Phenolic Biphenyl Derivatives from the Heartwood of *Sorbus aucuparia* (L)

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From the heartwood of *Sorbus aucuparia*, Rosaceae, mountain ash or rowan tree (Swedish rönn), two biphenyl derivatives have been isolated by solvent extraction. They occur in almost equal amounts and constitute up to 7% by weight of the dry heartwood. One of these compounds, aucuparin, has the composition $C_{18}H_{20}(OH)(OCH_3)_2$ and melts at 101–101.5°. (Methyl ether, $C_{18}H_{22}(OCH_3)_2$, m.p. 88–89°. Acetate, $C_{18}H_{18}(OOCOCH_3)(OCH_3)_2$, m.p. 150–151°).

The other compound, methoxyaucuparin, has the composition $C_{18}H_{18}(OH)(OCH_3)_2$ and melts at 120–122°. (Methyl ether $C_{18}H_{20}(OCH_3)_2$, m.p. 71.5–72°. Acetate $C_{18}H_{18}(OOCOCH_3)(OCH_3)_2$, m.p. 119–120°).

On oxidation with permanganate aucuparin gives benzoic acid and methoxyaucuparin affords 2-methoxybenzoic acid. The U.V. spectra of the aucuparins show that they are hydroxybiphenyl derivatives and the N.M.R. spectra that they contain one symmetrical dimethoxy-hydroxyphenyl group. The aucuparins give no colour reaction with bisdiazoitated benzidine and hence cannot be 2,6-dimethoxy-4-hydroxy-phenyl derivatives. Aucuparin is therefore 3,5-dimethoxy-4-hydroxybiphenyl (I: $R = H$) and methoxyaucuparin is 3,5,2'-trimethoxy-4-hydroxybiphenyl (II: $R = OCH_3$).

Aucuparin methyl ether was synthesised by mixed Ullmann coupling of 3,4,5-trimethoxyiodobenzene and methyl 2-bromobenzoate followed by hydrolysis of the reaction product and isolation of the 2'-carboxy-3,4,5-trimethoxybiphenyl, $C_{18}H_{18}(OCH_3)COOH$, m.p. 136–137°, which was then decarboxylated with Adkins' catalyst in boiling quinoline. The 3,4,5-trimethoxybiphenyl thus obtained was identical with aucuparin methyl ether.

Similarly, using methyl 3-iodo-4-methoxybenzoate instead of methyl 2-bromobenzoate, 5'-carboxy-3,4,5,2'-tetramethoxybiphenyl, $C_{18}H_{18}(OCH_3)COOH$, m.p. 216–217.5°, was obtained. On decarboxylation this gave 3,4,5,2'-tetramethoxybiphenyl identical with methoxyaucuparin methyl ether.

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\begin{align*}
\text{OCH}_3 \\
\text{OH} \\
\text{OCH}_3
\end{align*}
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R = H \\
R = OCH_3
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