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GAS–LIQUID CHROMATOGRAPHY–MASS SPECTROMETRY STUDIES ON PINE KRAFT BLACK LIQUORS

III. THE LIBERATION OF CARBOXYLIC ACIDS IN THE INITIAL PHASE OF PULPING

KLAUS NIEMELÄ
Laboratory of Wood Chemistry, Helsinki University of Technology, SF-02150 Espoo (Finland)

SUMMARY

Pine-wood chips were treated with sodium hydroxide at a rather low temperature (40°C) and the products obtained in solution were analysed by capillary gas–liquid chromatography–mass spectrometry. In addition to fatty and resin acids, which were the main products, 22 hydroxy monocarboxylic, 18 dicarboxylic and 6 aromatic carboxylic acids were identified as their trimethylsilyl derivatives. Hydroxy monocarboxylic acids (0.09–0.16% of wood) were primarily carbohydrate degradation products, whereas the dicarboxylic acid fraction (0.07–0.10% of wood) was mainly composed of oxalic and C_5–C_{10} alkanedioic acids, which were obviously autoxidation products of fatty acids. Aromatic acids included benzoic acid and five lignin-related compounds, of which guaiacylglycolic and guaiacylglyceric acids had not been identified earlier after alkali treatment of softwood.

INTRODUCTION

Recent capillary gas–liquid chromatography–mass spectrometry (GLC–MS) studies have revealed the presence of about 100 carboxylic acids (excluding fatty and resin acids) in the spent liquors ("black liquors") from alkaline pulping of wood[1,2]. Most of these compounds are known as polysaccharide or lignin degradation products; however, the presence of certain hydroxy monocarboxylic and dicarboxylic acids has remained unexplained. To obtain further information on the formation of these compounds during the initial phase of alkaline pulping, pine-wood chips have been treated with alkali at a relatively low temperature.

EXPERIMENTAL

Alkaline treatments

Industrial pine-wood (*Pinus sylvestris*) chips (2–4 mm fraction) were carefully hand-sorted to remove knots, pieces of bark and other irregular materials. The early stages of alkaline pulping were simulated by treating samples of 30 g of these chips with 120 ml of 0.7 *M* sodium hydroxide in rotating autoclaves at 40°C for 40 and 80 min. The yields of wood residues were 97.2 and 95.5%, respectively.

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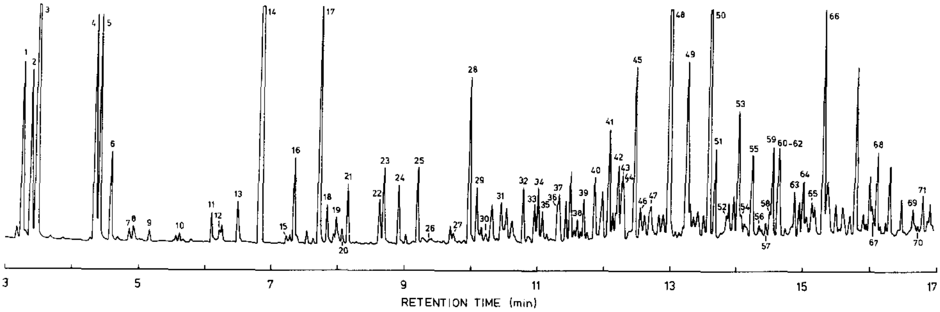

Fig. 1. Separation on an SE-54 fused-silica capillary column of the trimethylsilylated compounds obtained after sodium hydroxide treatment of pine chips at 40°C for 40 min. Carboxylic acids: 1, lactic; 2, hexanoic; 3, glycolic; 4, 2-hydroxybutanoic; 5, oxalic; 6, 3-hydroxypropanoic; 7, 3-hydroxybutanoic; 8, heptanoic; 10, malonic; 11, 4-hydroxybutanoic; 12, benzoic; 13, octanoic; 15, maleic; 16, succinic; 17, glyceric; 18, fumaric; 19, nonanoic; 20, *C*-methyltartronic; 21, 2-hydroxyheptanoic; 22, tartronic; 23, glutaric; 24, 3-deoxytetronic; 25, 2-deoxytetronic; 26, decanoic; 27, 2-deoxy-3-*C*-methyltetraric; 28, malic; 29, adipic; 30, 3,4-dideoxypentonic; 32, erythronic; 33, *C*-(hydroxymethyl)tartronic; 34, threonic; 35, 2,3-dideoxypentaric; 36, tartaric; 37, pimelic; 38, 4-hydroxybenzoic; 40, xyloisosaccharinic; 41, 3-deoxy-*erythro*-pentonic (+ unidentified); 43, 3-deoxy-*threo*-pentonic; 44, *C*-(2-hydroxyethyl)tartronic; 45, suberic; 46, 3,6-dideoxy-*ribo*-hexonic; 47, 3,6-dideoxy-*arabino*-hexonic; 49, vanillic; 50, azelic; 51, a pentonic; 53, citric; 54, myristic; 57, β-galactometasaccharinic; 58, α-galactometasaccharinic; 59, β-glucoisosaccharinic; 60, guaiacylglycolic; 61, α-glucoisosaccharinic; 62, sebacic; 68, palmitic; 69, ferulic; 70, guaiacylglyceric and 71, margarinic acids. Other compounds: 9, dodecamethylpentasiloxane (artifact); 14, glycerol; 31, vanillin; 39, a pentopyranose; 42, vanillyl alcohol; 48, arabinitol; 52, dihydroconiferyl alcohol; 55, pinitol; 56, guaiacylglycol; 63, 64, hexopyranoses; 65, coniferyl alcohol; 66, a hexitol; 67, guaiacylglycerol.

GLC

The conversion of non-volatile compounds into their per(trimethylsilyl) (TMS) derivatives was carried out as previously described[3], by using samples of 3 ml of the spent liquor. D-Xylitol (0.2 mg) was added as the internal standard. The separations were performed with a Model 5880 A gas chromatograph (Hewlett-Packard, Avondale, PA, U.S.A.) equipped with a flame ionization detector and an SE-54 fused-silica capillary column (25 m × 0.32 mm I.D.). The temperature programme was 3 min at 90°C, 10°C/min to 250°C and 15 min at 250°C. The temperature of both the injection port and the detector was 260°C. The carrier gas was hydrogen at 2 ml/min. Fig. 1 shows an example of the separation. It should be pointed out that resin acids, long-chain fatty acids and some other compounds are eluted later and are not shown in the chromatogram.

GLC-MS

The mass spectra were recorded[1] at 70 eV with a Model JMS-DX303 instrument (JEOL, Akishima, Japan) in combination with a Model 5790 A gas chromatograph (Hewlett-Packard) and the same column as above. Most of the compounds could be identified on the basis of previous studies[1,2]. The identities of alkanedioic acids could be confirmed by data presented recently by Herrmann *et al.*[4]. The identification of pinitol was based on the published[5] mass spectrum and retention index. The mass spectrum of the TMS derivative of guaiacylglycol differed slightly from that reported by Hattox and Murphy[6]: *m*/*z* 400 (M^+, 2%), 385 (4), 297 (benzylic ion,

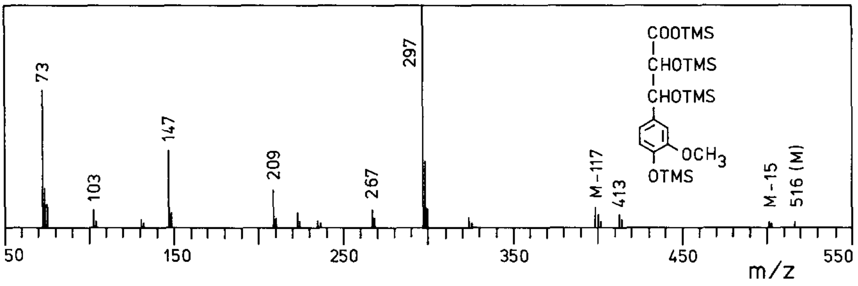

Fig. 2. Mass spectrum at 70 eV of the per(trimethylsilyl) (TMS) derivative of guaiacylglyceric acid.

100), 267 (5), 193 (3), 147 (14), 123 (3), 103 (5) and 73 (72). The mass spectrum of the TMS derivative of guaiacylglyceric acid is shown in Fig. 2.

RESULTS AND DISCUSSION

The total yield of the low-molecular-weight compounds which could be deter-

TABLE I

YIELDS OF HYDROXY MONOCARBOXYLIC ACIDS OBTAINED ON TREATMENT OF PINE CHIPS WITH SODIUM HYDROXIDE

The figures are given as mg/l in the liquor. + = Traces detected.

Carboxylic acid	*40 min*	*80 min*	*Found in black liquor**
Glycolic	70	81	Yes
Lactic	17	59	Yes
3-Hydroxypropanoic	10	10	Yes
2-Hydroxybutanoic	21	41	Yes
3-Hydroxybutanoic	2	3	Yes
4-Hydroxybutanoic	3	3	Yes
Glyceric	28	27	Yes
2-Hydroxyheptanoic	7	7	Yes
3-Deoxytetronic	8	9	Yes
2-Deoxytetronic	7	7	Yes
3,4-Dideoxypentonic	3	6	Yes
Erythronic	5	6	Yes
Threonic	5	5	No
Xyloisosaccharinic	8	19	Yes
3-Deoxy-*erythro*-pentonic	5	8	Yes
3-Deoxy-*threo*-pentonic	7	12	Yes
3,6-Dideoxy-*ribo*-hexonic	+	5	Yes
3,6-Dideoxy-*arabino*-hexonic	+	8	Yes
Galactometasaccharinic	+	4	Yes
β-Glucoisosaccharinic	9	24	Yes
α-Glucoisosaccharinic	6	13	Yes
Total amount (mg/l)	221	357	
(% of wood)	0.09	0.16	

* Pine kraft black liquor.

mined by GLC corresponded to 1–2% of the wood, of which fatty and resin acids constituted the major part. In addition, small amounts of miscellaneous compounds were identified. The main wood losses were, however, obviously caused by deacetylation of galactoglucomannans and dissolution of hemicelluloses[7].

Hydroxy monocarboxylic acids

Of the 22 hydroxy monocarboxylic acids identified (Table I), all, except threonic acid, had been found earlier in pine kraft black liquor[2]. The origins of 3-hydroxybutanoic[8] and 2-hydroxyheptanoic[9] acids remain unexplained, and further studies are thus necessary to clarify whether these acids originate from native wood constituents. The rest of the acids are known as carbohydrate degradation products.

It is known that, under oxidative alkaline conditions, large amounts of glycolic, glyceric, 3-hydroxypropanoic, 2-deoxytetronic and 3-deoxypentonic acids are formed from xylan[10,11] and glucomannans[12,13]. The relatively high concentrations of these acids after treatment for 40 min thus probably depends on the presence of oxygen in the autoclaves. On prolonged treatment, more lactic, 2-hydroxybutanoic, 3,4-dideoxypentonic and isosaccharinic acids were formed, which are characteristic products from non-oxidative alkaline degradation of polysaccharides[7]. 3,6-Dideoxyhexonic acids originate from rhamnose moieties present in xylan[14].

TABLE II

YIELDS OF DICARBOXYLIC ACIDS OBTAINED ON TREATMENT OF PINE CHIPS WITH SODIUM HYDROXIDE

The figures are given as mg/ml in the liquor. + = Traces detected.

Carboxylic acid	*40 min*	*80 min*	*Found in black liquor**
Oxalic	30	33	Yes
Malonic	+	2	Yes
Succinic	10	14	Yes
Glutaric	9	8	Yes
Adipic	8	6	No
Pimelic	8	8	No
Suberic	19	23	No
Azelaic	60	64	Yes
Sebacic	6	8	No
Maleic	+	+	No
Fumaric	4	5	Yes
Tartronic	6	13	Yes
C-Methyltartronic	+	2	Yes
C-(Hydroxymethyl)tartronic	4	3	Yes
C-(2-Hydroxyethyl)tartronic	4	4	Yes
Malic	15	19	Yes
2,3-Dideoxypentaric	3	7	Yes
2-Deoxy-3-*C*-methyltetraric	+	+	Yes
Total amount (mg/l)	186	219	
(% of wood)	0.07	0.10	

* Pine kraft black liquor.

Dicarboxylic acids

The length of the treatment time had surprisingly little effect on the concentrations of dicarboxylic acids (Table II), of which C_5–C_{10} alkanedioic acids are of special interest. Recently, glutaric and azelaic acids were identified[2] in pine kraft black liquor, but their origins could not be clarified. On the basis of the present results, it seems likely that the formation of these acids, together with their homologues, takes place at the beginning of pulping.

Most probably, these alkanedioic acids are autoxidation products of unsaturated fatty acids. Oleic and linoleic acids are the main fatty acids[15] of *Pinus sylvestris,* and it is well known[16–18] that azelaic acid is the main oxidation product of unsaturated C_{18} fatty acids. Various other dicarboxylic acids are formed as well, although in minor amounts. It is still unclear, however, whether the alkanedioic acids are formed mainly during the storage of the chips or during the treatment with alkali. Terashima *et al.*[19] obtained traces of azelaic acid from *Pinus densiflora* after seasoning for 5 years, and this compound was considered as an autoxidation product of oleic acid.

The presence of adipic, pimelic, suberic and sebacic acids in pine kraft black liquors has not yet been confirmed, but at least adipic and sebacic acids have been found[20] in tall oil. The rest of the dicarboxylic acids either originate from native wood constituents[21,22] (oxalic, succinic, fumaric and malic acids), or are products from polysaccharide degradation. Tartronic acid derivatives can be formed from xylan under oxidative conditions[23], and possible sources of 2,3-dideoxypentaric acid are pectic substances[24] or 4-*O*-methyl-D-glucuronic acid groups of xylan.

Aromatic carboxylic acids

Of the six aromatic acids identified (Table III), benzoic, 4-hydroxybenzoic and vanillic acids have previously been isolated[25,26] from softwood. Ferulic acid belongs to the widely distributed[27] class of cinnamic acid derivatives. The presence of traces of two α-hydroxy acids having a guaiacyl nucleus was surprising and their origins remain unclear.

TABLE III

YIELDS OF AROMATIC CARBOXYLIC ACIDS OBTAINED ON TREATMENT OF PINE CHIPS WITH SODIUM HYDROXIDE

The figures are given as mg/l in the liquor. + = Traces detected.

Carboxylic acid	*40 min*	*80 min*	*Found in black liquor**
Benzoic	+	+	Yes
4-Hydroxybenzoic	3	3	Yes
Vanillic	19	24	Yes
Ferulic	+	+	No
Guaiacylglycolic	3	3	No
Guaiacylglyceric	+	1	No
Total amount (mg/l)	25	31	

* Pine kraft black liquor.

Other compounds

Although this study mainly concentrated on the identification of carboxylic acids, various other compounds were also detected. Among these were vanillin, vanillyl alcohol, coniferyl alcohol, dihydroconiferyl alcohol, guaiacylglycol and guaiacylglycerol. The identification of small amounts of vanillin[25,26,28,29] and guaiacylglycerol[29–31] in softwood has repeatedly been reported, and dihydroconiferyl alcohol was recently detected[32] in *Pinus contorta*. Possibly all the guaiacyl compounds identified are native constituents of wood, even though their formation during the storage of the chips cannot be ruled out. The detection of arabinitol, pinitol and some other alcohols (which were not as yet identified) will be discussed in more detail elsewhere.

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