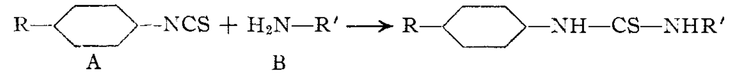
TABLE II



Cpd.	R, reagent A	R″, reagent B	Yield, %	M. p., °C.	Formula	Analyses, % sulfur Calcd.	Analyses, % sulfur Found
VII	Carboxy[a]	*p*-Sulfonamidophenyl[b]	94	213–215; 263–268 (dec.)[c]	$C_{14}H_{13}N_3O_4S_2$	18.25	18.17
VIII	Carboxy[a]	*p*-Sulfon-(2-thiazolyl)-amidophenyl[d]	71	185; 195–200 (dec.)[c]	$C_{17}H_{14}N_4O_4S_3$	22.14	22.11
IX	Carboxy[a]	*p*-Sulfon-(2-pyridyl)-amidophenyl[d]	84	175–179 (dec.)	$C_{19}H_{16}N_4O_4S_2$	14.96	14.97
X	Sulfonamido	*p*-Sulfon-(2-thiazolyl)-amidophenyl[e]	90	214–217 (dec.)	$C_{16}H_{15}N_5O_4S_4$	27.31	27.22
XI	Sulfonamido	6-Methoxy-8-quinolyl[e]	98	189–190 (dec.)	$C_{17}H_{16}N_4O_3S_2$	16.51	16.61
XII	Sulfon-(2-pyridyl)-amido	2-Thiazolyl[f]	82	167–170	$C_{15}H_{13}N_5O_2S_3$	24.57	24.51

[a] Browne and Dyson, ref. 2. [b] Recrystallized from dioxane–acetone. [c] Melted at 213–215°, resolidified and remelted at higher temperature. [d] Recrystallized from dioxane–water. [e] Due to extreme insolubility in organic solvents, the compound was dissolved in dilute sodium hydroxide, treated with norite, reprecipitated slowly with dilute acid, filtered and washed thoroughly with water, alcohol and acetone. [f] Reaction medium, dioxane–acetone; recrystallized as in *e*.

taining 50 cc. of concentrated hydrochloric acid. To this 13.4 g. (0.12 mole) of thiophosgene was added in one portion. Stirring was begun immediately and continued until all of the red color of thiophosgene had disappeared and the product appeared as a white crystalline precipitate. This was filtered, washed thoroughly with water, and recrystallized from acetone–water. The product consisted of 22 g. of white platelets melting with decomposition at 212–214°.

4 - Carboxy - 4′ - sulfonamido - thiocarbanilide (VII).—Twenty grams (0.11 mole) of *p*-isothiocyanobenzoic acid[2] and 20 g. (0.12 mole) of sulfanilamide were dissolved in 800 cc. of dry acetone and refluxed for forty hours. (During this time it became necessary to remove the product several times by filtration to avoid severe bumping.) The "crude" product so obtained was recrystallized from dioxane–acetone; however, its melting point was not altered by this treatment. The thiourea so obtained consisted of 37 g. of a fine white powder. On heating, the product melted at 213–215° and immediately resolidified. Final melting with decomposition occurred at 263–268°.

Acknowledgment.—The authors wish to take this opportunity to express their appreciation to The Wm. S. Merrell Co., whose generous support made this work possible.

Summary

Six new aromatic isothiocyanates and six new thioureas, all derived from pharmacologically well-known sulfonamides, have been prepared and characterized.

CHAPEL HILL, NORTH CAROLINA

RECEIVED JUNE 24, 1946

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

Hydrogenation of Lignin over Raney Nickel[2]

BY J. F. SAEMAN AND E. E. HARRIS

The hydrogenation of lignin in dioxane solution over copper–chromium oxide has been carried out by Harris, D'Ianni and Adkins[3] and subsequently by others.[4,5] A number of new compounds of theoretical and practical interest resulted from their work. In this paper is described an investigation of the hydrogenation of methanol lignin over Raney nickel performed at the Forest Products Laboratory.

Raney nickel promotes greater activity toward aromatic structures than does copper chromium oxide. It was believed that this would lead to the formation of hydroaromatics from which structurally significant ether linkages would be less easily cleaved. Early experiments were carried out with the lignin in dioxane solution at temperatures below 210°, but no significant yield of volatile products was formed. Experiments with this solvent were discontinued because an explosive decomposition of the dioxane is liable to occur[6] at higher temperatures.

An absorption of 1 mole of hydrogen per 45 g. of lignin was obtained in ethanol at a temperature of 240,° but the product was almost exclusively a resin with a very high boiling point. At higher temperatures the ethanol is decomposed.

To avoid the complications caused by unstable solvents, lignin was hydrogenated, using water and hydrocarbons as non-solvent vehicles. In such liquids the lignin melts and reacts in the liquid phase. As hydrogenation progresses, part or all of the products may go into solution, depending on the nature of the vehicle. Advantages in speed and economy of catalyst result from the use of a hydrogen donor vehicle, such as decahydronaphthalene. In aqueous systems the use of alkali has a protective effect on the catalyst,[7] but it results in the production of more complex mixtures.

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(1) Maintained at Madison, Wisconsin, in coöperation with the University of Wisconsin.

(2) Abstracted from a thesis submitted by J. F. Saeman to the Faculty of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1942.

(3) E. E. Harris, J. D'Ianni and H. Adkins, THIS JOURNAL, **60**, 1467 (1938).

(4) H. Adkins, R. L. Frank and E. S. Bloom, *ibid.*, **63**, 549–555 (1941).

(5) J. R. Bower, L. M. Cooke and H. Hibbert, *ibid.*, **65**, 1192–1195 (1943).

(6) N. L. Drake, ed., "Organic Syntheses," John Wiley & Sons, Inc., New York, N. Y., 1941,Vol. 21, p. 16.

(7) E. E. Harris, J. F. Saeman and E. C. Sherrard, *Ind. Eng. Chem.*, **32**, 440 (1940).

The work described in this report is confined to the use of water alone as a vehicle. As in the work done previously using copper-chromium oxide,[3] the lignin used was obtained from extractive-free green aspen wood by treatment with methanol containing 2% hydrogen chloride.

Small-scale experiments showed that the conversion of lignin to gases or very low-boiling products became excessive if the temperature of hydrogenation exceeded 250°. High yields were favored by interrupting the reaction before the pressure had dropped to a constant value, and by the use of catalyst-to-acceptor ratios as high as 1 to 1. The use of such large amounts of catalyst was justified because the principal interest was in the nature of the products.

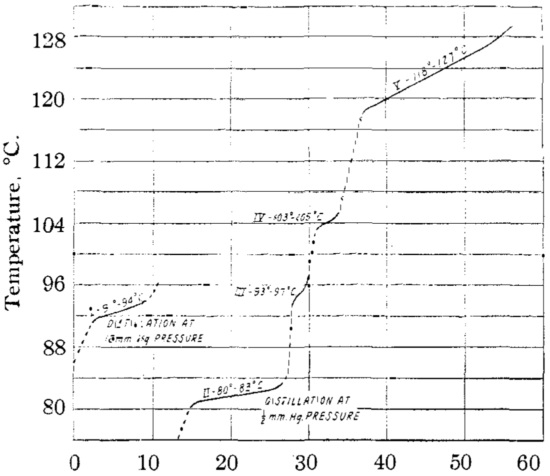

Fig. 1.—Distillation of water-soluble hydrogenation products from one kilo of lignin.

Experimental

A kilo of lignin was hydrogenated in 100-g. batches in an 1800 ml. bomb using a 1-to-1 catalyst-to-acceptor ratio. Water was added to each batch to make a total volume of 1000 ml. Hydrogen was admitted under a pressure of 3000 p. s. i. and the reaction carried out at 250°. The reaction was interrupted at the end of five hours when the rate of pressure drop was 75 pounds or less per hour.

The aqueous layers from these hydrogenations were combined, and the water was removed by distillation. The first distillate contained an insoluble oil, which was added to the water-insoluble material. The aqueous distillate was extracted with ether to recover any dissolved material and the water layer was then discarded. The water-soluble material with a boiling point above 100° was distilled under a vacuum. A distillate of 57.6 g. was obtained with a boiling point below 160° (2 mm.). A residue of 68.9 g. remained undistilled.

The water-insoluble material was dissolved from the bomb with alcohol and dioxane. The catalyst was filtered off, the solvent was removed by distillation at atmospheric pressure, and the remaining material distilled under a vacuum. A total of 206.2 g. boiled below 175° (2 mm.). A residue of 266.7 g. remained. Recovery of the combined water-soluble and water-insoluble products with a boiling point above 100°, amounted to 60% of the starting material. To ensure complete saturation of the distilled materials, the water-soluble and water-insoluble products were separately rehydrogenated in ethanol solution at 130 to 135°, using 4 g. of Raney nickel catalyst per 100 ml. of solution. Hydrogen absorption was insignificant.

The rehydrogenated water-soluble distillate, after removal of the alcohol, was shaken with water and benzene to separate the material of limited water solubility that it contained.

The water-insoluble material was treated similarly with water and ether to remove compounds of high water solubility. This separation was not definite because compounds of intermediate solubility distributed themselves between both layers.

Fractionation of Water-Soluble Material

The water-soluble material was fractionally distilled through a modified Widmer column carrying a helix 15 cm. long with 13 turns. The lowest boiling, 91-94° (10 mm.), fraction and the next, 80-83° (0.5 mm.), fraction were separated after one more distillation; each of the succeeding fractions required an additional fractionation. The final distillation curve is shown in Fig. 1.

Fractionation of Water-Insoluble Material

The water-insoluble material was fractionated into four cuts and then redistilled. No constant boiling cut could be obtained below a temperature of 83° (10 mm.). After two distillations a fraction (I) boiling as shown in the distillation curve (Fig. 2) was obtained. This was redistilled and a sample boiling at 84.7-85.5° (10 mm.) was taken for analysis. A fraction boiling at 94-96° (10 mm.) was separated, and the pressure was reduced to 0.5 mm. A fraction boiling at 86-89° (0.5 mm.) was obtained, but above this it was impossible to obtain any definite fraction by distillation alone. The higher boiling material, amounting to 33.3 g., was fractionated into petroleum ether soluble and insoluble portions by treatment with 125 ml. of petroleum ether, b. p. 40-60°, and cooling in ice and salt. Five grams of viscous liquid separated. The material that was soluble in petroleum ether was distilled, but the only inflection in the boiling curve occurred at 122-127°. This fraction appeared to be impure, however, and it occurred in too small an amount to be satisfactorily purified.

A composite boiling curve is shown in Fig. 2.

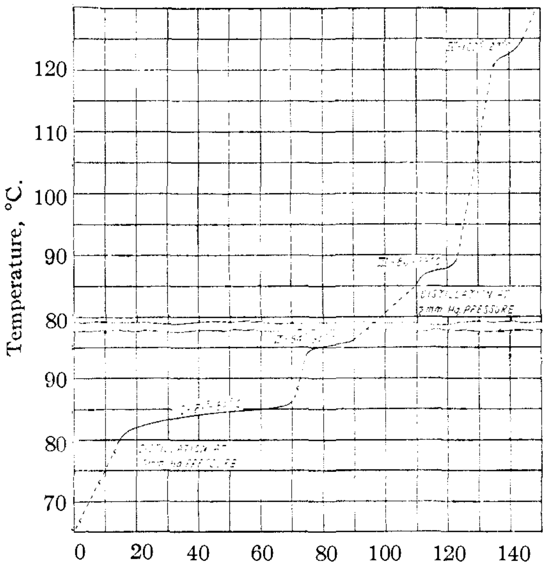

Fig. 2.—Distillation of water-insoluble hydrogenation products from one kilo of lignin.

Characterization of Water-Insoluble Products

Fraction I, b. p. 84.5-85.5° (10 mm.) (45.0 g.).—This, the largest distillable fraction, was identified as 4-ethylcyclohexanol. An α-naphthyl-urethan was prepared and found to melt at 143°. The corresponding derivative from a sample of synthetic 4-ethyl-cyclohexanol melted at 144°. The mixed melting point was 143.5°. Synthetic 4-ethyl-cyclohexanol was prepared by the hydrogenation of *p*-hydroxy-acetophenone.

Fraction II, b. p. 94-96° (10 mm.) (16.5 g.).—This fraction consisted chiefly of 2-methoxy-4-ethylcyclohexanol, together with a small amount of 4-propylcyclohexanol.

Anal. Calcd. for 2-methoxy-4-ethylcyclohexanol, $C_8H_{14}(OCH_3)(OH)$: C, 68.4; H, 11.4; OCH_3, 19.6; OH, 10.8. Calcd. for 4-propylcyclohexanol $C_8H_{15}(OH)$: C, 76.1; H, 12.7; OCH_3, 0.0; OH, 12.0. Found: C, 68.8; H, 11.4; OCH_3, 13.9; OH, 11.1. Analyses for OH were carried out with an acetic anhydride–pyridine reagent.

The 3,5-dinitrobenzoate prepared from this fraction had a m. p. of 125-128°, undepressed by admixture with the 3,5-dinitrobenzoate of authentic 2-methoxy-4-ethylcyclohexanol, m. p. 125.5-127.5°.

Anal. Calcd. for $C_{16}H_{20}O_7N_2$: C, 54.9; H, 5.7; N, 8.0. Found: C, 54.5; H, 5.7; N, 8.3.

The main portion of the phenylurethan from Fraction II had m. p. 110-112°, and a mixed m. p. determination with the corresponding derivative of authentic 2-methoxy-4-ethylcyclohexanol, of m. p. 112.5°, was not depressed. A small portion of the phenylurethan from Fraction II, obtained by fractional recrystallization, melted at 129°. A phenylurethan prepared from synthetic 4-*n*-propylcyclohexanol, m. p. 130.5°, melted at 130° when mixed with the former specimen. Fraction II boiled in the same range as 4-*n*-propylcyclohexanol.

Synthetic 2-methoxy-4-ethylcyclohexanol, b. p. 93–95° (10 mm.), was prepared by rearranging guaiacol acetate to 3-methoxy-4-hydroxy-acetophenone[8] and hydrogenating the latter over Raney nickel in ethanol at 190°.

Fraction III, b. p. 86-89° (0.5 mm.) (9.8 g.).—This fraction was not satisfactorily purified nor identified.

Anal. C, 73.7; H, 11.71; OH, 11.3; OMe, 2.55.

A *p*-nitrophenylurethan was prepared and melted at 230-236°.

Anal. C, 55.7; H, 5.44; N, 12.23.

The Characterization of Water-Soluble Products

Fraction I, b. p. 91-94° (10 mm.) (6.9 g.).—This fraction consisted chiefly of ethylene glycol. The benzoate had a melting point of 72°, undepressed by mixture with ethylene glycol dibenzoate, m. p. 73°. The phenylurethan melted at 156°, m. p. of phenylurethan of ethylene glycol, 157°; mixed melting point undepressed.

Fraction II, b. p. 80–83° (0.5 mm.) (12.1 g.).—This fraction consisted chiefly of diethylene glycol.

Anal. Calcd. for diethylene glycol, $O(C_2H_4OH)_2$: C, 45.2; H, 9.4; OH, 32.1. Found: C, 51.1; H, 9.9; OH, 26.8. Methoxyl analysis gave erratic results averaging 30.4%. Similar erratic results were obtained with methoxyl-free diethylene glycol.

The α-naphthylurethan prepared from this fraction had a melting point of 141-142°, undepressed by admixture with an authentic sample of bis-α-naphthylurethan of diethylene glycol, m. p. 141-142°.

Anal. Calcd. for $C_{26}H_{24}O_5N_2$: C, 70.30; H, 5.41; N, 6.31. Found: C, 69.84; H, 5.42; N, 6.59.

The 3,5-dinitrobenzoate of the fraction melted at 149°.

Anal. Calcd. for $C_{18}H_{14}O_{13}N_4$: C, 43.75; H, 2.84; N, 11.30. Found: C, 43.8; H, 3.06; N, 11.49. Melting point undepressed by an authentic sample of diethylene glycol bis-(3,5-dinitrobenzoate), m. p. 149°.

Fractions III and IV were present in quantities too small to be purified and characterized.

Fraction V-A, b. p. 118-122°, **and V-B**, b. p. 122-127°.—Both of these fractions contained some 3-(4-hydroxycyclohexyl)-propanol-1.

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.30; H, 11.40. Found: Fraction V-A: C, 64.85; H, 10.78. Fraction V-B: C, 64.52; H, 10.57. Crystals separated from V-A: C, 67.28; H, 11.09. The crystalline material melted at 89-93°.

An authentic sample of 3-(4-hydroxycyclohexyl)-propanol-1 deposited crystals after long standing, with a melting point of 89-93°, mixed melting point with the unknown was unchanged. The structure of this compound had previously been established by Harris, D'Ianni and Adkins[3] and by Bowden.[9] A 3,5-dinitrobenzoate was prepared that melted at 130-137°.

Anal. Calcd. for bis-dinitrobenzoate of $C_9H_{18}O_2$: C, 50.6; H, 4.00; N, 10.4. Found: C, 50.0; H, 4.42; N, 10.79.

The melting point reported by Harris, D'Ianni and Adkins[3] for this compound was 130-144°.

Analysis of the water-soluble resinous material that boiled above 130° (0.5 mm.) showed the composition: C, 63.83; H, 9.32. This corresponds to the empirical formula $C_{3.0}H_{3.5}O$.

Summary

Methanol aspen lignin was hydrogenated over Raney nickel at 250°, under a pressure of 400 atmospheres. In the course of four to five hours 1 mole of hydrogen was absorbed per 33 g. of lignin. Conditions for satisfactory hydrogenation were critical. Good yields of distillable products were favored by using large catalyst-to-acceptor ratios, and by interrupting the reaction before the pressure drop ceased.

A yield of 24% of volatile products was obtained which was separated into water-soluble and water-insoluble fractions.

From the material of high water solubility ethylene glycol, diethylene glycol, and 3-(4-hydroxy-cyclohexyl)-propanol-1 were separated and identified. Among the water-insoluble materials, 4-ethyl-cyclohexanol, 4-*n*-propylcyclohexanol and 2-methoxy-4-ethyl-cyclohexanol were found. Besides this methoxyl compound, the presence of other ethers as impurities in the various fractions was indicated by methoxyl and hydroxyl analysis.

MADISON, WISCONSIN RECEIVED[10] AUGUST 24, 1946

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(8) C. Coulthard, J. Marshall and F. Pyman, *J. Chem. Soc.*, 280 (1930).

(9) E. Bowden and H. Adkins, THIS JOURNAL, **62**, 2422 (1940).

(10) Original manuscript received April 22, 1946.