paper chromatography[7,8] indicated that vanillin, syringaldehyde, and p-hydroxybenzaldehyde were the only identifiable phenolic aldehydes present in this fraction, and quantitative paper chromatography and spectrophotometry[8] gave the following results: vanillin, 12.5%; syringaldehyde, 12.5%; and p-hydroxybenzaldehyde, 1.7%.

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[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

Studies on the Chemistry of Aspenwood. VIII.[1] An Investigation of the Neutral Extractives of Commercial Aspen Spent Sulfite Liquor[2]

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The "neutral" portion of the ether extractives of a commercial spent sulfite liquor from the pulping of mixed aspenwood (*Populus tremuloides, P. grandidentata,* and *P. tacamahaca*) was found to contain esters of long-chain fatty alcohols, sterols, glycerol, and phenolic acids with saturated and unsaturated long-chain fatty acids and phenolic acids together with some of their constituent components.

In the previous paper in this series[1] the large scale fractionation into bisulfite-soluble, bicarbonate-soluble, alkali-soluble, and neutral fractions of the ether extractives of a commercial spent sulfite liquor from the ammonia-base pulping of peeled mixed aspenwood (*Populus tremuloides, P. grandidentata,* and *P. tacamahaca*) was described. The present paper describes studies on the "neutral" fraction which were those materials which passed through the Craig machine countercurrent to 21% sodium bisulfite, 8% sodium bicarbonate, and 4% sodium hydroxide solutions, and which represented 35% of the original ether extractives.

The crude "neutral" fraction was evaporated to dryness, and the residual dark brown viscous oil was boiled with excess petroleum ether (b.p. 30–60°), and the clear petroleum ether extract was decanted. Evaporation of this petroleum ether extract yielded 90% of the "neutral" fraction as a yellow oily product. Subsequent extraction of the residue from the petroleum ether boiling with boiling benzene and then with boiling ether yielded 8% benzene-soluble and 1% ether-soluble fractions, respectively. The present study was concerned only with the petroleum ether-soluble portion. This crude fraction was chromatographed on alumina and eluted successively with petroleum ether (b.p. 65–110°), benzene, chloroform, 95% ethanol, and 1% acetic acid in ethanol. Fractions were analyzed by reverse-phase chromatography on mineral oil-impregnated paper in aqueous acetic acid and "peracid" developers and spots were located and identified by means of ultraviolet examination before and after exposure to iodine vapors, phosphomolybdic acid spray reagent, and the mercury stain.[3,4] The petroleum ether eluate representing 27% of the recovered fractions appeared to contain saturated compounds of relatively high molecular weight, probably alcohols or sterols. A small amount of fatty acid was also indicated. The benzene eluate (35%) appeared to comprise mainly saturated compounds, probably fatty alcohols, glycerides, and triglycerides. Some unsaturated material was indicated along with carboxylic acids. The chloroform eluate (17%) appeared to comprise predominantly sterol materials similar to β-sitosterol. The 95% ethanol eluate (7%) appears to be a mixture of unsaturated fatty acids, mostly linoleic and linolenic. The fraction eluted with 1% acetic acid in ethanol (13%) was composed of a mixture of saturated and unsaturated long-chain aliphatic acids. Linoleic, palmitic, stearic, arachidic, behenic, and lignoceric acids were identified. In addition, data indicated saturated fatty acids even higher than C_{24}.

Thus, the presence of saturated fatty acids with even chain lengths from 16 to 24 carbon atoms and higher was demonstrated in the so-called "neutral" fraction of the extractives of aspen spent sulfite liquor. Therefore, it appears that the fraction is actually not neutral at all, but contains a sizable amount of acidic materials. The finding of these acids in this "neutral" fraction indicates that probably much larger amounts are to be found in the bicarbonate-soluble and alkali-soluble fractions reported earlier.[1] To date, these other fractions have only been investigated for their aromatic constituents and not for their aliphatic components.

The paper chromatographic analysis of the fractions eluted from the above alumina column indicated that considerable overlap of individual fraction composition took place and that many ma-

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(1) For paper VII of this series, see I. A. Pearl and D. L. Beyer, *J. Org. Chem.*, **26**, 546 (1961).

(2) This paper represents a portion of the results obtained in the research program sponsored by the Sulphite Pulp Manufacturers' Research League and conducted for the League by The Institute of Paper Chemistry. Acknowledgment is made by the Institute for permission on the part of the League to publish these results.

(3) M. A. Buchanan, R. V. Sinnett, and J. A. Jappe, *Tappi,* **42**, 578 (1959).

(4) M. A. Buchanan, *Anal. Chem.*, **31**, 1616 (1959).

terials present were still subject to saponification. Accordingly, the crude product was saponified with 1*N* ethanolic potassium hydroxide and separated into acids and unsaponifiables amounting to 41 and 22% of the crude petroleum ether-soluble product. Glycerol was identified in the aqueous solution. Fractional crystallization from methanol yielded crystals of saturated long-chain aliphatic alcohols containing 26 carbon atoms which were identified by means of infrared absorption spectra, carbon and hydrogen analyses, and reverse-phase chromatography under high temperature conditions.[5] Paper chromatography of the methanolic filtrates indicated sterol and fatty acid material, but no isolations were made. Reverse-phase chromatography of the acids indicated the presence of myristic, palmitic, stearic, arachidic, behenic, and lignoceric saturated acids along with oleic, linoleic, linolenic, and arachidonic unsaturated acids. Paper chromatography of the acid fraction in the normal manner[6,7] indicated the presence of vanillic, syringic, ferulic, *p*-coumaric, and *p*-hydroxybenzoic acids.

The finding of acidic materials again in the "neutral" or unsaponifiable portion indicated that the resulting alkaline solution was not strong enough to keep the long-chain fatty acids in solution during a continuous ether extraction. Therefore, the experiment was repeated with 2*N* ethanolic potassium hydroxide, and under the same volume conditions, the unsaponifiables were found to be free of acidic constituents. In this second experiment, saturated long-chain aliphatic alcohols containing 27 and 28 carbon atoms were found in addition to the other compounds found in the first saponification experiment.

Thus, it appears that the "neutral" portion of the ether extractives of commercial aspen spent sulfite liquor contains esters of long-chain fatty alcohols, sterols, glycerol, and phenolic acids with saturated and unsaturated long-chain fatty acids and phenolic acids together with some of their constituent components. It should be noted that the present paper describes only those compounds which have been identified and does not report the many components of most of the fractions which have not been identified as yet. Studies on these neutrals are continuing, and results will be reported in forthcoming papers.

EXPERIMENTAL[8]

Preliminary studies on entire "neutral" fraction. A sample (102 g.) of the crude "neutral" fraction from the Craig machine fractionation of mixed aspen (*Populus tremuloides, P. grandidentata,* and *P. tacamahaca*) commercial spent sulfite liquor ether extractives[1] was boiled under reflux with 2000 ml. petroleum ether (b.p. 30–60°), and the clear petroleum ether extract was decanted from the viscous residue. The petroleum ether solution was evaporated in a rotating evaporator under reduced pressure to yield 91.5 g. (90%) of yellow oily product. The viscous residue left after petroleum ether boiling and decanting was boiled with 1000 ml. of benzene, and the benzene was decanted and evaporated to yield 8.4 g. (8%) of benzene-soluble material. Subsequent boiling with anhydrous ether and decanting yielded 0.8 g. of ether-soluble material. A petroleum ether solution of 9.15 g. of the petroleum ether-soluble fraction was absorbed on alumina[9] and packed on the top of a column of 430 g. of alumina 45 mm. in width. The column was developed under gravity with 2000 ml. of each of the following solvents in order: petroleum ether (b.p. 65–110°), benzene, chloroform, 95% ethanol, and 1% acetic acid in 95% ethanol. Five hundred-milliliter fractions were collected in the effluent. All fractions were evaporated to dryness under reduced pressure in the rotating evaporator, weighed, and subjected to reverse-phase chromatography on mineral oil-treated papers developed with aqueous acetic acid and "peracid" developers.[3,4] Spots were located and identified by examining under ultraviolet light before and after exposure to iodine vapors, spraying with silver nitrate and phosphomolybdic acid spray reagents, and treating with the mercury stain.[3,4] Yield data and qualitative interpretation of chromatograms were as follows: petroleum ether eluates (2.19 g.), saturated compounds of relatively high molecular weight, probably long-chain alcohols or sterols, and a small amount of saturated and unsaturated long-chain fatty acids; benzene eluates (2.81 g.), mostly saturated compounds, probably fatty alcohols, glycerides, triglycerides, other esters, and carboxylic acids along with a little unsaturated material; chloroform eluates (1.35 g.), predominantly sterol materials similar to β-sitosterol; 95% ethanol eluates (0.58 g.), unsaturated fatty acids, mostly linoleic and linolenic acids; and ethanolic acetic acid eluate (1.07 g.), a mixture of saturated and unsaturated fatty acids comprising linoleic, palmitic, and stearic acids, with smaller amounts of arachidic, behenic, and lignoceric acids. Spots for saturated fatty acids higher than C_{24} were also obtained in the last fraction.

Saponification of petroleum ether-soluble "neutral" fraction. Forty grams of the petroleum ether-soluble fraction was boiled under reflux with 500 ml. of *N* ethanolic potassium hydroxide 10 hr., and the ethanol was removed by distillation and replaced with water. The alkaline aqueous solution was extracted exhaustively with ether, and the ether was dried and distilled to yield 8.6 g. of unsaponifiable material. The aqueous raffinate was acidified with dilute sulfuric acid and extracted exhaustively with ether to yield 16.1 g. of acidic material. The residual aqueous solution was neutralized with sodium bicarbonate and evaporated to dryness. The residue was extracted with 95% ethanol. The ethanol was evaporated, and the residue dissolved in water and deionized with a mixed bed ion-exchange resin. The aqueous solution was evaporated to yield glycerol as a colorless sirup, identified by paper chromatography in the 8:2:1 ethyl acetate–pyridine–water developer along with authentic glycerol and spraying with permanganate-periodate reagent.

Unsaponifiable material from petroleum ether-soluble "neutral" fraction. The entire fraction was boiled with methanol and filtered hot. The crystals which separated upon cooling were filtered and recrystallized several times from acetone to give colorless crystals melting at 78°. Infrared absorption ($\lambda^{\mathrm{KBr}}_{\mathrm{max}\,\mu}$ 2.95, 3.45, 3.52, 6.82, 7.24, 7.93, 9.45, 13.71, 13.91) indicated a long-chain fatty alcohol. High-tempera-

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[5] S. Fiker and V. Hajek, *Chem. listy,* **52,** 549 (1958).

[6] I. A. Pearl, D. L. Beyer, B. Johnson, and S. Wilkinson, *Tappi,* **40,** 374 (1957).

[7] I. A. Pearl, D. L. Beyer, and B. Johnson, *Tappi,* **41,** 255 (1958).

[8] All melting points are uncorrected. Analyses were performed by Huffman Microanalytical Laboratories, Wheatridge, Col. Infrared spectra were determined by Mr. Lowell Sell.

[9] All alumina employed was adsorption-grade Alumina (80–200 mesh) obtained from Fisher Scientific Co., Fair Lawn, N. J.

ture reverse-phase chromatography on paraffin–mineral oil impregnated paper with glacial acetic acid saturated with paraffin–mineral oil according to Fiker and Hajek[5] indicated a C_{26} long-chain fatty alcohol. The recorded[10] melting point for hexacosanol is 78°.

Anal. Calcd. for $C_{26}H_{54}O$: C, 81.60; H, 14.22. Found: C, 81.56; H, 14.01.

The methanol filtrate from the above crystals was evaporated to dryness, and the residue was recrystallized from acetone, chromatographed through acid-washed Magnesol,[11] and recrystallized several times from acetone to yield colorless crystals melting at 76.5–77°. The infrared curve was identical with that of hexacosanol except for the trace bands of magnesium silicate from the Magnesol column which could not be removed. High-temperature reverse-phase paper chromatography by the Fiker and Hajek[5] procedure indicated a C_{20} long-chain fatty alcohol.

Acids from petroleum ether-soluble "neutral" fraction. A sample (2.0 g.) of the acid fraction was chromatographed on alumina, and the column was eluted successively with petroleum ether (b.p. 65–110°), benzene, chloroform, 95% ethanol, and 1% acetic acid in 95% ethanol. The last eluate containing only acidic materials was evaporated under reduced pressure to yield 1.37 g. of product. The material was subjected to reverse-phase chromatography on mineral oil-treated paper in 85% acetic acid at room temperature along with known saturated and unsaturated fatty acids. The papers were examined by means of ultraviolet light before and after iodination and by means of the mercury stain.[3] Confirmatory chromatograms were run in the "peracid" developer.[4] The following acids were found: myristic (85% acetic acid R_f 0.65), palmitic (R_f 0.54), stearic (R_f 0.15), arachidic (R_f 0.09), behenic (R_f 0.04), lignoceric and/or higher (R_f 0.00), arachidonic (R_f 0.39), oleic (R_f 0.50), linoleic (R_f 0.66), and linolenic (R_f 0.74).

Paper chromatography in the butanol saturated with 2% aqueous ammonia, 10:3:3 butanol-pyridine–water, and benzene saturated with formic acid developers and comparison with known compounds[6, 7] indicated the presence of vanillic, syringic, ferulic, *p*-coumaric, and *p*-hydroxybenzoic acids.

Saponification of petroleum ether-soluble "neutral" fraction with strong alkali. Fifty grams of the petroleum ether–soluble fraction was boiled under reflux with 500 ml. 2*N* ethanolic potassium hydroxide for 15 hr., and then the ethanol was distilled and replaced with water. The alkaline solution was extracted exhaustively with ether as before, but in this case, chromatography of the ether extract gave no evidence of acidic materials. This unsaponifiable material was obtained as a light tan oil which deposited colorless platelets upon standing. The fraction was diluted with a little petroleum ether (b.p. 30–60)° and filtered. The oil-free crystals were recrystallized several times from ether at −60° to yield colorless platelets melting at 78–90°. Infrared absorption spectra indicated a long-chain fatty alcohol, and high-temperature reverse-phase chromatography by the Fiker and Hajek procedure[5] indicated a C_{27} alcohol.

Anal. Calcd. for $C_{27}H_{56}O$: C, 81.74; H, 14.23. Found: C, 81.75; H, 14.19.

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[10] T. Koyama, and T. Morikita, *Kumamoto Pharm. Bull.*, **1955**, No. 2, 69; *Chem. Abstr.*, **50**, 11228 (1956).

[11] I. A. Pearl and E. E. Dickey, *J. Am. Chem. Soc.*, **73**, 863 (1951).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

The Reaction of Some Silanols and Siloxanes with *n*-Octyl Alcohol

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The acid- or base-catalyzed reaction of a number of silanols and siloxanes with *n*-octyl alcohol under nonequilibrium conditions was studied by observing the amount of water formed and the quantitative rate at which it was formed. The reaction is nearly always complicated by simultaneous selfcondensation of the silanol, and by further attack of the reagent upon the siloxane that is formed. By noting the positions at which pronounced "knees" appear in the water-evolution rate curves, and by independently determining the rates of alcoholysis of the siloxanes (when this was feasible), conclusions were reached concerning the extent of selfcondensation of the silanol compared to that of reaction with the alcohol. The nature of the catalyst, the number of alkyl or aryl substituents on silicon, the steric or inductive effects of these substituents, and the ring size (in case of the cyclic polysiloxanes) are all of importance. A number of *n*-octoxysilanes and *n*-octoxysiloxanes were isolated and identified.

INTRODUCTION

Although silanols are known to be involved in most syntheses of organosilicon polymers, the reactions that they undergo have been only scantily considered. The reactions by which silanols are prepared can usually be reversed. For example, some years ago Sommer, Pietrusza, and Whitmore[1] converted triethylsilanol to chlorotriethylsilane, to triethylsiloxyl acetate, to bis(triethylsiloxyl) sulfate, and to sodium triethylsilanolate. Alkali silanolates can be obtained from certain silanols by treatment either with the alkali amide, or with concentrated alkali metal hydroxide.[2] Sauer[3] prepared trimethylsiloxymagnesium iodide from

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[1] L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 2282 (1946).

[2] (a) J. F. Hyde, U. S. Patent **2,567,110**, Sept. 4, 1951; (b) W. S. Tatlock and E. G. Rochow, *J. Am. Chem. Soc.*, **72**, 528 (1950); (c) W. S. Tatlock and E. G. Rochow, *J. Org. Chem.*, **17**, 1955 (1952); (d) J. F. Hyde, O. K. Johannson, W. H. Daudt, R. F. Fleming, H. B. Laudenslager, and M. P. Roche, *J. Am. Chem. Soc.*, **75**, 5615 (1953).

[3] R. O. Sauer, *J. Am. Chem. Soc.*, **66**, 1707 (1944).