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

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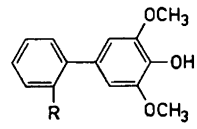
From the heartwood of *Sorbus aucuparia*, Rosaceae, mountain ash or rowan tree (Swedish rönn), two biphenyl derivatives have been isolated by solvent extraction. They occur in almost equal amounts and constitute up to 7 % by weight of the dry heartwood. One of these compounds, aucuparin, has the composition $C_{12}H_7(OH)(OCH_3)_3$ and melts at 101–101.5°. (Methyl ether, $C_{12}H_7(OCH_3)_3$, m.p. 88–89°. Acetate, $C_{12}H_7(OCOCH_3)(OCH_3)_2$, m.p. 150–151°). The other compound, methoxyaucuparin, has the composition $C_{12}H_6(OH)(OCH_3)_3$ and melts at 120–122°. (Methyl ether $C_{12}H_6(OCH_3)_4$, m.p. 71.5–72°. Acetate $C_{12}H_6(OCOCH_3)(OCH_3)_3$, 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 bisdiazotised benzidine and hence cannot be 2,6-dimethoxy-4-hydroxyphenyl 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, $C_{12}H_6(OCH_3)_3COOH$, 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, $C_{12}H_5(OCH_3)_4COOH$, m.p. 216–217.5°, was obtained. On decarboxylation this gave 3,4,5,2′-tetramethoxybiphenyl identical with methoxyaucuparin methyl ether.



I: R = H
II: R = OCH_3

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