

HYDROGENATION OF DOUGLAS FIR,
PSEUDOTSUGA TAXIFOLIA, BRITT., WAX

by

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HYDROGENATION OF DOUGLAS FIR,
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INTRODUCTION

Bark, a major by-product in logging operations, constitutes about 9 to 15% of the wood and often presents serious disposal problems. The potential annual yield of Douglas Fir bark alone, as a by-product of the lumber industry in Oregon and Washington, is about 125 million cubic feet. The only use of the whole bark is as a fuel after it has been pressed to remove most of the water. In some instances the bark must be burned as a waste for purposes of disposal.

Since the whole bark has limited applications and is available in such vast quantities, it is only natural that it has been subjected to numerous investigations to determine the chemical composition and possible utilization of this material. Mechanical separation, destructive distillation and solvent extraction procedures have so far been developed pursuant to this problem.

Grondal et al, (9,p.24) effected a mechanical separation by chopping the bark into pieces, drying, then grinding in a coarse burr mill. The resulting material was then subjected to alternate screening and grinding processes. With this method the bark is separated into three components; cork, bast fibers, and an amorphous powder. Other procedures of a similar nature have been

reported (6,p.14).

The cork content of Douglas Fir bark varies with the age as well as the position of the bark on the tree and can range from 25 to 50% of the total bark. This cork is similar chemically to that of the Mediterranean Oak but has a higher extractive content (10,p.66). Mediterranean Oak is the chief source of cork for use in bottle stoppers, etc., in this country. Cork granules have been combined with commercial binder to form composition cork which compares favorably in some instances with that from Mediterranean Oak. Flaky cork particles have been used successfully in the smoke curing of meats and in phenolic resin manufacture. A commercial process for the mechanical separation of the bark has been developed and the cork fraction is sold as a soil conditioner (1,p.61).

East fibers, present in the bark in quantities from 35-48%, are short, pointed, spindle shaped brown particles. They are produced commercially and used in the plastics industry as an ingredient in impact grades of thermosetting compounds and in cold molded plastics. Addition of this material increases the strength and decreases shrinkage. In addition, this material has been found to be of value as an ingredient of magnetsite flooring and as an absorbant filler for explosives. Experimental work

is being done in its application to tile flooring, buffing and abrasive compounds, hard rubber, and asphalt compounds (4,p.88). These fibers have been investigated and their chemical nature established by Kurth and Kiefer (15,p.19). The fibers have a low extractive content as compared to the cork, particularly with respect to dihydroquercetin and waxes. Analytical data indicate that these fibers may be a lignocellulose material similar to wood in composition.

The amorphous powder has found application as an ingredient in match scratcher compounds and as a conditioning agent in insecticide dusts. The powder prevents sticking and agglomeration and adjusts the specific gravity of insecticide dusts. A mixture of fine cork particles (20%), bast fibers (40%), and the fine powder (40%), is prepared commercially and is used as an ingredient in match ignition compounds, as well as a chemical ingredient in phenolic adhesives. Other possible applications are being studied (4,pp.90,92).

Destructive distillations were carried out by Kurth and Ratnam on the total bark at temperatures from 745 to 910°F. for 2 to 10 hours (16,p.519). Among the products isolated were charcoal, acetic acid, acetone and methanol, the latter two components being present in less than one per cent. The yield of charcoal from the

bark was higher than that from the waste wood.

Solvent extraction procedures have been developed for Douglas Fir bark to find utilizable chemicals and as a means of studying the chemical composition. Clark and co-workers (2,p.3143) extracted hogged Douglas Fir waste containing approximately 30% of bark with benzene. They obtained a brown and black wax-like mixture of long chain aliphatic alcohols and acids as well as some unidentified material. The mixture was reextracted with petroleum ether to yield a light brown material of higher melting point than the original mixture. Kurth and co-workers (14,p.185) have extracted tannins, dihydroquercetin, phlobaphene and waxes by their procedure which involved the extraction of the total bark or the cork with benzene, ethyl ether, alcohol, and hot water, in the order named.

Ether extraction of the residue from a benzene extraction of the total bark or cork yields dihydroquercetin, a flavone with pharmacological properties which furthermore is an effective antioxidant against rancidification of fats, oils, and dairy products (13, p.436).

Tannin and a red, amorphous, phlobaphene are extracted with alcohol from the residue of the first two extractions. Phlobaphene is an anhydride of tannin and can be removed by taking advantage of its insolubility in

hot water. The tannin from Douglas Fir has been used by leather companies in Oregon for quite some time. Tannin is also used by the petroleum industry to control the consistency of oil well drilling mud.

The material obtained by the initial benzene extraction is a brown wax which can be separated further into a hexane soluble fraction and a hexane insoluble fraction. The hexane soluble fraction is a tan colored, hard, non tacky wax melting at 58-60°C. Saponification studies (12,p.1648) have shown it to be composed of lignoceryl alcohol, phytosterol, lignoceric acid, ferulic acid, and a small amount, if any, of oleic acid. The hexane insoluble fraction of the benzene extracted wax, on the other hand, is dark brown in color and has been found to be more complex in chemical composition than the hexane soluble fraction (10,pp.60-61).

Although the wax from the benzene extractives of Douglas Fir bark possess many desirable properties and appear to be similar to Carnuba wax in many aspects, it is discolored, particularly the hexane insoluble fraction. This discoloration may be caused by the phlobaphene components. For this reason hydrogenation studies were undertaken in an attempt to convert any phenolic material into a carbocyclic derivative and thus perhaps improve the color of the wax.

EXPERIMENTAL

In order to determine the activity of the catalyst and the suitability of the conditions for the hydrogenation of the aromatic components present in the wax, hydrogenations were performed on phenol and eugenol, especially since the latter is a constituent of lignins.

Eugenol (4 grams), 1 teaspoon of Raney nickel slurry (about 3 grams), were washed into the glass liner of the bomb with absolute ethanol, and hydrogenated for 6 hours at 2575 psi and 190°. The reaction mixture was then filtered, the ethanol evaporated, and the residue distilled in vacuo. The product, boiling at 104-106° (12mm), was identified as octahydroeugenol (75% yield) (17,p.3732).

Phenol (30 grams) dissolved in 50 cc of ethanol was hydrogenated over Raney nickel (1 teaspoon of slurry) at 2000 psi and 150° for 7 hours. The reaction mixture was filtered, then evaporated. The residue was added to aqueous sodium hydroxide, then extracted with ether. The ether was removed and the product distilled yielding 26.2 grams of cyclohexanol (87%).

Hydrogenation studies were limited to three types of waxes which for purposes of discussion will be designated in this thesis as: wax number 1 (the benzene extractive of Douglas Fir bark), wax number 2 (the

hexane soluble fraction of wax number 1), and wax number 3 (the hexane insoluble fraction of wax number 1).

The general procedure employed in these studies was as follows: the glass liner of the Parr Hydrogenation Apparatus was charged with 2 grams of wax, 2 grams of catalyst, and 0 to 100 cc of solvent. The hydrogen pressure was adjusted to pressures varying from 1400 to 2500 psi and the rocker then set in motion while the bomb was brought to the experimental temperatures; heating and shaking continued for periods of 5 to 44 hours. At the end of this time the bomb was opened and the product removed. Isolation consisted of removing the catalyst by filtration and the solvent by evaporation on a water bath with or without vacuo.

In the experiments with no solvent, the reaction mixture was digested with hot solvent, i.e., benzene in experiments 4 and dioxane in experiments 5, 6, 7 and 8. The resulting suspension was filtered to remove the catalyst and the filtrate in turn evaporated.

Twenty milliliters of water were added as a dispersing agent in experiments 9, 10 and 11. Since lignin has been hydrogenated in an aqueous suspension (18, p.2508), a trial of these conditions was suggested by Dr. Kurth. The water was removed from the rest of the reaction mixture by filtration and the solid was then

digested with hot solvent (dioxane in experiments 9 and 10, and benzene in experiment 11).

The results obtained in experiments using wax number 1 are tabulated in Table I.

Hydrogenations on wax number 2 were performed with cyclohexane as a solvent. The procedure followed for the isolation of the product was essentially the same as that described for wax number 1. A 1:1 ratio of catalyst to wax was used with copper chromite and 5% catalyst was used in the low pressure hydrogenations. Results from these studies are given in Table II.

The results from the series of experiments on wax number 3, whose iodine number (Hanus) is 31.4, are tabulated in Table III. In experiments 17 to 26, ethanol was used as a solvent, and the procedure for the isolation of the product was slightly modified. The reaction mixture was filtered hot, using a fluted filter, into a flask containing boiling ethanol; the hot alcohol vapors prevented solidification of the product. The filtrate was then added to cold water and the resulting suspension filtered using suction. The precipitate was dried in an air stream after most of the water had been removed.

Experiments 27 and 28 were carried out with the wax dispersed in water. The isolation procedure was that followed in experiment 5. Experiments 29, 30 and 31 used

TABLE I
HYDROGENATION OF BENZENE SOLUBLE WAX

<u>Exp.</u>	<u>Temp.</u> <u>°C.</u>	<u>Press</u> <u>psi</u>	<u>Time</u> <u>hrs.</u>	<u>Catalyst</u>	<u>Solvent</u>	<u>M.P.</u>	<u>Color</u>
1	200	2450	8	CuCr	dioxane	-	dark brown
2	250	2500	9	"	"	-	grey ¹
3	160	1600	10	"	"	55-57	grey
4	200	1500	11	"	none	-	dark brown
5	160	1450	9	Raney nickel	"	39-44	dark brown
6	170	1550	9	"	"	47-54	dark brown
7	170	1750	6	"	"	48-53	tan ²
8	210	1700	9.5	"	"	-	light tan ³
9	160	1450	44	"	sus-pended water	50-55	yellow ⁴
10	170	1500	5.5	"	"	47-51	dark brown ⁵
11	170	1575	5	"	"	-	dark brown

¹Instead of evaporating the dioxane after removal of the catalyst, the dioxane solution was added to cold water. This yielded a dark grey precipitate which darkened on standing.

²The product was less soluble in dioxane than that from previous runs.

³After removal of the water, the solid was washed with alcohol before digestion with hot dioxane.

⁴The residue from the dioxane evaporation was almost colorless and was soluble in ether.

⁵The Hanus iodine number of the product was 22.2 and that of the original wax was 32.2.

TABLE II

HYDROGENATION OF HEXANE SOLUBLE WAX

<u>Exp.</u>	<u>Temp.</u> <u>°C.</u>	<u>Press</u> <u>psi</u>	<u>Time</u> <u>hrs.</u>	<u>Catalyst</u>	<u>I₂ No.</u>	<u>Color</u>
12	200	1500	6	CuCr	9.84	unchanged ¹
13	200	1700	19	"	-	light tan ²
14	200	1550	15	"	-	white ³
15	160	2450	18	"	5.0	light yellow ⁴
16	25	26	8	Pd on charcoal	7.84	unchanged ¹

¹Hubl's iodine number; Hubl's iodine number on unhydrogenated wax is 17.2.

²M.P. 57-62°.

³M.P. 54-58°.

⁴The iodine number was determined by the Hanus method (11, pp. 393-394). The iodine number of the untreated wax by this method is 24.5.

TABLE III
HYDROGENATION OF HEXANE INSOLUBLE WAX

<u>Exp.</u>	<u>Temp.</u> <u>°C.</u>	<u>Press</u> <u>psi</u>	<u>Time</u> <u>hrs.</u>	<u>Catalyst</u>	<u>I₂ No.</u>	<u>H₂</u> <u>absorp.</u>	<u>Color</u>
17	60	2000	21	Raney nickel	27.8	50	red brown ¹
18	100	2000	16	"	25.4	100	brown ¹
19	150	2000	11	"	25.2	50	brown ¹
20	200	2000	14	"	18.9	275	brown ¹
21	250	2000	22	"	21.3	300	black ²
22	100	2000	17	CuCr	24.3	100	tan ³
23	150	2000	22	"	25.6	100	brown
24	200	2000	18	"	32.3	325	brown
25	250	2000	23	"	29.7	450	black
26	250	2000	14	"	28.0	400	black
27	200	1700	8	Raney nickel	-	-	dark brown
28	200	1700	8	"	-	-	yellow oil ⁴
29	250	1650	28	Raney nickel, CaO	-	-	brown oil ⁵
30	160	2850	7	"	-	-	red brown
31	190	2700	9	Raney nickel	-	-	brown

¹A yellow product was obtained, which darkened rapidly on exposure to air.

²The reaction product was tan colored, and darkened upon standing.

³This product, after standing in the atmosphere, turned black.

⁴Dioxane was used to digest the reaction mixture.

⁵Ether was used to digest the reaction mixture.

dioxane as solvent, which had been purified by the procedure described by Fieser (5,p.369). The products in experiments 29 to 31 were isolated by the general procedure.

In order to note the changes in the composition of the wax due to hydrogenation a sample of wax number 3 was hydrogenated under conditions given in experiment 31, and both the hydrogenated and untreated product were saponified, according to the procedure of Hergert and Kurth (10,p.61).

The results of this study are given in Table IV.

TABLE IV

<u>Fraction</u>	<u>Hydrogenated wax</u>	<u>Untreated wax</u>
Non saponifiable	15.5%	16.4%
Acids:		
hexane soluble	46.3%	30.2%
benzene soluble	19.5%	31.4%
ether soluble	5.4%	10.12%
ether insoluble residue	<u>14.4%</u>	<u>11.9%</u>
	104.6	109.42

Since Hergert (10,p.61) had reported the isolation of an unsaturated acid, m.p. 40-45, neutral equivalent 282 in the benzene soluble fraction of the acids obtained through saponification of wax number 3, hydrogenation experiments were undertaken using the sample of the same

material.

Ten grams of the benzene extract of the acid fraction of the saponified wax number 3, 1 teaspoon (about 3 grams) of Raney nickel catalyst in ethyl alcohol was hydrogenated for 12 hours at 100° and 1700 psi pressure. The reaction mixture, after removal of catalyst, was refluxed in alcoholic potassium hydroxide for 2 hours, evaporated to remove ethanol, acidified, and filtered. The precipitate was recrystallized from isopropyl ether. A yellow brown amorphous solid was obtained which upon drying yielded a dark brown solid (m.p. 61-67°, neutral equivalent 374).

This material was extracted with boiling hexane, which upon cooling yielded a white precipitate (m.p. 68-70°, neutral equivalent 279.5). The residue from the hexane extraction yielded yellow crystals from a mixture of isopropyl ether and ethyl acetate melting at 65-68° with a neutral equivalent of 293.5. Both of these fractions gave a negative bromine test for unsaturation, showing that hydrogenation was effective as far as the unsaturated acids are concerned.

Sulfonation and nitration experiments were undertaken in order to estimate the amount of aromatic material in (a) wax number 3, (b) acids obtained by saponification of wax number 3, and (c) the alcohols from the saponification of wax number 3.

The procedure for the sulfonation reaction consisted of the following:

Ten grams of the wax or one of its components were added portionwise with stirring to a solution of 6 cc of concentrated sulfuric acid, 26.8 cc of glacial acetic acid and 67.2 cc of acetic anhydride, according to the directions of Friese (7,p.1066), who sulfonated lignin under identical conditions. The stirring was continued for 9 hours, after which the reaction mixture was filtered through a sintered glass funnel and the insoluble residue washed with glacial acetic acid. Tests for sulfur were performed on the insoluble portion in all three experiments. Negative results, as expected, were obtained in all cases.

The filtrate was concentrated at reduced pressure to about 50 cc and then added to 300 cc of water. The excess sulfate was precipitated by bringing the aqueous solution to pH 8 with barium hydroxide. The resulting suspension was warmed and filtered using filter aid and the filtrate in turn freed of barium ion by passage through an IR100 ion exchange column. This converted the water soluble barium salts to the free acids. The precipitate, together with the filter aid, was resuspended in water, acidified with hydrochloric acid, refiltered and the filtrate basified to see if any insoluble barium salts

were present; no precipitation was observed, thus indicating that only barium sulfate had been removed.

The eluent from the IR100 column was evaporated to dryness yielding a dark, hygroscopic substance. Since the presence of sulfur in the residue from this evaporation had been indicated by sodium fusion, the sulfur was determined quantitatively.

This sulfur containing residue was then hydrolyzed to determine the amount of sulfate esters, if any, that were present. Since the aromatic sulfonic acids are not easily hydrolyzable they would not be hydrolyzed but would remain intact.

The residue was refluxed with 5.6 grams of potassium hydroxide in 100 cc of water for 8 hours. The reaction mixture was cooled and examined for base insoluble components by extraction with ether. Evaporation of the ether extract left a thin film of residue so small it could not be weighed on the Trip balance.

The basic aqueous residue from the ether extraction was acidified with hydrochloric acid and extracted again, this time with chloroform to see if any acid insoluble compounds were present. Evaporation of this solvent also left a very small residue thus indicating the presence of very little simple sulfate esters.

The acidified aqueous residue was then tested for free sulfate ion. After extraction with chloroform, the aqueous solution was diluted to 500 cc and the free sulfate was determined on a 50 cc aliquot. The free sulfate should come from aromatic sulfate esters which have also been sulfonated to form water soluble sulfonic acids.

The results of the sulfonation studies are presented in Table V.

TABLE V

Samp.	Wt. used (A)	Wt. insol. material	Wt. residue IR100 eluent evaporation (B)	Total sulfur (as %A)	(as %B)	%SO ₃ H	%SO ₄
a)	10	7	3.3	5.67	17.2	87.8	12.2
b)	10	.5	9.0	12.8	14.2	96.1	3.9
c)	10	7.0	6.5	7.46	15.5	86.0	14.0

The conditions for the nitration experiments were identical with those of Friese for the nitration of lignin (8,p.1468). The experimental procedure was as follows:

The acid fraction of saponified wax number 3 (10 grams) was added portionwise to a stirred solution of 72 cc of acetic anhydride, 10 cc of glacial acetic acid, and 14 cc of concentrated nitric acid. Stirring was

continued for six hours, the reaction mixture then filtered through a sintered glass funnel. The insoluble material was washed with glacial acetic acid, then water, and the washings added to the original filtrate. The insoluble fraction, weighing 3.23 grams (30.8% of total), melted at 72-73° and gave a negative test for nitrogen.

Addition of the water washings to the original filtrate caused precipitation of a pale yellow solid. This material was removed by filtration, and washed with water until the washings were neutral (weight 7 grams, 67% of total, nitrogen content 5.57%). With drying in vacuo over calcium chloride the product became dark red in color.

The aqueous filtrate from the removal of the yellow nitration product was then passed through an IR4B ion exchange column and the eluent evaporated to dryness (weight residue 0.25 grams, 2.2% of total).

Reductions were performed on the nitration product in an effort to convert the nitro groups to amino groups. Two methods were tried, catalytic hydrogenation and a stannous chloride-hydrochloric acid mixture.

The red solid from the nitration reaction (4 grams), 0.2 gram of platinum oxide catalyst and 70 cc of ethanol were hydrogenated at room temperature at 35.75 psi for

5 hours. The decrease in pressure at the end of 4 hours was 34.25 psi.

The reaction mixture was filtered and the ethanol evaporated. The residue was added to 100 cc of 2 N hydrochloric acid, the resulting suspension heated to boiling with stirring. Upon cooling, a dark brown, wax-like material was observed and was removed by filtration (weight 3.7 grams). This material gave a positive nitrogen test and a positive ferric chloride test for phenols. The filtrate was evaporated to dryness, yielding a small amount of residue.

Stannous chloride (2.8 grams) in 3 cc of concentrated hydrochloric acid was added to a stirred solution of 4 grams of the nitration product in 60 cc of ethanol. The mixture was refluxed on the steam bath for 1 hour, then added to a solution of 3.6 grams of sodium hydroxide in 10 cc of water. The ethanol was removed by evaporation, and the residue added to 50 cc of 2 N sodium hydroxide. The resulting mixture was cooled and the insoluble matter extracted with ether, and the ether evaporated. The residue, 1.2 grams of a yellow wax-like material, contained nitrogen and gave negative ferric chloride test for phenols.

The aqueous residue was filtered to remove an insoluble paste (.4 gram) and the filtrate was acidified

to precipitate the insoluble acids, and reextracted with ether. Evaporation of the ether extract yielded a dark brown solid weighing 1.3 grams and containing nitrogen. A ferric chloride test for phenols gave a dark brown coloration.

A fine brown precipitate was observed in the aqueous layer which was insoluble in the ether. The acidic aqueous residue was filtered to remove the fine precipitate. A fusion test showed this material to be mostly inorganic. This precipitate was washed with ethyl acetate and the ethyl acetate evaporated. The residue from this evaporation was very small, weighing about 0.03 gram.

DISCUSSION OF RESULTS

The reduction of phenol and eugenol to cyclohexanol and octahydroeugenol with Raney nickel indicated that the catalyst was sufficiently active to bring about the reduction of aromatic nuclei.

Copper chromite acts somewhat preferentially in reducing carbon-oxygen bonds while being relatively inactive toward aromatic nuclei, and was used in these experiments for purposes of comparison.

Hydrogenations on wax number 1, catalyzed by copper chromite, yielded unstable products which darkened on standing. Higher reaction temperatures with this catalyst gave less stable products. This wax, as well as wax 3, contains a phlobaphene-like phenolic material and conversion of these waxes into a stable, light colored product appears to be dependent on the conversion of this material into carbocyclic compounds. Raney nickel, which is selective toward reduction of carbon-carbon double bonds as well as aromatic nuclei, should be well suited for this purpose. With this catalyst, wax 1, originally brown in color, was converted to a light tan product. The best results with this catalyst were obtained with no solvent and at high reaction temperatures. Since the wax is a liquid at the reaction temperatures used in this study, a solvent is not essential. The presence of water in the

hydrogenation media did not seem to improve the product.

Wax number 2 is much less complex in composition, containing none of the phlobaphene present in waxes 1 and 3 (12,p.1686). The original color is tan, much lighter than waxes 1 and 3. Hydrogenation with copper chromite was effective in removing the color and reducing the iodine number from 24.6 to 5.0 (note 5, Table II). Low pressure hydrogenation was not effective in color removal but did reduce the iodine number from 17.2 to 7.84 (note 1, Table II).

Wax number 3, having the largest amount of the phlobaphene-like phenolic material, could not be reduced to a stable, light colored product under the conditions cited. Hydrogenations over Raney nickel did decrease the color but the products were unstable and darkened considerably upon exposure to air.

The hydrogen absorbed in experiment 21, Table III, performed with Raney nickel catalyst corresponds to approximately 1.2 moles of hydrogen. The iodine number of the untreated wax indicates about 0.49 mole of unsaturation which was decreased by 0.16 mole with hydrogenation. With copper chromite as catalyst, (experiment 26, Table III), the hydrogen absorbed was 1.56 moles and the decrease in olefinic linkages by iodine number 0.043 mole.

These results are difficult to correlate with the dark products obtained. The small olefinic bond decrease and the high hydrogen absorption would indicate reduction of aromatic nuclei had taken place but such reaction products should be more stable than the phenolic material originally present. It is possible that a small amount of difficultly hydrogenated material is present and is causing the discoloration upon exposure of the product to air.

A comparison of the relative quantities of acid fractions obtained by saponification of hydrogenated and untreated wax 3 indicates hydrogenation caused a change in solubility characteristics of the acids. The amount of acids soluble in the less polar solvents has increased with hydrogenation as would be expected.

Hydrogenation of the benzene soluble fraction of the acids from wax 3 and subsequent fractional crystallization yielded two fractions, which were separated on the basis of hexane solubility, both giving a negative test for unsaturation, melting at 68° to 70° and 65° to 68° with neutral equivalents of 279.5 and 293, respectively. Hergert and Kurth (10,p.61) reported the presence of unsaturated hydroxy acids melting from 40 to 45° with a neutral equivalent of 282 and a saturated hydroxy acid melting from 79 to 81° with a neutral equivalent of

274 in untreated wax 3.

Although the agreement is not close it appears that the acid m.p. 68-70° must be the one described by Hergert and Kurth with m.p. 79-81°, as judged by neutral equivalents and solubility data (10,p.61).

The results of the sulfonation experiments indicate that some sulfate esters as well as sulfonic acids were formed.

As was expected the acid component of the wax contained the bulk of the aromatic material although some was present in the alcohol fraction. The sulfate esters may arise from some sulfonation of the olefinic linkages of the alcohols.

The presence of sulfonic acids in the alcohol component indicates some aromatic material was present in this hydrolysis product in addition to the lignoceryl alcohol and physosterol reported by Hergert and Kurth (10,p.61).

The magnitude of the sulfur content would indicate that the wax consists largely of aromatic material which supports the observation of Hergert and Kurth who reported the wax to contain about 25% of phenolic material alone (10,p.61).

Nitration experiments confirm the presence of an aromatic component in the wax. Furthermore, judging by

the magnitude of the nitrogen in the nitrated acids, the aromatic content is large, thus confirming the results of the sulfonation studies.

The product from the catalytic reduction was removed from an acidic media. This product also gave a positive ferric chloride test for phenols and contained nitrogen.

The product from the stannous chloride reduction of the nitrated acids was obtained in two fractions. The fraction extracted from the basic mixture was found to contain nitrogen and gave a negative ferric chloride test for phenols. The material extracted from the acidic suspension contained nitrogen and gave a positive ferric chloride test. The phenolic fraction is sufficiently acidic to be extractable from an acidic solution even with an amino group.

SUMMARY

The wax extracted with benzene from the bark of Douglas Fir (Pseudotsuga taxifolia, Britt.) and its two fractions, the hexane soluble and hexane insoluble wax, was hydrogenated over copper chromite and Raney nickel catalysts in an effort to remove their color.

The brown wax (extracted with benzene from the bark) was hydrogenated over Raney nickel to a light tan colored product, and the hexane soluble fraction of this wax, tan in color, was converted to a white wax with copper chromite.

The hexane insoluble fraction, red brown in color, was quite difficult to hydrogenate to a product that was light colored and would not darken upon standing.

Saponifications were performed on hydrogenated and untreated hexane insoluble wax. A comparison of the relative quantities of the acid fractions showed increased solubility of the acids in the less polar solvents with hydrogenation.

The benzene soluble acids from the hexane insoluble wax, known to contain unsaturated acids, was hydrogenated and the product tested for unsaturation. Negative results indicated hydrogenation was removing olefinic bonds.

Sulfonations on the hexane insoluble wax and its two saponification products yielded sulfonic acids in both the acid and the alcohol fraction.

Nitration experiments on the acid fraction of the hexane insoluble wax yielded a red solid containing 5.57% nitrogen. Reduction of the nitration product with stannous chloride gave base insoluble and acid insoluble products, both containing nitrogen. Catalytic reduction of the nitration product yielded an acid insoluble product.

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