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COMPOSITION OF NONPOLAR EXTRACTIVES IN BARK OF
NORWAY SPRUCE AND SCOTS PINE

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ABSTRACT

The composition of nonvolatile extractives soluble in petroleum ether was investigated separately for inner and outer bark of Norway spruce (*Picea abies* (L.) Karst) and Scots Pine (*Pinus silvestris* (L.)). The bark extractives of one spruce and one pine tree were prefractionated by thin-layer chromatography and the detailed composition of free and esterified fatty acids, free and esterified sterols, triterpenoid alcohols and fatty alcohols, resin acids and diterpene aldehydes was determined by gas chromatography. Bark of four other trees was analysed by a routine method based on direct gas chromatography of the extracts. Fatty acids, resin acids and sterols accounted for ca 80% of extractives in inner bark and for 50% in outer bark. Qualitative differences between the extractives in inner and outer bark were noticed. The total amount of fatty and resin acids was about 1.5% of spruce and pine bark dry weight and the amount of sterols was 0.2-0.5%. These levels are low considering possible technical recovery and utilization of extractives from the bark.

INTRODUCTION

Norway spruce (*Picea abies* (L.) Karst.) and Scots pine (*Pinus silvestris* (L.)) are the principal pulp wood species in Northern and Central Europe. Their bark constitutes a huge stock of waste

material which is readily available at pulp mills or sawmills. So far no large scale uses other than burning have been developed.

A detailed knowledge of the chemistry of bark is necessary for the development of alternative uses of bark. The nonpolar extractives is a compound group of interest for chemical utilization.

Norin and Winell conducted comprehensive studies on the nonpolar extractives of both Norway spruce¹ and Scots pine². A large number of extractive constituents were isolated and identified. Weissman later verified the presence of several of these components³. These studies were carried out on whole bark. No information on the extractive composition of the anatomically different inner and outer bark tissues has been reported for Norway spruce or Scots pine.

The aim of the present investigation was to learn more about the composition of nonpolar extractives from inner and outer bark, respectively. Quantitation of the components was performed in order to determine the potential for the possible recovery and utilization of bark extractives.

EXPERIMENTAL

Sampling and Sample Handling

Bark samples were taken from 5 living trees each of Norway spruce and Scots pine in a mixed softwood forest in SW Finland. The samples were taken in October, and were taken at 1.5 m height above the ground. The tree diameters ranged from 22 to 39 cm for the spruce trees and 24 to 36 cm for the pine trees. The bark samples were stored at -16°C until analysis was carried out.

After manual separation of outer and inner bark, the samples were freeze-dried. The proportion of dry outer and inner bark was determined by weighing. The bark samples were ground to less than 0.7 mm diameter particles with a Cyclo-Tec laboratory mill.

Extraction

Dry bark powder (about 1 g or 10 g) was extracted with a Soxhlet apparatus for 20 h using petroleum ether (bp. 40-60°C). Internal standard substances (see Table 1 and Figure 2) were added to the solvent before extraction.

Analytical Schemes

The bark extractives of one spruce and one pine tree (tree number 1) were analysed according to a detailed procedure originally developed for wood extractives in our laboratory⁴. In this procedure, the extractives are prefractionated by preparative thin-layer chromatography (TLC) followed by gas chromatography (GC) of the fractions (Figure 1 and Table 1). Bark of the other trees (tree numbers 2-5) was analysed by a routine method based on direct gas chromatography (GC) also developed for wood extractives in our laboratory⁵ (Figure 2).

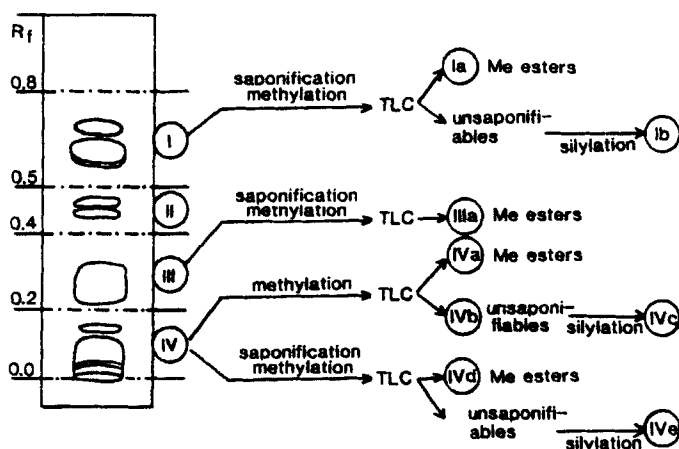


FIGURE 1. Fractionation of extractives by thin-layer chromatography on silica gel. Solvent system: petroleum ether: diethyl ether 85:15 v/v. For other details see ref. 4.

TABLE 1
Extractive TLC-fractions Utilized for GC-analysis

Fraction	Constituents	Internal standard	GC-column, temperature
Ia	Fatty acids from esterified sterols and fatty alcohols	Heptadecanoic acid (as methyl ester) from cholesteryl heptadecanoate	capillary BDS, 190°C
Ib	Sterols and fatty alcohols from fatty acid esters	Cholesterol (as TMS ether) from cholesteryl heptadecanoate	capillary SE-30, 150-280°C, 40C/min
II	Diterpene aldehydes and resin acid methyl esters	Methyl heptadecanoate	capillary BDS, 190°C
IIIa	Triglyceride fatty acids	Heptadecanoic acid (as methyl ester) from glyceryl triheptadecanoate	capillary BDS, 190°C
IVa	Free fatty and resin acids	Heptadecanoic acid (as methyl ester)	capillary BDS, 190°C
IVb	Free diterpene alcohols		1% XE-60, 100-180°C, 40C/min
IVc	Free sterols, triterpene alcohols and fatty alcohols	Cholesterol (as TMS ether)	capillary SE-30, 150-280°C, 40C/min
IVd	Fatty acids from polar esters (i.e. mono- and diglycerides) (+ free fatty and resin acids)	Heptadecanoic acid (as methyl ester)	capillary BDS, 190°C
Ive	Fatty alcohols from ferulic acid esters (+ free fatty alcohols)	Cholesterol (as TMS ether)	capillary SE-30, 150-280°C, 40C/min

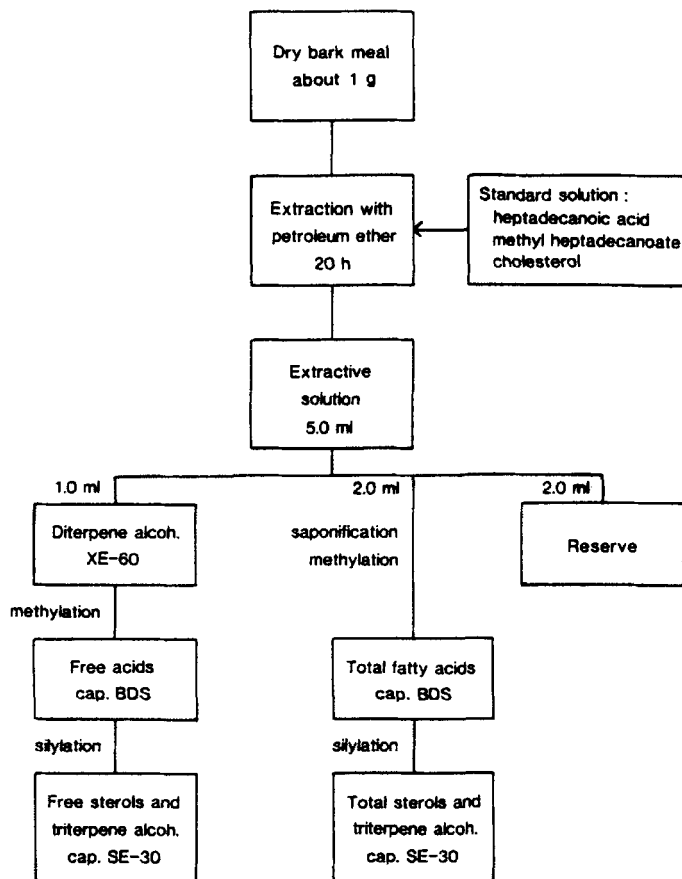


FIGURE 2. Scheme for routine analysis of nonpolar extractives. For additional information see ref. 5.

RESULTS

The proportion of outer bark varied between 45 and 57% for the five spruce and between 83 and 92% for the five pine bark samples. The content of nonpolar extractives in spruce bark was 1.8-2.9% (on dry weight basis) of inner and 2.0-4.8% of outer bark. The corresponding figures for pine were 5.0-7.2% for inner and 2.1-3.6% for outer bark (Figure 3).

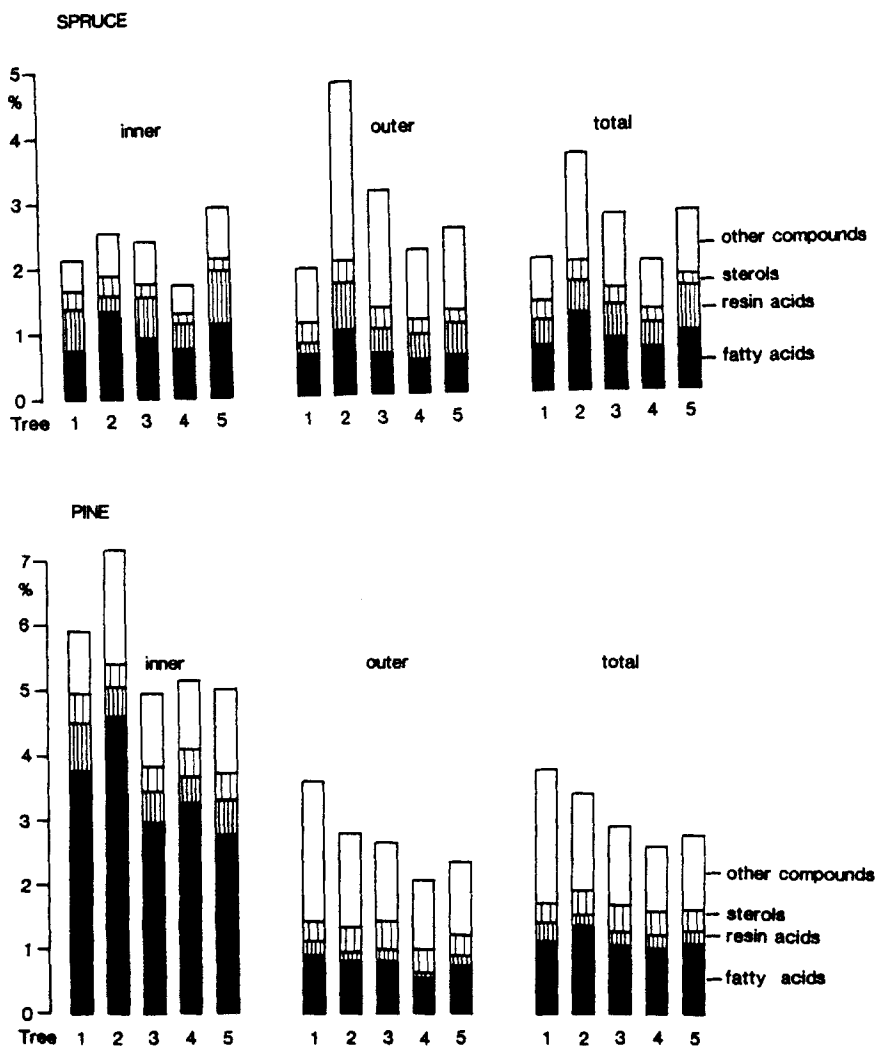


FIGURE 3. Amount and composition of extractives soluble in petroleum ether in bark from five spruce and five pine trees (% of dry bark).

Fatty Acids

The highest content of total fatty acids was found in pine inner bark (Figure 3). Detailed analysis revealed that they were present here principally in the form of triglycerides (Table 2). In pine outer bark, the mono- and diglyceride fatty acid content exceeded that of the triglycerides. In the outer bark of spruce the content of fatty acids was only slightly higher than in the inner bark. The triglycerides dominated in both bark fractions of spruce. The content of free acids was higher in outer bark than in inner bark both for pine and spruce. The opposite was true for steryl esters (Table 2). The fatty acids in triglycerides and steryl esters were predominantly unsaturated (Figure 4). Oleic, linoleic, and pinolenic acids were the principal components. Among the free fatty acids and the mono- and diglycerides, saturated acids dominated with arachidic (20:0), behenic (22:0), and lignoceric (24:0) acids as the main components. On a whole bark basis, oleic, linoleic, and pinolenic acids accounted for more than 70% of the fatty acids. Over 30 fatty acid components were separated and identified. The unsaturated anteiso-branched fatty acids 5,9-19:2, 9,12-19:2, 5,9,12-19:3 and the normal-chain acids 7,11,14-20:3 and 5,9,12,15-18:4, previously identified in spruce wood⁶, were now detected also in bark. All except the 18:4 acid were found also in pine bark.

Resin Acids

The resin acids amounted to about 0.5% of the whole bark (Figure 3) of spruce. Pine bark contained less of these acids due to their low concentration in the outer bark. Abietic-type acids constituted over 75% of the resin acids in both spruce and pine (Table 3). Levopimaric and palustric acids dominated in inner bark of both species and dehydroabietic acid in outer bark.

Sterols and Triterpene Alcohols

The content of free sterols and triterpene alcohols was higher in outer bark than in inner bark both for spruce and pine

TABLE 2

Content of Main Extractive Components Soluble in Petroleum Ether
(mg/g dry bark) for Tree Number 1

Component	Spruce bark		Pine bark	
	inner	outer	inner	outer
FATTY ACIDS	7.57	6.36	37.83	9.04
Triglyceride	4.86	2.60	33.40	1.71
Mono- and diglyceride	0.84	1.74	2.26	5.46
Stery1 ester	1.44	0.60	1.54	0.19
Free	0.43	1.42	0.63	1.68
RESIN ACIDS	6.26	1.94	7.16	2.39
STEROLS AND TRITERPENE ALCOHOLS	2.94	2.98	4.50	2.98
Free	0.72	1.91	2.56	2.73
Esterified	2.22	1.07	1.94	0.25
DITERPENE ALCOHOLS	1.24	0.30		
DITERPENE ALDEHYDES	0.33	0.10	0.21	0.11
FATTY ALCOHOLS	0.13	1.24	1.33	1.25
Ferulate-	0.08	0.94	1.26	1.01
Wax-	0.03	0.07	0.03	0.09
Free	0.02	0.23	0.04	0.15
GLYCERYL RESIDUES ¹⁾	0.32	0.31	1.76	0.68
TOTAL (GC)	18.79	13.23	52.79	16.45
WEIGHED EXTRACTIVES	21.40	19.54	59.06	36.11

1) Approximated calculation

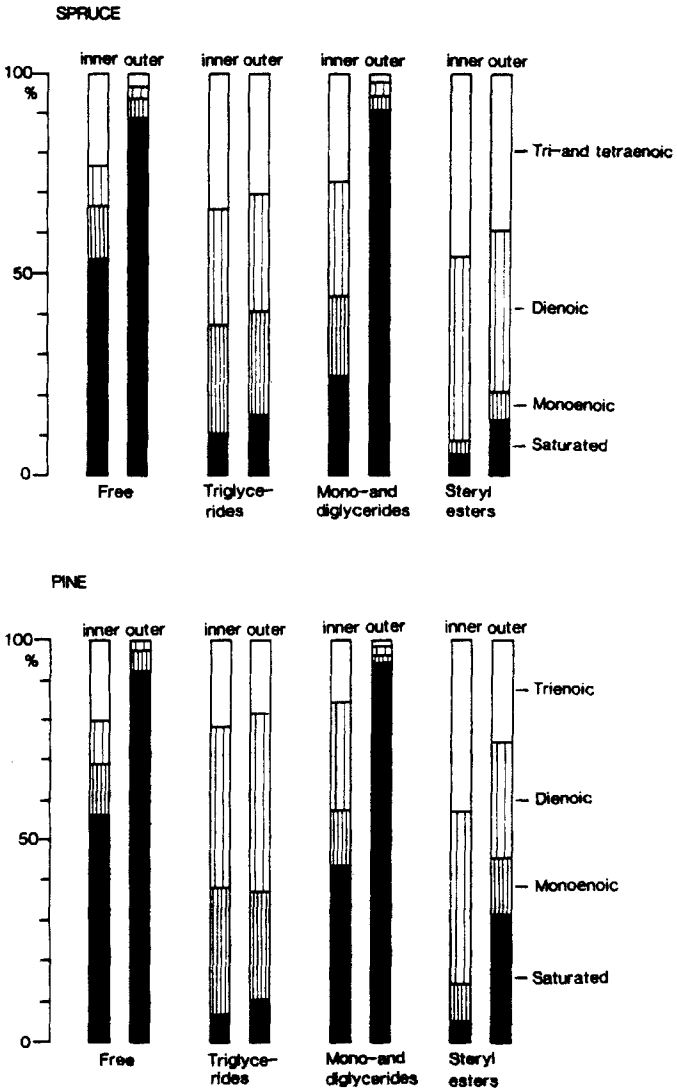


FIGURE 4. Distribution of fatty acids (tree number 1).

TABLE 3

Composition of (Free) Resin Acids (Tree Number 1) (%)

Acid	Spruce bark		Pine bark	
	inner	outer	inner	outer
Pimaric	-	1.6	8.7	14.1
Sandaracopimaric	2.2	2.7	1.7	2.4
Levopimaric	19.0	10.2	29.3	10.5
Palustric	24.9	16.9	16.4	6.9
Isopimaric	17.9	19.2	6.9	7.6
Abietic	11.6	9.0	13.6	12.6
Dehydroabietic	10.8	32.4	9.9	41.1
Neoabietic	13.6	8.0	13.5	4.8
	100.0	100.0	100.0	100.0

(Table 2). Steryl esters were more abundant in inner bark. β -sitosterol, campesterol and β -sitostanol dominated in the esters. Triterpene alcohols of the serratene type were present in free form in both spruce and pine bark and they occurred almost exclusively in outer bark.

Diterpene Aldehydes

The following aldehydes were found in pine bark: pimaral, palustral, levopimaral, isopimaral, abietal, dehydroabietal, and neoabietal. All these, except pimaral, occurred also in spruce. Palustral was the predominant aldehyde in spruce inner bark, and pimaral in pine inner bark. Dehydroabietal was the main component in the aldehyde fraction of the outer bark both in spruce and pine.

Diterpene Alcohols and Fatty Alcohols

Thunbergol and *cis*-abienol occurred in spruce bark, particularly in inner bark (Table 2). Pine bark contained pimarol in smaller amounts. Behenyl and lignoceryl alcohols were present in both spruce and pine in the free form, but also in the form of esters with fatty acids or with ferulic acid.

DISCUSSION

The contents of petroleum ether soluble extractives on a whole bark basis were only slightly lower than the figures for methylene chloride soluble extractives (3.5% for spruce and 3.7% for pine) obtained by Norin and Winell^{1,2}. It is obvious that spruce and pine bark on a whole bark basis contain about equal amounts of nonpolar extractives. Inner bark of pine contained significantly more extractives than outer bark. However, for spruce there were no clear differences in extractive content between inner and outer bark.

Fatty acids, resin acids, and sterols accounted for ca 80% of the nonpolar extractives in inner bark, but only for ca 50% in outer bark. The remaining part consisted of small amounts of diterpene alcohols and aldehydes, fatty alcohols, in addition to larger amounts of unidentified extractives. This material probably is composed of oxidized and polymerized extractives which could not be eluted under the used GC conditions. Similar unaccounted for material found in loblolly pine bark extractives was classified by Pearl and Buchanan as "nebulous material known as phenolic acid and bark lignin"⁷.

Most of the constituents previously identified by Norin and Winell^{1,2} were found also in the present study. The volatile mono- and sesquiterpenoids were not investigated now. Alkanes were detected neither in spruce nor in pine bark. If alkanes do occur, their sum content must be much below 1% of the extractives. *cis*-Abienol and thunbergol, which are the predominant neutral diterpenoids in oleoresin of spruce wood^{4,8}, were now proved to occur also in bark, primarily in inner bark.

The diterpene aldehydes have not previously been found in spruce bark, although they have been detected in the wood and oleoresin^{4,8}. Among the wood extractives which were not found in the bark were the artenol-type triterpene alcohols.

There are distinct quantitative differences between the extractives in inner and outer bark. The much higher content of tri-

glycerides and steryl esters and the lower content of free fatty acids in inner bark than in outer bark resemble the distribution of extractives in sapwood and heartwood, respectively.

The amounts of oleoresin-derived components, primarily the resin acids and other diterpenoids, were about three times higher in inner bark than in outer bark. The outer bark contained smaller amounts of easily oxidizable components like abietic-type resin acids and *cis*-abienol. The serratene-type triterpene alcohols seem to be specific outer bark constituents. The C₂₀ - C₂₄ saturated fatty acids were also much more abundant in outer bark.

The amounts of fatty and resin acids together were on the 1.5% level for both spruce and pine bark. The amount of sterols was 0.2-0.5%. These levels of fatty acids, resin acids, and sterols are not very encouraging in view of technical recovery and utilization of extractives from the bark. Obviously the recovery of nonpolar extractives from bark can be feasible only if it can be integrated with a broader chemical utilization of the bark.

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