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4-(β-D-GLUCOPYRANOSYLOXY)BENZOIC ACID, A CHARACTERISTIC PHENOLIC CONSTITUENT OF THE APIACEAE

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Key Word Index—*Pimpinella anisum*; Apiaceae; *Illicium verum*; Illiciaceae; 4-(β-D-glucopyranosyloxy)benzoic acid; prep. HPLC; chemotaxonomy.

Abstract—A characteristic phenolic glucoside of the Apiaceae was isolated from anise seeds. Its structure was established as 4-(β-D-glucopyranosyloxy)benzoic acid. The compound is widely distributed among the Apiaceae and is also present in staranise (Illiciaceae).

INTRODUCTION

Spices and other plants of the Apiaceae contain *p*-hydroxybenzoic acid derivatives. Preliminary examination [1] indicated the presence of large amounts of *p*-hydroxybenzoic acid, especially in anise seeds. As a result of the present work *p*-hydroxybenzoic acid glucoside **1** was isolated from *Pimpinella anisum* (Apiaceae) in a pure state. It was characterized as the 4-glucoside. *p*-Hydroxybenzoic acid glucoside has previously been found in conifers, i.e. in species of *Larix* [2–4], *Abies* [2, 5] and *Pinus* [5–7], but the compound was not completely

Table 1. Concentrations of 4-(β-D-glucopyranosyloxy)benzoic acid in Apiaceae and staranise

Species	Part	Content (ppm fr. wt)
Anise (*Pimpinella anisum*)	fruit	730
		800
		830
		870
		1010
		1080
Dill (*Anethum graveolens* var. *hortorum*)	fruit	42
		188
	leaf	11
	stalk	3
Fennel (*Foeniculum vulgare* var. *dulce*)	fruit	106
		30
Sweet Fennel (*Foeniculum vulgare* var. *azoricum*)	leaf sheath	16
Coriander (*Coriandrum sativum*)	fruit	8
		16
		30
Caraway (*Carum carvi*)	fruit	37
		42
Lovage (*Levisticum officinale*)	leaf	3
Carrot (*Daucus carota* ssp. *sativus*)	fruit	65
	root	11
Parsley (*Petroselinum crispum* ssp. *crispum*)	fruit	165
	herb	3
Celeriac (*Apium graveolens* var. *rapaceum*)	fruit	56
	tuberous root	20
		3
Staranise (*Illicium verum*)	fruit	730
		770
		840

Where more than one value is given, plant samples were of varying origin.

characterized. However, its synthesis has been described by Helferich and Lutzmann [8].

RESULTS AND DISCUSSION

From whole anise seeds nearly 1 g of **1** was isolated pure by means of repeated prep. HPLC. Its purity was established by HPLC on different columns before and after derivatisation (as the benzoate) [9] and after silylation by capillary GC. The structure of **1** was established by acid hydrolysis with 2 N HCl yielding equal amounts of glucose and *p*-hydroxybenzoic acid. The presence of a β-glucosidic linkage was confirmed by hydrolysis of **1** with β-glucosidase. The structure of **1** was further supported by spectral measurements (IR, ^{1}H and ^{13}C NMR) and comparison with literature standards [10]. By analytical HPLC, **1** was shown to be a characteristic phenolic constituent of the Apiaceae. From anise seeds the greatest amounts were obtained. Compound **1** was found to occur in all ten species investigated, especially in the fruits (Table 1). The glucoside is extremely stable in the dried fruits, since 1000 ppm (0.1%) of the glucoside were detected in four-year-old anise seeds. Of the investigated spices and vegetables, anise and staranise seeds contain the highest amounts of the glucoside. Although the staranise (*Illicium verum*) belongs to a different family (Illiciaceae), anise and staranise are very similar in their volatile oil constituents. The glucoside was not detected in cloves (*Syzygium aromaticum*; Myrtaceae), allspice (*Pimenta dioica*, Myrtaceae) or cardamom (*Elettaria cardamomum*; Zingiberaceae).

EXPERIMENTAL

Analyt. HPLC: A Merck LiChrosorb RP-18-column (5 μ, 25 × 0.4 cm i.d.) was used. Other chromatographic data were: UV detection, wave length: 254 nm, flow: 1 ml/min, eluent: 2% HOAc in H_2O. The glucoside eluted after 14 min, well separated from other compounds [11]. ^{1}H and ^{13}C NMR spectra were recorded in D_2O and $CDCl_3$ (acetate) at 300 MHz. Chemical shifts are given in δ values (ppm) with TMS as internal standard. UV spectra were run in MeOH.

Isolation of **1**. Whole anise seeds (100 g) were crushed, with water cooling, in a mill and extracted several times with 80% MeOH using an Ultraturrax. After filtration, the filtrate was concd to a small vol. (5 g anise/ml) under red. pres. at 40°. Large amounts of chlorophyll which precipitated were separated on cottonwool. After repeated filtration the viscous residue was used for prep. HPLC.

Prep. HPLC. The residue was chromatographed on a reversed-phase column filled with RP-18, 10 μ material (Chrompak) as stationary phase with 2% HOAc–dist. H_2O as eluent by a flow of nearly 12 ml/min (detector wavelength: 254 nm). Two ml were injected on the column. Fractions of the peak containing **1** were repeatedly collected and carefully freeze-dried.

This chromatographic procedure was repeated once more to purify the isolated compound, an amorphous powder, mp 211–212° (lit. 209–210°). λ_{max}^{MeOH} nm: 246. IR ν_{max}^{KBr} cm^{-1}: 3100–3600 (OH), 1680 (C=O), 1620, 1595, 1520, 1460 (benzene ring), 1250 Ar–O–Ether. ^{1}H NMR (D_2O): δ8.0 (2H, *d*, aromatic H), 7.2 (2H, *d*, aromatic H), 5.2 (1H, *d*, acetal H), 3.5–4.5 (6H, *m*, CHOH and CH_2OH protons). ^{13}C NMR (D_2O): δ63.5 (CH_2OH), 72.4, 75.8, 78.5, 79.2 (CHOH), 102.5 (acetal carbon), 119, 134.1 (aromatic C), 128.1 (aromatic C), 163.3 (aromatic C–O), 173.7 (COOH). The tetra-acetate (prepared via Ac_2O–pyridine) was purified by prep. HPLC. ^{1}H NMR ($CDCl_3$): δ2.0 (12H, *s*, OAc), 7.0 (2H, *d*, aromatic H), 8.1 (2H, *d*, aromatic H), 5.1–5.4 and 3.8–4.4 (4 + 3H, both *m*, CH_2OAc and CHOAc groups). ^{13}C NMR ($CDCl_3$): δ20.5–20.6 (Me from OAc), 168.5, 169.1, 169.3, 169.5, 170.2 (COOH and CO from OAc).

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