Minor Components in Tall Oil

I. Neutral Carbonyl Compounds

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In a short communication Erdtman and Westfelt [1] reported on the composition of the higher neutral terpenes from wood of Scots pine (*Pinus silvestris*). Among carbonyl compounds, they isolated dehydroabietinal, abietinal, pimarinal, and isopimarinal. Swedish tall light oil was also investigated, but none of the mentioned carbonyl compounds was found therein. Sandermann and Weissmann [2] examined tall light oil and found isopimarinal and fellandral.

In the course of our work on tall oil we have investigated the neutral carbonyl compounds in crude tall oil, tall oil distillate from continuous distillation of crude tall oil, and tall oil fatty acids (with low resin acid content) obtained by batch distillation of tall oil distillate.

By converting the carbonyl compounds to the corresponding alcohols and carboxylic acid methyl esters and comparing relative retention data with those obtained with known mixtures of alcohols and methyl esters we managed to identify pimarinal, isopimarinal, dehydroabietinal, abietinal, and a peak probably being palustrinal. The results were confirmed by mass spectrometric data * using a combined gas chromatograph/mass spectrometer (*cf.* Table 1). Apart from the mentioned compounds the samples contained some minor components. In the tall oil fatty acid sample three of these components by mass spectrometry were shown to have a molecular weight of 256. These smaller components were not identified in the present investigation.

Experimental. Gas chromatography and mass spectrometry. The gas chromatographic analyses were performed on a Perkin-Elmer Model 116 equipped with a hot wire detector. The column used was packed with 7 % Versamid 900 on Chromosorb W 60–80 mesh. This type of liquid phase has been used for gas chromatographic separation of resin acid methyl esters.[3] The authors operated it at 250°C but we found 220°C satisfactory for our purpose. A reason for us to choose this column packing was, except good separation capability, its low bleeding which made it suitable for use in gas chromatograph combined with mass spectrometer. The column packing was delivered to Dr. Ryhage, Karolinska Institutet, Stockholm, and used by him when carrying out the mass spectrometry analyses for us.

The order of elution on Versamid 900 at 220°C is: methyl pimarate/pimarinal/acetyl pimarinol = 1.00/1.05/1.42. The relative retention times for the resin acid methyl esters are (methyl pimarate 1.00): methyl palustrate, 1.17; methyl isopimarate, 1.27;

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Table 1. Gas chromatography of carbonyl compounds. Column: Versamid 900, temp: 220°C Carrier: Helium, 140 ml/min.

Compound	R1/P	MW	CTO	TOD	TOFA
	0.24		0.4	2.1	0.1
	0.29	256	0.7	6.5	0.4
	0.37			1.7	0.1
	0.43	256	1.1	13	0.4
	0.48				1.4
	0.55	256		4.5	1.7
	0.63			3.2	0.7
	0.78			1.8	
	0.88	286	0.3		1.1
Pimarinal	1.00	286	45	39	20
Palustrinal (?)	1.16	286	7.5	6.2	6.1
Isopimarinal	1.33	286	18	10	16
Dehydroabietinal	1.54	284	11	12	21
Abietinal	1.75	286	16		31

Table 2. Content of carbonyl compounds in tall oil and tall oil distillation products.

Product	Acid value	% Resin acids	% Unsaponifiables	% Carbonyl compounds In unsaponifiables	% Carbonyl compounds In product
Crude tall oil	148	34.5	11.5	9.9	1.1
Tall oil distillate	177	10.6	9.9	22	2.2
Tall oil fatty acids	195	2.0	2.8	23.5	0.6

methyl dehydroabietate, 1.54; methyl abietate, 1.74.

The relative retention times for the aldehydes are given in Table 1 and those of the acetates are (acetyl pimarinol, 1.00): acetyl palustrinol, 1.12; acetyl isopimarinol, 1.26; acetyl dehydroabietinol, 1.53; acetyl abietinol, 1.74.

Norin and Westfelt [4] have given retention data for the mentioned type of compounds on a column consisting of 1 % E 301 on Gaschrom P operating at 150°C.

Isolation of carbonyl compounds. The unsaponifiable fractions from the various sources were isolated by saponification with 2 N alcoholic KOH followed by extraction with petroleum ether in a continuous extractor. From the unsaponifiable fractions the carbonyl compounds were isolated with Girard's Reagent T according to a method described by Sandermann and Weissmann.[5]

Oxidation of aldehydes. The oxidation of aldehydes to the corresponding carboxylic acids was carried out with chromic acid in acetic acid according to the method described in Ref. 6. The acids thus obtained were methylated with ethereal diazomethane.

Reduction of aldehydes. The reduction of aldehydes to the corresponding alcohols was carried out using sodium borohydride in aqueous methanol according to the standard procedure. The alcohols thus formed were acetylated in the usual way (refluxing with acetic anhydride).

Reduction of resin acid methyl esters. For comparison, resin acids of known composition were methylated (ethereal diazomethane) and the esters reduced with lithium aluminium hydride in ether solution according to the usual procedure.

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Phase Transitions and Structure of Lithium Cryolite

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In a recent publication [1] it was shown that the sodium, potassium, rubidium and cesium compounds of the cryolite family, M_3AlF_6, all are polymorphic. The sodium compound Na_3AlF_6 changes from a monoclinic to a cubic symmetry at 560°C while the other compounds K_3AlF_6, Rb_3AlF_6, and Cs_3AlF_6 change from a tetragonal to a cubic symmetry at 327°C, 357°C, and 287°C, respectively. In their high-temperature forms they all belong to the space group $Fm3m-O_h^5$.

A preliminary examination of the lithium compound will here be reported.

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