preparation of the acetonide VIII) gave 75 mg. of XII from aqueous ethanol, m.p. 142.5–144.5° (lit. 141–143.5°,[8a] 136–138°[8b]).

*16β-Hydroxy-16α-methyl-19-nortestosterone* (XIII). Reduction of 1.5 g. of XI with lithium and liquid ammonia as described above (*cf.* the preparation of II) gave a solid which crystallized from methylene chloride–methanol to give 1.14 g. (75%) of the dihydro product as colorless needles, m.p. 183–195°; $\nu_{max}$ 1698 and 1669 cm.$^{-1}$ Treatment of 500 mg. of the latter with hydrochloric acid in refluxing aqueous methanol as described above gave a semicrystalline solid which crystallized from acetone–petroleum ether to give 400 mg. (84%) of XIII, m.p. 175.5–179°. A sample for analysis was recrystallized thrice from acetone–petroleum ether and had m.p. 176–179.5°; $[\alpha]_D + 34°$; $\lambda_{max}$ 240 m$\mu$ ($\epsilon$ 16,800); $\nu_{max}$ 1670, 1618, 1263, 1208, 1130, and 1063 cm.$^{-1}$

*Anal.* Calcd. for $C_{19}H_{28}O_3$ (304.41): C, 74.96; H, 9.27. Found: C, 74.75; H, 9.31.

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## Studies on the Chemistry of Aspenwood. XIII.[1] Further Studies on the Neutral Extractives of Commercial Aspen Spent Sulfite Liquor[2]

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In a previous paper on the neutral extractives of a spent sulfite liquor from the commercial ammonia-base pulping of peeled mixed aspenwood (*Populus tremuloides*, *P. grandidentata*, and *P. tacamahaca*)[3] the finding of 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 was reported. Studies on crude "neutrals" and saponified "neutrals" were reported. The present paper reports additional studies on these same materials.

Re-evaluation of the fatty-acid fraction of the original "neutrals" indicated the presence of myristic and lauric acids in addition to the previously reported palmitic, stearic, arachidic, behenic, and lignoceric saturated fatty acids reported earlier. The original "neutrals" were re-examined for phenolic acids, but none could be found by means of paper chromatographic procedures.

Further studies on the saponification of the petroleum ether-soluble "neutrals" with both *N* and 2*N* ethanolic potassium hydroxide were made. Lauric and capric acids were found in addition to previously reported saturated fatty acids. The presence of $C_{22}$, $C_{24}$, $C_{25}$, and $C_{26}$ long-chain saturated fatty alcohols was indicated by the high-temperature reverse-phase chromatographic procedure of Fiker and Hajek[4] and confirmed by low-temperature reverse-phase chromatography of *p*-phenylazobenzoic acid esters of the mixed alcohols.

Even after saponification with strong ethanolic alkali, the "neutral" fraction obtained by continuous extraction with ether or ethyl acetate contained substantial amounts of acidic materials. Linoleic, oleic, arachidonic, lauric, and capric acids in addition to two unidentified unsaturated fatty acids were found in the mother liquors from the crystallization of the long-chain fatty alcohols in these "neutral" fractions. Thus, it is apparent again that the so-called "neutral" fraction obtained by extraction of an alkaline saponification mixture with an immiscible solvent may actually contain acidic materials in the form of fatty acids. Although the distribution coefficient of these fatty acid compounds between aqueous alkaline solution and ethyl acetate or ether is in favor of the aqueous alkaline solution, continuous extraction with the immiscible solvent will remove a portion of these acids.

The acids and phenols fraction obtained after saponification of the original "neutrals" was found to contain substantial amounts of vanillic, syringic, *p*-hydroxybenzoic, and ferulic acids in addition to several unidentified phenolic acids. Thus, it appears that the extractives of the mixed aspens employed in the original sulfite cook contain esters of fatty acids with all of these phenolic acids, and that the ester linkage is between the carboxyl group of the fatty acids and the phenolic group of the phenolic acids. Furthermore, the carboxyl groups of the phenolic acids must be esterified with aliphatic long-chain alcohols. Apparently, these esters are hydrolyzed to a certain extent during the sulfite cook because all the same products were found free in the ether extractives of the original liquor before saponification,[5] but some pass through the sulfite cook and can be hydrolyzed only by subsequent saponification with strong alkali.

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(1) For paper XII of this series, see I. A. Pearl and L. R. Busche, *Tappi*, **43**, 970 (1960).

(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.

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## EXPERIMENTAL[6]

*Additional studies on original "neutral" fraction.* The 1% acetic acid in 95% ethanol eluate of the alumina column chromatogram of this fraction noted earlier[3] was submitted to reverse-phase chromatography on mineral oil-treated paper at 37° with "peracid" developer.[7] In addition to the $C_{16}$ to $C_{24}$ saturated fatty acids reported earlier[3] this fraction contained myristic and lauric acids with $R_f$ values of 0.65 and 0.82, respectively.

*Additional studies on unsaponifiables from petroleum ether-soluble "neutral" fraction.* This fraction was boiled with methanol and filtered hot as described earlier.[3] The filtrate deposited hexacosanol melting at 78° upon cooling. The hexacosanol was filtered, and the filtrate was cooled to −70°. The crystals which separated were filtered and chromatographed reverse-phase at 37° on mineral oil-impregnated paper with 85% acetic acid. The chromatograms indicated the presence of $C_{26}$ and higher long-chain fatty alcohols. No individual spots were apparent, but the spot for long-chain fatty alcohols appeared as a continuous spot from the origin to $R_f$ 0.34, the $R_f$ for the $C_{26}$ alcohol. Infrared spectra of this crystalline material indicated only long-chain fatty alcohols.

The methanol filtrate from the crystallization at −70° was chromatographed reverse-phase in the same manner. The chromatograms were dried and scanned under ultraviolet light before and after iodine vapor treatment and examined by means of the mercury stain.[8] Linoleic acid ($R_f$ 0.66), oleic acid ($R_f$ 0.57), arachidonic acid ($R_f$ 0.40), and two unidentified unsaturated acids with $R_f$'s 0.30 and 0.02 were found. Reverse-phase chromatography with the "peracid" developer at 37° indicated the presence of lauric acid ($R_f$ 0.82) and capric acid ($R_f$ 0.94) in this fraction.

*Additional studies on acids from petroleum ether-soluble "neutral" fraction.* Chromatography of the crude fraction on Whatman No. 1 paper in butanol–2% aqueous ammonia and in 10:3:3 butanol-pyridine-water and location of spots with bisdiazotized benzidine, diazotized *p*-nitroaniline, and Mäule reagents as described earlier[9] indicated the presence of vanillic, syringic, *p*-hydroxybenzoic, and ferulic acids.

The crude fraction was chromatographed on a column of alumina and eluted successively with petroleum ether (b.p. 65–110°), benzene, chloroform 95% ethanol, and 1% acetic acid in 95% ethanol as before.[3] Again, the 1% acetic acid in ethanol eluate contained almost the entire fraction. Reverse-phase chromatography with "peracid" developer at 37° indicated the presence of lauric acid in addition to the previously reported acids in this fraction.

*Additional studies on the unsaponifiables from the saponification of petroleum ether-soluble "neutral" fraction with strong alkali.* The oil filtrate and petroleum ether washings from the $C_{27}$ alcohol reported previously[3] were evaporated to dryness and dissolved in anhydrous ether. Fractional crystallization by stepwise concentration and cooling of the ether solution yielded several crystalline fractions melting from 77 to 83°. Infrared spectra of all fractions were essentially identical and indicated only long-chain fatty alcohols. High-temperature reverse-phase chromatography by the Fiker and Hajek[4] method indicated the presence of $C_{22}$, $C_{24}$, $C_{25}$, and $C_{26}$ long-chain saturated fatty alcohols. These fractions were also examined by the new reverse-phase procedure employing *p*-phenylazobenzoyl esters of the alcohols.

*p-Phenylazobenzoyl ester chromatographic procedure.* The esters were prepared by a modification of the procedure of Woolfolk, Beach, and McPherson.[10] A mixture of excess *p*-phenylazobenzoyl chloride, known or unknown alcohol, and pyridine was boiled under reflux for 4 hr. The red reaction mixture was poured with vigorous stirring into a mixture of ice and saturated sodium bicarbonate solution, and the mixture was allowed to stand a short while. The crystalline precipitate was filtered, washed with water, and air dried.

Approximately 100 μg. of the crystalline ester was spotted on Whatman No. 1 paper impregnated with mineral oil (7 g. of mineral oil dissolved in 100 ml. of ether). The paper was developed with glacial acetic acid saturated with mineral oil at 37° for 15 hr. Compounds appeared as weak orange spots in ordinary light, but, under ultraviolet light, the compounds gave dark spots against a light background, and were discernible even in small concentration. During the 15-hr. developing time, the solvent front moved off the paper, thus precluding the possibility of $R_f$ determination. Instead, mobilities of individual compounds were recorded with reference to stearyl (octadecyl) alcohol and are denoted $R_{st}$ values. The $R_{st}$ values were determined for the *p*-phenylazobenzoyl esters of several authentic long-chain saturated fatty alcohols[3] as follows: $C_{26}$, 0.24; $C_{24}$, 0.41; $C_{22}$, 0.53; $C_{20}$, 0.76; and β-sitosterol, 0.42.

Chromatography of the 77–83° melting crystalline fractions by this procedure confirmed the occurrence of the alcohols noted by the Fiker and Hajek procedure.

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# Methyl Glycoside Formation from β-D-Glucopyranose Pentanitrate

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By reaction of tetra-*O*-acetyl-α-D-glucopyranosyl chloride with silver nitrate, Skraup and Kremann[2] obtained tetra-*O*-acetyl-β-D-glucopyranosyl nitrate, a compound showing a close similarity to the corresponding chloride,[3] for like the latter it readily anomerizes in polar solvents to the α-D form. Tetra-*O*-acetyl-α-D-glucopyranosyl nitrate itself resembles the acetylated glucosyl halides in that it reacts with methanol under the influence of a variety of bases to give methyl tetra-*O*-acetyl-β-D-glucopyranoside[4,5] and with sodium acetate in acetic anhydride to give penta-*O*-acetyl-β-D-glucopyranose.[4]

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