All the published information indicates, however, that cobalt–magnesia catalysts do not measure up to the cobalt–thoria catalysts in yield of liquid hydrocarbons. Yields of 150 cc. per cubic meter of gas are now normal in the latter case whereas with cobalt–magnesia catalysts the yields reported are less than 100 cc. of liquid per meter cube.

It appears, therefore, that the thoria in a Fischer catalyst exerts a promoter action more specific than that of merely dispersing the cobalt. In other words, good availability of cobalt to carbon–carbon bonds, associated in the Fischer process with the reduction of the carbon monoxide to hydrocarbon radicals, is not a sufficient condition for a good Fischer catalyst. There must be present a promoter, such as thoria, which will give to the catalyst suitable properties, presumably for catalyzing the polymerization of the hydrocarbon radicals to the desired products. More evidence for the specific action of the promoter is found in the type of hydrocarbon product resulting from cobalt catalysts with different promoters. The data in the literature indicate that alumina as a promoter gives rise to a light spirit, thoria to the normal Fischer spirit, and manganese oxide to paraffin wax. In these cases, obviously, the promoter is exercising an influence upon the extent of polymerization that takes place.

This suggests that, although it is a better dispersing agent for the cobalt (which undoubtedly initiates the reduction of carbon monoxide to hydrocarbon radicals), the magnesia is less efficient than thoria in bringing such radicals into the polymerizing reactions which ultimately yield the Fischer spirit.

Summary

1. The rate of the hydrogenation-decomposition of ethane has been studied on a cobalt–thoria–copper–kieselguhr catalyst, and upon four cobalt–magnesia catalysts containing varying proportions of the components.

2. The results indicate that, for this reaction, cobalt is somewhat less active than nickel, but much more active than copper.

3. This reaction on cobalt is inhibited by hydrogen, but to a less extent than the same reaction on nickel. The dependence of the rate on hydrogen concentration varies with the nature of the second component of the catalyst.

4. The cobalt–magnesia catalysts are markedly more active in this reaction than the cobalt–thoria–copper catalyst. In the range of composition studied, the activity of the catalysts of the cobalt–magnesia series increased with increasing cobalt content.

5. These results have been discussed in connection with the work of previous investigators on nickel and copper.

6. The use of the hydrogenation-decomposition of ethane as an index to the availability of cobalt in catalysts for the Fischer synthesis of higher hydrocarbons from water gas has been discussed.

Studies on Lignin and Related Compounds. XXXV. The Ethanolysis of Spruce Wood

BY A. B. CRAMER,[1] M. J. HUNTER[2] AND HAROLD HIBBERT

The isolation from extracted lignins of various aromatic products[3a] such as veratric, dehydrodiveratric and isohemipinic acids[3b]; protocatechuic acid and gallic acid[3c]; catechol, phenol, o-cresol, guaiacol, creosol, 1-vinyl-3-methoxy-4-hydroxybenzene, 1-n-propyl-3-methoxy-4-hydroxybenzene[3d] has led to the formation of certain theories of lignin structure, which would seem to be based on unsatisfactory and very incomplete experimental evidence. Up to quite recently there has been a general tendency to ascribe a highly complex structure, or series of closely related structures, to lignin, but there is now a growing opinion[4] that lignin may possibly exist in the wood

(1) Post-graduate student and holder of Hibbert–Cole Fellowship.

(2) Post-graduate student and holder of Dow Chemical Company Fellowship.

(3) (a) For review see "Chemistry of Lignin," M. Phillips, Chem. Rev., **14**, 103 (1934); (b) Freudenberg and co-workers, Ber., **71**, 1821 (1938); **69**, 1415 (1936); (c) Hibbert and co-workers, THIS JOURNAL, **58**, 345, 348 (1936); **59**, 2447 (1937); **60**, 565 (1938); Can. J. Research, **16B**, 54, 68 (1938); (d) Phillips and Goss, Ind. Eng. Chem., **24**, 1436 (1932).

(4) Hilpert and co-workers, Ber., **67**, 1157 (1934); **68**, 16, 371, 380, 1575 (1935); **69**, 680 (1936); **70**, 108, 413, 514 (1937); Z. angew. Chem., **49**, 54 (1936); Cellulosechemie, **16**, 92 (1935); **17**, 124 (1936).

as a simple substance of low molecular weight, and which, due to its unstable character, very readily undergoes condensation–polymerization reactions yielding the more complex materials isolable in the form of "extracted" lignins. Hilpert considers this original substance to be some type of carbohydrate, but the experimental evidence of other workers does not support this point of view.

Unfortunately, the earlier belief that lignin exists as a highly polymerized complex substance, already pre-formed in the wood, led workers to consider that the water-insoluble amorphous product obtained by the customary extraction methods was the only form in which lignin could be isolated. Precipitation into water has been an almost invariable step in all extraction or purification methods, and invariably the efficiency of an extraction process has been judged by the amount of water-insoluble product formed. The possibility of the isolation of other substances not precipitated by dilution with water has been overlooked, and this has resulted in the practice of discarding the precipitating liquors. The latter, as shown in the present communication, contain aromatic products in considerable amount and their presence would seem to be very important from the point of view of lignin structure. In this and accompanying researches the water-soluble constituents obtained by the action of various hydroxylic solvents on wood have been subjected to a thorough investigation. This communication deals only with the action of ethanol and hydrochloric acid on spruce wood meal.

The liquors obtained by precipitation of the ethanolysis extract of spruce wood meal into water yielded, on ether extraction, the following products.

		% Based on wt. of dry wood meal	% Based on wt. of "Klason lignin" originally present
I	Aldehydes	0.54	1.9
II	Acids	.46	1.6
III	Phenols (distilled)	.92	3.3
IV	Neutral product	.41	1.4
		2.33	8.2

Up to the present only the lower-boiling phenolic constituent has been identified definitely, but all of the remaining products are under investigation.

The phenolic substance is a thick distillable sirup (b. p. 130–150° at 0.010 mm.) which could not be crystallized. On treatment with diazomethane it gave a well-defined crystalline product, m. p. 81–82°, having the empirical for-

mula $C_{13}H_{18}O_4$. Grignard machine analysis showed the presence in this of one carbonyl group (13% enolized in pyridine solution) per molecular weight of 238. Alkoxyl analysis showed presence of one ethoxyl and two methoxyl groups per mole of 238. The methylated ketone also yielded a well-defined crystalline 2,4-dinitrophenylhydrazone corresponding to the formula $C_{19}H_{21}O_5N_4$ indicating an addition of one hydrazine residue per molecular weight of 238. Alkaline permanganate oxidation of the ketone yielded veratric acid, proving the presence of the veratryl group. Consideration of these analytical data indicated the substance to be one of four products, namely
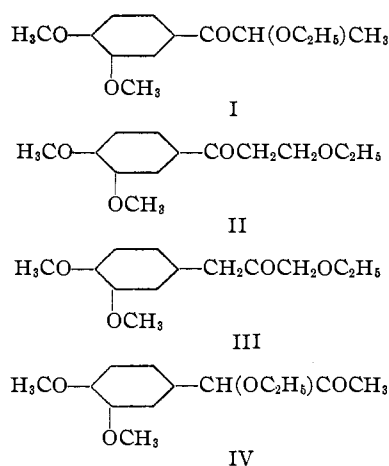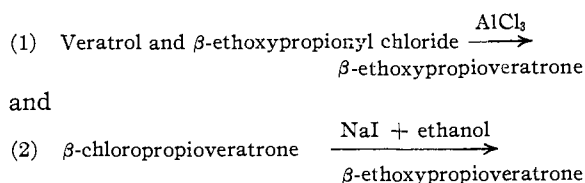

none of which has been reported previously in the literature.

A negative iodoform test excluded Formula IV, while of the remaining three, α-ethoxypropioveratrone (I) and β-ethoxypropioveratrone (II) seemed the most probable, especially in view of the isolation of vanillin as a fission product of extracted lignin.[3c]

Following an extensive series of investigations the synthesis of both substances has been accomplished and the methylated water-soluble, low-boiling phenol constituent definitely identified as α-ethoxypropioveratrone (I).

Synthesis of β-Ethoxypropioveratrone.—This was carried out by two different methods as indicated below

(1) Veratrol and β-ethoxypropionyl chloride $\xrightarrow{\text{AlCl}_3}$ β-ethoxypropioveratrone

and

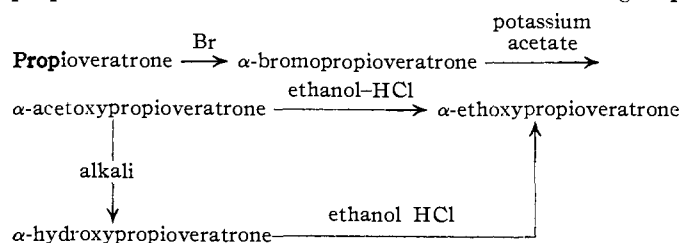(2) β-chloropropioveratrone $\xrightarrow{\text{NaI + ethanol}}$ β-ethoxypropioveratrone

Using the first method, many experiments were necessary before the desired conditions were found, since there is a marked tendency for demethylation and loss of ethoxyl to occur during the reaction, the net result being the liberation of free hydroxyl groups and consequently a very pronounced tendency of the resulting product to undergo condensation–polymerization reactions.

The second procedure provided a much smoother reaction and gave good yields of the β-ethoxy compound.

The crystalline β-ethoxypropioveratrone obtained by both syntheses was identical in every respect, but differed from the natural diazomethane-methylated ethanolysis derivative, as shown by its melting point and mixed melting point determinations.

Synthesis of α-Ethoxypropioveratrone.—Attempts to synthesize the α-ethoxy compound directly by the Friedel–Crafts reaction from α-ethoxypropionyl chloride and veratrol were unsuccessful in spite of numerous variations in the procedure used. The crystalline reaction product curiously enough had the same melting point as the natural substance but showed a lowering of 15–20° in a mixed melting point determination. Grignard machine analysis showed absence of a carbonyl group and both methoxyl and carbon-hydrogen values indicated that the substance was not the desired product.

The α-ethoxy compound was finally synthesized by the following series of reactions starting with propioveratrone

Propioveratrone $\xrightarrow{\text{Br}}$ α-bromopropioveratrone $\xrightarrow[\quad]{\text{potassium acetate}}$

α-acetoxypropioveratrone $\xrightarrow{\text{ethanol–HCl}}$ α-ethoxypropioveratrone

| alkali

α-hydroxypropioveratrone $\xrightarrow{\text{ethanol HCl}}$

The yield, when synthesized from the hydroxy compound, was much lower, namely, around 12% as compared with that of approximately 80% from the acetate directly.

The synthetic product thus obtained was identical in all respects with the natural product isolated from spruce wood meal.

Theoretical Discussion

The manner of synthesis of α-ethoxypropioveratrone suggests the mechanism of ethoxyl addition

to α-hydroxypropioveratrone. It appears highly improbable that the postulated hydroxyl group in the side chain exists free in the wood. The fact that the extremely mild treatment with ethanol and hydrochloric acid polymerizes such a large part of the unethylated material makes it appear that practically none of the latter would survive the much more severe treatment of the extraction process. On the other hand, since the acetate gives a comparatively good yield of the ethylated compound under the same conditions, this suggests that, *in situ*, the hydroxyl is masked in some manner, possibly as a glycoside. It is suggested that, by a similar kind of ester or ether interchange reaction, the ketone is transformed into an ethoxyl derivative, in which form it is isolated. The results thus provide a solution of a long-outstanding problem, namely, the reason for the interaction of the organic extractant with the lignin constituents of wood. For some considerable time it has been known that hydroxylic solvents such as alcohols, glycols and glycerol derivatives[5,6] react with lignin during the extraction process. The investigations outlined above indicate a simple mechanism for such an addition.

Relationship of α-Hydroxypropiovanillone to "Extracted" Lignins.—The synthesis of α-hydroxypropiovanillone has now been carried out.[7] It is an extraordinarily reactive substance which readily undergoes condensation–polymerization reactions under the influence of dilute acids at room temperature. The aliphatic hydroxyl group is especially reactive, while the phenolic hydroxyl group, due to its position *para* to a carbonyl group, exerts an outstanding influence on the properties of the latter, as in the case of vanillin, which in the Grignard machine shows only 0.65 active hydrogen and 0.33 RMgX added per mole vanillin in isoamyl ether solution, while values of 0.99 and 0.21, respectively, are obtained in dioxane.[8]

On warming with dilute sulfuric acid, α-hydroxypropiovanillone is converted into a light-brown condensation product possessing many of the properties of, if actually not identical with, Freudenberg "Cuproxam" lignin.[9] It therefore seems reasonable to suggest that "native" lignin

(5) Hägglund and Urban, *Cellulosechemie*, **8**, 69 (1927).

(6) Hibbert and co-workers, *Can. J. Research*, **2**, 357, 364; **3**, 65 (1930); **13**, 28 (1935); THIS JOURNAL, **55**, 4720 (1933).

(7) Publication to be made in the immediate future.

(8) M. Lieff, Ph.D. Thesis, McGill University, 1938.

(9) Freudenberg, *Ber.*, **71**, 1810 (1938).

in wood is present to a large extent either (a) in the form of simple building units of this type, or, on the other hand, (b) as more complex substances which readily undergo fission into this and other simple building units.

The fact that recent work carried out by Peniston and McCarthy in these Laboratories on an oak lignin extracted under very mild conditions proves that it is possible to reconvert such a lignin, by the above ethanolysis technique, into the same "type mixture" of oils described in this communication, and in high yield (about 36%), would seem to be a strong argument in favor of the first theory (existence in wood of *simple* building units). It is thus of considerable interest that the theory of lignin as a condensation-polymer of a simple unit, namely
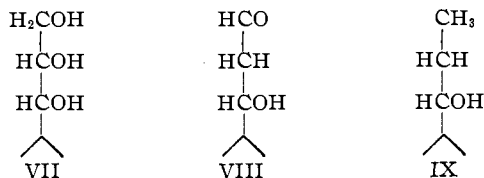
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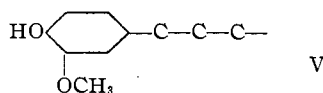
first put forward by P. Klason[10] some thirty years ago and supported so energetically by Freudenberg[11] in recent years, should find strong support in the present investigation.

Klason was of the opinion that lignin is essentially a polymer, or condensation product, of coniferyl aldehyde or alcohol, or both.[1a] On the other hand, Freudenberg for many years held the view[11] (p. 134) that it is a *linear condensation polymer* (VI) derived from a di- or trioxypropylguaiacol.
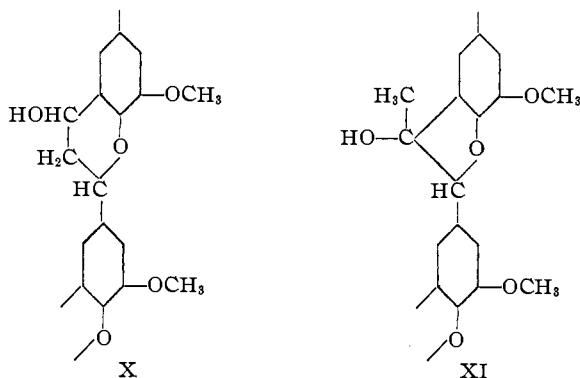
VI
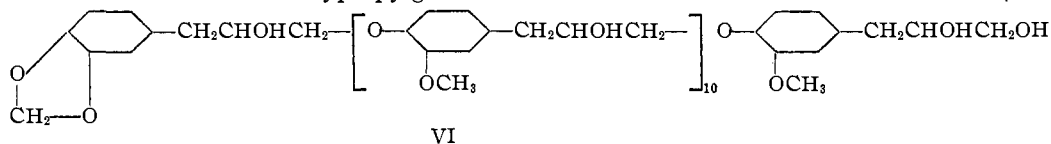
The recent isolation in these Laboratories of vanillin, acetovanillone and guaiacol from spruce lignin sulfonic acid[3c] rendered such a mode of linkage highly improbable, and in his most recent communication Freudenberg[12] has abandoned this view of lignin structure in favor of the new theoretical, polymeric types (X) and (XI), derived theoretically from the dioxyphenylpropanes (VIII and IX).

H$_2$COH	HCO	CH$_3$
HCOH	HCH	HCH
HCOH	HCOH	HCOH
VII	VIII	IX

X   XI

It is the writers' belief that this theoretical conception also will have to be abandoned in favor of the view that all extracted lignins are condensation polymers, derived in large measure, possibly entirely, from the building units (XII) and (XIII) or their dismutation isomers.
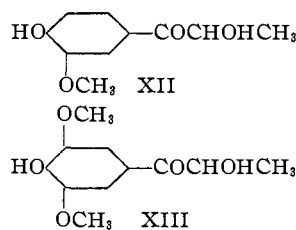
In soft woods only (XII) is concerned, while in hard woods both (XII) and (XIII) take part in the formation of "extracted" lignins.

The fact that substances similar to (XII) and (XIII) are known to undergo, readily, tautomeric changes of the types (XIV), (XV) and (XVI)[13]

RCOCHOHR′ $\rightleftarrows$ RC(OH)=C(OH)R′ $\rightleftarrows$
    XIV   XV
                                            RCHOHCOR′
                                                XVI

would indicate the possibility of a similar equilibrium transformation of XVII into XVIII
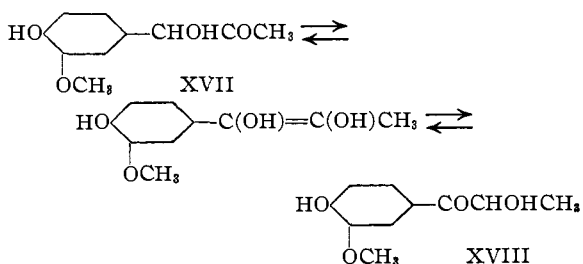
(10) Klason, *Arkiv Kemi Mineral Geol.*, **3**, No. 5, 17 (1908).
(11) Freudenberg, "Tannin, Cellulose, Lignin," Verlag von Julius Springer, Berlin, 1933.
(12) Freudenberg, *Ber.*, **70**, 501 (1937).

(13) Favorsky, *Bull. soc. chim.*, **39**, 215 (1926); Kohler and Kimball, THIS JOURNAL, **56**, 729 (1934); Kohler and Leers, *ibid.*, **56**, 981 (1934); Philip G. Stevens, Dissertation, Harvard University, 1929.

with the result that the isomer XVII and not XVIII may actually prove to be the building unit of "extracted" lignins as suggested recently by Freudenberg[12] on purely theoretical grounds and as one phase of his numerous theoretical speculations in this field.　Experiments are in progress to settle this matter.

The only previous experimental evidence indicating the presence in "extracted" lignins of the grouping (V) is that provided by Phillips and Goss[3d] in the small amounts of C_6—C—C—C— substances isolated by them in their work on the pyrolysis of corn cob lignin.

In this and the following investigation, experimental procedures are given for the first time for the isolation of such type substances (V) in high yield, and by the use of very mild extraction media.　In the previous absence of such data, the formulation of any theoretical structure for lignin either "native" or "extracted" has appeared to one of us (H. H.) as somewhat premature.

Experimental

Ethanolysis of Spruce Wood.—Finely-divided spruce wood meal (50 mesh, 8% moisture content) was extracted for seventy-two hours with a mixture of equal volumes of ethanol (97%) and benzene; then for seventy-two hours with ethanol (97%) alone; finally for twenty-four hours with water. The "resin content" was in this way decreased from some 4.5% to less than 0.5%. The wood meal was air-dried, and later vacuum-dried (50° at 40 mm.) for twenty-four hours, leaving a product with a moisture content of 4% and a lignin content (Klason) of 28.6%.

Four hundred and fifty grams of material were mixed with 3 liters of absolute ethanol containing 3% hydrochloric acid and refluxed for forty hours. The mixture was filtered and the residual wood washed with 2 liters of ethanol; weight of residual wood meal, 263 g., containing 24.7% lignin (Klason).

The combined ethanol extract and washings were concentrated under reduced pressure (15–20 mm.) to 500 cc. and this solution then poured with vigorous stirring into 2500 cc. of water. Insoluble ethanol lignin precipitated as a light brown, flocculent amorphous substance. This was filtered off and the resulting filtrate then continuously extracted with ether for forty-eight hours. The ether extract after concentration left an orange-brown colored sirup. The precipitated lignin was macerated thoroughly with five 100-cc. portions of ether and these ether solutions united, concentrated and added to the main ether concentrate. Total yield of residual oil left after complete removal of the ether was 26 g.

These oils were now redissolved in 200 cc. of ether, the solution filtered from the small amount of insoluble lignin-like material and the ether solution extracted with five 20-cc. portions of sodium bisulfite solution (20%). Both the ether and the combined aqueous solutions were backwashed and the respective aqueous and ether solu-

tions combined. The bisulfite solution was decomposed by addition of dilute sulfuric acid in slight excess and the sulfur dioxide removed at 30° under reduced pressure. The resulting aqueous solution on continuous extraction with ether yielded 2.1 g. of an aldehydic constituent. The bisulfite extracted ether solution was then shaken with five 20-cc. portions of a saturated sodium bicarbonate solution and this backwashed with ether. On neutralization of the aqueous bicarbonate solution, extraction with ether, and removal of the solvent, an oily acidic substance remained; wt. 2 g.

The ether solution left after bicarbonate extraction was then shaken 4–5 times with successive quantities of about 30 cc. of 2% sodium hydroxide, or a total quantity of about 150 cc. of alkali. The ether and water solutions were carefully backwashed as above.

The alkaline extract was neutralized immediately by addition of 10% sulfuric acid and extracted continuously for twenty-four hours with ether. Evaporation of the ether left a mixture of phenols in the form of a reddish-brown oil which could not be caused to crystallize; wt. 12.1 g.

On distillation the main portion (4.2 g.) distilled over at 130–150° (0.015 mm.) as a clear yellow oil, leaving behind a black undistillable tarry substance, wt. 7.4 g. Methylation of 4 g. of this distillable phenolic product with an ether solution of diazomethane (50% excess) yielded, after removal of the ether, a white crystalline product, which, after recrystallization, first from alcohol (50%) and then from petroleum ether (60–70°), gave a white, and apparently homogeneous, crystalline substance melting sharply at 81–82°; yield 80–85%.

Use of a larger excess of diazomethane resulted in secondary reactions with formation of a different product which could not be crystallized.

Methylation of the crude phenolic fraction with dimethyl sulfate prior to distillation gave a crude methylated product which on distillation yielded a much higher percentage of the crystalline methylated product (63%) with a consequently lower yield of the undistillable fraction. The distillate in this case was a clear yellow oil which solidified completely on seeding with the methylated product obtained by the treatment with diazomethane.

This methylated product was readily soluble in organic solvents: ether, alcohol, benzene, hot petroleum ether. Treatment with alkaline hypoiodite gave a negative iodoform reaction. With 2,4-dinitrophenylhydrazine it gave a crystalline hydrazone, m. p. 140–141°.

Analysis of the crystalline methyl ether. Calcd. for $C_{13}H_{18}O_4$: C, 65.5; H, 7.6. Found: C, 65.5; H, 7.7. Grignard analysis. Calcd. addition for one carbonyl group per mole (238), 1.0. Found: addition, 0.85; active hydrogen, 0.13. Calcd. alkoxyl for $C_9H_7O(OCH_3)_2OC_2H_5$: total alkoxyl (calcd. as methoxyl), 39.0; methoxyl, 26.0; ethoxyl, 18.9. Found: total alkoxyl, 38.7; methoxyl, 25.8; ethoxyl, 19.3.

Preparation of 2,4-Dinitrophenylhydrazone.—2,4-Dinitrophenylhydrazine (0.419 g.) was suspended in 10 cc. of absolute ethanol, 0.3 cc. of a solution of absolute ethanol containing 25% hydrochloric acid added, and the mixture warmed, cooled and filtered. To the clear solution was added 0.5 g. of the ketone dissolved in 1 cc. of ethanol.

The heavy orange-yellow precipitate (0.45 g.) which formed immediately was filtered off. After repeated recrystallization first from 50% ethanol, then from chloroform, finally from petroleum ether (60–70°), it melted at 140–141°.

Anal. Calcd. for $C_9H_7(OCH_3)_2OC_2H_5$=NNHC$_6$H$_4$-(NO$_2$)$_2$: C, 54.5; H, 5.32; N, 13.4; alkoxyl (calcd. as methoxyl), 22.25. Found: C, 54.5; H, 5.51; N, 13.7; alkoxyl, 22.0.

Oxidation of the Methylated Product to Veratric Acid.— The crystalline methylated phenol product (0.5 g.) was dispersed in 100 cc. of water and 1 cc. of 30% alkali added. The mixture was warmed on the steam-bath and finely powdered potassium permanganate (2.59 g.) added slowly with vigorous stirring over a period of two hours. The excess permanganate was destroyed by addition of a few drops of methanol. The hot reaction mixture was then filtered, the filtrate was extracted with ether, and the aqueous solution acidified with dilute sulfuric acid. The acidified solution was extracted with ether, the ether extract dried over sodium sulfate and concentrated. The brownish-white solid residue was recrystallized from water, yielding a colorless crystalline product, m. p. 181°. Mixed melting point with an authentic sample of veratric acid showed no depression; yield, 0.10 g. (27%).

Synthesis of β-Ethoxypropioveratrone II.—This product was synthesized by two methods.

Method 1.—This consisted of a Friedel–Crafts reaction between β-ethoxypropionyl chloride and veratrol.

(a) **Preparation of β-Ethoxypropionyl Chloride.**— Potassium cyanide (43.2 g.) was dissolved in 60 cc. of water in a three-necked flask equipped with a mercury-seal stirrer, a dropping funnel and a condenser; 227 cc. of 95% ethanol was added to the solution, followed by 65 g. of β-bromoethyl ether. The mixture was refluxed with stirring for three hours, allowed to cool and 292 cc. of water added. The solution was then extracted seven times with 200 cc. of chloroform and the extract fractionated through an 18-inch (46-cm.) fractionating column. The nitrile distilled at 75–77° (23 mm.); yield, 31.3 g. (74.5%).

The nitrile (12 g.) in 50 cc. of concentrated hydrochloric acid (sp. gr. 1.18) was heated on the steam-bath for one hour. On cooling a heavy precipitate of ammonium chloride formed. The solution was diluted with an equal volume of water, saturated with ammonium chloride and extracted with ether. The ether solution yielded 7.5 g. of the β-ethoxypropionic acid boiling at 121° (20 mm.); yield 70%. The acid (7.5 g.) was mixed with 30 cc. of thionyl chloride and dry nitrogen was bubbled through the solution for three hours. The solution was fractionated, yielding 7.5 g. of β-ethoxypropionyl chloride boiling at 64–67° (30 mm.).

(b) **Condensation with Veratrol.**—β-Ethoxypropionyl chloride (15 g.), veratrol (16 cc.) and carbon disulfide (35 cc.) were mixed together in a three-necked flask equipped with a condenser, calcium chloride tube and mechanical stirrer. Eighteen grams of anhydrous aluminum chloride was added in small portions to this mixture during the course of approximately an hour, the mixture being stirred vigorously throughout. The reaction vessel was then cooled in an ice-water bath, the temperature of the mixture at no time exceeding 20°. After addition of all of the aluminum chloride the mixture was allowed to

stand overnight, with stirring, at room temperature. Two layers had formed and the upper one, consisting mainly of carbon disulfide, was decanted off. The lower thick, sirupy layer was then decomposed by addition of cracked ice, the resulting dark-colored, heavy oil dissolved in ether and the solution extracted with dilute alkali. The alkali-extracted ethereal solution was dried over sodium sulfate, the ether removed and the residue repeatedly extracted with boiling petroleum ether (60–70°). A white crystalline product crystallized out from this solution on cooling; m. p. 45–48°; yield, 28%. Repeated recrystallization of this product, alternately from petroleum ether and aqueous alcohol (50%), gave a product melting sharply at 50–51°.

Anal. Calcd. for $C_9H_7O(OCH_3)_2(OC_2H_5)$: C, 65.5; H, 7.6; OCH$_3$, 39.0. Found: C, 65.4; H, 7.8; OCH$_3$, 38.8. This product formed a 2,4-dinitrophenylhydrazone, m. p. 167–168°. Calcd. for $C_{19}H_{21}O_7N_4$: C, 54.5; H, 5.3; OCH$_3$, 22.25. Found: C, 54.4; H, 5.4; OCH$_3$, 22.34.

Method 2 consisted in the direct conversion of β-chloropropioveratrone by means of sodium iodide and ethanol.

(a) **Preparation of β-Chloropropioveratrone.**—This was prepared by the method of Freudenberg:[14] yield 68%; m. p. 115°.

(b) **Conversion into the Ethoxy Derivative.**—β-Chloro-propioveratrone (1.5 g.), sodium iodide (10 g.) and ethanol (50 cc.) were refluxed together for thirty-six hours. The mixture was concentrated to about 20 cc. and 200 cc. of ether added. The resulting mixture was then washed, first with thiosulfate solution, then with water. After drying over sodium sulfate the ether was evaporated off, leaving a crystalline residue (yield 52%). The colorless, crystalline solid melted at 50–51°; mixed melting point with product obtained from Method 1 showed no depression; m. p. of the 3,4-dinitrophenylhydrazone, 167–168°.

Synthesis of α-Ethoxypropioveratrone

Method 1. Attempted Synthesis by the Action of Aluminum Chloride on a Mixture of α-Ethoxypropionyl Chloride and Veratrol.—The reaction was carried out using the same procedure as in the synthesis of the β-ethoxy compound, using a mixture of 8.5 g. of ethoxypropionyl chloride, 9.6 cc. of veratrol, 25 cc. of carbon disulfide and 10.8 g. of aluminum chloride. The reaction product was isolated in the same manner and recrystallized from petroleum ether (60–70°): yield 2.5 g.; m. p. 81–82°. This melting point, by a remarkable coincidence, is identical with that of the natural ketone. However, a mixed melting point gave a depression of 15–20°, indicating the two were not identical. *Anal.* Calcd. for C_9H_7O-$(OCH_3)_2(OC_2H_5)$: C, 65.5; H, 7.6; OCH$_3$, 39.0. Found: C, 71.04; H, 7.72; OCH$_3$, 40.4. Treatment in the Grignard machine gave no reaction for either active hydrogen or carbonyl. These results clearly indicated the substance was not the desired α-ethoxypropioveratrone. Numerous attempts to effect a synthesis of the latter by alterations in the conditions of reaction were fruitless. It was finally synthesized by the following method.

Method 2.—This consisted in first brominating propioveratrone, followed by conversion of this into the corre-

(14) Freudenberg and Kentscher, *Ann.*, **440**, 36 (1924).

sponding acetate and then replacement of the acetate by the ethoxyl radical.

Propioveratrone.—This was prepared by the method of Martegioni:[15] yield 45%; m. p. 59–60°.

Preparation of α-Bromopropioveratrone,—Propioveratrone (15 g.) was dissolved in 500 cc. of chloroform and into this 12 g. of bromine, dissolved in 25 cc. of chloroform, was dropped slowly with vigorous stirring, at room temperature, over a period of about one hour. On completion of the addition the reaction product was stirred for an additional hour and then refluxed for thirty minutes. The chloroform was removed and the residual crystalline product recrystallized, first from petroleum ether (60–70°) and then from ethanol: yield 76%; m. p. 89°.

Anal. Calcd. for $C_9H_7OBr(OCH_3)_2$: C, 48.35; H, 4.78; Br, 29.9; OCH_3, 22.4. Found: C, 48.39; H, 4.97; Br, 29.9; OCH_3, 22.3.

Attempts were then made to prepare the ethoxy compound directly from this bromo compound by treatment with (1) sodium ethoxide, and (2) silver nitrate and ethanol, but all such attempts were unsuccessful. (3) A further attempt was made to prepare the α-ethoxy compound by the process used above in the case of the β-ethoxy derivative (Method 2). The α-bromo compound was treated with sodium iodide and ethanol and gave unexpectedly iodopropioveratrone, a well-defined colorless crystalline compound, m. p. 95°, which decomposed spontaneously in sunlight.

Anal. Calcd. for $C_9H_7OI(OCH_3)_2$: C, 41.3; H, 4.10; OCH_3, 19.5. Found: C, 41.6; H, 4.10; OCH_3, 19.4.

Conversion of α-Bromopropioveratrone into the α-Acetate of Propioveratrone.—Pure bromopropioveratrone (10 g.) and anhydrous potassium acetate (7.5 g.) were mixed with anhydrous ethanol (85 cc.) and the mixture refluxed for four hours. The major part of the ethanol (*ca.* 60 cc.) was then distilled off under reduced pressure. The residual material was diluted with ether, filtered, and the solvent removed by concentration under reduced pressure. The residual product was extracted with boiling ether and the ether removed, leaving 7.6 g. of a clear yellow sirup, which solidified on standing. Recrystallization, alternately from petroleum ether and aqueous ethanol (50–60%), gave a pure crystalline acetate, m. p. 65–66°.

Anal. Calcd. for $C_{11}H_{10}O_3(OCH_3)_2$: C, 61.8; H, 6.37; OCH_3, 24.5. Found: C, 61.6; H, 6.48; OCH_3, 24.6.

Conversion of α-Acetoxypropioveratrone into α-Ethoxypropioveratrone.—The crystalline acetate (5 g.) was refluxed for eighteen hours with 125 cc. of absolute ethanol containing 2% dry hydrochloric acid and the alcohol then removed under reduced pressure. The residual light brown sirup solidified completely on inoculation with the natural product. On distillation at 140–150° (bath temperature), the resulting material solidified completely on inoculation; m. p. 74–78° (yield 97%). Recrystallized from ethanol and water it melted at 81–82°. A mixed melting point with the original synthetic product showed no depression. The dinitrophenylhydrazone melted at 140–141°; mixed melting point with the 2,4-dinitrophenylhydrazone of the natural product showed no depression.

(15) Martegioni, *Gazz. chim. ital.*, **42**, 346 (1912).

Anal. α-Ethoxypropioveratrone. Calcd. for $C_9H_7O(OCH_3)_2(OC_2H_5)$: C, 65.5; H, 7.6; OCH_3, 39.0. Found: C, 65.3; H, 7.7; OCH_3, 38.9. Dinitrophenylhydrazone. Calcd. for $C_{15}H_{11}O_4N(OCH_3)_2(OC_2H_5)$: C, 54.5; H, 5.51; N, 13.4; OCH_3, 22.25. Found: C, 54.3; H, 5.70; N, 13.7; OCH_3, 22.2.

Preparation of α-Hydroxypropioveratrone from the Synthetic Acetate.—The acetate (13 g.) and freshly precipitated barium carbonate (9 g.) were mixed with 500 cc. of water and refluxed for eight hours. The reaction product was acidified with dilute hydrochloric acid to dissolve the barium carbonate and the solution then extracted continuously with ether for thirty-six hours. The ether extract was dried over fused potassium carbonate, the ether removed and the residual oils distilled at a bath temperature of 140° and pressure 0.010 mm.; yield, 9 g. (83%).

Anal. Calcd. for $C_9H_8O_2(OCH_3)_2$: C, 62.7; H, 6.66; OCH_3, 29.55. Found: C, 62.3; H, 6.73; OCH_3, 29.40.

Ethylation of the α-Hydroxy Compound with Ethanol–Hydrochloric Acid. Expt. I.—The hydroxy compound (1 g.) was dissolved in absolute ethanol (25 cc.) and dry hydrogen chloride was passed into the solution at 0° until saturated. The solution, which first turned green and then black, was poured immediately into water and the resulting dark brown product separated. This could not be crystallized due to the far-reaching decomposition which had taken place.

Expt. II.—The hydroxy compound (1 g.) was dissolved in absolute ethanol (25 cc.) and dry hydrogen chloride passed into the solution at 0° until this just commenced to turn green, this change corresponding to a concentration of about 8% hydrochloric acid. On pouring into water a light-colored amorphous product was formed, which was filtered off, and dried. When this was heated to a bath temperature of 170–180° (0.010 mm.), an oily distillate was obtained which immediately solidified to a non-crystallizable vitreous resin.

Expt. III.—The hydroxy compound (1 g.) was dissolved in 25 cc. of absolute ethanol containing only 0.5% hydrochloric acid. The solution was allowed to stand at room temperature for forty-eight hours, during which time it changed color from a clear yellow to a dark brown. It was then refluxed for half an hour and the solvent removed under reduced pressure, leaving a black tar-like residue. This was extracted with boiling petroleum ether (30–50°) and the crystalline product, separating on cooling, then recrystallized repeatedly first from aqueous ethanol (50–60%), then from petroleum ether (30–50°). The final product melted at 80–81° and showed no depression in melting point on mixing with the natural product. The yield was small, varying from 7 to 12%. The dinitrophenylhydrazone melted at 141°; mixed melting point with the hydrazone of the natural product showed no depression.

Summary

1. Ethanolysis of spruce wood with ethanol–

hydrochloric acid gives, in addition to the water-insoluble "ethanol lignin," a mixture of distillable oils in amount equal to about 8.2% of the weight of (Klason) lignin present in the original wood.

2. The mixture contains aldehydic, acidic, phenolic and neutral products. The principal constituent has been identified by analysis and synthesis as α-ethoxypropioveratrone.

3. Evidence is adduced to show that this product is probably derived from α-hydroxypro-

piovanillone either present, as such, in the wood, or formed as a fission product from a relatively simple molecular complex.

4. It is suggested that this derivative (α-hydroxypropiovanillone), or a dismutation isomer of it, forms the true building unit from which "extracted" lignins from soft woods are derived by condensation-polymerization reactions brought about by the extractant.

MONTREAL, CANADA   RECEIVED DECEMBER 10, 1938

Studies on Lignin and Related Compounds. XXXVI. Ethanolysis of Maple Wood

BY M. J. HUNTER,[1] A. B. CRAMER[2] AND HAROLD HIBBERT

Previous work in these laboratories has resulted in the isolation of a considerable number of aromatic fission products from "extracted" lignins, mostly lignin sulfonic acids. Thus, from spruce lignin sulfonic acid, vanillin,[3] acetovanillone[4] and guaiacol[5] have been obtained, while from maple lignin sulfonic acid, syringic aldehyde,[6] acetosyringone,[4b] pyrogallol 1,3-dimethyl ether,[7] in addition to vanillin[6] and guaiacol,[7] have been isolated.

A sharp characteristic difference is thus to be found between soft and hard woods in that lignin constituents of the former are distinguished by containing only the guaiacyl (I), while the latter contain both the guaiacyl (I) and syringyl (II) radicals.
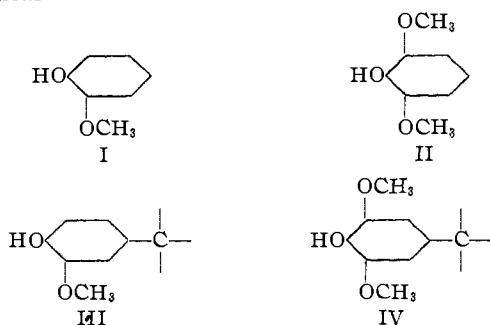
Moreover, the structure of these products indicates the presence of at least *one* carbon atom in the side chains of (III) and (IV).

In the preceding communication[8] experimental evidence is given indicating that the side chain of the building-unit in the case of spruce wood lignin is that shown in (V). The possibility, however, is not to be overlooked that the α-hydroxypropiovanillone (V) containing this side-chain may be in equilibrium, in the native lignin, with the isomeric dismutation forms portrayed in VI and VII.
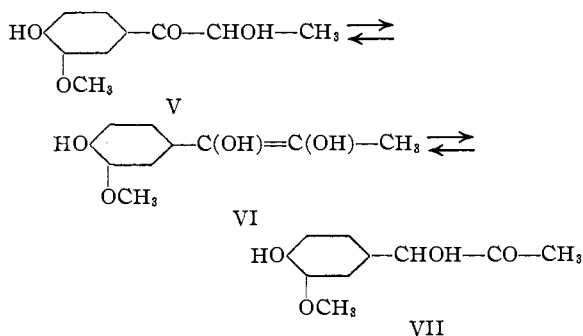
It was therefore to be anticipated, in the light of the above, that in the case of hard woods the water-soluble ethanolysis fractions would be found to contain, in addition to α-ethoxypropiovanillone (VIII), the corresponding syringyl

(1) Postgraduate student and holder of Dow Chemical Company Fellowship.

(2) Postgraduate student and holder of Hibbert–Cole Fellowship.

(3) Tomlinson and Hibbert, THIS JOURNAL, 58, 345 (1936).

(4) (a) Buckland, Tomlinson and Hibbert, Can. J. Research, B16, 54 (1938); (b) Leger and Hibbert, THIS JOURNAL, 60, 565 (1938).

(5) Leger and Hibbert, Can. J. Research, B16, 68 (1938).

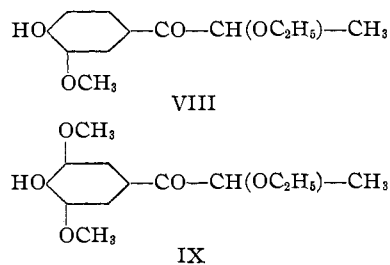(6) Hawkins, Wright and Hibbert, THIS JOURNAL, 59, 2447 (1937).

(7) Leger and Hibbert, Can. J. Research, B16, 151 (1938).

(8) Cramer, Hunter and Hibbert, THIS JOURNAL, 61, 509 (1939).