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3-(4-HYDROXY-3,5-DIMETHOXYPHENYL)-PROPANAL FROM *SORBUS AUCUPARIA* SAPWOOD

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Key Word Index—*Sorbus aucuparia*; Rosaceae; mountain ash; phenols; 3-(4-hydroxy3,5-dimethoxyphenyl)-propanal.

Abstract—3-(4-hydroxy-3,5-dimethoxyphenyl)-Propanal (dihydrosinapic aldehyde) has been isolated from the sapwood of *Sorbus aucuparia* in a yield of 2×10^{-4}%. Its structure has been elucidated spectroscopically.

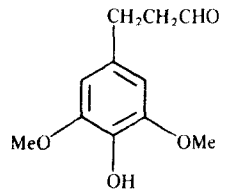
INTRODUCTION

Sorbus aucuparia L., mountain ash (Rosaceae), is a common tree in Northern Europe. From the heartwood of *S. aucuparia*, Erdtman *et al.* have isolated the biphenyls aucuparin and dimethoxyaucuparin [1, 2]. The same group isolated a lignan xyloside, lyoniside, from the sapwood [3]. In connection with our studies on the aucuparins [4, 5], we have studied the wood constituents of *S. aucuparia*. In this communication, we report the isolation and structure elucidation of a novel dihydrocinnamic aldehyde from *S. aucuparia* sapwood.

RESULTS AND DISCUSSION

The title compound **1** was isolated in 2×10^{-4}% yield from the sapwood (see Experimental). Its UV spectrum ($\lambda_{max} = 280$ nm) is typical for substituted aromatic compounds. The IR spectrum shows absorption at 1732 cm^{-1}, indicating a non-conjugated carbonyl function. In the NMR spectrum of the substance, two identical aromatic methoxyl groups give rise to a six-proton singlet at δ3.90 ppm. A broad singlet (1H) at δ5.4 is probably due to a hydroxyl proton, and a two-proton singlet at 7.20 ppm indicates two identical aromatic protons. These observations are in good accordance with NMR spectra of other syringyl (4-hydroxy-3,5-dimethoxyphenyl) systems [2, 5]. A multiplet at δ2.8 (4H) and a narrow one at δ9.75 (1H) would seem to indicate an oxygenated three-carbon side chain, either with a carboxylic acid or an aldehyde function as end group. The IR spectrum is, however, different from the one reported for 3-(4-hydroxy-3,5-dimethoxyphenyl)-propanoic acid [6], indicating an aldehyde structure.

This is substantiated by the mass spectrum, with a molecular ion at *m/z* 210 (0.6% intensity), which corresponds to a formula of $C_{11}H_{14}O_4$. Other important ions are found at *m/z* 182 and 181 [M − CO and M − CHO], and at *m/z* 167 (base peak; M − CH_2CHO, stabilized by rearrangement to a tropylium ion). Loss of the whole side chain is less favoured, as demonstrated by an intensity of



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0.9% for the *m/z* 153 peak. Thus, the isolated substance is 3-(4-hydroxy-3,5-dimethoxyphenyl)- propanal, or dihydrosinapic aldehyde (**1**). It appears that shikimate metabolites with the syringyl moiety are characteristic for *Sorbus aucuparia*, since the biphenyls aucuparin and methoxyaucuparin, which probably are partially shikimate-derived [7], and the lignan lyoniside have this substitution pattern as well.

In contrast to cinnamic aldehydes, dihydrocinnamic aldehydes are rare in Nature. Dihydrocinnamic aldehyde itself was reported from oil of cinnamon in 1902 [8]. It has since then been found in several other plants. To our knowledge, only two other dihydrocinnamic aldehydes are known as natural products. 4-Isopropyl-α-methyldihydrocinnamic aldehyde is an aroma component in nutmeg [9] and blackberries [10], while dacrinial (4-hydroxy-3-methoxy-5-(3-methyl-2-butenyl)-dihydrocinnamic aldehyde) has been reported from *Dacrydium franklini* [11].

Dihydrosinapic aldehyde, **1**, was, however, recently reported as a constituent of beechwood smoke condensate by Wittkowski *et al.* [12]. It would appear debatable whether this constitutes evidence for its presence as a natural product. Dihydroferulic aldehyde (4-hydroxy-3-methoxydihydrocinnamic aldehyde) was reported, as well. Identification of the substance was based solely on GLC-MS of the trimethylsilylated smoke condensate. We found that after being kept in a refrigerator for one month, the substance had decomposed. Thus, it must be regarded as somewhat unstable.

EXPERIMENTAL

Droplet countercurrent chromatography (DCCC) was carried out on a Büchi B670 instrument equipped with 300 columns (0.5 m × 3 mm). For prep. TLC, DC-Alufolien, silica gel $60F_{254}$, layer thickness 0.2 mm (Merck, Darmstadt, F.R.G.) were employed.

S. aucuparia stems were collected in Bjoa, Ølen community, Norway, by the senior author. A voucher sample (KEM8606-1) has been deposited in the Institute of Pharmacy, Department of Pharmacognosy, the University of Oslo.

Sapwood of *S. aucuparia* (2.9 kg) was extracted with a total of 21 l EtOAc in a Soxhlet. Evapn of solvent furnished 49 g crude extract, which was suspended in MeOH–H_2O (19:1, 300 ml). Washing with hexane (3 × 350 ml), addition of water (95 ml) and extraction with $CHCl_3$ (3 × 300 ml) gave 24 g purified extract. Of this extract, 10 g was separated by DCCC in 2 g batches (solvent system: $CHCl_3$–MeOH–H_2O, 7:13:8; descending mode). In each run, 120–130 25 ml fractions were collected. Fractions 3–6, pooled from 5 runs (total weight 785 mg) showed presence of aromatic protons (NMR) and were purified by repeated prep. TLC in different solvent systems (CH_2Cl_2–HOAc, 99:1; toluene–Me_2CO, 9:1; CH_2Cl_2–Me_2CO, 9:1). Substances were detected by UV irradiation (254 nm).

Compound **1** was obtained in 4.4 mg yield (2×10^{-4}%) as a colourless oil. UV λ_{max}^{MeOH} 280 nm (log ε 3.75). IR ν_{max}^{KBr} 3400, 2960, 2925, 2860, 1732, 1468, 1260–1290 cm^{-1}. NMR (60 MHz, d_6-acetone): δ 2.8 (4H, *m*), 3.90 (6H, *s*), 5.4 (1H, broad *s*), 7.20 (2H, *s*), 9.75 (1H, narrow *m*). MS (IP 70 eV, m/z (% intensity)): 210 (0.6, M), 182 (13, M−CO), 181 (9.8, M–CHO), 178 (1.5, M−MeOH), 167 (100, M−CH_2CHO), 155 (1.2), 153 (0.9, M−CH_2CH_2CHO), 151 (5.0), 132 (7.1), 113 (39), 112 (29), 104 (21).

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