

Investigations on Tall Oil of Southern Pine Wood

Part 2: Tall Oil Pitch

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Abstract. The residue from tall oil distillation, known as tall oil pitch (TOP), was investigated by GC/MS analysis. Several separation techniques such as preparative TLC and extractions from solutions of different pH were applied. Apart from about 4 % distilled free acids (fatty and diterpenoid) and 5 % steroids (sitosterol and sitostadiene) two new fatty acids C-26 and C-28 could be detected. About 1 % of lignin like material could be isolated after continuous extraction with chloroform.

Introduction

The composition of tall oil pitch (TOP) has not been studied intensively so far. Holmbom and Erä (1978) have investigated the compositions of different TOPs mainly with respect to the presence of free and esterified acids and unsaponifiables like higher alcohols and sterols.

In this work TOP was investigated to obtain more information on the possible reaction products in tall oil, which originated from the distillation process. As lignin degradation products were found to be present in the distilled and fractionated tall oil fatty acids (Traitler, Kratzl, 1979), lignin material should also be present in raw tall oil and – after distillation – in the residue TOP.

Results and Discussion

In the first experiment TOP was distilled under reduced pressure (ca. 0.1 pascal) at 155 °C, when ca. 4 % of distillable material was isolated. The distillate was methylated

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Table 1. Composition of the distillate of TOP

Compound	Retention time	% Amount of distillate
Methylhexadecanoate	18.0	1.2
Methyloctadecanoate	20.8	5.3
Methylpimarate	23.4	3.1
Methylisopimarate	23.6	9.9
Methyldehydroabietate	24.1	35.2
Methylabietate	25.1	35.0
Methyl diterpenoate	26.0	2.1

and subsequently submitted to GC/MS analysis and found to consist of fatty and diterpenoid acids (mainly dehydroabietic and abietic acid). Table 1 gives a list of the identified substances in this fraction.

TOP was only partly soluble in chloroform and after filtration the dark brown insoluble residue was continuously extracted in a Soxhlet extractor for 15 hours. The elemental analysis of the dried residue showed an amount of methoxyl groups of 7.84% compared to 14.28% methoxyl in kraft lignin, indicating a demethoxylated lignin material.

Other methods were tried to obtain a satisfactory fractionation of TOP especially with regard to the required identification by means of gas chromatography and mass spectroscopy. Steam distillation gave only a very small amount of distillate which was rather similar to that obtained by distillation in vacuum.

A mixture of an aqueous solution of NaHCO_3 and TOP was extracted with benzene. The aqueous layer yielded only 0.2% extractable material after acidification. The benzene extract, which was practically all the total pitch, was evaporated to dryness and after dissolving in methanol, it was reacted with an ethereal solution of diazomethane. After evaporation of all solvents only part of the mixture could be dissolved in ether. The other part was totally soluble in chloroform. The ethereal solution could be analyzed by GC/MS whereas the chloroform solution could not be separated by gas chromatography, probably due to high molecular weight substances.

A similar treatment of TOP was carried out with an aqueous solution of KOH followed by an extraction with benzene. The water fraction, after acidification, yielded ca.14% solid material, which was treated in the same way as before. Table 2 gives a list of compounds of KOH-soluble substances which could be identified by GC/MS analysis.

Also found was 7-oxo-dehydroabietic acid which seems to be an oxidation product formed during the fractionation processes (Enoki, 1975). The mass spectrum of the methylated compound (Fig. 1) shows a similar fragmentation pattern like methyl dehydroabietate.

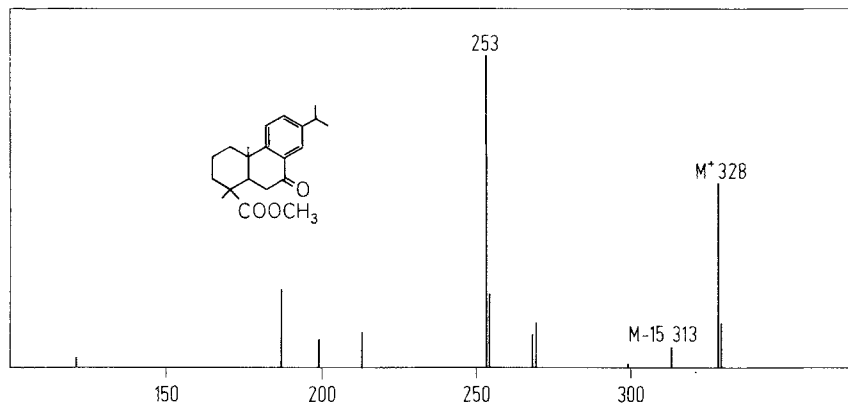
The benzene fraction, after methylation, also gave ether- and chloroform-soluble portions; the latter could not be successfully separated by gas chromatography. On the whole it appears that the separate fractions of the bicarbonate-extractions and the

Table 2. Composition of KOH-soluble fraction of TOP

Compound	Retention time	% Amount of distillate
Methylhexadecanoate	15.2	2.7
Methylheptadecanoate*	16.9	0.3
Methyloctadecadienoate	18.6	7.9
Methyloctadecadienoate (isomer)	18.8	11.0
Methyloctadecanoate	18.9	2.8
Methyloctadecanoate	19.3	0.6
Methylditerpenoate	20.3	2.0
Methylnonadecanoate	21.8	0.7
Methylditerpenoate	22.1	0.9
Methylditerpenoate	22.6	2.9
Methyldehydroditerpenoate	22.7	6.5
Methyldehydroditerpenoate	23.2	18.0
Methylditerpenoate	24.2	17.1
Methyldehydroditerpenoate	25.2	1.1
Oxo-methyldehydroabietate	27.1	(see Fig. 1) 2.5
β -Sitostadiene	40.5	6.9
β -Sitosterol	50.4	7.3

* Probably an artifact of the distillation process. The detection sensitivities of the two different analyses are due to different spectroscopical systems which have been more advanced in the latter case (Varian CH 7 and Varian 311 A)

KOH-extractions are of similar constitution but with varying concentrations of the different components. The ether soluble portion of the benzene fraction of the KOH-extraction was separated by preparative thin layer chromatography (TLC). To obtain an optimum separation analytical plates (Merck, silica-gel on glass; 0.25 mm layer) were used. A mixture of chloroform/methanol (9 : 1) was applied as solvent. To visualize

**Fig. 1.** Mass spectrum of 7-oxo-methyldehydroabietate

the single components, the plates were sprayed with water. The separated zones were removed from the plates and eluated with methylene chloride/methanol (1 : 1); the separate fractions could be identified by mass spectroscopy. High resolution mass spectroscopy is an excellent technique for accurate characterisation of single substances. By means of the "peak-matching" method it was possible to obtain the exact molecular weight (\mp a few millimasses) and via the molecular weight also the most probable formula of a compound. The measurements were carried out on a Varian SM 1 (Mattauch-Herzog geometry) and on a Varian MAT 311 A (Inverse Nier-Johnson geometry). The signals (peaks) of the unknown and of a known ion of exactly defined mass are alternately projected on the screen of an oscilloscope and are visible at the same time. The acceleration potential of one ion can then be changed with a potentiometer until both of the peaks appear at the same position. When this is achieved, the deflection radii are equal. At a constant field H the equation $m_1 : m_2 = U_2 : U_1$ is valid for single charged ions. Perfluoro kerosene (PFK) was used as a standard, because it has a large number of well defined known fragment ions in almost every needed mass region.

Apart from β -sitosterol (MW 414.3862; based on ^{12}C isotope) there were two substances with molecular weights of around 396. Compound one with MW 396.3737 (due to β -sitostadiene) and compound two with MW 396.3946 due to a C-26 saturated fatty acid. Another compound with MW 424.4240 was found to be a C-28 saturated fatty acid (ca. 0.1 %).

Saponification of TOP by a modified Sandermann process (1940) with methanolic KOH for 15 hours, extraction with benzene and fractional crystallisation yielded 5 % of pure β -sitosterol apart from other products like the above mentioned C-26 saturated fatty acid (ca. 1 %).

Depending on the reaction conditions of saponification this number probably may vary to a great extent. The two acids could not be detected via gas chromatography.

Experimental

Distillation of TOP: 33 g TOP were distilled under reduced pressure (ca. 0.1 pascal) in a "Kugelrohr" distillation at a temperature of 155°C for 7 hours to yield 1.32 g (4 %) yellow, resinous material. The whole distillate was methylated with freshly prepared diazomethane and analyzed by GC/MS. See Table 1. The GC conditions were: 100°C , $6^\circ/\text{min.}$; 20 m SE-30 glass capillary column, Carlo Erba Fractovap 2300.

Extraction of TOP with chloroform: TOP (60 g) was mixed with chloroform (ca. 100 ml) and the insoluble material removed. The solid residue was extracted in a Soxhlet apparatus with chloroform for 15 hours and then dried over P_2O_5 and silica gel, to yield 0.5 g (0.8 %) of a brown, crystalline substance. The elemental analysis gave the following data:

	Residue	Corrected for ash	Kraft lignin
C	50.19	62.01	65.95
H	4.38	5.41	5.42
O	24.20	29.90	24.39
S	1.85	2.29	1.39
N	0.32	0.40	—
OCH ₃	7.84	9.69	14.28
ash	26.45	—	—

Extraction of TOP with aqueous NaHCO₃: A mixture of TOP (10 g) and saturated aqueous solution of NaHCO₃ (200 ml) was heated to ca. 70 °C and stirred for 30 minutes. After cooling, the mixture was extracted with benzene and solid NaCl added to separate the emulsion formed. The water layer was acidified with 6N HCl and the precipitate filtered, washed with little 6N HCl and then with water. After drying, the yield was 20 mg of solid product. The benzene layer was evaporated to dryness and after reaction with diazomethane mixed with ether to form an ether-soluble material with the remainder totally soluble in chloroform.

Extraction of TOP with aqueous KOH: A mixture of 10 g TOP and a 10 % aqueous KOH-solution (300 ml) was treated the same way as above to yield ca. 14 % of solid product. Methylation of the benzene layer also gave ether- and chloroform-soluble portions. Table 2.

Isolation of β -sitosterol from TOP: TOP (100 g) and a solution of KOH (25 g) in methanol (175 ml) were refluxed for ca. 15 hours. After cooling the mixture, water (100 ml) was added, followed by extraction with three 150 ml portions of benzene. Emulsification was avoided by gentle shaking. The combined organic layers were dried over Na₂SO₄ and the solvent was totally evaporated. The oily, semi-crystalline and slightly tan coloured residue was mixed with a mixture of methanol and methylene chloride (1 : 1, ca. 50 ml), heated and cooled slowly. Repeated fractional crystallisation yielded 5.2 g pure β -sitosterol, mp. 136–7 °C. Another compound which could be isolated from the crude benzene fraction was 1.1 g C-26 saturated fatty acid, mp. 73–4 °C.

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