9-Hydroxypiperitone β-D-Glucopyranoside and Other Polar Constituents from Dill (*Anethum graveolens* L.) Herb

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A methanolic extract from dill (*Anethum graveolens*) herb was subjected to XAD-2 adsorption chromatography. The methanolic eluate was fractionated with the all liquid chromatographic technique of multilayer coil countercurrent chromatography (MLCCC). After acetylation of MLCCC subfractions and flash chromatography, final purification of dill herb constituents was achieved by preparative and/or analytical HPLC. Nine compounds were obtained in pure form, including the β-D-glucopyranosides of 9-hydroxypiperitone, *p*-menth-2-ene-1,6-diol, and 8-hydroxygeraniol. Structure elucidation is based on electrospray ionization ion trap multiple mass spectrometry (ESI-MS/MS) as well as one- and two-dimensional nuclear magnetic resonance spectroscopy.

Keywords: *Dill herb; glycosides; 9-hydroxypiperitone β-D-glucopyranoside; p-menth-2-ene-1,6-diol β-D-glucopyranoside; 8-hydroxygeraniol β-D-glucopyranoside; dill ether; multilayer coil countercurrent chromatography*

INTRODUCTION

Dill ether (2,3,3a,4,5,7a-hexahydro-3,6-dimethylbenzofuran **1**) belongs together with (+)-4*S*-α-phellandrene **2**, myristicin **3**, and (*Z*)-3-hexenol **4** to the primary odorants of dill herb (Blank and Grosch, 1991; Blank et al., 1992; Charles et al., 1995; Huopalahti, 1986; cf. Figure 1). The chemical structure of benzofuran derivative **1** was elucidated more than 20 years ago by Bélafi-Réthy and Kerényi (1977). In 1984, the absolute stereochemistry of the naturally occurring isomer was determined as 3*S*,3a*S*,7a*R* (Brunke and Rojahn, 1984). Several chemical syntheses of dill ether **1**—including enantioselective routes—have been published (Ohloff et al., 1966; Müller, 1993; Reichert et al., 1998). Moreover, separations of dill ether stereoisomers using enantioselective capillary gas chromatography (high-resolution gas chromatography; HRGC) have been reported (König et al., 1990; Reichert et al., 1998). Despite these efforts, knowledge about the biosynthesis of dill ether **1** is still limited. On the basis of HRGC—isotopic ratio mass spectrometric (IRMS) measurements, it has been concluded that dill ether **1** and α-phellandrene **2** are closely related biogenetically (Faber et al., 1997). Further details concerning the generation of benzofuran derivative **1** in dill herb are not known because labeling and feeding experiments of putative precursor substances have not yet been published. This paper concerns the isolation and characterization of 9-hydroxypiperitone β-D-glucopyranoside from dill herb, which can be converted into a known synthetic progenitor of dill ether **1** by simple reduction.

EXPERIMENTAL PROCEDURES

Chemicals. All commercial chemicals used were of analytical grade quality. Solvents were redistilled before use.

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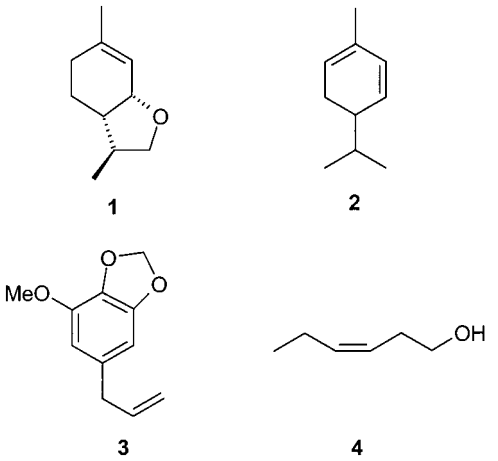

Figure 1. Structure of primary odorants in dill herb (Huopalahti, 1986): dill ether (**1**), α-phellandrene (**2**), myristicin (**3**), *cis*-hexenol (**4**).

Plant Material. Ten kilograms of fresh dill (*Anethum graveolens* L.; Apiaceae) herb was obtained from the local market. After freezing, the main stems were cut off, yielding 5.6 kg of herb material.

Preparation of a Glycosidic Extract. The herb material was mixed in small portions with a total of 15 L of methanol. After filtration, the organic solvent was removed under reduced pressure and the aqueous residue was extracted with pentane and diethyl ether to remove pigments and volatile compounds. The water layer was diluted to 1.8 L and applied onto an Amberlite XAD-2 column (Günata et al., 1985). After rinsing with 5 L of distilled water, the retained compounds were eluted with 2 L of methanol. The eluate was concentrated under reduced pressure. Freeze-drying yielded 12.6 g of a glycosidic extract.

Multilayer Coil Countercurrent Chromatography (MLCCC). A first fractionation of the eluate was achieved by MLCCC using the multilayer coil separator-extractor manufactured by P. C. Inc. (Potomac, MD) equipped with a single coil (length of tubing, 85 m; diameter of tubing, 2.6 mm; volume, 360 mL). The solvent system was $CHCl_3$/MeOH/H_2O

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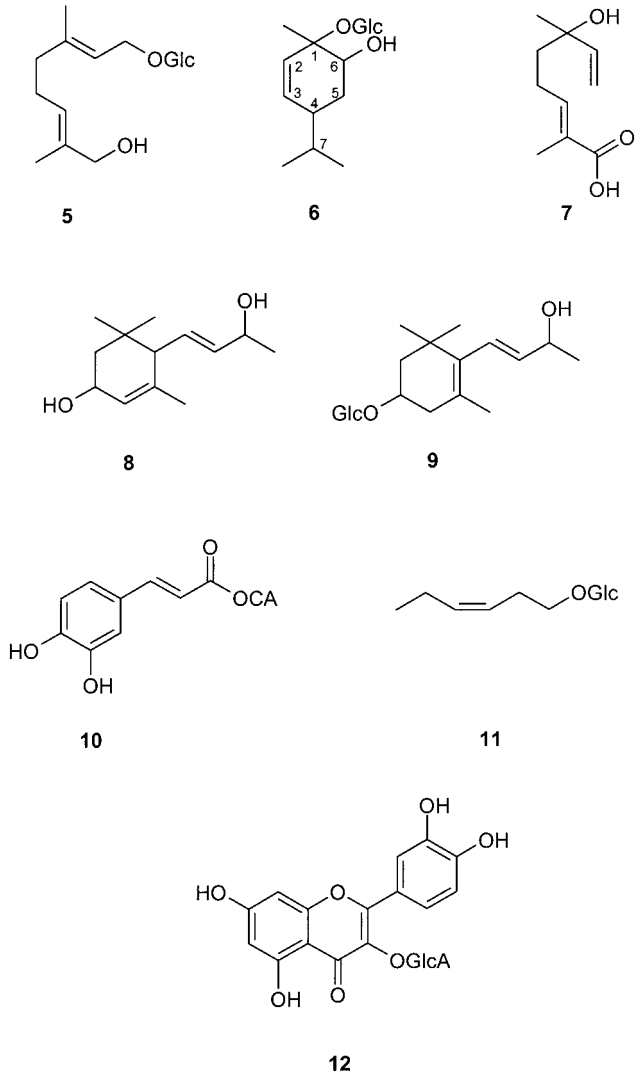

Figure 2. Structures of isolated compounds from dill herb: 8-hydroxygeraniol *β*-D-glucoside (**5**), *p*-menth-2-ene-1,6-diol *β*-D-glucoside (**6**), (*E*)-2,6-dimethyl-6-hydroxy-octa-2,7-dienoic acid (**7**), 3-hydroxy-α-ionol (**8**), 3-hydroxy-*β*-ionol 3-*O*-*β*-D-glucopyranoside (**9**), chlorogenic acid (**10**), (*Z*)-3-hexenyl-*β*-D-glucopyranoside (**11**), and quercetin 3-*O*-*β*-D-glucuronide (**12**). Abbreviations: Glc, *β*-D-glucopyranoside, QA, quinic acid, GlcA, *β*-D-glucuronic acid.

(7/13/8, v/v/v), and the more dense phase was used as stationary phase. The elution mode was tail-to-head at a flow rate of 1.5 mL/min, and the revolution speed was set at 800 rpm. Each time, 2−3 g of the extract were dissolved in the solvent system and separated by MLCCC. Fractions were pooled in five combined fractions on the basis of a thin-layer chromatography (TLC) analysis on SiO_2 plates.

Acetylation. The combined fractions of five MLCCC separations were concentrated and freeze dried. The residue was acetylated (acetic anhydride/pyridine) at ambient temperature overnight. Unreacted acetic anhydride was destroyed by addition of methanol under ice cooling. Pyridine was removed using methanol and toluene as tractants (Winterhalter et al., 1991).

Column Chromatography. Further separation of MLCCC subfractions was achieved with a glass column (3.5 × 55 cm) filled with SiO_2 (Merck SiO_2 60, 70−230 mesh). Elution was made with solvents of increasing polarity (i.e., pentane/diethyl ether, ethyl acetate and methanol).

High-Performance Liquid Chromatography (HPLC). Purification of compounds was achieved by preparative and analytical HPLC on silica gel as well as RP-18 material using the solvent systems *tert*-butyl methyl ether/hexane or methanol/water, respectively.

Table 1. ^{1}H NMR Spectral Data of Isolated Compound 6 ($CDCl_3$, 360 MHz)

δ	signal	*J* (Hz)	atom
0.89	3 H, d	3	Me-C7
0.91	3 H, d	3	Me-C7
1.51	1 H, s		Me-C1
1.68	1 H, m		H C7
1.74	1 H, m		H_a C5
1.80	1 H, m		H_b C5
1.98	1 H, obscure		H C4
1.93, 2.00, 2.01, 2.03, 2.08	5 × 3 H, 5s		H_3 acetates (5×)
3.68	1 H, ddd	10/4.7/2.5	H C5′
4.11	1 H, obscure		H C6
4.15	1 H, dd	2.5/12	H_a C6′
4.25	1 H, dd	4.7/12	H_b C6′
4.58	1 H, d	8	H C1′
4.95	1 H, dd	8/9.5	H C2′
5.08	1 H, dd	9.5/10	H C4′
5.21	1 H, dd	9.5/9.5	H C3′
5.68	1 H, d	10/3	H C2
5.95	1 H, d	10/2	H C3

Table 2. ^{13}C NMR Spectral Data of Isolated Compound 6 ($CDCl_3$, 90 MHz)

δ	DEPT	atom
19.4/19.6	CH_3	2Me-C7
20.5−21.5	CH_3	CH_3CO (5×)
22.1	CH_3	Me-C1
24.9	CH_2	C5
31.4	CH	C7
37.8	CH_2	C4
62.1	CH_2	C6′
68.8	CH	C4′
71.6	CH	C2′
71.9	CH	C5′
73.0	CH	C3′
76.9	CH	C6
79.0	C	C1
98.8	CH	C1′
129.1	CH	C2
132.4	CH	C3

Isolation of Dill Herb Constituents. The following compounds were obtained in pure form (cf. Figure 2): 8-hydroxygeraniol *β*-D-glucopyranoside **5** (7 mg, isolated as hexaacetate; Kitagawa et al., 1983), (*E*)-2,6-dimethylocta-6-hydroxy-2,7-dienoic acid **7** (1 mg; Marco et al., 1993), 3-hydroxy-α-ionol **8** (2 mg, isolated as diacetate; Behr et al., 1978), 3-hydroxy-*β*-ionol 3-*O*-*β*-D-glucopyranoside **9** (2 mg, isolated as hexaacetate; Winterhalter et al., 1991), chlorogenic acid **10** (∼70 mg, isolated as triacetate; Zapesochnaya et al., 1992), (*Z*)-3-hexenyl-*β*-D-glucopyranoside **11** (1.5 mg, isolated as pentaacetate; Kobayashi et al., 1994), and quercetin 3-*O*-*β*-D-glucuronide **12** (3.2 mg, isolated as triacetate; Möhle et al., 1984). Spectral data for **5** and **7**−**12** were identical with published data.

p-Menth-2-ene-1,6-diol *β*-D-glucopyranoside **6** was isolated as the pentaacetate) (2 mg): electrospray ionization mass spectrometry (ESI-MS); positive mode): pseudo molecular ion at *m*/*z* 565 $[M(542) + Na]^+$. The nuclear magnetic resonance (NMR) spectral data are presented in Tables 1 and 2.

9-Hydroxypiperitone *β*-D-glucopyranoside **21** was isolated as the tetraacetate (90 mg; cf. Figure 3); ESI-MS (positive mode): pseudo molecular ion at *m*/*z* 521 $[M(498) + Na]^+$ and 499 $[M + H]^+$. The NMR spectral data are presented in Tables 3 and 4. High-resolution mass spectral data were recorded with a Finnigan MAT 8200 in peak matching mode: 498.20998 ($C_{24}H_{34}O_{11}$, theoretical 498.21011).

Degradation of 8-Hydroxygeraniol (cf. Figure 4). Approximately 70 mg of 8-hydroxygeraniol (**5a)** were diluted with 100 mL of 0.2 M citric acid − phosphate buffer (pH 2.5) and subjected to a simultaneous distillation−extraction (SDE) treatment, using the SDE head described by Schultz et al. (1979). The organic layer was dried over anhydrous Na_2SO_4

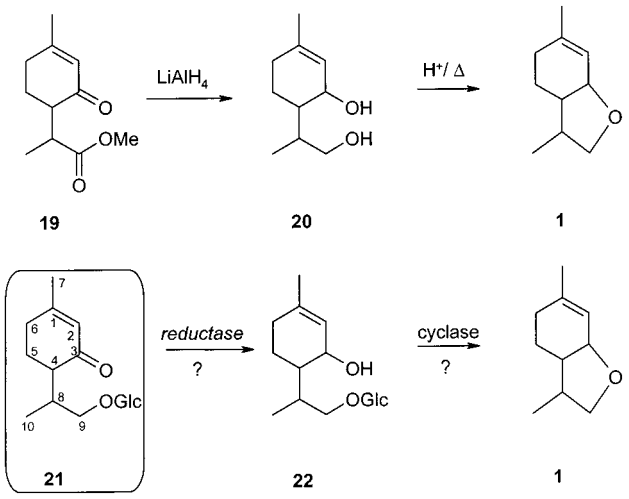

Figure 3. Known synthetic routes to dill ether **1** (Müller 1993) and the postulated generation from the newly isolated 9-hydroxy-piperitone β-D-glucopyranoside (**21**).

Table 3. ^{1}H NMR Spectral Data of Isolated Compound 21 ($CDCl_3$, 300 MHz)

δ	signal	J (Hz)	atom
0.79	3 H, d	7	H_3 C10
1.74	1 H, m		H_a C5
1.90	1 H, m		H_b C5
1.91	3 H, br s		H_3 C7
1.99, 2.01, 2.02, 2.08	4 × 3 H, 4s		H_3 acetates (4×)
2.30	2 H, m		H_2 C6
2.32	1 H, m		H C4
2.57	1 H, dddd	4.5/6/7/8.5	H C8
3.41	1 H, dd	6/10	H_a C9
3.67	1 H, ddd	9.8/4.5/2.5	H C5′
3.73	1 H, dd	8.5/10	H_b C9
4.12	1 H, dd	2.5/12	H_a C6′
4.26	1 H, dd	4.5/12	H_b C6′
4.50	1 H, d	8	H C1′
4.96	1 H, dd	8/9.5	H C2′
5.07	1 H, dd	9.5/9.8	H C4′
5.18	1 H, dd	9.5/9.5	H C3′
5.83	1 H, br s		H C2

Table 4. ^{13}C NMR Spectral Data of Isolated Compound 21 ($CDCl_3$, 90 MHz)

δ	DEPT	atom
12.7	CH_3	C10
20.5−20.7	CH_3	CH_3CO (4×)
22.6	CH_3	C5
24.1	CH_3	C7
30.6	CH_2	C6
30.9	CH	C8
46.1	CH	C4
62.0	CH_2	C6′
68.5	CH	C4′
71.3	CH	C2′
71.7	CH	C5′
72.5	CH_2	C9
72.8	CH	C3′
100.8	CH	C1′
126.8	CH	C2
160.4	C	C1
200.5	C	C3

and carefully concentrated (Vigreux column) prior to HRGC and HRGC−MS analyses.

Deacetylation and Enzymatic Hydrolysis. 9-Hydroxypiperitone β-D-glucoside was obtained after deacetylation using sodium methanolate solution (Winterhalter et al., 1991). For neutralization, an ion-exchange resin (Dowex 50 W × 8) was used. ESI-MS (positive mode): pseudo molecular ion at *m/z* 353 $[M(330)+Na]^+$. Enzymatic hydrolysis using sweat almond emulsin in citric acid/phosphate buffer medium (pH 5) at 37 °C overnight liberated 9-hydroxypiperitone as aglycone. HRGC−MS: *m/z* 168 (1, M^+), 150 (3, $M^+ - H_2O$), 138 (5), 135 (5), 123 (10), 110 (100), 95 (50), 82 (50).

Reduction of 9-Hydroxypiperitone-β-D-glucoside. For the reduction of the deacetylated glucoside, $NaBH_4$ in methanol at 50 °C was used. ESI-MS of glucoside **22** (positive mode): pseudo molecular ion at *m/z* 355 $[M(332) + Na]^+$.

Mass Spectrometry. Mass spectra were recorded using Bruker Esquire LC−MS (ion trap) system and ESI in the positive mode. Dry gas was nitrogen and the parameters were set as follows: capillary, 2500 V, end plate, 2000 V; capillary exit, 90 V; skimmer 1, 30 V. Fragmentation experiments were performed by isolation of the molecule ions, using different fragmentation amplitudes.

NMR Spectroscopy. A complete set of spectral data could be recorded on Bruker AMX-360 and AMX-300 spectrometers. The spectra were recorded in $CDCl_3$. Signals were assigned using ^{1}H, ^{13}C, DEPT, correlation spectroscopy (COSY) as well as HMQC and HMBC experiments. For known compounds, spectra were recorded in $CDCl_3$, CD_3OD, and dimethyl sulfoxide (DMSO) to enable comparison with published data.

HRGC−MS. A Carlo-Erba Vega gas chromatograph equipped with a DB1 capillary column (30 m × 0.25 mm i.d.; film thickness, 0.25 μm) was used. Splitless injection was employed. Injector temperature was kept at 180 °C to avoid thermal destruction of the labile diol in the injector. The temperature program was from 70 to 300 °C at 6 °C/min. The chromatograph was directly coupled to a Finnigan MAT 4515 mass spectrometer; the temperature of the ion source was 270 °C, and the electron energy was 70 eV. Volumes of 1 μL were co-injected with a Kovats standard for calculation of retention indices.

RESULTS AND DISCUSSION

Dill ether **1** is considered a key flavor compound of fresh dill herb (Bélafi-Réthy and Kerény, 1977; Schreier et al., 1981; Brunke and Rojahn, 1984; Brunke et al., 1991; Blank and Grosch, 1991; Nitz et al., 1991) because of its low flavor threshold and typical 'dill note'. With regard to the biosynthetic pathways, it has been assumed that the monoterpene hydrocarbon α-phellandrene **2** and dill ether **1** are closely related (Faber et al., 1997). However, formation of the benzofuran derivative **1** requires the introduction of an oxygen function into the monoterpene skeleton of **2**. This requirement prompted us to search for oxygenated monoterpenoids that may act as intermediates in pathways leading to dill ether **1**.

A methanolic extract was prepared from dill herb. The polar secondary metabolites were enriched by adsorption on Amberlite XAD-2 (Günata et al., 1985). After prefractionation of the isolate by MLCCC, the subfractions were acetylated and purified by liquid chromatography. Figure 2 shows the structures of some compounds that have been completely characterized using MS and NMR spectroscopy. The isolated compounds **5**−**12** belong to different classes of natural products, they are, monoterpenoids (**5**−**7**), norisoprenoids (**8**, **9**), cinnamic acid derivatives (**10**), aliphatic compounds (**11**), and flavonoids (**12**).

Identification of *p*-Menth-2-ene-1,6-diol β-D-Glucopyranoside (6). Whereas compounds **5** and **7**−**12** are known, glucoside **6** is reported here for the first time. Compound **6** can be considered as an oxidation product of α-phellandrene, which is a major volatile constituent of dill herb oil.

Identification of 8-Hydroxygeraniol β-D-Glucopyranoside (5) and (*E*)-2,6-Dimethyl-6-hydroxy-2,7-octadienoic Acid (7). Two known oxygenated monoterpenes were obtained in pure form from the methanolic

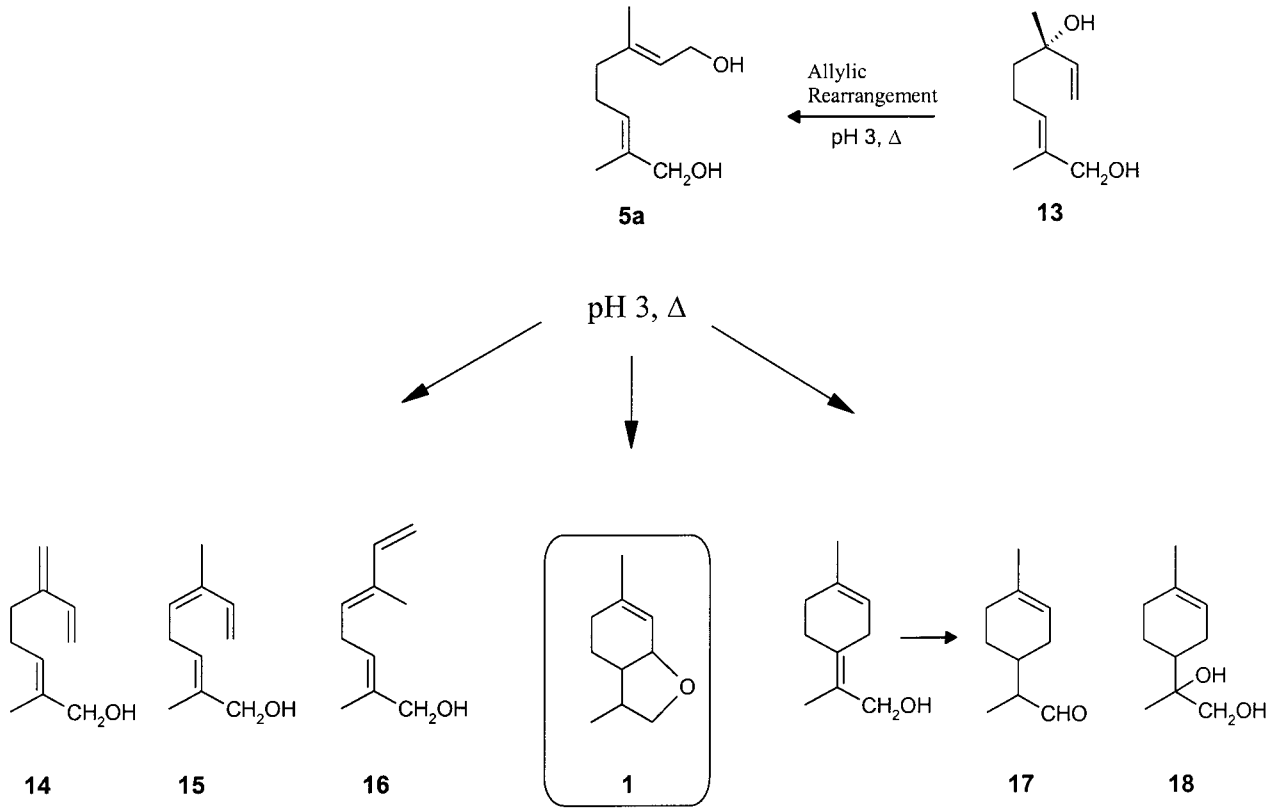

Figure 4. Acid-catalyzed degradation of 8-hydroxygeraniol (**5a**) and 8-hydroxylinalool (**13**).

dill herb extract. Importantly, both compounds have earlier been recognized as aroma progenitors in grapes and wine. In biomimetic studies, the allylic rearrangement product of 8-hydroxygeraniol **5a**, 8-hydroxylinalool **13**, had been converted into a series of aroma compounds, including the target benzofuran **1** (Strauss et al., 1988). Although only trace amounts of dill ether **1** were formed from diol **13**, the hydrolysate was characterized by an intense dill note. Dill ether **1** is also obtained as a degradation product of aglycon **5a**, together with the tentatively identified trienols **14**−**16** as well as isomeric *p*-menthenals **17** and uroterpenol **18** (cf. Figure 4). In a similar reaction, acid **7** is converted into the intensely odorous wine lactone (Winterhalter and Bonnländer, 2000).

It is evident that hydrolytic degradation of 8-hydroxygeraniol **5a** gives rise to the formation of trace amounts of dill ether **1**. But it is also clear that this pathway can be excluded for the formation of genuine **1** in dill herb for two reasons: Formation of dill ether from **5a** only occurs under drastic reaction conditions (pH 2.5, 100 °C), and more important, the chemical pathway of dill ether formation from **5a** will not proceed in an enantioselective way, which is necessary to exclusively form the naturally occurring 3*S*,3a*S*,7a*R*-configured isomer of **1**. Hence, other pathways for dill ether formation have to be considered.

Identification of 9-Hydroxypiperitone *β*-D-Glucopyranoside (21). Glucoside **21** has been identified here for the first time in nature. The structure of **21** has been unambiguously deduced from extended NMR studies. Because glucoside **21** could not be obtained in crystalline form, its absolute stereochemistry still remains to be elucidated. The novel natural product was easily converted into dill ether **1** by chemical means. $NaBH_4$-reduction followed by enzymatic hydrolysis gave rise to diol **20**, which is a known synthetic progenitor of dill ether **1** (Müller, 1993). Final proof for the precursor function of glucoside **21**, however, requires feeding experiments with a labeled specimen of **21**.

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