6β-Hydroxyteuscordin and 2β-, 6β-Dihydroxyteuscordin
Two New Diterpenoids from Teucrium scordium L.

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Teucrium scordium L., Lamiaceae, Clerodane Type, Furanoid Diterpene

Two new furanoid diterpenes of clerodane type, 6β-hydroxyteuscordin (1) and 2β,6β-dihydroxyteuscordin (3) have been isolated from Teucrium scordium var. scordium, Lamiaceae. Their structures and stereochemistry have been determined on the basis of chemical reactions and spectroscopic evidence.

Recently, we have described the isolation, structures and stereochemistry of teuscordinon [1] and 6-ketoteuscordin and 6α-hydroxyteuscordin [2] from Teucrium scordium L. In continuation of this work, we have isolated two new diterpenoids, 6β-hydroxyteuscordin (1) and 2β,6β-dihydroxyteuscordin (3).

6β-Hydroxyteuscordin, C20H22O6, m.p. 229–231 °C, [α]D20 = 74.68° (c 0.158, acetone). MS: m/e 358 (M+).

IR (KBr, cm−1): 3440 (broad), 1770 and 1750 (two γ-lactones), 1660 (double bond), 3140, 2960, 1720–1740 and 1240 cm−1 for two ester groups. Absorption at 1720–1740 cm−1 is characteristic for 6-acetoxy groups.

The presence of a hydroxyl group in 1 was disclosed by treating with trichloroacetylisocyanate. The corresponding NH singlets appeared at δ 10.02 and 10.10. The δH–1H couplings of C–6H showed that the H-6 in 1 is equatorial whereas the orientation of OH group is axial. Oxidation of 1 with chromium trioxide gave only teuscordinon (2) [1], identical to the high field OH group in 2. Oxidation of 1 with Jones reagent to the 2-keto-6β-hydroxyteuscordin (5), C20H22O7, m.p. 185–187 °C, m/e 372 (M+).

Acetylation of 3 gave a diacetate (4), C24H24O9, m.p. 185–187 °C. The spectroscopic properties of 4 revealed the presence of a diacetate (CDCl3, δ): 1.92 (3H, s, COOMe) and 2.04 (3H, s, COOMe). The IR spectrum of 4 contained an intensive band at 1720–1740 and 1240 cm−1 for two ester groups.

The two hydroxyl groups in 3 were also proved with trichloroacetilisocyanate. The corresponding >NH singlets appeared at δ 10.02 and 10.10. The 2β,6β-dihydroxyteuscordin (3) was oxidized with Jones reagent to the 2-keto-6β-hydroxyteuscordin (5), C20H22O7, m.p. 223–225 °C, m/e 372 (M+).
In the \( ^1H \) NMR spectrum of 5 the signal from the 2-proton vanished, while the doublet from the 3-proton appeared as a singlet at 6.70. Furthermore the \( ^1H-^1H \) couplings of 10-H in 5 are different (\( J = 4 \) and 14 Hz) from the values found for 3 (\( J = 2.5 \) and 14 Hz). These facts showed unambiguously that one of the hydroxil group is at C-2, \( \beta \)-oriented. The coupling of H-2 and H-6 indicated \( \beta - \)OH supported by deshilding of H-10 and C-20 deshilding of H-19 (Table 1). On the base of the \( ^1H \) NMR data for the 6-proton (\( \delta = 4.35, 1H, t, J = 3 \) Hz) the other hydroxil group is at C-6, \( \beta \)-oriented. These data correspond with the values reported on related molecules of known geometry [3-6].

### Table I. \( ^1H \) NMR spectral data of compound (400 MHz), CDCl\(_3\), TMS as internal standard) [7].

<table>
<thead>
<tr>
<th>1(^{-})H</th>
<th>10(^{-})H ( \delta )</th>
<th>1(^{-})H</th>
<th>10(^{-})H ( \delta )</th>
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<td>( 2.05 ) d br</td>
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<tr>
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<td>( 2.41 ) dd</td>
<td>( 12 ) - H</td>
<td>( 5.37 ) dd</td>
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<tr>
<td>( 6.87 ) d</td>
<td>( 14 ) - H</td>
<td>( 6.41 ) dd</td>
<td>( 3) - Ha</td>
</tr>
<tr>
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<td>( 7.48 ) s br</td>
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<td>( 11) - Ha</td>
<td>( 2.41 ) dd</td>
<td>( 15 ) - H</td>
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<td>( 12 ) - H</td>
<td>( 5.37 ) dd</td>
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<td>( 21)</td>
<td>( 2.87 ) d</td>
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</table>

\( J \) (Hz): \( 1,1' = 1,10 = 14; 12 = 1',2 = 4; 1',10 = 2; 2,3 = 6.5; 2,0H = 6.7 = 6.7' = 15; 7,8 = 13; 7',8 = 4; 8,17 = 7; 11,11' = 14; 11,12 = 8; 11',12 = 9.5.\)

### Experimental

The melting points are uncorrected and have been determined with a Kofler microhostage apparatus. IR spectra were recorded on KBr pellets. \( ^1H \) NMR spectra were obtained on a JEOL PS-100 instrument at 100 MHz in CDCl\(_3\), C\(_5\)D\(_5\)N or CD\(_3\)COCD\(_3\) with TMS als internal standart. Merck silica gel (0.05 to 0.2 mm) was used for TLC.

### Isolation of 1 and 3

The CHCl\(_3\) extract (6.0 g) was passed over silica gel column. Elution with CHCl\(_3\)-MeOH (98:2) yielded 1 (118 mg). After recrystallization from acetonether colourless crystals were obtained. Further elution with CHCl\(_3\)-MeOH (93:7) leads to the isolation of 3 (800 mg) as crystals, which were recrystallized from acetone-ether.

### Oxidation of 1 to 2

To a solution of 1 (50 mg) in pyridine (3 ml) was treated with chromium trioxide (60 mg) at room temperature for 35 h. The reaction mixture was poured into water and extracted with chloroform. The usual treatment of the extract gave a crystalline product (2) (42 mg), which was recrystallized from acetone dichlormethane to yield pure substance identical with teuscordinon (mixed m.p., IR and \( ^1H \) NMR).

### Acetylation of 3

The diol (3) (100 mg) was treated with acetic anhydride (1.5 ml) and pyridine (2-3 drops) at room temperature overnight. The crude diacetate (96 mg) was purified by crystallization and recrystallization from acetone dichloromethane to yield pure substance, C\(_{24}\)H\(_{26}\)O\(_9\), m.p. 185-187 °C, \( \nu_{\text{max}} \) 1720-1740 (intensive) and 1240 cm\(^{-1}\), \( \delta = 1.92 (3H, s, COOMe), 2.04 (3H, s, COOMe)\), 5.25 (1H, dd, \( J = 4\) and 12 Hz, H-2), 5.20 (1H, t, \( J = 3\) Hz, H-6) and 2.98 (1H, dd, \( J = 2.5 \) and 14.0 Hz, 1a-H).

### Jones oxidation of 3 to 5

To a solution of 3 (100 mg) in acetone was added some drops of Jones reagent and the mixture was stirred for 10 min under ice-cooling. The mixture was added to cold aqueous sodium chloride and extracted with ether. The usual treatment of the extract gave a crystalline product (98 mg), which was recrystallized from methanol to yield pure substance, C\(_{20}\)H\(_{20}\)O\(_7\), m.p. 223-225 °C, m/e 372 (M\(^+\)).

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[7] The authors are grateful to Prof. Dr. F. Bohlmann (Institut für Organische Chemie der Technischen Universität Berlin-12) for recording of the \( ^1H \) NMR spectra.