycosides, will be reported elsewhere.

RESULTS AND DISCUSSION

(−)-Massoniresinol (**1**), $C_{20}H_{24}O_8$, $[M]^+$ 392, $[\alpha]_D^{25}$ −31.4°, was isolated from the ethyl acetate fraction of the needles of *P. massoniana*, as described previously [1]. The compound gave a yellow-green colour with diazotized sulphanilic acid spray reagent on silica gel HF_{254} plates similar to that given by (+)-lariciresinol and (−)-olivil. The ^{1}H NMR spectrum of **1** showed the presence of seven protons apart from six aromatic protons and two aryl methoxyl groups. These protons were comprised of an oxymonobenzylic proton (*s*, δ5.01), and the protons of a benzylic methylene group (*s*, δ2.93) and two methylene groups, attached to oxygen atoms (*m*, δ3.6–4.0). On acetylation with acetic anhydride and pyridine at room temperature overnight, a triacetate (**2**), $[M]^+$ 518, $[\alpha]_D^{25}$ −13.2°, was obtained. The ^{1}H NMR spectrum of **2** showed one aliphatic and two aromatic acetoxyl groups. The seven proton signals mentioned above appeared as a singlet for one proton at δ5.07 and three double-doublets of an AB pattern for three methylene groups. The downfield shift of one of the methylene groups to δ4.28 and 4.45 on acetylation of compound **1** indicated the presence of a

*Part 11 in the series "The Constituents of Conifer Needles". For Part 10 see ref. [1].

†Present address: Research Institute of Chemical Processing and Utilization of Forest Products, Chinese Academy of Forestry, Shao Shan Road, Nanjing, The People's Republic of China.



1 $R_1 = R_2 = OH$, $R_3 = H$
2 $R_1 = R_2 = OH$, $R_3 = Ac$
3 $R_1 = R_2 = OMe$, $R_3 = Me$
4 $R_1 = OH$, $R_2 = R_3 = H$

Table 1. ^{13}C NMR spectral data of (−)-olivil (4) and 1

C	4	1	C	4	1
1′	135.46	131.26	1″	130.50	130.26
2′	111.82	113.17	2″	115.52	115.58
3′	148.65*	148.65	3″	149.08*	148.65
4′	147.27	147.27	4″	146.27	146.29
5′	115.85	115.88	5″	115.85	115.88
6′	120.84	121.83	6″	124.03	124.22
2	85.76	86.27 *d*	4a	40.68	40.25 *t*
3	61.92	82.18 *s*	4	82.61	82.48 *s*
3a	60.86	64.58 *t*	5	78.01	74.98 *t*
OMe	56.55	56.55 *q*	OMe	56.55	56.55 *q*

*Signals may be reversed.

primary hydroxyl group in compound **1**. Furthermore, no decoupling of these signals was observed upon irradiation of any pair of doublets. This implied that these methylene groups and the oxymonobenzylic proton were separated by oxygen or fully substituted carbon atoms. On methylation (MeI, DMSO, NaH), **1** gave a pentamethyl ether **3** ($[M]^+$ 462). Its ^1H NMR spectrum indicated three aliphatic and four aromatic methoxyl groups. The fact that **1** gave a triacetate, but a pentamethyl ether, revealed the presence of two tertiary alcohol groups in **1**, which were not acetylated under the acetylation conditions used. Also, the ^1H NMR spectrum of **1** in DMSO-d_6 clearly showed two singlets and one triplet (lost on addition of D_2O) for the three hydroxyl groups. From the above data, the structure **1** was proposed for the new lignan, named massoniresinol.

^{13}C NMR analysis of **1** and the known compound (−)-olivil (**4**) (Table 1) provided further confirmation for the proposed structure. The chemical shifts of **4** were assigned on the basis of literature data [2, 3]. The assignments of **1** were made by comparison with those of **4** and its off-resonance spectrum. The ^{13}C NMR spectrum of **1** clearly showed that, in addition to twelve aromatic and two methoxyl carbons, there were six carbon atoms in **1**, and two of them were fully substituted. As expected, according to the known effects of hydroxyl group substitution on the α,β,γ and δ carbons, C-3, C-2, C-3a, C-2′ and C-6′ shifted downfield, and C-5, C-1′ and C-4a shifted upfield in comparison with the related chemical shifts of **4**.

The absolute configuration of **1** was elucidated by comparison of its CD spectrum with that of **4**. The similarity between the two CD spectra defined the same configuration of (−)-massoniresinol as that of (−)-olivil [4, 5]. Thus (−)-massoniresinol was (2*R*,3*S*,4*R*)-3,4-dihydroxy-2-(4-hydroxy-3-methoxyphenyl)-4-(4-hydroxy-3-methoxybenzyl)-3-tetrahydrofuranmethanol.

EXPERIMENTAL

The general procedures and instruments used were all as described in the previous paper [1].

(−)-Massoniresinol was isolated from the same EtOAc extract of *P. massoniana* needles as reported previously [1]. Thus, fraction VI from the Sephadex LH-20 column, eluted with 50% EtOH, was rechromatographed on a silica gel (230–400 mesh) column with 2-butanone–H_2O. The related subfraction was purified by prep. TLC on silica gel HF_{254} developed with $CHCl_3$–MeOH–H_2O (80:15:1) to yield the chromatographically homogeneous compound **1** (0.04 g).

(−)-Massoniresinol (**1**), amorphous, $[\alpha]_D^{22}$ −31.4° (MeOH; *c* 0.79). ^1H NMR (CD_3OD): δ2.93 (2H, *s*, H-4a), 3.6–4.0 (4H, *m*, H-3a, H-5), 3.85 (6H, *s*, 2 × OMe), 5.01 (1H, *s*, H-2), 6.7–7.1 (6H, *m*, aromatic protons); MS (probe, 70 eV) *m/z*: 392 $[M]^+$; CD (*c* 100 mg/100 ml MeOH, 190–400 nm): $[\theta]_{305}$ 0, $[\theta]_{285}$ 6800, $[\theta]_{255}$ 800, $[\theta]_{235}$ 19000, $[\theta]_{220}$ 1200, $[\theta]_{207}$ 7500, $[\theta]_{202}$ 0, $[\theta]_{198}$ −800. Cf. (−)-olivil, CD (*c* 75 mg/100 ml MeOH 190–400 nm): $[\theta]_{305}$ 0, $[\theta]_{285}$ 7000, $[\theta]_{254}$ 900, $[\theta]_{235}$ 18200, $[\theta]_{220}$ 1000, $[\theta]_{206}$ 8000, $[\theta]_{200}$ 0, $[\theta]_{195}$ −2100.

Massoniresinol triacetate (**2**) was obtained on acetylation (Ac_2O–pyridine) of **1**. Amorphous, $[\alpha]_D^{25}$ −13.2° ($CHCl_3$; *c* 0.38); ^1H NMR ($CDCl_3$): δ2.05 (3H, *s*, –OAc), 2.31 (6H, *s*, 2 × Ar–OAc), 2.81 (1H, *d*, J = 14 Hz, H_A-4a), 3.02 (1H, *d*, J = 14 Hz, H_B-4a), 3.70 (1H, *d*, J = 9 Hz, H_A-5), 3.98 (1H, *d*, J = 9 Hz, H_B-5), 3.83 (6H, *s*, 2 × OMe), 4.28 (1H, *d*, J = 11 Hz, H_A-3a), 4.45 (1H, *d*, J = 11 Hz, H_B-3a), 5.07 (1H, *s*, H-2), 6.8–7.1 (6H, *m*, aromatic protons); MS (probe, 70 eV) *m/z*: 518 $[M]^+$.

Massoniresinol pentamethyl ether (**3**) was obtained on methylation (MeI/DMF, NaH) of **1**. ^1H NMR ($CDCl_3$): δ2.75 (1H, *d*, J = 14 Hz, H_A-4a), 3.27 (1H, *d*, J = 14 Hz, H_B-4a), 3.06 (3H, *s*, –OMe), 3.43 (6H, *s*, 2 × –OMe), 3.88 (12H, *s*, 4 × Ar–OMe), 3.70–4.14 (4H, *m*, H-3a, H-5), 4.83 (1H, *s*, H-2), 6.75–7.10 (6H, *m*, aromatic protons); MS (probe, 70 eV), *m/z* (rel. int.): 462 $[M]^+$ (3), 311 (1), 238 (43), 207 (23), 181 (93), 151 (100).

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