3270); and, in direct comparison with the spectral curves of Deyrup[17]:

	Dihydrotriacanthine	Synthetic 3-Isopentyladenine
pH 1		
$\lambda_{max}^{C_2H_5OH}$	277 mμ (ε 18,700)	277 mμ (ε 17,500)
$\lambda_{min}^{C_2H_5OH}$	239 (3,350)	238 (3,400)
pH 7		
$\lambda_{max}^{C_2H_5OH}$	273 (12,700)	274 (12,600)
$\lambda_{min}^{C_2H_5OH}$	247 (3,240)	246 (3,170)

Acknowledgment.—The authors are happy to record particular appreciation to Miss Gertrude B. Elion, Burroughs Wellcome and Co., Tuckahoe, N. Y., for providing us with details for the synthesis of 3-methyladenine.

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[17] J. A. Deyrup, Ph.D. thesis, University of Illinois, 1961.

Model Compounds for Comparison with Native Lignin. II. 3-Phenyl-1-propyl α-Ethylbenzyl Ether and 3-Phenyl-1-propyl α-Ethylveratryl Ether[1]

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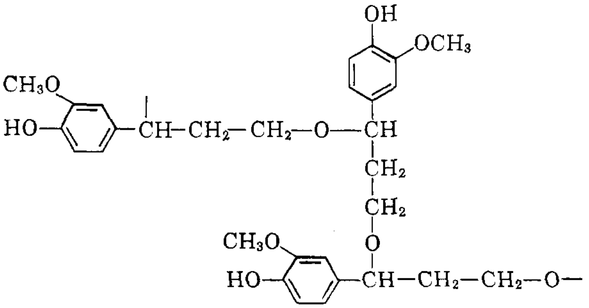
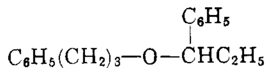
The difference in reactivity of 3-phenyl-1-propyl α-ethylbenzyl ether (I) and 3-phenyl-1-propyl α-ethylveratryl ether (II) is ascribed to the activating influence of the 3,4-dimethoxy substitution present in II. Lignin, in which the 3-methoxy-4-hydroxyphenyl nucleus is prominent, has a chemical reactivity closely approached by 3-phenyl-1-propyl α-ethylveratryl ether (II) in the studies that have been made. The presence of this benzyl γ-propyl ether structure in lignin may be regarded as a definite possibility.

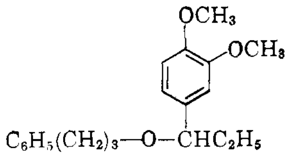
There is general agreement among the investigators of the structure of lignin that the fundamental unit present is a substituted benzene ring with a three carbon atom side chain. However, the mode of linkage of the units has not been determined. Numerous types of linkage have been proposed and this prior work has been summarized by Brauns.[3] Although the ether linkage has been suggested as a possibility, substituted dipropyl ethers linked in the α, β, or γ positions have not been synthesized. The present investigation concerns the synthesis of ethers with linkages between the α-carbon of one propyl group and the γ-carbon of another propyl group. Model compounds of this type, specifically 3-phenyl-1-propyl α-ethylbenzyl ether (I) and 3-phenyl-1-propyl α-ethylveratryl ether (II), were selected for study in order to compare their properties with those recorded in the literature for lignin. This particular type of ether was selected because hydrogenolysis of II should yield 3-phenyl-1-propanol and 1-(3,4-dimethoxyphenyl)propane. The selective hydrogenolysis of the α-ether linkage has been shown by Beets and Van Essen.[4,5] Such a structure would be in agreement with the hydrogenolysis products obtained from lignin.[3] A possible polymeric structure incorporating these α,γ-ether linkages is the following:





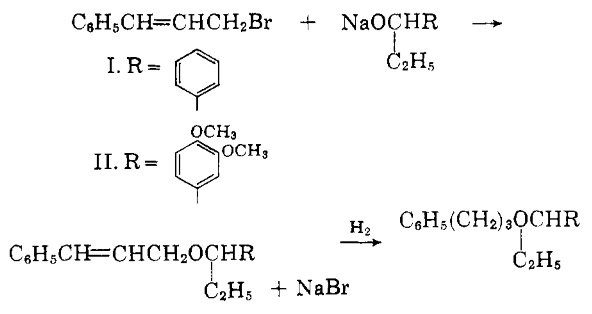
$C_6H_5(CH_2)_3{-}O{-}\overset{\displaystyle C_6H_5}{\overset{|}{C}}HC_2H_5$

I



II

The synthesis of 3-phenyl-1-propyl α-ethylbenzyl ether (I) was accomplished by the intermediate



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[1] For the previous paper in this series, see M. F. Browne and R. L. Shriner, *J. Org. Chem.*, **22**, 1320 (1957).

[2] From the Ph.D. thesis submitted to the Graduate College of the State University of Iowa. Allied Chemical Corporation Fellow, 1953–1954. Present address: Phillips Petroleum Co., Bartlesville, Okla.

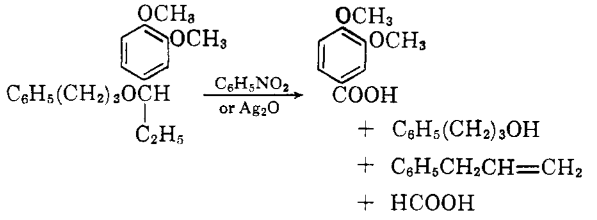
[3] F. E. Brauns, "The Chemistry of Lignin," Academic Press, Inc., New York, 1952. F. E. Brauns and D. A. Brauns, "The Chemistry of Lignin, Supplement Volume Covering the Literature for the Years 1949–1958," Academic Press, Inc., New York, 1960.

[4] M. Beets, *Rec. trav. chim.*, **70**, 20 (1951).

[5] M. Beets and R. Van Essen, *Rec. trav. chim.*, **70**, 25 (1951); E. Drukker and M. Beets, *Rec. trav. chim.*, **70**, 29 (1951).

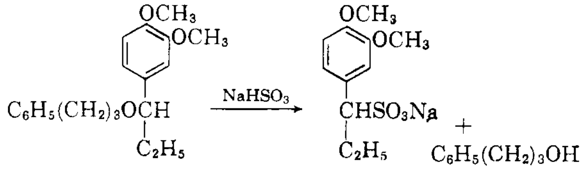
preparation of cinnamyl α-ethylbenzyl ether, which yielded I by catalytic reduction at low pressure. The synthesis of 3-phenyl-1-propyl α-ethylveratryl ether (II) was similarly accomplished by the reduction of cinnamyl α-ethylveratryl ether.

3-Phenyl-1-propyl α-ethylbenzyl ether (I) did not react with nitrobenzene under alkaline conditions. 3-Phenyl-1-propyl α-ethylveratryl ether (II) was oxidized under these conditions to yield veratric acid, formic acid, and 3-phenyl-1-propanol; a definite indication of the presence of allylbenzene was noted. Acetic acid—from the terminal ethyl group—aldehydes, and ketones were not detected in the product mixture. Partial dehydration of 3-phenyl-1-propanol would account for the presence of allylbenzene but the exact source of formic acid remains in question. Quantitative recovery of the oxidation products was not achieved and argument from this direction is precluded. A small amount of unchanged model compound II was recovered. Isolated lignin and lignosulfonic acid are oxidized similarly by nitrobenzene under alkaline conditions to yield vanillin as the chief product.[6-9]



3-Phenyl-1-propyl α-ethylbenzyl ether (I) did not react with silver oxide but 3-phenyl-1-propyl α-ethylveratryl ether (II) was oxidized to yield the same mixture of products that was obtained through the use of nitrobenzene. Lignin preparations are known to yield vanillic acid as the chief product when oxidized by silver oxide.[10]

3-Phenyl-1-propyl α-ethylbenzyl ether (I) was not cleaved by sodium bisulfite solutions when heated under pressure. 3-Phenyl-1-propyl α-ethylveratryl ether (II) was cleaved under these conditions to yield 3-phenyl-1-propanol and sodium α-ethylveratryl sulfonate. The acid sulfite cooking of lignin is believed to involve sulfonation of the α-carbon atom of the three carbon side chain.[11,12]



Experimental

Cinnamyl α-Ethylbenzyl Ether.—Absolute ethanol (69 g., 1.5 moles) and sodium (23 g., 1 g.-atom) were added to 50 ml. of anhydrous xylene. When the sodium had dissolved, α-ethylbenzyl alcohol (136 g., 1 mole) of 2 l. of xylene were added. The mixture was distilled until the distillate was ethanol-free. Finely ground potassium iodide (1 g.) and 3-bromopropenylbenzene (138 g., 0.7 mole) were added, the mixture was refluxed for 4 hr., cooled, and filtered. The filtrate was washed bromide-free with distilled water, dried, and distilled. Cinnamyl α-ethylbenzyl ether (125 g., 70.8%) was collected at 116–120°/0.15 mm. A sample for analysis was redistilled through a 6-in. carborundum column, b.p. 124°/0.35 mm. n^{20}_D 1.5684, d^{20}_4 1.05.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.86; H, 8.21.

3-Phenyl-1-propyl α-Ethylbenzyl Ether (I).—Cinnamyl α-ethylbenzyl ether (50.2 g., 0.2 mole), platinum oxide (0.4 g.), and 100 ml. of 95% ethanol were shaken with hydrogen at low pressure until reduction was complete. The product mixture was distilled to yield 46.3 g. (91.0%) of 3-phenylpropyl α-ethylbenzyl ether, b.p. 110–115°/0.04 mm., n^{20}_D 1.5358. A 10-g. sample for analysis was dissolved in 30 ml. of cyclohexane, washed with three 5-ml. portions of aqueous ceric nitrate solution, with two 10-ml. portions of distilled water, with two 5-ml. portions of 80% sulfuric acid at 10°, with two 10-ml. portions of distilled water, with five 10-ml. portions of 5% aqueous sodium hydroxide, and with four 10-ml. portions of distilled water. The solution was dried, the cyclohexane distilled, and the residue fractionated using a 6-in. carborundum column retaining the center cut, b.p. 110°/0.18 mm., n^{20}_D 1.5530, d^{20}_4 0.988.

Anal. Calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.97; H, 8.27.

Cinnamyl α-Ethylveratryl Ether.—Following the procedure for cinnamyl α-ethylbenzyl ether, but with a 2-hr. reflux period, cinnamyl α-ethylveratryl ether was prepared using absolute alcohol (50.6 g., 1.1 moles), sodium (13.8 g., 0.6 g.-atom), α-ethylveratryl alcohol (117.6 g., 0.6 mole), 1.5 l. of anhydrous xylene, potassium iodide (1 g.), and 3-bromopropenylbenzene (98.5 g., 0.5 mole). A 98-g. (62.8%) yield was obtained boiling at 150–160°/0.11 mm.

3-Phenyl-1-propyl α-Ethylveratryl Ether (II).—Following the procedure for the preparation and purification of 3-phenyl-1-propyl α-ethylbenzyl ether (I), cinnamyl α-ethylveratryl ether (57.9 g., 0.186 mole) was reduced to yield 3-phenyl-1-propyl α-ethylveratryl ether (II) (55 g., 94.4%), b.p. 125–130°/0.3 mm. n^{20}_D 1.5395. A sample for analysis was purified as was the analytical sample of I, b.p. 95–100°/0.05 mm. η^{20}_D 1.5271, d^{20}_4 0.984.

Anal. Calcd. for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34. Found: C, 76.23; H, 8.49.

The Action of Alkaline Nitrobenzene.—A mixture of distilled water (152 g.), sodium hydroxide (75 g.), nitrobenzene (123 g., 1 mole), and 3-phenyl-1-propyl α-ethylbenzyl ether (I) (25.4 g., 0.1 mole) was refluxed for 8 hr. The mixture was acidified with dilute sulfuric acid and extracted with ether. The residue obtained upon evaporation of the ether was steam distilled. The steam distillate was extracted with benzene and the extracts concentrated to 25 ml. Negative tests for carbonyl compounds were obtained with phenylhydrazine and a saturated 2,4-dinitrophenylhydrazine solution. Acids could not be extracted with aqueous sodium hydroxide from either the steam distillate or steam distillation residue. All mixtures containing organic components were combined, dried, and distilled to yield nitrobenzene and 20.2 g. of I collected at 105–107°/0.02 mm., n^{20}_D 1.5345 (sample charged, n^{20}_D 1.5358).

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(6) K. Freudenberg, *Z. angew. Chem.*, **52**, 362 (1939).

(7) H. Richtzenhain, *Acta Chem. Scand.*, **4**, 206 (1950).

(8) L. Schulz, German Patent 111,993 (1940).

(9) W. L. Faith, D. B. Keyes, and R. L. Clark, "Industrial Chemicals," 2nd ed., John Wiley and Sons, Inc., New York, 1957, pp. 787–793.

(10) I. A. Pearl, *J. Am. Chem. Soc.*, **71**, 2196 (1949).

(11) G. H. Tomlinson II, and H. Hibbert, *J. Am. Chem. Soc.*, **58**, 348 (1936).

(12) K. Freudenberg, M. Meister, and E. Flickenger, *Ber.*, **70**, 500 (1937).

A mixture of distilled water (76 g.), sodium hydroxide (38 g.), nitrobenzene (61.5 g., 0.5 mole), and 3-phenyl-1-propyl α-ethylveratryl ether (II) (15.7 g., 0.05 mole) was refluxed for 8 hr. The mixture was saturated with carbon dioxide and enough water added to keep the bicarbonate in solution. The aqueous layer obtained by ether extraction was acidified with dilute hydrochloric acid to Congo red, extracted with ether, and the extracts dried and evaporated to yield veratric acid (0.7 g. after recrystallization from water). A mixed melting point with an authentic sample showed no depression, m.p. 179.5–180.5°. The original ether extracts of the product mixture were dried, evaporated, and the residue dissolved in 150 ml. of 95% ethanol to which were added 300 g. of granular tin and 600 ml. of concd. hydrochloric acid. The mixture was refluxed for 45 min., diluted with 1-l. of water, and extracted with ether. The extracts were neutralized with 5% sodium bicarbonate and washed with water until bicarbonate-free. Ether, ethanol, and water were removed under reduced pressure. Distillation of the residue through a 6-in. carborundum column yielded a lower boiling fraction (2.5 g.) b.p. 60–66°/0.034 mm., n^{20}D 1.5204[13] and 3-phenyl-1-propyl α-ethylveratryl ether (II) (1.3 g.) b.p. 100–130°/0.018 mm., n^{20}D 1.5392 (sample charged, n^{20}D 1.5395). The acidified aqueous solution from which veratric acid had been extracted was diluted with water to a 2-l. volume and placed on a steam bath for 1 hr. as nitrogen was bubbled through it. Negative tests for carbonyl compounds were obtained on this solution with a saturated 2,4-dinitrophenylhydrazine solution and phenylhydrazine. A 400-ml. aliquot of this solution was stirred with 60 g. of freshly precipitated silver oxide until chloride free and acidified with 85% phosphoric acid; 200 ml. of the solution were distilled. The Duclaux constants, 4.12, 4.49, 4.40, suggest the presence of formic acid.[16] Formic acid (0.23 g.) was detected by the method of Houben-Weyl.[17]

The Action of Silver Oxide.—Conductivity water was used exclusively in work with silver oxide. A solution of sodium hydroxide (20 g., 0.5 mole) in 150 ml. of water was stirred rapidly with a solution of silver nitrate (42.5 g., 0.25 mole) in 250 ml. of water. The precipitated silver oxide was washed nitrate-free and covered with 400 ml. of water. Sodium hydroxide (40 g., 1 mole) and 3-phenyl-1-propyl α-ethylbenzyl ether (I) (12.7 g., 0.05 mole) were added. The mixture was refluxed for 4 hr. Silver oxide was collected on a filter, washed with ether, and the washings were combined with the filtrate. The aqueous layer was saturated with sulfur dioxide, acidified to Congo red with dilute hydrochloric acid, and extracted with ether; the extracts were dried and evaporated without residue. The original ether solution was washed free of sodium hydroxide, dried, and evaporated. Negative results were obtained on the residue for carbonyl compounds with saturated 2,4-dinitrophenylhydrazine solution and for alcohols with ceric nitrate solution. 3-Phenyl-1-propyl α-ethylbenzyl ether (I) (10.2 g.), b.p. 98–101°/0.013 mm. n^{20}D 1.5352 (sample charged, n^{20}D 1.5358) was recovered on distillation of the residue through a 6-in. carborundum column.

3-Phenyl-1-propyl α-ethylveratryl ether (II) (15.7 g., 0.05 mole) was treated with silver oxide as above. The aqueous layer of the product mixture was saturated with sulfur dioxide, acidified to Congo red with dilute hydrochloric acid and extracted with ether. The extracts were dried and the ether was evaporated. A residual brown oil was recrystallized from water to yield 0.2 g. of veratric acid. A mixed melting point with an authentic sample showed no depression, m.p. 180–181°. The original ether solution was dried, the ether evaporated, and the residue distilled through a 6-in. carborundum column. A lower boiling fraction (2.7 g.), b.p. 66–70°/0.056 mm., n^{20}D 1.5202[13] and 3-phenyl-1-propyl α-ethylveratryl ether (II) (4.3 g.), b.p. 120–130°/0.08 mm., n^{20}D 1.5380 (sample charged, n^{20}D 1.5395) were obtained. The acidified aqueous solution from which veratric acid had been extracted was diluted with water up to 1.5 l. It was placed on a steam bath and nitrogen was bubbled through it for 1 hr. Negative tests for carbonyl compounds were obtained on this solution with saturated 2,4-dinitrophenylhydrazine solution and with phenylhydrazine. A 200-ml. volume of this solution was treated with excess 0.5 *M* barium chloride, filtered, made slightly basic with sodium hydroxide, stirred with 60 g. of freshly precipitated silver oxide, filtered, acidified with 85% phosphoric acid, and distilled. The Duclaux constants, 7.5, 6.0, 6.0, suggest the presence of acetic acid[16] but the anilide could not be prepared. Formic acid (0.064 g.) was detected by the method of Houben-Weyl.[17]

The Action of Sodium Bisulfite.—3-Phenyl-1-propyl α-ethylbenzyl ether (I) (6 g., 0.024 mole) and 300 ml. of sodium bisulfite solution (2.8% sodium hydroxide, 8% sulfur dioxide in water) were heated to 130–150° for 72 hr. No reaction occurred. Repeating the procedure, exactly, twice, but using a saturated solution of sodium bisulfite yielded 4 g. of sulfur. Excess sulfur dioxide was removed by drawing air through the mixture. It was then carefully neutralized with dilute sodium hydroxide and extracted with ether. The ether extracts were washed with water and dried. The ether was evaporated and the residue was distilled through a 6-in. carborundum column. 3-Phenyl-1-propyl α-ethylbenzyl ether (I) (7.1 g.), b.p. 100–105°/0.02 mm., n^{20}D 1.5363 (sample charged, n^{20}D 1.5358) was recovered. The aqueous phase was distilled. Negative tests for alcohols with ceric nitrate solution and for carbonyl compounds with 2,4-dinitrophenylhydrazine solution were obtained on the distillate. The distillation residue was dried and extracted for 48 hr. with absolute ethanol. Evaporation of the ethanol left a slight residue of sodium hydroxide.

3-Phenyl-1-propyl α-ethylveratryl ether (II) (6 g., 0.019 mole) and 300 ml. of sodium bisulfite solution (2.8% sodium hydroxide, 8% sulfur dioxide in water) were heated to 130–150° for 72 hr. This procedure was repeated exactly, and the product mixtures were combined. Excess sulfur dioxide was removed by drawing air through the mixture. It was then carefully neutralized with dilute sodium hydroxide and extracted with ether. The ether extracts were washed with water and dried. The ether was evaporated and the residue distilled through a 6-in. carborundum column. 3-Phenyl-1-propanol (1.9 g.), b.p. 63°/0.023 mm., n^{20}D 1.5252[14] (characteristic odor and positive alcohol test with ceric nitrate solution) and 3-phenyl-1-propyl α-ethylveratryl ether (II) (1.9 g.), b.p. 110–125°/0.03 mm., n^{20}D 1.5405 (sample charged, n^{20}D 1.5395) were collected. The aqueous phase was distilled and negative tests for alcohols with ceric nitrate solution and for carbonyl compounds with 2,4-dinitrophenylhydrazine solution were obtained on the distillate. The distillation residue was evaporated and the resulting solids were extracted for 48 hr. with absolute ethanol. Evaporation of the ethanol extracts left a residue (2 g.) which contained sulfur and methoxyl groups. It was purified by adding ether to a hot, concd. ethanol solution until cloudy. Chilling this mixture to 5° for 2 hr. resulted in the crystallization of sodium α-ethylveratryl sulfonate (1.1 g.), m.p. 284–285°.

Anal. Calcd. for $C_{11}H_{15}O_5SNa$: C, 46.80; H, 5.36; Na, 8.14; S, 11.36. Found: C, 46.32; H, 5.37; Na, 7.49; S, 11.16.

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[13] The presence of 3-phenyl-1-propanol n^{20}D 1.5268[14] and allylbenzene n^{20}D 1.5042[15] was indicated by refractive index, by a positive ceric nitrate test for alcohols, and by a positive test for unsaturation with bromine in carbon tetrachloride.

[14] R. L. Shriner and P. R. Ruby, *Org. Syntheses*, **33**, 76 (1953).

[15] J. F. McKenna and F. J. Sowa, *J. Am. Chem. Soc.*, **59**, 470 (1937).

[16] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, Inc., New York, 1956, p. 204.

[17] Houben-Weyl, "Analytical Methods," Vol. 2, Eugen Muller ed., Georg Thieme, Stuttgart, 1953, p. 980.