

## 4,2'-Dihydroxy-3,5-dimethoxybiphenyl, a New Phenol from the Wood of *Salix caprea* L.

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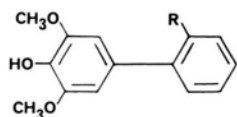
*Salix caprea*, Salicaceae, Biphenyl,  
Wood Constituent, Stress Compound

The title substance has been isolated in a 0.0003% yield from wood of *Salix caprea* L. which, after felling, had been kept outdoors for one year. Its structure has been elucidated by spectroscopical and chemical methods.

### Introduction

The wood of *Salix caprea* L. (Salicaceae) is reputed to be very resistant to rotting [1]. For this reason, the wood has found use in wet and marshy areas as fence poles. To our knowledge, no work has been published on the wood constituents of *S. caprea*. We have made an investigation of the wood of this tree in order to identify the substances responsible for the resistance to rot producing microorganisms.

Several flavonoids and biphenyls [2] have been isolated and identified. In this communication, we report the isolation of a new phenol, 4,2'-dihydroxy-3,5-dimethoxybiphenyl (**1**). This substance is closely related to aucuparin (**2**) and methoxyaucuparin (**3**) which we have isolated previously from the same source. [2].



- 1:** R = OH  
**2:** R = H  
**3:** R = OCH<sub>3</sub>

### Materials and Methods

*Salix caprea* was collected in July 1982 in Nordre Land community, Oppland, Norway. Samples have been deposited in the herbarium of the Institute of Pharmacy, Department of Pharmacognosy, The University of Oslo. After being felled, the tree trunks were kept outdoors for one year.

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After removal of the bark and cambium, the wood was cut to pass through a 4 mm sieve and extracted with ethyl acetate in a Soxhlet extractor. The extract was partitioned between equal amounts of hexane and methanol/5% water, and the methanolic phase was taken to dryness and chromatographed on a Si gel column. The fractions eluted with toluene/ethyl acetate (1:1) were rechromatographed on Si gel, yielding crude **1** with toluene/10% acetone. Pure **1** was obtained by preparative TLC (Si gel F<sub>254</sub>, 0.2 mm thickness, eluent toluene/ethyl acetate, 1:1), yield 20 mg from 5.8 kg wood, m.p. 148–150 °C after recrystallization from methanol. Methylation of the substance was carried out with a surplus of diazomethane in ether/ethanol at ambient temperature for two hours.

### Results and Discussion

The UV spectrum of the isolated substance (MeOH,  $\lambda_{\max}$  291 and 262 nm,  $\log \epsilon$  4.00 and 4.07) and its IR spectrum (KBr,  $\nu_{\max}$  3300, 1605, 1338, 1224 and 754  $\text{cm}^{-1}$ ) point to a close relationship with the previously isolated substances **2** and **3**. Its <sup>1</sup>H NMR spectrum (60 MHz, d<sub>6</sub>-acetone) shows two identical aromatic methoxyl groups ( $\delta$  3.87), a two-proton singlet at  $\delta$  6.77 (H-2 and H-6), and a multiplet (4H) at  $\delta$  6.8–7.3. The aromatic methoxyl groups are found at  $\delta$  3.92 in **2** and 3.90 in **3**, but the latter substance shows, in addition, a methoxyl group at  $\delta$  3.81. H-2 and H-6 show signals at  $\delta$  6.74 and 6.77 in **2** and **3**, respectively. Finally, the four-proton multiplet in **1** is nearly identical to the one in **3**, but clearly different from the five-proton multiplet in **2**.

The MS shows a molecular mass of 246.0902 (calculated value for C<sub>14</sub>H<sub>14</sub>O<sub>4</sub> 246.0893). The molecular ion is base peak, other important ions are found at  $m/z$  231 (11%, M–CH<sub>3</sub>), 213 (3%, M–H<sub>2</sub>O–CH<sub>3</sub>), 203 (8%), 171 (16%), 131 (9%) and 115 (11%). Cleavage of the bond between the phenyl nuclei seems to be unfavoured, signals at  $m/z$  153 (0.1%) and 93 (1.0%) being of low intensity. This phenomenon is observed in **2** and **3**, as well.

Final confirmation of the structure of **1** was obtained by methylation with diazomethane, furnishing a substance identical with **3** (TLC, co-TLC, IR). Steric hindrance may be the reason for the lack of reactivity of the 4-OH group.

Biphenyls such as **1**, **2** and **3** may well play an important role in the resistance of *S. caprea* wood to rotting. Recently, **2** has been reported as a phytoalexin in loquat, *Eriobotrya japonica* [3]. This substance shows a strong antifungal and antibacterial effect [3, 4]. Since we have been unable to isolate **1** from fresh *S. caprea* wood, while **2** and **3** are present



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in trace amounts only, it would seem possible that biphenyls are formed as a result of fungal attack in *S. caprea*, too. Thus, they may be regarded as stress compounds [5].

In a paper on biphenyls in *E. japonica* [4], a substance called hydroxyaucuparin has been referred to. No data were given for this substance, and no for-

mula was proposed. It would seem possible that this substance is identical with **1**.

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