CHEMICAL COMPOSITION OF LIPOPHILIC EXTRACTIVES FROM NON-WOOD FIBERS USED FOR MANUFACTURING HIGH QUALITY PAPER PULPS

Ana Gutiérrez, Isabel M. Rodríguez and José C. del Río
Instituto de Recursos Naturales y Agrobiología de Sevilla, CSIC, P.O. Box 1052, E-41080-Seville, Spain

ABSTRACT. The chemical composition of lipophilic extractives from fibers of three annual plants, namely hemp (*Cannabis sativa*), flax (*Linum usitatissimum*) and kenaf (*Hibiscus cannabinus*) that are commonly used for high quality paper pulp production was studied. The cloroform soluble fractions of the acetone extracts of the fibers were analyzed by gas chromatography-mass spectrometry. The main compounds identified were series of *n*-alkanes, *n*-fatty acids, *n*-aldehydes, *n*-fatty alcohols and waxes. On the other hand, free and esterified sterols and triterpenols, steroid hydrocarbons, steroid and triterpenoid ketones, as well as sterol glycosides were also found in the fibers studied here.

I. INTRODUCTION

Consumption of wood is increasing worldwide as demand for paper in response to population and economic growth. Interest in alternative sources of fiber is increasing as concerns about the adequacy of future supplies of wood fibers are growing. One source of industrial fiber is agricultural crops, either in the form of residues or plants grown specifically for fiber. Flax, hemp, abaca, kenaf, jute and sisal are used in the manufacturing of high-quality pulps for specialty papers.

On the other hand, it is well known that lipophilic extractives present in raw materials cause significant technical and environmental problems in the pulp and paper industry. They form the so-called "pitch" deposits in circuits, equipment and final product, and are responsible for reduced production levels, higher operating costs and increased incidence of quality defects (1). Moreover, the increasing need for recirculating water in pulp mills is aggravating these problems. While many studies of the composition of lipids from several wood species have been published (2-5), little information regarding the lipophilic extractive composition of many of these non-wood fibers can be found in the literature (6,7). In the present study, we report the chemical composition of lipophilic extractives from fibers of the herbaceous annual plants hemp, flax and kenaf that are commonly used in paper pulp manufacture. The lipid extracts of the fibers were analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS).

II. EXPERIMENTAL

Samples. Fibers of flax (*Linum usitatissimum*), hemp (*Cannabis sativa*) and kenaf (*Hibiscus cannabinus*) were supplied by CELESA (Spain). The fibers contained about 20-25% of core fibers. The samples were milled using a knife mill, and Soxhlet extracted with acetone in for 8 h. The extracts were evaporated to dryness, and resuspended in chloroform for chromatographic analysis of the lipophilic fraction. When required, silylation with bis-(trimethylsilyl)trifluoroacetamide (BSTFA) was used.

GC and GC-MS. The GC analyses were performed in a Hewlett-Packard HP-5890 using a short fused silica capillary column (DB-5HT, J&W; 5 m x 0.25 mm, 0.1 μm film thickness). The oven was heated from 100°C (1 min) to 350°C (3 min) at 15°C/min. The injector (split-splitless) and detector (FID) temperatures were set at 300°C and 350°C respectively. The carrier gas was Helium and the injection was performed in splitless mode. The GC-MS analyses were performed on a Model GC 8000 Top gas chromatograph coupled to a quadrupole mass spectrometer detector (ThermoQuest Finnigan, Model Voyager) equipped with a fused silica capillary column (DB-5HT, J&W; 15 m x 0.25 mm, 0.1 μm film thickness). The oven was heated from 120°C (1 min) to 380°C (5 min) at 10°C/min. The injector and transfer line temperatures were set at 300°C and 350°C respectively. Helium was used as the carrier gas and the injection was performed in splitless mode. Peaks were quantified by area. Compounds were identified by comparing their mass spectra with mass spectra in the Wiley and Nist libraries, by mass fragmentography and, when possible, by comparison with standards.

III. RESULTS AND DISCUSSION

The lipophilic extracts from flax, hemp and kenaf fibers accounted for 1.8, 0.8 and 1%, respectively. The underivatized and silylated extracts were analyzed by GC and GC-MS using short and medium length high

temperature capillary columns, respectively, with thin films, according to the method previously described (8). This method enables the elution and analysis of high molecular weight lipids such as waxes, sterol esters and triglycerides. The relative percentages (based on GC peak areas) of the different classes of compounds identified in the three fibers are shown in **Figure 1**.

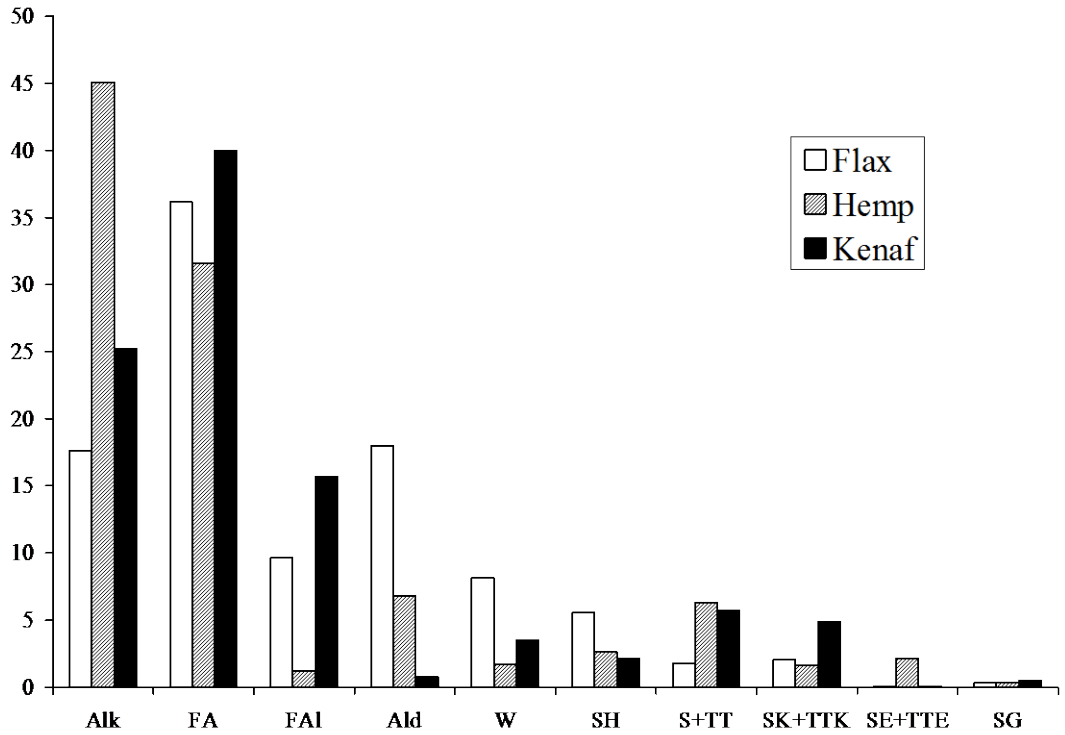

Fig. 1. Distribution (percentages) of the main classes of lipophilic extractives (alkanes, Alk; fatty acids, FA; fatty alcohols, FAl; aldehydes, Ald; waxes, W; steroid hydrocarbons, SH; sterols, S; triterpenols, TT; steroid ketones, SK; triterpenoid ketones, TTK; sterol esters, SE; triterpenol esters, TTE; and sterol glycosides, SG) found in flax, hemp and kenaf fibers.

The most predominant lipids in flax, hemp and kenaf fibers were series of long chain *n*-fatty acids (36, 32 and 40%, respectively) and *n*-alkanes (18, 45 and 25%, respectively). Significant amounts of series of *n*-aldehydes (18%) and *n*-fatty alcohols (16%) were found in flax and kenaf, respectively. Minor amounts of waxes, steroids and triterpenoids were also present in these fibers. No triglycerides were found in appreciable amounts in the samples studied here.

The identities of the main lipophilic compounds found in these fibers are summarized in **Table 1**. Fatty acids ranging from C_{14} to C_{32} were identified in all fibers. Palmitic acid (C_{16}) was the most abundant in flax and hemp fibers and together with linoleic acid ($C_{18:2}$) were the most predominant in kenaf fibers. Palmitic acid was also the major fatty acid found in the extract from several flax fibers by Morrison *et al.* (7). A series of *n*-alkanes (from C_{21} to C_{33}) were identified in all samples with strong odd carbon atom number predominance. Nonacosane (C_{29}) was the most abundant in flax and hemp fibers while hentriacontane (C_{31}) predominated in kenaf fibers. Hentriacontane was also the major alkane found in the bark extract from kenaf fibers by Seca *et al.* (6). *n*-Alkanes with even numbers of carbon atoms (C_{26}, C_{28} and C_{30}) were also identified albeit in lower amounts. *n*-Fatty alcohols ranging from C_{18} to C_{32} were present in all fiber extracts with strong even carbon atom predominance. Octacosanol (C_{28}) was the most abundant fatty alcohol in flax and kenaf. Similar amounts of triacontanol (C_{30}) and octacosanol were found in hemp. Octacosanol was also the major fatty alcohol found in the bark extracts from kenaf and flax fibers by Seca *et al.* (6) and Morrison *et al.*(7), respectively. A series of *n*-aldehydes ranging from C_{21} to C_{32} were identified in these fibers with strong even carbon atom predominance. Aldehydes were especially abundant in flax and hemp with octacosanal (C_{28}) and triacontanal (C_{30}) predominating in flax and hemp, respectively. Waxes (from C_{46} to C_{60}) were also identified in all fibers but were

especially abundant in flax. The waxes constituted a complex mixture and consisted of high molecular weight fatty acids (ranging from C_{16} to C_{30}) esterified to high molecular weight fatty alcohols (from C_{24} to C_{38}).

Table 1. Relative composition of the main compounds (percentages of GC peak areas) identified in the lipophilic extracts of flax, hemp and kenaf fibers.

	Flax	**Hemp**	**Kenaf**
***n*-Alkanes**	**18**	**45**	**25**
n-Heptacosane	3	4	<1
n-Nonacosane	11	34	2
n-Hentriacontane	1	4	19
Steroid hydrocarbons	**6**	**3**	**2**
Stigmasta-3,5,22-triene	1	1	1
Stigmasta-3,5-diene	4	1	<1
Fatty acids	**36**	**32**	**40**
Palmitic acid	14	16	13
Linoleic acid	2	6	14
Oleic acid	6	3	6
Stearic acid	6	3	2
***n*-Fatty alcohols**	**10**	**1**	**16**
n-Hexacosanol	2	<1	2
n-Octacosanol	4	<1	11
n-Triacontanol	1	<1	3
***n*-Aldehydes**	**18**	**7**	**1**
n-Octacosanal	8	2	<1
n-Triacontanal	4	3	<1
Sterols/ Triterpenols	**2**	**6**	**6**
Sitosterol	1	3	3
Motiol	0	0	<1
Glutinol	0	0	2
β-Amyrin + α-Amyrin	<1	2	<1
Steroid/ Triterpenoid Ketones	**2**	**2**	**5**
Stigmast-4-en-3-one	1	<1	2
β-Amyrenone + α-Amyrenone	<1	<1	<1
Waxes	**8**	**2**	**4**
Sterol /Triterpenol esters	**<1**	**2**	**<1**
Sitosterol esters	<1	<1	<1
Glutinol esters	0	0	<1
β-Amyrin + α-Amyrin esters	<1	2	<1
Sterol glycosides	**<1**	**<1**	**<1**
Campesteryl glucopyranoside	<1	<1	<1
Stigmasteryl glucopyranoside	<1	<1	<1
Sitosteryl glucopyranoside	<1	<1	<1

Among sterols, sitosterol predominated in both free and esterified form in all samples. Minor amounts of other free sterols, such as stigmastanol, stigmasterol and campesterol were also found in flax, hemp and kenaf. Triterpenols such as β- and α- amyrins were also present in both free and esterified form in the three fibers. In

contrast, two triterpenols namely glutinol and motiol were only identified in the kenaf fiber. The identification of these two triterpenols was made according to Seca *et al*. (6), who also identified them in kenaf fibers. On the other hand, several steroid hydrocarbons (such as stigmasta-3,5 diene, stigmasta-3,5,22-triene) and steroid and triterpenoid ketones (such as stigmast-4-en-3-one, stigmastan-3-one, stigmasta-7,22-dien-3-one and β- and α-amyrenones) were identified in these samples. Finally, several sterol glycosides, such as campesteryl, stigmasteryl and sitosteryl glucopyranosides were also identified in flax, hemp and kenaf fibers, although in very low amounts.

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