

Demethylation of Pinosylvin Monomethyl Ether

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The heart wood of Scots pine (*Pinus silvestris*) contains approximately 1 % of the mixed phenols pinosylvin and pinosylvin monomethyl ether. The relation of these two phenols appears to be rather constant (1 : 3—1 : 4)¹. The isolation of the crude mixture is quite simple² but the separation of the mixture is laborious.

Since pinosylvin, generally, is more toxic and more important for physiological investigation, the conversion of the monomethyl ether (or the mixture) into pure pinosylvin is a matter of importance. Previous attempts to employ hydriodic acid or hydrobromic acid showed that these reagents were unsuitable for the demethylation of pinosylvin monomethyl ether:

The facile demethylation of the monomethyl ether has now been accomplished by means of pyridine hydrochloride, introduced as demethylating agent by Prey³. The yield of pure pinosylvin was about 90 %. Unfortunately the method is not suited for the demethylation of the crude, distilled phenol mixture. A lot of resinous, strongly coloured material is formed and the pinosylvin cannot be obtained in a pure state without considerable loss of substance. Thus the yield of pure pinosylvin never exceeded 50 % of the theoretical value, determined by oxidizing the phenol mixture with potassium permanganate and isolating the benzoic acid formed. (I am indebted to Mr. A. Frank for these determinations.) The isolation of pinosylvin monomethyl ether of sufficient purity, however, is facile.

EXPERIMENTAL

Pinosylvin monomethyl ether (13 g) and pyridine hydrochloride (26 g) were heated to 180° on a salt bath for two hours. The hot mixture was poured into 2 N hydrochloric acid (250 ml) and extracted with ether (3 · 150 ml). The brown ether solution was dried over anhydrous sodium sulfate and filtered through a column of aluminium oxide (10

cm · 5 cm²). The faintly yellow filtrate was evaporated to dryness and the residue recrystallized twice from benzene. M. p. 154–155° (uncorr.). Concentration of the mother liquors yielded a second crop of pure pinosylvin. Total yield 11.0 g (90 %).

SUMMARY

The demethylation of pinosylvin monomethyl ether in a good yield by means of pyridinium hydrochloride is described.

REFERENCES

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3. Prey, V. *Ber.* 74 (1941) 1219.

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