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.

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[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, ($M\mathrm{D}_{\mathrm{calcd.}}$), the values of the atomic refractions used were those of Swietoslawski.[3] The observed Molecular Refractions ($M\mathrm{D}_{\mathrm{obs.}}$) 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.

TABLE I

TETRALIN DERIVATIVES

Compound	Yield, %[e]	Empirical formula	B. p., °C. (5 mm.)	d^{20}_4	n^{20}_D	$r_{D\,\mathrm{obs.}}$	M_D		$E\Sigma$	M. p. of picrate, °C.[d]	Analyses, %[c]			
											Carbon		Hydrogen	
							Calcd.	Obs.			Calcd.	Found	Calcd.	Found
6-*n*-Propyl[a]	57	$C_{13}H_{18}$	110–112	0.9400	1.5291	0.328	56.55	57.18	0.361		89.6	89.9	10.4	9.9
6-*n*-Butyl	54	$C_{14}H_{20}$	126–127.5	.9341	1.5234	.328	61.16	61.91	.398		89.4	89.5	10.6	10.1
6-*n*-Amyl	64	$C_{15}H_{22}$	140–141.5	.9226	1.5179	.328	65.76	66.44	.336		89.0	89.1	11.0	10.5
6-*n*-Propyl-7-ethyl[a]	53	$C_{15}H_{22}$	134–135	.9366	1.5270	.328	65.76	66.36	.296		89.0	88.3	11.0	11.3
6,7-Di-*n*-propyl[a]	55	$C_{16}H_{24}$	144–146	.9282	1.5220	.328	70.36	71.07	.328		88.8	88.7	11.2	10.9
6-*n*-Butyl-7-ethyl	60	$C_{16}H_{24}$	146–147	.9309	1.5230	.328	70.36	71.01	.300		88.8	88.6	11.2	10.9
6-*n*-Butyl-7-*n*-propyl	62	$C_{17}H_{26}$	157–158	.9307	1.5210	.327	74.96	75.36	.174		88.6	88.3	11.4	10.7
6,7-Di-*n*-butyl	60	$C_{18}H_{28}$	164–165.5	.9228	1.5172	.328	79.57	80.16	.242		88.5	88.2	11.5	11.1
6,7-Di-*n*-amyl	56	$C_{20}H_{32}$	181–183	.9088	1.5110	.329	88.77	89.80	.378		88.2	88.0	11.8	11.2
6-*n*-Decyl	62	$C_{20}H_{32}$	204–206	.9011	1.5052	.329	88.77	89.64	.319		88.2	88.5	11.8	11.4
Naphthalene Derivatives														
2-*n*-Butyl	48	$C_{14}H_{16}$	133–134	0.9626	1.5740	0.343	60;40	63.20	1.518	73–74	91.2	91.6	8.8	8.4
2-*n*-Amyl	57	$C_{15}H_{18}$	148–149.8	.9526	1.5648	.342	64.97	67.75	1.401	57–58	90.8	90.6	9.2	9.0
2-*n*-Propyl-3-ethyl[a]	45	$C_{15}H_{18}$	142.5–144.5	.9660	1.5701	.340	64.97	67.36	1.204	89–90.5	90.8	90.3	9.2	9.3
2,3-Di-*n*-propyl[a]	48	$C_{16}H_{20}$	151–152	.9626	1.5691	.341	69.58	72.30	1.270	80–82	90.5	90.7	9.5	9.5
2-*n*-Butyl-3-ethyl	49	$C_{16}H_{20}$	153–154	.9271	1.5730	.345	69.58	73.25	1.728	65–66	90.5	90.7	9.5	9.0
2-*n*-Butyl-3-*n*-propyl	57	$C_{17}H_{22}$	162–163.5	.9488	1.5680	.345	74.25	78.33	1.798	52–53	90.2	90.7	9.8	9.5
2,3-Di-*n*-butyl	52	$C_{18}H_{24}$	172–173	.9500	1.5593	.340	78.80	81.73	1.219	35–37	89.9	90.1	10.1	9.7
2,3-Di-*n*-amyl	51	$C_{20}H_{28}$	197–198.6	.9317	1.5474	.341	88.00	91.40	1.265	31–32	89.5	89.6	10.5	10.4
2-*n*-Decyl[b]	59	$C_{20}H_{28}$	213–214	.9220	1.5394	.340	88.00	91.26	1.213	46–47	89.5	89.3	10.5	10.6

[a] Smith and Lo, THIS JOURNAL, **70**, 2209 (1948). [b] M. p. 13°. [c] All analyses by Oakwold Laboratories, Alexandria, Va. [d] Picrates not analyzed. [e] % Yield: for monoalkyl tetralins and naphthalenes, calculated on basis of tetralin as starting material; for dialkyl tetralins and naphthalenes, calculated on basis of monoalkyl tetralin as starting material.

of lines (I and II) is less than one degree, *i. e.*, there are two pairs of parallel lines.

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Summary

1. Seven new 6-*n*-alkyl and 6,7-di-*n*-alkyl tetralins have been synthesized and their physical constants determined.

2. Six new 2-*n*-alkyl and 2,3-di-*n*-alkyl naphthalenes have been synthesized and their physical constants determined.

3. Five other monoalkyl and dialkyl tetralins and naphthalenes have been synthesized and are reported here both for comparison with the same compounds reported by Smith and Lo in a current issue of THIS JOURNAL and to make available additional data not reported for these compounds.

4. Values for the specific refraction, the observed molecular refraction, the theoretical molecular refraction, and the specific exaltation have been calculated for nineteen monoalkyl and dialkyl tetralins and naphthalenes.

5. There is a well-defined linear relationship between the boiling points and the number of carbon atoms when the data are segregated into groups according to molecular types.

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