4-Octynoic acid (Table II).—In a typical malonic ester synthesis 280 g. (1.74 mole) of 1-bromo-2-hexyne was added to a solution of 1.5 l. of absolute alcohol, the sodium ethoxide prepared from 41.5 g. (1.8 mole) of sodium, and 320 g. (2 mole) of ethyl malonate. After refluxing for eight hours the product was treated as usual to yield 240 g. (57%) of ethyl 2-hexynylmalonate, b. p. 134–134° at 5 mm., and 75 g. (13%) of ethyl di-(2-hexynyl)-malonate, b. p. 168–170° at 5 mm., $n^{25}D$ 1.4600.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 65.0; H, 8.3. Found: C, 65.3, 65.2; H, 8.2, 8.2. Calcd. for $C_{19}H_{28}O_4$: C, 71.2; H, 8.7. Found: C, 71.2, 71.3; H, 8.8, 8.7.

In another experiment partial saponification occurred during isolation of the products from the reaction mixture and there was isolated a small amount of ethyl di-(2-hexynyl)-acetate, b. p. 135–137° at 3 mm.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.4; H, 9.7. Found: C, 77.0, 77.0; H, 9.7, 9.8.

On alkaline hydrolysis 2-hexynylmalonic acid, m. p. 109–110° with dec., and di-(2-hexynyl)-malonic acid, m. p. 138–139° with dec., were obtained. The neutralization equivalents were 92, 91 (theory, 92) and 131, 131 (theory, 132), respectively.

Anal. Calcd. for $C_9H_{12}O_4$: C, 58.9; H, 6.5. Found: C, 59.0, 59.0; H, 6.6, 6.7. Calcd. for $C_{15}H_{20}O_4$: C, 68.2; H, 7.6. Found: C, 68.4, 68.5; H, 7.6, 7.6.

Heating at 150 to 170° until the evolution of carbon dioxide ceased afforded 4-octynoic acid in 93% over-all yield from ester. The di-2-hexynylacetic acid was not isolated as such but was converted into the amide, m. p. 63–64°.

Anal. Calcd. for $C_{14}H_{21}ON$: C, 76.8; H, 9.6; N, 6.4. Found: C, 76.9, 77.0; H, 10.1, 10.1; N, 6.5, 6.5.

2-Octynoic Acid.—In a manner similar to the above, ethyl 2-heptynylmalonate, b. p. 146 at 5 mm., was prepared in 66% yield.

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.1; H, 8.7. Found: C, 64.9; H, 8.5.[22]

(22) The remaining malonic ester was saponified before the poor analytical result was obtained, hence we were unable to secure a good analysis.

On hydrolysis 2-heptynylmalonic acid, m. p. 93–94°, neutral equivalent 99 (theory, 99), was obtained.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.6; H, 7.1. Found: C, 59.9, 59.5; H, 7.1, 7.3.

Preparation of Methyl Esters.—The acetylenic acids were obtained in over 90% yields after refluxing for twelve hours in an excess of methanol containing small amounts of *p*-toluenesulfonic acid.

Ozonization of Octynoic Acids.—The octynoic acids were oxidized in acetic acid in an ozonizer of the Henne–Perilstein type[23] using a flow rate of 23 l. of oxygen, containing 1 g. of ozone, per hour. Only the dibasic acid fractions were isolated. The acids were checked by melting point and neutralization equivalent. The yields from solutions of about 4 g. of acids in 50 cc. of acetic acid (ozonized for four hours at room temperature) were as follows: 7-octynoic acid, 46% pimelic acid; 6-octynoic acid, 52% adipic acid; 5-octynoic acid, 71% glutaric acid; 4-octynoic acid, 67% succinic acid; and 3-octynoic acid, 80% malonic acid. No attempt to isolate maximum amounts of these dibasic acids was made.

Hydrogenation of Octynoic Acids.—The octynoic acids, 0.8 to 1.4 g., were dissolved in 20 cc. of pure ethyl alcohol and reduced over 0.20 g. of Adams platinum catalyst in a quantitative manner using an apparatus similar to that described by Joshel.[24] In each case almost exactly the theoretical amount of hydrogen was absorbed in times which varied from 150 to 300 minutes. 5-Octynoic acid was hydrogenated on a larger scale in a shaking device (Parr Instrument Company). In each case the saturated acid, obtained in almost theoretical yield, proved to be *n*-octanoic acid. Comparison was always effected by means of the amide, m. p. and mixed m. p., 103–104°.

Summary

The synthesis of 7-, 6-, 5-, 4- and 3-octynoic acids and the preparation and chemical behavior of many of the new acetylenic intermediates are described.

(23) Henne and Perilstein, THIS JOURNAL, **65**, 2183 (1943).

(24) Joshel, *Ind. Eng. Chem., Anal. Ed.*, **15**, 590 (1943).

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[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

Native Lignin. II. Native Aspen Lignin[1,2]

BY M. A. BUCHANAN, F. E. BRAUNS AND R. L. LEAF, JR.

The isolation of native lignin fractions from black spruce and western hemlock has been described by Brauns.[3] These two preparations represent softwood (gymnosperm) lignin and are similar in nature. It is well known that hardwood (angiosperm) lignin differs from softwood lignin in that the former contains a greater amount of methoxyl and is built up of both syringyl and guaiacyl nuclei, whereas only the latter are found in softwood lignins. In recent years, the hardwoods have become increasingly important as a source of wood pulp. Consequently, it was of interest to isolate and investigate the native lignin fraction from a typical hardwood.

Native aspen lignin was isolated by means of neutral ethanol under conditions designed to prevent any change in the lignin during its isolation and purification. The crude lignin contained 17.6% methoxyl, which agrees with the value of 17.5% reported by Lovell and Hibbert[4] for a lignin preparation extracted from aspen with neutral alcohol. These investigators separated their product into three fractions by a fractional distribution between water, methanol, chloroform and carbon tetrachloride. They obtained one fraction having a methoxyl content of 18.4%, but apparently did not investigate their lignin further.

(1) For paper I of this series see F. E. Brauns, THIS JOURNAL, **61**, 2120–2127 (1939).

(2) Presented before the Division of Cellulose Chemistry at the 114th meeting of The American Chemical Society, Portland, Oregon, September 13–16, 1948.

(3) F. E. Brauns, *J. Org. Chem.*, **10**, 211–215 (1945).

(4) E. L. Lovell and H. Hibbert, THIS JOURNAL, **63**, 2070–2073 (1941).

Purification of the crude native aspen lignin by repeated precipitations into water and into ether increased the methoxyl content to a constant value of 19.5%. The purified lignin on treatment with 72% sulfuric acid under the conditions of the lignin determination gave approximately 90% of a "Klason lignin." The composition corresponds very well with those normally obtained from Klason lignin isolated directly from hardwoods.[5] The isolated native aspen lignin, therefore, undergoes changes similar to those produced in native spruce lignin on treatment with 72% sulfuric acid. The exact nature of these changes is not known, but they may involve loss of some fragment of the lignin molecule, in addition to loss of water as a result of condensation.

Treatment of the purified native aspen lignin with methanol containing hydrogen chloride resulted in a product having a methoxyl content slightly higher than the value (25.6%) reported by Harris[6] for methanol lignin prepared directly from aspenwood.

Methylation of the purified native aspen lignin with diazomethane indicates the introduction of 1.5 methoxyl groups per six methoxyl groups originally present. On the other hand, diazomethylation of the methanol native aspen lignin introduced one additional methoxyl group. Under these conditions, diazomethane methylates only acidic hydroxyl groups. Methanol in the presence of hydrogen chloride methylates carboxyl groups and forms acetals with aldehydic or ketonic carbonyl groups and, therefore, the above results indicate the presence of one phenolic group per six methoxyl groups in the original aspen lignin. The additional 0.5 methoxyl group introduced by diazomethane may represent the methylation of one enolic group per 12 original methoxyl groups. However, the methoxyl content of the methanol derivative suggests that there may be as many as 2.5 carbonyl groups per 12 original methoxyl groups.

Complete methylation of the diazomethane-methylated native aspen lignin and acetylation of the original lignin suggests that it contains six hydroxyl groups. However, *p*-toluenesulfonyl chloride reacts with one or two less groups than does acetic anhydride under similar conditions.

A spruce lignin building unit containing four methoxyl groups has been postulated which agrees very well with the analytical results of a number of derivatives.[1] Attempts to postulate a similar unit for aspen lignin have not been entirely satisfactory. If one assumes a unit of aspen lignin containing six methoxyl groups, the unit weight is calculated to be approximately 950 on the basis of the methoxyl content of the native aspen lignin. The carbon and hydrogen data suggest that a unit of this size contains 50 carbon, 56 hydrogen, and 18 oxygen atoms. This combination corresponds to a unit weight of 945. Calculated values for a unit of this size are compared with the observed values in Table I. The data for the original native aspen lignin, as well as those for the completely methylated and acetylated products, agree rather well with the calculated values. However, the diazomethane-methylated material, the methanol lignin, and the phenylhydrazine reaction product do not correspond to the introduction of an integral number of groups. This suggests that either the true unit is a multiple of 945 or that the native aspen lignin is not homogeneous. If the lignin is non-homogeneous, any attempts to derive a unit weight can represent only an average composition of the material. Hence, the 945 unit is only tentative in nature and may require revision when more data are available.

Absorption Spectra.—Methylation of the native aspen lignin reduces the absorption in the visible range by a factor of about four (Fig. 1). Ultraviolet absorption spectra were determined by means of a Beckman Model DU spectrophotometer. The results, expressed as specific extinction (optical density/concentration in grams per liter), are shown in Fig. 2. Methylation has but little effect on the absorption in the ultraviolet region. The native aspen lignin differs from spruce lignin in that it does not have a well-defined maximum at about 280 mmu. It does show a slight inflection at 275 mmu but does not have the minimum at approximately 260 mmu. The aspen lignin curve may be composed of the same general absorption bands which are responsible for the spruce lignin curve. If this is true, the bands are broadened sufficiently to remove the characteristic maximum and minimum.

Patterson and Hibbert[7] likewise found a broadening of the absorption bands in the case of certain hardwood lignin products obtained by the ethanolysis of maplewood.

The infrared spectrum of native aspen lignin has been determined and will be reported later. Its general nature is similar to that reported for native spruce lignin.[8]

Experimental

Isolation of Native Aspen Lignin.—A 17-year old aspen (*Populus tremuloides*) tree having a butt diameter of 5.25 inches was felled shortly after leafing. The wood was immediately converted into sawdust. A 59-pound portion of sawdust (containing 50.6% moisture and 2.4% ethanol-soluble material) was extracted with 95% ethanol at room temperature. One to two gallons of the alcoholic extract was removed from the bottom of the percolator per day, which was then replenished with fresh ethanol. After three weeks, approximately half of the original

(5) Wise, "Wood Chemistry," Reinhold Publishing Corp., New York, N. Y., 1944, p. 297.

(6) E. E. Harris, THIS JOURNAL, **58**, 894-896 (1936).

(7) R. F. Patterson and H. Hibbert, *ibid.* **65**, 1869-1873 (1943).

(8) E. J. Jones, *ibid.*, **70**, 1984-1985 (1948).

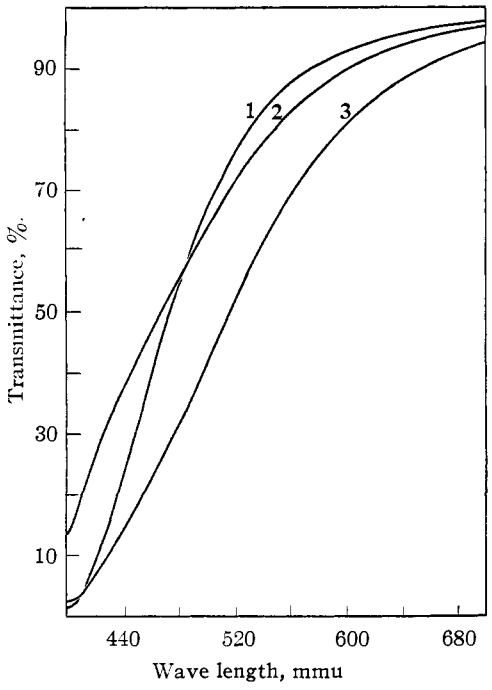

Fig. 1.—Spectral transmittance curves for a dioxane solution: 1, diazomethane-methylated product (concn. 25.0 g./l.); 2, aspen native lignin (concn. 6.3 g./l.); 3, aspen native lignin (concn. 12.5 g./l.).

ethanol-soluble material had been removed from the sawdust and the extraction was discontinued. The alcoholic solutions were concentrated under reduced pressure to a volume of 3 liters. This removed the alcohol and caused precipitation of considerable water-insoluble material.

TABLE I

ANALYTICAL RESULTS

	Number of groups introduced	Calculated for 945 unit ($C_{30}H_{36}O_{18}$), % MeO	Other	Found, % MeO	Other
Native aspen lignin (N. A. L.)	...	19.7	C, 63.5 H, 6.0	19.5	63.2 5.9
N. A. L. methylated with CH_2N_2[a]	1.5	24.1	..	24.1	..
Completely methylated N. A. L.[b,c]	6	36.2	..	36.1	..
Methanol N. A. L.[c]	2.5	26.2	..	26.1	..
Methanol N. A. L. methylated with diazomethane[a]	1[d]	28.8	..	28.8	..
Acetylated N. A. L.[e]	6	15.5	..	15.4	..
Tosylated N. A. L.[e]	4 5	11.9 10.8	S, 8.2 S, 9.3	11.8	9.0
"Phenylhydrazone" of N. A. L.[c]	0.5	18.8	N, 1.4	18.5	1.5
"Klason" N. A. L.[f]	...	..	..	20.5	C, 63.9 H, 5.5

[a] Methylated in dioxane solution to constant methoxyl content. [b] N. A. L. methylated with dimethyl sulfate. [c] Prepared according to Brauns.[1] [d] Number of groups introduced by diazomethane. [e] N. A. L. treated with 2.5 parts *p*-toluenesulfonyl chloride and 15 parts pyridine for 24 hours at room temperature. [f] N. A. L. treated with 72% sulfuric acid under conditions of the lignin determination; yield 90%.

The aqueous mixture was extracted directly with ether, which removed 179.1 g. of ether-soluble material.

The extracted mixture was filtered and the moist precipitate dissolved in dioxane.[9] The resulting solution was dehydrated by distilling under reduced pressure with fresh dioxane. The dry dioxane solution was adjusted to approximately 10% solids and was added dropwise (in small portions) with vigorous stirring to 30 volumes of anhydrous ether. The precipitated product was washed thoroughly with low boiling petroleum ether to remove all traces of ethyl ether. This crude product contained 17.6% methoxyl. It was purified by reprecipitating from a 10% solution in 1:1 methanol–acetone into 10 volumes of water. Eighty per cent. of the material was recovered as a water-insoluble product which, after an additional precipitation into ether, contained 19.2% methoxyl. The yield at this stage was 87.7 g. or 0.7% of the original wood (oven-dry basis). After three additional precipitations into ether, the product contained 19.5% methoxyl (ash-free basis) and 0.12% ash. Additional precipitations into water or into ether did not change the methoxyl content. The analysis of this and other derivatives is given in Table I.

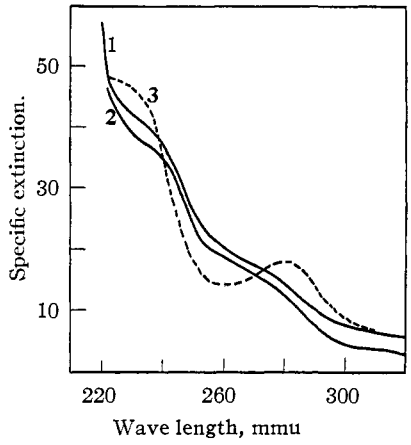

Fig. 2.—Ultraviolet absorption spectra of dioxane solutions: 1, aspen native lignin (concn. 0.021 g./l.); 2, diazomethane-methylated aspen, native lignin (concn. 0.021, g./l.); 3, spruce native lignin[10] (concn. 0.03 g./l.).

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Summary

A native hardwood lignin has been isolated from aspenwood. After purification, the product contains 19.5% methoxyl. On treatment with 72% sulfuric acid, using the Klason procedure, the methoxyl content is increased to 20.4%. A unit of native aspen lignin containing six methoxyl groups also contains six hydroxyl groups, one of which is phenolic in nature. The ultraviolet absorption spectrum of the aspen lignin differs from that of softwood lignins in that no well-defined maximum is present.

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(9) All dioxane used in this investigation was purified by refluxing and distilling over sodium.

(10) J. S. Barton, Ph.D. dissertation, The Institute of Paper Chemistry, 1947.