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DISTRIBUTION OF HIGH FATTY ACIDS IN THE CROSS SECTION OF THE OAK TRUNK (*QUERCUS ROBUR* L.)

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ABSTRACT

High fatty acids were determined in the cross section of the trunk of common oak (*Quercus robur* L.) Gas chromatography was used to determine the content of high fatty acids in a hexane extract of sapwood, heartwood and wood close to the pith regions at three heights of the trunk. The content of hexane soluble substances in the sapwood zone as well as in heartwood zone does not differ significantly along the trunk. There is about 40% higher content of free fatty acids in the wood close to the pith regions than in the heartwood zone and more than two times higher than in the sapwood zone. There are more acids determined as total acids in the sapwood zone than in the heartwood zone and wood close to the pith.

KEY WORDS: sapwood, heartwood, hexane extract, free high fatty acids, total high fatty acids

INTRODUCTION

Heartwood has been the subject of numerous studies, as it is known to be harder and accounting for a greater share in wood material. Distribution of the extractives in the wood of the (*Quercus petraea* L.) oak trunk in its cross section was also investigated by Krutul and Sacharczuk (1997). Oak wood close to the pith features a higher percentage of the extractives soluble in an alcohol-benzene mixture as compared with the wood of the outer layer of the tree. Gao et al. (1995) identified non-volatile lipid substances isolated from the extracts of the sapwood and heartwood of pine. It follows from the data obtained that the sapwood contains five times less of the acetone extractives as compared with the heartwood region. The major fatty acids occurring in the extract studied are: oleic, linoleic, linolenic, and palmitic acids. In the sapwood the four mentioned acids account for an 85% of total fatty acids, and in the heartwood, for a 65%. In the studies on oak wood extracts the most interest was given to the content and composition of the tannins present, as they occur in the wood in the largest amount and moreover they highly affect wood properties.

The type and content of extractives in wood are very important from the viewpoint of wood processing in pulp and paper industry, which process significant amount of hardwood, including oak wood. Wandelt et al. (1976) state that, the oak wood is of the highest importance among hardwood species intended for management.

The extractives have an influence on the pulp colour and sometimes cause liquors foaming (McMillin 1969, Łapiński and Kikiewicz 1971).

Properties of fatty acids in the wood are very important in cellulose industry. According to Brandal and Lindheim (1966) long hydrocarbon chain extractives decrease the mechanical strength of pulp, as they block reactive groups on the surface of the fibres. Additionally, it was discovered that high content of fatty acids involve difficulty in glueing of lime and birch wood (Proszyk and Przybylak 1986).

The oak wood increase material resources in pulp and paper industry and has a significant meaning in wood recycling.

In the case of raw source, which properties connected with the kind and quantity of extractives differ significantly from typical, there may be neccesity of technological process adaptation to other reqirements.

No data are available in the literature on the extracts with non-polar solvents and on the contents of extractives distribution along the trunk.

The purpose of this work is to examine the distribution of high fatty acids along the trunk as well as over the cross-section of the trunk.

MATERIAL AND METHODS

Three about 80-year-old (*Quercus robur* L.) oak trunks were obtained from the Mazovia-Podlasie region. Habitat conditions: brown, loamy soil of class I, stocking density 1.3, tree stand composed of pine, spruce and oak. Three ca. 50 mm thick disks were cut off from each of the trunks at their butt (0.1 m), height of 20.0 m and 23.0. Samples of individual heartwood or sapwood and wood close to the pith were obtained from particular disks. The samples were then ground and the fraction passing 1.0-mm and remaining on 0.49 mm mesh sieve was taken for analysis (Prosiński 1984).

The extractives content was determined using a Soxhlet apparatus (7 h) with hexane as a solvent. The extract was evaporated using a rotary vacuum evaporator. The total fatty acid content in the hexane extracts was determined by GC-MS (gas chromatography - mass spectrometry) as their methyl esters. A HP model 5890 series II chromatograph was used, equipped with a flame-ionization detector and a capillary column, with a BPX 70 cyanopropyl polar phase. Tridecanoic acid was used as internal standard. Column size: 50 m x 0.25 mm , sample injection at a 50:1 split ratio. Conditions of the GC analysis: helium flow at a pressure of 200 kPa, flow rate of the detector-flame feeding gases: hydrogen, 25 $cm^3.min^{-1}$; air, 300 $cm^3.min^{-1}$; programmed column heating over 140°C for 1 min, then 1.5°C.min^{-1} to 210°C for 15 min.

The free fatty acid content was determined without their previous esterification. The HP 1 capillary column containing polymethylsilicone phase was used. Separation conditions: helium flow through the column at a pressure of 75 kPa, flow rate of the detector-flame feeding gases: H_2, 25 $cm^3.min^{-1}$; air, 300 $cm^3.min^{-1}$, programmed heating of the column over 180°C for 5 min, then 4°C.min^{-1} to 240°C for 10 min.

RESULTS AND DISCUSSION

The oak wood used in the study had an average density ranging from 0.592 to 0.797 $g.cm^{-3}$, which is situated within the range typical of this species (Fig. 1). Presented results are the average of all of the three tested oak trunks.

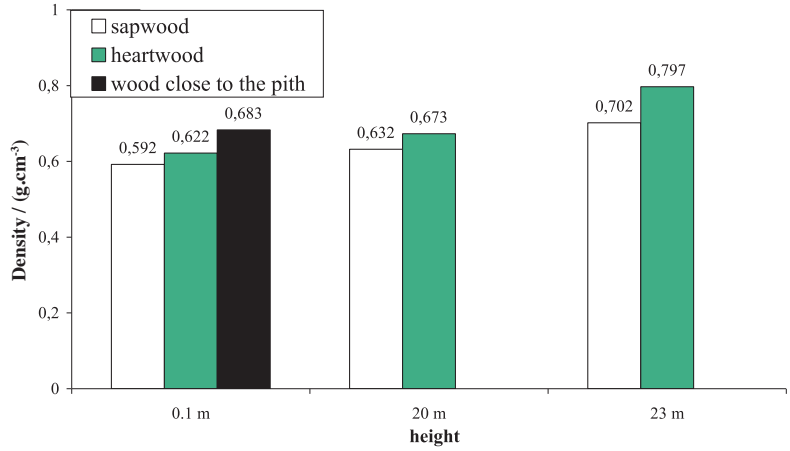

Fig.1: Average wood density

There is slightly higher content of hexane soluble substances in heartwood zone than in the sapwood, as this is shown on the Fig. 2. The content of hexane soluble substances may be connected with wood density, as it follows from Figs. 1 and 2.

It should be emphasized that the content of the extractives determined in the alcohol-benzene (1:1) extract in oak wood is nearly ten times higher than in the case of a non-polar solvent, like hexane. When an alcohol-benzene mixture was used in the extraction of oak wood, significant differences were observed in the content of these substances along the trunks, as well as their several times greater quantity in the heartwood, compared with the sapwood (Krutul and Buzak 1986, Krutul and Sacharczuk 1997, Krutul 1997).

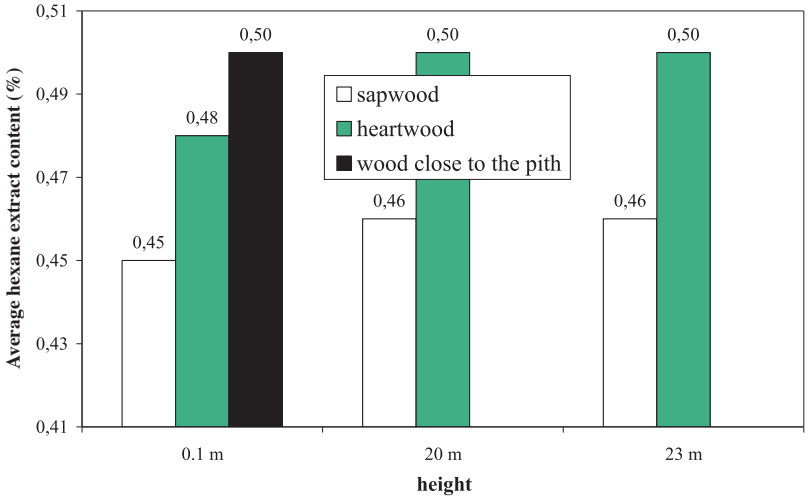

Fig. 2: Hexane extract content relative to the mass of dry wood for oak wood

The content of hexane-soluble substances, both in the sapwood and heartwood, remains unchanged along the trunks. To confirm that there is no influence of trunk height on the free fatty acids content in the heartwood zone, the following hypothesis was verified H_0: $\bar{x}_1 = \bar{x}_2 = \bar{x}_3$ against the alternative hypothesis H_1: $\bar{x}_1 \neq \bar{x}_2 \neq \bar{x}_3$ $\bar{x}_1$ is the average content of free fatty acids in samples taken from the first population (the lowest height), $\bar{x}_2$ - the second population (the middle height), $\bar{x}_3$ - the third population (the highest height). The results of calculations are: $\bar{x}_1 = 0.338$; $\bar{x}_2 = 0.342$; $\bar{x}_3 = 0.345$; $\bar{x} = 0.342$, where $\bar{x}$ is the mean value of average contents at all heights of the trunk. Following parameters was calculated: the value of random variable

$$F = \frac{\frac{Q_G}{k-1}}{\frac{Q_R}{n-k}} = 9.11 \times 10^{-3} \tag{1}$$

(where k is the number of populations, n is the number of all samples taken from three populations), the value of sum square

$$Q_G = \sum_{i}^{k} \left(\bar{x}_i - \bar{\bar{x}}\right)^2 n_i = 7.08 \times 10^{-4} \tag{2}$$

(where n_i is the size of i-th sample) and the value of residual sum square

$$Q_R = \sum_{i=1}^{k} \sum_{j=1}^{n_i} \left(x_{ij} - \bar{x}_i\right)^2 = 0.932 \tag{3}$$

(where x_{ij} is the sample from i-th group of j-th number).

Statistical F value with the significance level $\alpha = 0.05$ taken from tables (Krysicki et al., 1999) amounts to $F(1\text{-}\alpha, k\text{-}1, n\text{-}k) = F(0.95, 2, 24) = 3.40$. The set $\langle F(1\text{-}\alpha, k\text{-}1, n\text{-}k, +\infty)$ is the critical region.

Calculated value of F does not belong to the critical region so there is no reason, with a significant level $\alpha = 0.05$, to reject the H_0 hypothesis and accept H_1 hypothesis. Therefore the content of free fatty acids in the heartwood zone does not depend on the sampling along the trunk. Statistical values for free fatty acids in the sapwood zone are equal to: $\bar{x}_1 = 0.190$; $\bar{x}_2 = 0.191$; $\bar{x}_3 = 0.193$; $\bar{x} = 0.192$, $Q_R = 4.80 \times 10^{-5}$, $Q_G = 5.00 \times 10^{-6}$), $F = 1{,}25$.

Values of the corresponding parameters for total fatty acids in the heartwood zone are equal to: $\bar{x}_1 = 0.779$; $\bar{x}_2 = 0.782$; $\bar{x}_3 = 0.782$; $\bar{x} = 0.781$, $Q_R = 4.37 \times 10^{-4}$, $Q_G = 6.00 \times 10^{-6}$, $F = 0.160$.

Values of the corresponding parameters for total fatty acids in the sapwood zone are equal to: $\bar{x}_1 = 1.77$; $\bar{x}_2 = 1.78$; $\bar{x}_3 = 1.76$; $\bar{x} = 1.77$, $Q_R = 11.7 \times 10^{-3}$, $Q_G = 10.7 \times 10^{-4}$, $F = 1.10$.

Basing on the presented data, F does not belong to the critical region, so the statement is justified that with the significance level $\alpha = 0.05$ the content of free and total fatty acids in the sapwood as well as in the heartwood zone does not depend on the sampling along the trunk. Then it was assumed that mean content of free and total fatty acids in samples of sapwood, heartwood and wood close to the pith is equal for all heights of the trunk.

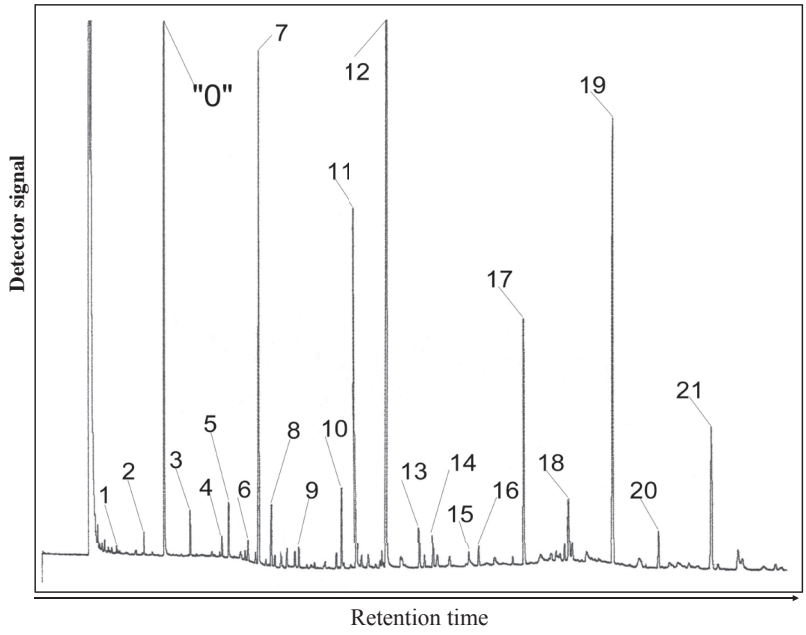

Fig. 3: A gas chromatogram of a sample of fatty acids as their methyl esters and tridecanoic acid as an internal standard "0". For peak identification see Tab. 1

Tab. 1: Fatty acids corresponding to individual chromatographic peaks on the chromatogram shown in Fig. 3

Peak no.	Acid [1]		Peak no.	Acid [1]	
1	Capric	10:0	12	Linoleic	18:2
2	Lauric	12:0	13	Linolenic	18:3
3	Myristic	14:0	14	Arachidic	20:0
4	Tetradecenoic	14:1	15	Eicosenoic	20:1
5	Pentadecenoic	15:0	16	Eicosadienoic	20:2
6	Pentadecenoic	15:1	17	Behenic	22:0
7	Palmitic	16:0	18	Tricosanoic	23:0
8	Palmitoleic	16:1	19	Lignoceric	24:0
9	Margaric	17:0	20	Pentacosanoic	25:0
10	Stearic	18:0	21	Cerotic	26:0
11	Oleic	18:1			

[1] with the number of carbon atoms and degree of unsaturation

In Fig. 3 is shown a chromatogram where the peak marked "0" corresponds to tridecanoic acid (C13) added to the sample as an internal standard. Gathered in Table 1 are the data related to the peaks corresponding to the fatty acids present in the sample. Free fatty acids were determined by gas chromatography in hexane extracts from the wood of the sap- and heartwood zones and close to the pith.

The results obtained for the high fatty acid content in the sapwood and heartwood and in the wood close to the pith regions are gathered in Tab. 2. The wood close to the pith features the highest free fatty acid content (468 mg.kg^{-1}), which are by ca. 40% higher in relation to the heartwood region and over twice that in the sapwood region. In the wood close to the pith the content of free fatty acids, which are palmitic, linoleic and lignoceric acids, is 33% higher as compared with heartwood and over three times higher than in the sapwood region. Free linoleic acid in the wood close to the pith region amounts to 186 mg.kg^{-1}, 60% more as compared with the heartwood region and over four times more than in the sapwood region. Likewise, in that region of the wood palmitic and lignoceric acids occur in higher amounts, notably by 27% and 18%, respectively, relative to the heartwood and three times and over twice the figures with respect to the sapwood region. In the case of other free fatty acids, these are in great amount in the wood close to the pith relative to the heartwood and sapwood regions (Tab. 2). In oak wood the following: palmitoleic, stearic, oleic, linolenic, behenic and cerotic acids occur in lesser quantities. Other acids in oak wood are present in trace amounts.

Tab. 2: Free fatty acids in oak sap-, heartwood and wood close to the pith in mg.kg^{-1} dry wood; D(x) – mean standard deviation

Acid [1)]		Acid content in sapwood		Acid content in heartwood		Acid content in wood close to the pith (butt section)	
		Average [mg.kg^{-1}]	D(x) [mg.kg^{-1}]	Average [mg.kg^{-1}]	D(x) [mg.kg^{-1}]	Average [mg.kg^{-1}]	D(x) [mg.kg^{-1}]
Lauric	12:0	3.2	0.4	2.6	0.5	4	0.2
Myristic	14:0	4.8	0.4	6.3	0.4	5.9	0.3
Pentadecanoic	15:0	4.2	0.3	3.6	0.5	5	0.3
Palmitic	16:0	26.1	0.9	61.2	2.8	78.2	1.2
Palmitoleic	16:1	20.4	0.8	14	1.5	22.1	1.2
Margaric	17:0	2.4	0.2	2.4	0.2	4	0.4
Stearic	18:0	12.1	0.3	12.2	0.3	14.5	0.7
Oleic	18:1	21.3	0.6	29.7	2.7	38	4
Linoleic	18:2	44.6	0.8	116.5	2.5	185.8	2.6
Arachidic	20:0	3.4	0.3	6.3	0.4	7	0.5
Behenic	22:0	16.3	0.4	30.4	0.9	35	3
Lignoceric	24:0	24.0	1.2	46.4	1.4	55	4
Pentacosanoic	25:0	3.9	0.2	4.1	0.3	5.1	0.4
Cerotic	26:0	5.0	0.2	6.2	0.2	8.1	0.5
Total acids:		192		342		468	

[1)] with the number of carbon atoms and degree of unsaturation

The total fatty acids content in oak wood in the heartwood and wood close to the pith regions is in practice the same, as it is shown in the Tab. 3. In the sapwood region the acids prevail by ca. 2.5 times relative to the heartwood and wood close to the pith regions. Linoleic acid is present in the highest amount of all the acids determined. In the sapwood it accounts for 1079 mg.kg^{-1}, in the heartwood for 312 mg.kg^{-1} and in the wood close to the pith region, for 287 mg.kg^{-1}. This corresponds to 61, 40 and 37%, respectively, of the total fatty acids present. Hafizoglu and Holmbom (1995) report that of the total fatty acids occurring in the Caucasian fir (*Abies nordmanniana*) wood linoleic acid is in the highest quantity. In the heartwood free linoleic acid content accounts for ca. 50% of total amount of that acid, whereas in the sapwood this acid occurs primarily in a bounded form. Also in the sapwood palmitic acid content is higher relative to the heartwood and the wood close to the pith regions by ca. 63% (Tab. 3).

Tab. 3: Total fatty acids in the sap-, heartwood and wood close to the pith of oak wood in mg.kg^{-1} dry wood; D(x) – mean standard deviation

Acid [1)]		Acid content in sapwood		Acid content in heart wood		Acid content in wood close to the pith (butt section)	
		Average [mg.kg^{-1}]	D(x) [mg.kg^{-1}]	Average [mg.kg^{-1}]	D(x) [mg.kg^{-1}]	Average [mg.kg^{-1}]	D(x) [mg.kg^{-1}]
Capric	10:0	6.1	0.7	4.1	0.7	4.1	0.5
Lauric	12:0	7.1	0.9	5.0	0.6	4.0	0.3
Myristic	14:0	15.4	1.0	11.9	1.0	9.2	0.5
Tetradecenoic	14:1	8.9	0.6	8.1	0.4	8.1	0.5
Pentadecanoic	15:0	10.4	1.1	5.2	0.4	6.1	0.6
Pentadecenoic	15:1	8.3	0.7	5.1	0.6	3.9	0.4
Palmitic	16:0	262.0	3.0	95.7	2.1	99.0	5.0
Palmitoleic	16:1	53.4	1.9	16.8	1.3	25.0	3.0
Margaric	17:0	14.3	1.0	5.2	0.6	6.0	0.5
Stearic	18:0	19.1	1.0	14.4	0.5	15.2	0.6
Oleic	18:1	34.0	1.5	48.1	0.9	45.6	2.7
Linoleic	18:2	1079.0	5.0	312.0	5.0	287.0	3.0
Linolenic	18:3	152.0	3.0	22.4	1.3	28.1	0.5
Arachidic	20:0	7.3	0.7	7.3	0.7	7.0	0.5
Eicosenoic	20:1	1.5	0.3	2.2	0.5	2.1	0.3
Eicosadienoic	20:2	7.4	0.8	4.0	0.5	5.0	0.6
Behenic	22:0	27.1	2.6	42.6	1.4	43.4	2.7
Tricosanic	23:0	18.3	0.8	9.1	0.7	10.0	0.9
Lignoceric	24:0	26.4	2.9	112.6	1.4	111.0	7.0
Pentacosanoic	25:0	4.5	0.4	7.1	0.8	9.1	0.7
Cerotic	26:0	6.2	0.5	42.3	1.2	40.5	1.1
Total acids:		1769		781		769	

[1)] with the number of carbon atoms and degree of unsaturation

More free fatty acids in the wood close to the pith as compared with the heartwood is a consequence of transformation of bounded fatty acids into free fatty acids. This may result from natural secondary processes occurring in the heartwood following the formation process.

CONCLUSION

1. The wood close to the pith characteristically contains by ca. 40% more free fatty acids relative to the heartwood and by over twice their content compared with the sapwood.
2. Of the free fatty acids present in wood: palmitic, linoleic and lignoceric acids are the major ones. In the wood close to the pith there are 33% more of these acids as compared with the heartwood and over three times more than in the sapwood.
3. Total fatty acids present in the sapwood account for more than by ca. 2.5 the amount in the wood close to the pith and heartwood regions. The content of these acids in the wood close to the pith and heartwood is essentially the same.
4. As the dependence of the fatty acids content on the trunk height was found not to be statistically significant, the height from which sample was taken for the analysis can be ignored.

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