[CONTRIBUTION FROM FOREST PRODUCTS LABORATORY,[1] FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Constituents of Extractive from Douglas-Fir Lignin Residue

BY IRA T. CLARK, J. R. HICKS AND ELWIN E. HARRIS

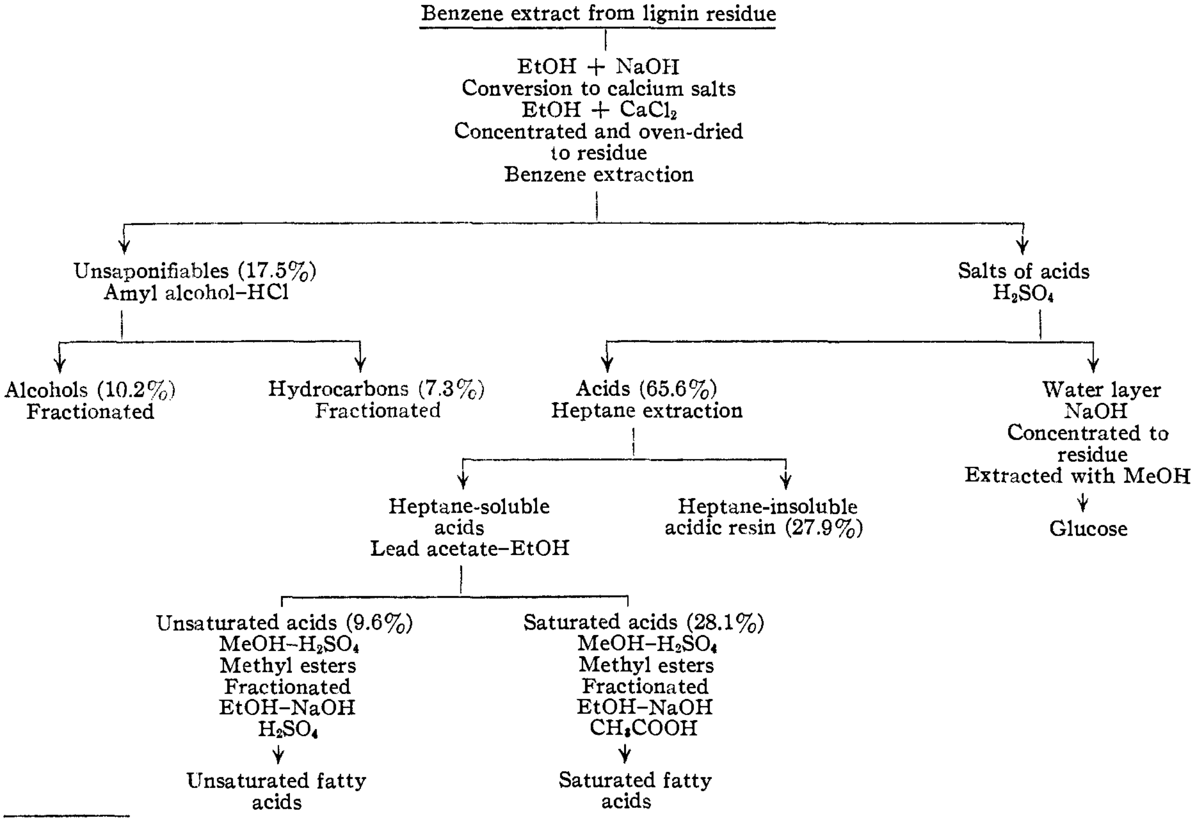
Earlier investigation[2] by the authors at the U. S. Forest Products Laboratory indicated the presence of wax extractive in Douglas-fir wood and bark and in the lignin residue from the dilute-acid hydrolysis of Douglas-fir wood waste.[3] Since potentially large quantities of the lignin residue are expected to be available from industrial processes, further investigation was undertaken to determine the constituents of its extractive in the interests of better utilization of this by-product.

Benzene, acetone or petroleum ether will extract fractions that differ in yield and characteristics.[2] The extractive used for the present investigation was removed from the Douglas-fir lignin residue by benzene. A separation procedure (Fig. 1) was followed that yielded saturated acids (28.1%), unsaturated acids (9.6%), an amorphous heptane insoluble acidic resin (27.9%), alcohols (10.2%), hydrocarbons (7.3%), and residual sulfuric acid, sugars, and losses (17%).

Fractional distillation of the alcohols, hydrocarbons, and methyl esters was used to separate the components of each group for identification. Since fractionation or crystallization methods do not readily separate a pure wax aliphatic compound from admixtures with its adjacent homologs, the method of Schuette, *et al.*,[4,5] for identifying components of binary-acid mixtures was used in this work. The presence of eicosanoic acid, docosanoic acid and tetracosanoic acid was thus indicated. Oleic acid, eicosanol-1 and docosanol-1 were isolated. Physical data obtained indicated the presence of docosane, tetracosane and hexacosane.

The foregoing compounds and similar ones have been known to exist in plants and in the wood, bark, and foliage of many species of trees. The fact that their relative insolubility in aqueous solutions leaves appreciable quantities of them with the lignin residue of processes that remove cellulose from wood by hydrolysis methods, must now be recognized, and their appearance in products of

FIG. 1.—SEPARATION OF EXTRACTIVE OF DOUGLAS-FIR LIGNIN RESIDUE



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[1] Maintained at Madison, Wis., in coöperation with the University of Wisconsin. Article not copyrighted.

[2] I. T. Clark, J. R. Hicks and E. E. Harris, THIS JOURNAL, **69**, 3142 (1947).

[3] E. E. Harris and E. Beglinger, *Ind. Eng. Chem.*, **38**, 890 (1946).

[4] H. A. Schuette and H. A. Vogel, *Oil and Soap*, **17**, 155 (1940).

[5] H. A. Schuette, B. M. Christenson and H. A. Vogel, *ibid.*, **20**, 263 (1943).

chemical processing of such lignin residues is not evidence that they were part of the lignin molecule.

TABLE I

SATURATED FATTY ACIDS FROM EXTRACTIVE OF DOUGLAS-FIR LIGNIN RESIDUE

				Synthetic binary acid mixture[4,5]	
Fraction, weight per cent.	Neutral equivalent	Composition of fraction,[a] mole per cent.	Resolidification point found, °C.	Composition, mole per cent.	Resolidification point, °C.
10.7	211	......	Indef.	......	....
10.5	234	......	Indef.	......	....
13.7	337.5	C_{20} 11.7 C_{22} 88.3	77.2	C_{20} 11.65 C_{22} 88.35	76.9
7.5	352.2	C_{22} 61.1 C_{24} 38.9	74.4	C_{22} 62.33 C_{24} 37.7	74.35
14.9	364.2	C_{22} 16.8 C_{24} 83.2	80.4	C_{22} 15.7 C_{24} 84.3	80.4
17.4	370.5	C_{22} 6.3 C_{24} 93.7	81.4	C_{22} 7.3 C_{24} 92.7	81.4
25.3	....	......	....	......	....

[a] Calculated from neutral equivalent.

TABLE II

HYDROCARBONS FROM EXTRACTIVE OF DOUGLAS-FIR LIGNIN RESIDUE

				Observed				Calculated	
Melting point, °C.	$n^{65}D$	Density at deg. C.	Mol. wt. (Rast)	Carbon, %	Hydrogen, %	Formula	Mol. wt.	Carbon, %	Hydrogen, %
40	1.4270	0.7773^{40}	307.9	85.21	14.90	$C_{22}H_{46}$	310.59	85.06	14.94
45	1.4287	$.7790^{46}$	323.6	84.75	15.05	$C_{23}H_{48}$	324.61	85.09	14.91
						$C_{24}H_{50}$	338.64	85.12	14.88
53	1.4312	$.7799^{53}$	342.5	85.20	14.77	$C_{25}H_{52}$	352.67	85.14	14.86
62.5	1.4358	$.7778^{65}$	367.3	84.96	14.80	$C_{26}H_{54}$	366.69	85.16	14.84

Experimental

Lignin Residue.—The lignin residue used for this work was the dried residual material from the Madison wood-sugar process.[3] The morphological structure of the wood was retained after hydrolysis. It was a roughly granular substance, of which 18% was held on a 12-mesh screen and 33% on a 20-mesh screen, and 49% of which passed through a 20-mesh screen. An average analysis by the Forest Products Laboratory 72% sulfuric acid method[6] showed 83.2% lignin, and 6.5% benzene–alcohol-soluble, 2.3% water-soluble, and 8% other non-lignin materials, chiefly cellulose. The water-soluble fraction included 0.1% sugars and 0.7% acid as sulfuric. Analysis varied slightly depending on hydrolysis treatment.

Extraction.—Extraction of the lignin residue (1–3% moisture) was made with benzene in a Lloyd continuous-type copper extractor having a capacity of 8 kg. of lignin residue and 28 liters of solvent. A charge was extracted for fifty hours, the extractive concentrate removed, and the extraction continued for another ten hours. This was found to be the limit of practical extraction.

Separation.—A 1695-g. portion of benzene extractive in 10 liters of ethanol was saponified with 1000 g. of sodium hydroxide. The resulting sodium salts were converted to calcium salts by using an excess of calcium chloride in ethanol. Most of the ethanol was then removed on a steam-bath, the mass air-dried at 80°, and the unsaponifiable fraction removed by benzene extraction in soxhlet extractors. This procedure was adopted after considerable difficulty had been experienced with emulsion formation in liquid–liquid extraction.

1. Acid Fraction (1112 g.)

A 925-g. portion of the acid fraction was extracted with heptane after recovery from the calcium salts. The heptane-insoluble fraction (388 g.) was an amorphous resin that failed to respond to crystallization or further separation. The heptane-soluble fraction (525 g.) was separated into a saturated-acid fraction (325 g.) and an unsaturated-acid fraction (112 g.) by the lead–salt method of Hilditch.[7] The methyl esters of each were prepared[8] and fractionated twice at 1 mm. of mercury in a 48-inch Stedman-type column.

Saturated Acids.—The methyl ester fractions were converted separately to acids by saponifying, boiling the resultant purified salts in acetic acid, precipitating in cold water, and water washing until neutral to litmus. Eicosanoic, docosanoic and tetracosanoic acids were identified in the fractions as binary mixtures by solidification temperatures and molecular-weight calculations (Table I) by using the data of Schuette, *et al.*,[4,5] for synthetic binary mixtures of these acids.

Unsaturated Acids.—Fractionation of the unsaturated acid methyl esters yielded one fraction (51% of the distillate) that upon conversion to the acid (by saponification, then decomposition of the salt with sulfuric acid), was identified as oleic acid. The flask residue (25% of starting material) was considerably polymerized, apparently from less readily distilled unsaturated acids.

Oleic Acid.—Neutral equivalent calcd.: 282.45. Found: 283.5. Iodine number calcd.: 90.07. Found: 89.6. The 9,10-dihydroxystearic acid was formed by oxidation with potassium permanganate at 0–10°.[9] M. p. 131° (literature 132°).

2. Unsaponifiable Fraction (297 g.)

A 100-g. portion of the unsaponifiable fraction was separated into hydrocarbons (37.4 g.) and alcohols (51.0 g.) by the method of Leys,[10] using a fuming hydrochloric acid–amyl alcohol mixture. It is possible that the reagent caused rearrangement or changes in the products. The alcohols were fractionated at 1 mm. of mercury in a 200-mm. × 8-mm. Stedman column at total reflux with intermittent product withdrawal at a rate of about 5 cc. per day.

Hydrocarbons.—Data on the four principal fractions of hydrocarbons obtained are given in Table II. Evidence indicates these fractions to be mixtures of the even-numbered hydrocarbons from C_{20} through C_{26}.

Alcohols.—Two fractions were obtained whose melting points corresponded closely to those for eicosanol-1 and docosanol-1, as shown below. They were converted to the corresponding acids by using soda-lime fusion, and identified by solidification point and molecular weight.

Eicosanol-1, m. p. 66.5°; corresponding acid: solidification temperature found 73.5°. Molecular weight calcd. for $CH_3(CH_2)_{18}COOH$: 312.52. Found: 313.4.

Docosanol-1, m. p. 70.5°; corresponding acid: solidification temperature found: 78.5°. Molecular weight calcd. for $CH_3(CH_2)_{20}COOH$: 340.58. Found: 338.4.

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(6) G. J. Ritter, R. M. Seborg and R. L. Mitchell, *Ind. Eng. Chem., Anal. Ed.*, **4**, 202 (1932).

(7) T. P. Hilditch, *Chem. Const. of Nat. Fats.*, Vol. V, p. 371.

(8) E. F. Armstrong and T. P. Hilditch, *J. Soc. Chem. Ind.*, **44**, 66T (1925).

(9) A. Lapworth and E. N. Mottram, *J. Chem. Soc.*, **127**, 1629 (1925).

(10) J. I. Lewkowitsch, "Chem. Tech. and Anal. Oils, Fats and Waxes." Vol. I, 6th ed., p. 615.

Water Soluble

The water-soluble fraction included the residual 0.1% reducing sugars and 0.7% sulfuric acid shown by analysis to remain with the lignin residue after hydrolysis. Examination of the water layer gave no indication of the presence of other compounds.

Summary

1. Solvent extraction has removed a wax extractive of high melting point from the lignin residue of the dilute-acid hydrolysis of Douglas-fir wood waste, a cheap, abundant material.

2. Analytical data obtained indicated the presence of eicosanoic, docosanoic, tetracosanoic and oleic acids; eicosanol-1, and docosanol-1; docosane, tetracosane and hexacosane.

3. The appearance of these compounds in the products of chemical treatments of this lignin residue indicates their carry-over from the original wood rather than evidence that they are derived from the lignin molecule.

4. Also appearing in the extractive were a heptane insoluble acidic resin, residual sugars and sulfuric acid.

MADISON, WISCONSIN RECEIVED JUNE 7, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MAINE]

Some New Alkyl Tetralins and Naphthalenes[1]

BY ROBERT T. HART AND SAMUEL A. ROBINSON

Considerable effort, particularly in recent years, has been devoted to the synthesis of pure hydrocarbons and to the correlation of their physical constants with molecular structure. A search of the literature, however, reveals a paucity of data available concerning the monoalkyl and dialkyl tetralins and naphthalenes. At the time of completion of this paper, only one compound, 2-*n*-butylnaphthalene, of the nineteen alkyl tetralins and naphthalenes described here had been previously reported. In a current issue of THIS JOURNAL,[2] however, five of the remaining eighteen compounds are described as intermediates in a problem of other scope. These are denoted by letter (a) in Table I and are included here both for purposes of comparison and because additional data not previously reported for these compounds are now made available.

The method of synthesis of this series of compounds is identical with that employed by Smith and Lo[2] with the exception that the appropriate acid chlorides rather than acid anhydrides were used as acylating agents.

In the calculation of the theoretical values for the Molecular Refractions, ($M\text{D}_{\text{calcd.}}$), the values of the atomic refractions used were those of Swietoslawski.[3] The observed Molecular Refractions ($M\text{D}_{\text{obs.}}$) were calculated by the Lorenz–Lorentz equation for specific refractivity, using the experimental values for density and refractive index. As can be seen from Table I, there exists a considerable exaltation of the observed molecular refractions over those calculated on the basis of molecular structure. This effect, expressed as "specific exaltation," $E\Sigma = 100\ EM/m$,[4] where EM is the molecular exaltation and m is the molecular weight, is about four and one-half times as large for the naphthalenes as for the tetralins. This is found to be in accord with the ratio of approximately four to one for the exaltations of the specific dispersions of naphthalene and tetralin respectively. Exaltation effects are usually ascribed to some constitutive peculiarity, in this case, conjugation of double bonds. The relatively large positive exaltation for naphthalene derivatives is interpreted as indicating "that only one ring in such compounds is truly aromatic, the other rings producing the exaltation characteristic of normal unsaturated conjugation."[5]

For the purpose of statistical analysis the boiling point data were divided into the four possible combination groups, monoalkyl and dialkyl tetralins and naphthalenes. The boiling point data used in the calculations were the means of the boiling point ranges observed. The "least squares" method of fitting straight lines to the paired observations of boiling point (y) *versus* the number of carbon atoms (x) gave the four following equations:

I. Monoalkyl
  1, Naphthalenes $y = -50.161283 + 13.193548x$
  2, Tetralins $y = -59.633625 + 13.258621x$
II. Dialkyl
  1, Naphthalenes $y = -21.026042 + 10.859375x$
  2, Tetralins $y = -4.598958 + 9.390625x$

An F-test[6] shows the fit of these lines to be significant. Moreover, the close fit of the points to the lines necessitated the use of the large number of decimals in order to apply the F-test, whereas the accuracy of the data itself would not justify these decimals. As important, in the practical sense, is the fact that the angle of intersection of each pair

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[1] A part of the research reported in this paper will be submitted by S. A. R. in partial fulfillment of the requirements for the degree of Master of Science in Chemistry, University of Maine, February, 1949.

[2] Smith and Lo, THIS JOURNAL, **70**, 2209 (1948).

[3] Swietoslawski, *ibid.*, **42**, 1945 (1920).

[4] Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 442.

[5] Brode and Leermakers, Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 1741.

[6] H. A. Freeman, "Industrial Statistics," John Wiley and Sons, Inc., New York, N. Y., 1942.