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# Extractives From the Bark of Scots Pine, *Pinus silvestris* L.

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The methylene chloride extract from the bark of Scots pine, *Pinus silvestris* L., has been investigated and found to consist of free and esterified fatty acids ($C_{12}-C_{24}$), resin acids of pimarane and abietane type, ferulic esters, fatty alcohols ($C_{18}-C_{24}$), alkanes ($C_{15}-C_{34}$), campesterol, β-sitosterol, stigmast-4-en-3-one, monoterpenes (α- and β-pinene, $\Delta^3$-carene, and *p*-cymene), sesquiterpenes (α- and γ-muurolene, γ-cadinene, α-longipinene, copaene, longifolene, β-copaene, and copaborneol), diterpenes (pimaradiene, isopimaradiene, pimaral, isopimaral, dehydroabietal, pimarol, isopimarol, and abietol), norditerpenes (*1* – *3*) and triterpenes of serratene type, 3β-methoxyserrat-14-en-21-one (*6*), 3α-methoxyserrat-14-en-21-one (*7*), 3β,21α-dimethoxyserrat-14-ene (*8*) and 3α,21α-dimethoxyserrat-14-ene (*9*).

The wood extractives, particularly the phenolic heartwood constituents of a number of *Pinus* species, have previously been studied and the taxonomic significance of various compounds have been discussed.[1–3] The lipophilic bark constituents of some American *Pinus* species have recently been studied: *P. ponderosa*, [4] *P. lambertiana*, [4–6] *P. densiflora*, [7] *P. contorta*, [5,8,9] *P. banksiana*,[5,6,10,11] *P. taeda*,[5,6] *P. palustris*,[6] and *P. radiata*.[12] The chemistry of *Pinus* bark appeared to be different from that of the wood.[4–12] Particularly the occurrence of triterpenes of serratene type in pine bark may be significant. It is therefore of interest to investigate further species belonging to the genus *Pinus*.

The aim of the present investigation was to examine the lipophilic bark constituents of *P. silvestris L.*, Scots pine. This pine has a wider distribution than any other pine and it is found throughout Europe, Western and Northern Asia. It occurs on a great variety of soils and in regions of the most diverse climates. On the lower part of the trunk the bark is fissured into irregular, longitudinal plates, reddish-brown or greyish-brown in colour. On the upper part of the tree it is light red or orange. The anatomy of the bark is rather complex and there is no definite distinction between inner and outer bark. However, most investigations which have so far been published, have been carried out on the whole bark from the cambial region to the outer bark.

Investigations on Scots pine bark, published before 1940, have been reviewed in a paper by Lehman and Wilke.[13] The chemical investigations published up to that date are of limited value and are largely concerned with fractionation according to solubility in various solvents and elemental analysis of the fractions.

Pajari[14] published an analysis of the ether extract of the bark. He isolated hydrocarbons, sterols, fatty and resin acids. In connection with an examination of the influence of bark on hardboard properties Andersson[15] separated an ether extract into component groups according to their chemical properties (waxes, saponifiables, unsaponifiables, fatty acids, resin acids, phenols, and other acids). Lindstedt and Misiorny[16] have studied the phenols of pine heartwoods. They also studied the bark of Scots pine but did not detect any of the characteristic heartwood phenols. Oksanen[17] made a careful examination of the phenols from the ether extract of pine bark. He has also analysed the volatile components in order to test them as pheromones.[18] He considers α-terpineol to be an attractant for the bark beetle (*Blastophagus piniperda*, L.) which attacks *P. silvestris*.

Sharkov[19] investigated the bark and studied the water extract, the ethyl alcohol extract, pectic substances, cellulose, uronic acids, pentosans, lignin, methoxyl content, fermentable sugars, and ash. A number of investigations have been carried out on the tannin fractions (*cf.* Gerngross and Gülbaran[20]) and the carbohydrates of the inner bark have been studied by Timell *et al.*[21]

## RESULTS AND DISCUSSION

The bark of *P. silvestris*, from the cambial region outwards, was collected from the lower part of the trunk. The bark was extracted with methylene chloride. This extract was separated into light petroleum soluble and insoluble fractions. The insoluble fraction consisted mainly of waxes and related substances. Upon hydrolysis mainly fatty acids, hydroxy fatty acids, and dicarboxylic acids were isolated. These constituents are probably derived from the cork suberin (*cf.* Ref. 22).

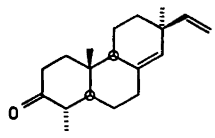
The light petroleum soluble fraction of the extract was further separated into free acids and a neutral fraction. The acid fraction consisted mainly of fatty acids (saturated $C_{12}-C_{24}$), resin acids and a waxy fraction which upon saponification yielded ferulic acid and fatty alcohols ($C_{13}-C_{22}$). The main fatty acid was behenic acid. The even numbered acids dominated. The resin acids were the same as those also present in the oleoresin.[23] Dehydroabietic acid was the main component. Wax alcohol esters of ferulic acid seem to be rather common in pine barks, as previously indicated in the review by Rowe *et al.*[11]

A large quantity of the extract consisted of waxes which could be isolated by silica gel chromatography of the crude neutral fraction. The waxes were saponified and separated into a neutral fraction and an acid fraction. The two fractions were analysed by GLC and TLC. The acid fraction was shown to contain saturated fatty acids and was similar in composition to that reported above for the free acids. The neutral fraction consisted of sterols (β-sitosterol and campesterol) and even numbered fatty alcohols $C_{18}-C_{24}$, $C_{22}$ dominating.

The crude neutral fraction of the light petroleum soluble bark extract was saponified and separated into an unsaponifiable fraction and acids. The unsaponifiable part was fractionated on silica. The following types of constituents were isolated: hydrocarbons, aldehydes, norditerpenes, alcohols, sterols, and triterpenes.

The hydrocabon fraction contained saturated and unsaturated compounds. The saturated fraction was shown (GLC, IR) to consist of alkanes with the odd chain lengths predominating. There were also small amounts of branched alkanes. The unsaturated hydrocarbons were of terpenoid nature and of the same type as those found in the wood.[24]

The aldehyde fraction consisted of three compounds: pimaral, isopimaral, and dehydroabietal. The same aldehydes together with abietal were also found in the wood.[24] The dominating aldehyde both in the bark and the wood is pimaral.

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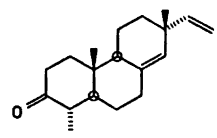


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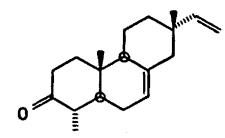


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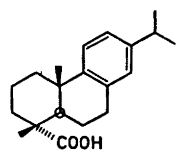


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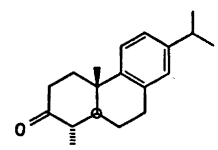


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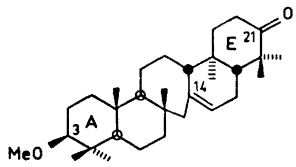
Three norditerpenes were isolated from the neutral fraction. One of these compounds has been characterized as 19-norpimara-8(14),15-dien-3-one (*1*). The structures of the other two are proposed to be 19-norisopimara-8(14),15-dien-3-one (*2*), and 19-norisopimara-7,15-dien-3-one (*3*). The isolation and structural elucidations of these norditerpene constituents have been reported in a previous paper.[25] Norditerpenes have also been isolated from the bark of *P. banksiana*.[26] Recently it has been shown that a microorganism isolated from the soil of a *P. maritima* forest is able to degrade dehydroabietic acid (*4*) to a norditerpene (*5*) of similar type to that found in pine bark.[27] It is therefore possible that the norditerpenes in the bark are artefacts formed by microbial degradation of resin acids.[25]

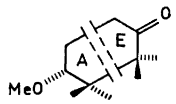
A number of alcohols, such as fatty alcohols, sterols, and terpenoid alcohols, were isolated. The fatty alcohols and sterols of the waxes were also found to be present in free form. The terpenoid alcohols occurred in unesterified form. Copaborneol, pimarol, isopimarol, and abietol were detected. These compounds are also characteristic wood constituents.[24]

A steroid derivative related to β-sitosterol was also isolated. It was shown to be stigmast-4-en-3-one. Rowe has found small amounts of oxidation products

of sterols, among them stigmast-4-en-3-one in the bark of *P. banksiana*.[5,10] He suggests that these products are artefacts formed by autoxidation. Autoxidation is to be expected in tree barks and it could be more widespread the older the trees are. However, a microbial transformation is also possible.




*6*




*7*


*8*


*9*

The presence of triterpenes of serratene type in the bark of the genus *Pinus* has been reported by Rowe.[6,9,10] From *P. silvestris* we isolated four serratene derivatives: 3$\beta$-methoxyserrat-14-en-21-one (*6*), 3$\alpha$-methoxyserrat-14-en-21-one (*7*), 3$\beta$, 21$\alpha$-dimethoxyserrat-14-ene (*8*), and 3$\alpha$, 21$\alpha$-dimethoxyserrat-14-ene (*9*). The occurrence of 3$\alpha$, 21$\alpha$-dimethoxyserrat-14-ene is noteworthy because it is the first natural 3-episerratenediol derivative.

The serratene derivatives *6*, *7*, *8*, and *9* were identified by comparison with authentic samples (TLC, GLC, IR, NMR, MS, m.p. and mixed m.p.). The 3$\alpha$,21$\alpha$-dimethoxyserrat-14-ene (*9*) was characterized and identified by comparison with a synthetic sample prepared from 3$\alpha$-methoxyserrat-14-en-21-one (*7*).

The NMR spectrum is very characteristic for a serratene derivative which has only seven angular methyl groups whereas normal pentacyclic triterpenes possess eight such grops. MS has a very characteristic fragmentation pattern which has been summarized in a paper by Kutney *et al.*[28] The seven-membered ring is the point of fragmentation and its cleavage gives rise to two main characteristic fragments. Fragments resulting from a retro Diels-Alder cleavage are found to a minor extent. ORD is very useful in the determination of the position of a keto function. Inubushi *et al.*[29] have shown that the ORD-curve of 3$\beta$-acetoxyserrat-14-en-21-one exhibits a negative Cotton effect with a molecular amplitude of $-32$, while serrat-14-en-3-one exhibits a positive Cotton effect with a molecular amplitude of $+30$.

The occurrence of triterpenes of serratene type in the genus *Pinus* may be of chemotaxonomical interest. Their occurrence in the bark of *Picea sitchensis* has been reported by Rogers and Rozon.[30] They have also been found in the bark of *Picea abies*.[31] A notable point is the fact that most of these compounds exist as methyl ethers, which is rather uncommon among known triterpenes.

## EXPERIMENTAL

Light petroleum refers to the fraction with the boiling-range 40 – 60°. NMR spectra were recorded using deuteriochloroform solutions (*ca.* 10 %) with internal standard (TMS). Chemical shifts are given in $\tau$ units. In all spectra (IR, NMR, and MS) only characteristic data are given.

*Extraction.* The air-dried bark (11.2 kg) was extracted with methylene chloride for 7 days. The bark was then dried and extracted with acetone for 5 days. Evaporation of the solvents gave 417 g (3.7 %) of methylene chloride extract and 143 g (1.3 %) of acetone extract. The acetone extract has not been investigated. The methylene chloride soluble part was soaked with light petroleum. The insoluble part (256 g) was a yellow powder. Some (2 g) of this material was saponified (20 % w/v of KOH in aqueous methanol, 5 h). The hydrolysate was diluted with water and extracted with several portions of ether. The ether extract (10 %) was found to consist mainly of fatty alcohols ($C_{20}-C_{24}$). The alkaline part was acidified and taken up in ether. The GLC analysis (1 % XE60) of this ether extract showed the presence of the following identifiable compounds: 30 % saturated fatty acids (23 % $C_{20}$, 63 % $C_{22}$, 14 % $C_{24}$); 9 % saturated hydroxy fatty acids (15 % $C_{20}$, 80 % $C_{22}$, 5 % $C_{24}$), and 4 % saturated dicarboxylic acids.

A part (50.0 g) of the light petroleum soluble fraction (161.0 g) was separated in the usual way into a neutral fraction (21.5 g) and an acidic fraction (28.5 g).

## Neutral fraction

The neutral fraction was saponified (20 % KOH in aqueous methanol, 5 h) to yield acids (7.0 g) and unsaponifiables (14.0 g).

When the unsaponifiable fraction was dissolved in ether and left overnight a crystalline part could be filtered off (0.50 g). This crystalline mixture was fractionated into three main compounds with $R_F$ 0.60, 0.64, and 0.68, respectively, by preparative TLC on silica with chloroform as eluent.

The compound with $R_F$ 0.60 was shown to be 3$\beta$-methoxyserrat-14-en-21-one (6)[9] by a direct comparison (m.p., mixed m.p., GLC, TLC, IR, NMR, ORD, and MS) with an authentic sample.

The compound with $R_F$ 0.64 had the following properties. M.p. 292 – 293° (evacuated capillary). $[\alpha]_D$ +18°, *c* 1.0 in chloroform. IR $cm^{-1}$ (KBr): 1100 ($-O-CH_3$) 850, 790 (trisubstituted double bond). NMR (recorded at 100 Mc/s; $\tau$-units): 4.64 (1H, unresolved multiplet, olefinic proton); 6.64 (6H, 2 singlet, $O-CH_3$); 7.20 and 7.40 (2H, quartets, $J=4$ cps and 11 cps, $H-C-OMe$); singlets at 9.0 – 9.4 corresponding to 7 angular methyl groups. MS: $M^+$ 470, 234, 221. The spectral data of this compound strongly suggest that it is a dimethoxyserrat-14-ene. The coupling constants ($J=11$ and 4 cps) in the signal patterns due to the protons geminal to the methoxyl groups indicate the presence of axial-axial and axial-equatorial couplings. The compound may thus be formulated as 3$\beta$,21$\alpha$-dimethoxyserrat-14-ene (*8*).[6] The structure was confirmed by a comparison (TLC, GLC, IR, NMR, MS, m.p. and mixed m.p.) with an authentic sample.

The compound with $R_F$ 0.68 (m.p. 295 – 298°, evacuated capillary; $[\alpha]_D$ +10°, *c* 0.2 in chloroform) was isolated in very small amounts (2 mg). The IR and NMR data were similar but not identical to those of 3$\beta$,21$\alpha$-dimethoxyserrat-14-ene, which indicated that it was a serratene derivative with methoxyl groups in positions 3 and 21. The structure of this compound was shown to be 3$\alpha$,21$\alpha$-dimethoxyserrat-14-ene (*9*) by comparison (TLC, GLC, IR, NMR, MS, m.p. and mixed m.p.) with an authentic sample which was prepared from 3$\alpha$-methoxyserrat-14-en-21-one (*7*) by reduction with lithium-aluminium-tri-*t*-butoxyhydride in dioxane.[32] The main reduction product, 3$\alpha$-methoxyserrat-14-en-21$\alpha$-ol, was separated by preparative TLC and without further purification methylated with methyl iodide and potassium *t*-butoxide in toluene to yield the 3$\alpha$,21$\alpha$-dimethoxyserrat-14-ene (*9*).

The unsaponifiable part was separated on a silica column with light petroleum ether mixtures. The separation was followed by TLC and the fractions were combined in a suitable manner.

*Fraction 1* (0.27 g) consisted of hydrocarbons. They were separated into saturated and unsaturated fractions by preparative TLC on silver nitrate impregnated silica with light petroleum as eluent. The saturated fraction (0.07 g) consisted of alkanes which were analysed by GLC on a 1 % SE 30 column and shown to be a complex mixture of mostly n-alkanes ($C_{15}-C_{34}$) with heneicosane and tricosane as main components (22 % $C_{21}$; 19 % $C_{23}$; 3 – 5 % for each of $C_{19}$, $C_{20}$, $C_{22}$, $C_{24}$, $C_{25}$, $C_{27}$, $C_{29}$, $C_{31}$, and $C_{33}$; 0.5 – 3 % for each of $C_{17}$, $C_{18}$, $C_{26}$, $C_{28}$, $C_{30}$, and $C_{32}$, and also branched $C_{28}$, $C_{29}$, $C_{30}$, and $C_{31}$; there were also traces of $C_{15}$, $C_{16}$, $C_{34}$ and some branched hydrocarbons). The unsaturated

fraction (0.2 g) was a complex mixture of mono-, sesqui- and diterpenes. They were analysed by GLC (1 % E 301 on Gas Chrom. P. and 1 % Reoplex on Chromosorb W.). The following compounds were identified by comparison of retention data with those of authentic samples: α- and β-pinene, $\Delta^3$-carene, *p*-cymene, α-longipinene, copaene, longifolene, β-copaene, α- and γ-muurolene, γ-cadinene, pimaradiene, and isopimaradiene.

*Fraction 2* (0.30 g) was separated by preparative TLC on silver nitrate impregnated silica with benzene as eluent. Three main compounds were isolated ($R_F = 0.21$, 0.40, and 0.63) and shown to be isopimaral ($R_F = 0.21$), pimaral ($R_F = 0.40$) and dehydroabietal ($R_F = 0.63$) by comparison of chromatographic (TLC, GLC) and spectral (IR, NMR) data with those of authentic samples. The remaining material appeared to be complex mixtures of hydrocarbons which were not further investigated.

*Fraction 3* (0.84 g) was chromatographed on a silver nitrate impregnated silica column with ether (10 %) in light petroleum as eluent. The separation was followed by TLC. One homogeneous fraction (0.16 g) could be isolated. It was dissolved in ether and left overnight. A white crystalline compound precipitated. This compound was proved to be 3β,21α-dimethoxyserrat-14-ene by a direct comparison (m.p., mixed m.p., IR, NMR, MS, TLC, and GLC) with an authentic sample.

The remaining part of fraction 3 was found to consist of norditerpenes. The investigation of these constituents has been reported in a previous paper.[25]

*Fraction 4* (0.42 g) was recrystallized from absolute ethanol yielding a compound which was shown to be 3α-methoxyserrat-14-en-21-one (7) [30] by a direct comparison (m.p., mixed m.p., IR, NMR, MS, GLC, and TLC) with an authentic sample.

*Fraction 5* (2.02 g) was analysed by TLC and GLC and found to contain 3β-methoxyserrat-14-en-21-one, fatty alcohols and an α,β-unsaturated ketone. The fatty alcohols were analysed as their TMS-derivatives by GLC (1 % XE 60). The following n-alcohols were detected: $C_{18}$ (1.5 %), $C_{20}$ (10 %), $C_{22}$ (63 %), $C_{24}$ (23 %), and $C_{26}$ (2.5 %).

The α,β-unsaturated ketone was isolated by preparative TLC on silica with light petroleum/ether (1:1) as eluent. IR ($cm^{-1}$, nujol): 1680 (α,β-unsaturated ketone); 1615 (trisubstituted double bond). NMR (τ): 4.2 (1H, broad singlet, olefinic proton); 7.6 (2H, multiplet, methylene adjacent to a keto function); 8.8 – 9.3 signals corresponding to 6 methyl groups. UV (nm): $\lambda_{max}$(EtOH) 240.5, ε 16 600; $[\alpha]_D$ ($CHCl_3$) +84° (*c* 0.65); m.p. 86.5 – 88.5°. MS $M^+$ 412, 370, 327, 289, 271, 229, 124 (100 %).

The compound was shown to be stigmast-4-en-3-one by comparison with literature [33] data (m.p. 88°; $[\alpha]_D$ ($CHCl_3$) +86°; UV (nm): $\lambda_{max}$(EtOH) 241, ε 17 000 – 20 000). The mass spectrum of stigmast-4-en-3-one and that of cholest-4-en-3-one [34] showed close similarities.

*Fraction 6* (1.52 g) was recrystallized from ethanol. The crystalline material was shown by TLC to consist of stigmast-4-en-3-one.

The rest of this fraction was a very complex mixture of alcohols of which the following could be identified by TLC and GLC (1 % E 301): pimarol, isopimarol, abietol, and copaborneol.

*Fraction 7* (2.47 g) was recrystallized from ethanol. The crystalline material was analysed by TLC and GLC after silylation and found to consist of β-sitosterol (94 %) and campesterol (6 %).

*Fractions 8* (1.24 g) and *10* (2.31 g) were not investigated.

*Fraction 9* (1.91 g) was absorbed on silica. Ether eluted four fractions 9.1 – 9.4 of which only one (9.2) was investigated. This fraction (850 mg) was further fractionated by preparative TLC (silica gel, 2 % MeOH in $CHCl_3$). Two fractions were isolated. The first ($R_F$ 0.2, 233 mg) was recrystallized from absolute ethanol and gave a crystalline mixture, m.p. 186 – 190°. GLC (1 % XE 60, 250°) of this mixture showed three main components, and spectral data (IR, NMR) indicated the presence of hydroxyl, methoxyl and angular methyl groups. GLC and MS data indicate that this mixture consists of triterpenes. Due to shortage of material these compounds have not been further investigated.

## Acidic fraction

The acidic fraction was shown by TLC to contain fatty acids, resin acids, and phenolic waxes. When the acidic fraction was dissolved in acetone and left overnight, fatty acids

precipitated. The acids were analysed as methyl esters by GLC (5 % BDS, 205°). Identifications were made by comparison of retention data with those of authentic samples. It was a complex mixture of saturated n-aliphatic ($C_{10}-C_{28}$) and branched acids. Behenic acid dominated (66 %). Other major acids were: $C_{20}$, 7 %; $C_{24}$, 20 %; $C_{26}$, 2 %. The percentage of the other acids was of the order 1 or less. The rest of the acidic part was treated with cyclohexylamine in acetone to precipitate the resin acids. The acid-amine complex was liberated with a saturated solution of boric acid in water. The resin acids were analysed as methyl esters by TLC [35] on silver nitrate impregnated silica (benzene as eluent) and by GLC (1 % XE 60, 180°). The following resin acids were detected: pimaric (5 %), isopimaric (5 %), levopimaric/palustric (8 %), dehydroabietic (58 %), abietic (9 %), and neoabietic acid (15 %).

Chromatography of the acid fraction after precipitation of resin acids yielded a waxy fraction isolated in large amounts (about 0.18 % of total dry bark). The fraction exhibited spectroscopic properties similar to a ferulic ester fraction described by Rowe *et al.*[11] Saponification of the fraction gave ferulic acid and a mixture of fatty alcohols ($C_{13}-C_{22}$) which were analysed by GLC.

*Isolation of waxes, free fatty alcohols, sterols, and terpenoid alcohols.* By chromatography of the crude neutral fraction (2.0 g) a wax fraction (0.8 g) was isolated. The waxes were saponified. The acidic part of the hydrolysate consisted of a mixture of fatty acids with a composition similar to that of the free fatty acids. The neutral part of the waxes consisted of β-sitosterol, campesterol, and fatty alcohols in proportions similar to that of the total free and esterified alcohol part. Free β-sitosterol, campesterol, fatty alcohols, and terpenoid alcohols were also obtained.

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