

Analysis of Lignans in Norway Spruce by Combined Gas Chromatography — Mass Spectrometry

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Keywords

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Summary

The acetone:water (9:1 v/v) soluble lignans of spruce wood (*P. abies* [L.] H. Karst.) were investigated by combined gas chromatography — mass spectrometry. Mass spectra of the trimethylsilyl-ethers of 12 separated lignans are presented and discussed. The studied wood sample contained approximately 0,5 per cent lignans of the guaiacyl type. Isolariciresinol (II), secoisolariciresinol (III), liovil (IV), α -conidendric acid (VIII), lignan A (IX), lariciresinol (XIII), two hydroxymatairesinol isomers (XIV and XV, major components), pinoresinol (XVI), matairesinol (XVII) and α -conidendrin (XIX) were identified together with minor amounts of lignan B (XII). Some of the compounds gave almost identical mass spectra indicating the presence of stereoisomers. Six unidentified lignans of the tetrahydrofuran series were also detected.

Schlüsselwörter (Sachgebiete)

Lignane
Gaschromatographie
Massenspektrometrie
Fichte
Picea abies (L.) H. Karst.

Analyse von Lignanen im Fichtenholz durch kombinierte Gaschromatographie — Massenspektrometrie

Zusammenfassung

Die Aceton-Wasser (9:1)-löslichen Lignane des Fichtenholzes wurden mit Hilfe der kombinierten Gaschromatographie — Massenspektrometrie untersucht. Die Massenspektren der Trimethylsilyl-äther von 12 isolierten Lignanen werden dargestellt und diskutiert. Die untersuchten Holzproben enthielten etwa 0,5 % Lignane vom Guajacyl-Typ. Isolariciresinol (II), Seco-isolariciresinol (III), Liovil (IV), α -Conidendrinsäure (VIII), Lignan A (IX), Lariciresinol (XIII), 2 Hydroxy-Matairesinol Isomere (XIV und XV, Hauptkomponenten), Pinoresinol (XVI), Matairesinol (XVII) und α -Conidendrin (XIX) wurden zusammen mit kleineren Mengen von Lignan B (XII) identifiziert. Einige Verbindungen ergaben stets identische Massenspektren, sie liegen also in stereoisomerer Form vor. Außerdem wurden 6 nicht identifizierte Lignane aus der Tetrahydrofuranreihe bestimmt.

Introduction

A number of guaiacyl lignans are present in spruce wood. In an early paper Freudenberg and Knof (1957) reported the occurrence of several main components making up approximately 0.4 per cent by weight of dry wood. The spruce oleoresin was investigated for lignans by Weinges (1960). In these studies the lignans were separated by liquid-liquid extraction using the countercurrent distribution technique.

The first description of gas chromatography (GC) of lignans was given by Ayres and Chater (1969), who found that the principal classes and geometrical isomers may usually be distinguished. Hereby less polar compounds and those where the polar groups could be blocked by methylation were studied.

Krahmer et al. (1970) used the GC of the trimethylsilyl (TMS) ethers for determination of the cellular distribution of lignans in *Tsuga heterophylla* wood. By this technique very small deposits in the heartwood could be analysed for hydroxymatairesinol, matairesinol and α -conidendrin. Similarly Shain and Hillis (1971) analysed sound and *Fomes annosus*-affected tissues of Norway Spruce. Hydroxymatairesinol, matairesinol, liovil and α -conidendrin were identified in sound heartwood and in the narrow reaction zone separating sound sapwood from wood incipiently decayed by *F. annosus* (Fr.) Cke. It was proposed that the high hydroxymatairesinol concentration in the reaction zone contributed to the resistance of the sapwood to *F. annosus* in vivo.

The same GC method was used by Hart et al. (1975), who studied the formation of lignans in sapwood of White Spruce in response to wounding.

Pelter et al. (1966) first applied mass spectrometry (MS) to the study of simple lignans. He stated that the mass spectra most often define the overall structure, and that positional isomers give different mass spectra. However stereoisomerism does seldom do more than slightly affect the intensity of some peaks, and this effect is too slight to be useful. The mass spectrometric fragmentation of lignans was later studied among others by Duffield (1967) and Pelter (1967, 1968).

Mass spectra of TMS ethers of spruce lignans have not been published.

The objective of this study was to develop methods for detailed qualitative analysis of lignan extracts to obtain a good reference standard mixture to be used for further investigations on wood extractives. The results will be applied in studies of the possible association between the lignan composition of spruce and resistance to *Fomes annosus*.

Experimental

Material and Extraction

A 65-year old spruce (*P. abies* [L.] H. Karst.) grown in Siilinjärvi in Central Finland was felled in March, 1975. A cross section of the trunk was taken at the height of 1 meter, and the wood sample was cut into small splinters, which were freeze-dried for two days. The dry material was ground to wood meal of 20 mesh particle size before extraction. To remove less polar components, 10 g of the wood meal was extracted in a Soxhlet apparatus for 24 hours using 150 ml petroleum ether (60–80°C). The lignans were then extracted in the