TABLE I[a]

PAPER CHROMATOGRAPHIC ANALYSIS OF LIGNIN OXIDATION PRODUCTS

Compound	R_f	Yield[b]	Compound	R_f	Yield[b]
Acetovanillone	0.72	0.03	5-Carboxyvanillin	0.39	0.09
p-Hydroxybenzaldehyde	0.68	0.15	*p*-Hydroxybenzoic acid	0.38	1.85
Acetosyringone	0.63	0.03	Vanillic acid	0.34	0.95
Vanillin	0.50	0.46	Syringic acid	0.30	0.31

[a] Descending development on Whatman No. 1 filter paper with butanol–ethanol–2% aq. ammonia (160:40:90). [b] Yield in % based on ash-free weight of peat soil.

We have been studying the composition of certain agriculturally important soils derived from peat as a starting model for our general research program on soil organic matter. Specifically, we have carried out selective oxidative degradation of artificially decomposed peat with a view to determining the constitution of peat lignin derivatives. In this note we wish to report some important qualitative data.

Despite certain reservations, it is generally conceded that the primary structural elements of lignin are derived from *p*-hydroxyphenyl, guaiacyl, or syringyl units.[6] These units are also to be found when peat soil derived from Sphagnum is oxidized by mercuric oxide in boiling alkali.

In the current theme of soil humus biogenesis, the lignin or lignin derivatives are considered to to be the most refractory of plant tissues. Our evidence shows that in peat soils where decomposition has been artificially promoted by the addition of lime, the lignin derivatives still retain their aboriginal microstructure. Our evidence further suggests the intriguing prospect of fractionating the lignin-humic complexes from soil organic matter by the use of commercial preparative methods—for example, the synthesis of lignosulfonic acids. This aspect of our work will be reported in due course.

EXPERIMENTAL

Sampling. The soil samples were obtained from Sphagnum peat farms located at Alfred, Ontario, which have been under cultivation for the last six years. Before cultivation the peat fields were treated with lime to reduce the acidity and to accelerate the "humification" of the organic matter.

Samples were taken at predetermined spots at depths of from 6 to 18 inches. They were air-dried, finely ground, and extracted with benzene-ethanol (2:1) mixture using a Soxhlet apparatus. Elemental analysis gave 53.25% C, 61.48% H, 1.90% N, 2.38% methoxyl, and 8.37% ash. Proximate analysis showed 21% lignin-humic complexes.[7]

Oxidation. The procedure is essentially that described by Pearl.[8] A 30-g. sample of peat soil was treated with 271.5 g. (1 mole) of mercuric chloride, 200 g. (5 moles) of sodium hydroxide in 1250 ml. of water. The reaction mixture was heated under reflux with stirring for 8 hr., acidified with sulfur dioxide and extracted with ether. The aqueous residue was further acidified with 45% sulfuric acid and exhaustively extracted with ether. The ether soluble materials were subsequently divided into 21% sodium bisulfite, 8% sodium bicarbonate, and 5% sodium hydroxide soluble fractions. The ether solutions were dried over anhydrous sodium sulfate and concentrated to 25 ml. Aliquot samples were then used for paper chromatographic analysis.

The yields of the bisulfite-, bicarbonate-, and alkali-soluble fractions based on ash-free organic matter were 9.8%, 6.0%, and 4.8%, respectively.

The positive identification, isolation, and quantitative analyses of the oxidation products listed in Table I were accomplished by established paper chromatographic techniques.[9-12] The aggregate yields of the compounds based on spectrophotometric estimation was 4.07% calculated on the ash-free weight of the peat soil.

For a general survey of the ether soluble peat oxidation products the most useful descending paper chromatographic solvent was found to be butanol-ethanol-2% aqueous ammonia (160:40:90 v/v). The R_f values of some pertinent compounds are listed in Table 1. The appropriate chromogenic reagents have appeared in the literature.[13]

With our ammoniacal solvent, the detection and quantitative isolation of the components in mixtures containing *p*-hydroxybenzaldehyde, acetovanillone, and acetosyringone could not be readily accomplished. Reliable results were, however, achieved by the use of borate buffered paper.[10]

Similarly, the presence of 5-carboxyvanillin interfered with the analysis of *p*-hydroxybenzoic acid and vanillic acid. In this instance, papers impregnated with a phosphate buffer at *p*H 7.4 afforded a convenient alternative method.[11]

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(6) F. E. Brauns, *The Chemistry of Lignin*, Academic Press Inc., New York, 1952.

(7) Material insoluble in 72% sulfuric acid, *cf.* Tappi Standard T-13m Method.

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

(9) I. A. Pearl, D. L. Beyer, B. Johnson, and S. Wilkinson, *Tappi*, 40, 374 (1957).

(10) D. E. Bland and C. Stamp, *Australian J. Appl. Sci.*, 6, 353 (1955).

(11) B. Leopold, *Acta Chem. Scand.*, 6, 38 (1952).

(12) J. L. Gardon and B. Leopold, *Pulp Paper Mag. Can.*, 57, T-148 (1958).

(13) I. A. Pearl and P. F. McCoy, *Anal. Chem.*, 32, 1407 (1960), and ref. 9 to 12.

Utility of the Methanesulfonyl Blocking Group. III. A New Synthesis of Dimesyl Protocatechuic Acid[1,2]

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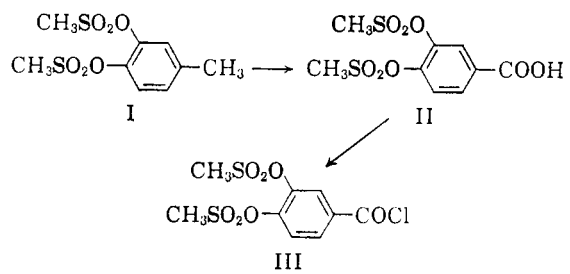
A synthesis of dimesyl[3] protocatechuic acid (II) from dimesyl protocatechualdehyde has been pre-

(1) J. H. Looker, *J. Org. Chem.*, 24, 1039 (1959).

(2) This investigation was supported by a research grant (CY-4750) from the National Cancer Institute, Public Health Service.

viously described.[1] Direct mesylation of protocatechuic acid can not be employed, since it and other phenolic acids give complex products containing ester linkages upon mesylation in pyridine.[1,4] Although synthesis of II from dimesyl protocatechualdehyde gives a satisfactory yield, it is not readily adaptable to large-scale preparations. Very pure protocatechualdehyde is required in the mesylation step, and in our hands, purification of large quantities of this aldehyde has proved inconvenient. The present note describes a synthesis of II from 4-methylcatechol, in which the remarkable stability of the mesyloxy group under acidic, oxidizing conditions is further demonstrated.

4-Methylcatechol was mesylated in pyridine in the usual manner, except that a somewhat higher temperature (*ca.* 80°) was employed. Oxidation of the dimethanesulfonate I under the previously described oxidizing conditions,[5] which consist of chromic acid in 88% sulfuric acid at temperatures as high as 110°, gave II in approximately 60% yield. The acid II has been converted to III with thionyl chloride. The intermediate III is of interest in the synthesis of natural products containing the catechol moiety.



EXPERIMENTAL

4-Methylcatechol dimethanesulfonate (I). To a 62 g. (0.5 mole) quantity of 4-methylcatechol in 100 ml. of reagent grade pyridine was added, dropwise, 90 ml. (1.1 moles) of methanesulfonyl chloride. The temperature rose to approximately 80°, and the reaction mixture became viscous and dark in color. After standing at room temperature for 90 min., 150 ml. of methanol was added. The resulting solution was poured slowly *without* stirring onto 200 ml. of concentrated hydrochloric acid and 800 g. of ice. The mixture was shaken gently until precipitation began, and then was stirred vigorously. Initial rapid stirring caused the product to precipitate in a very crude state which resisted ready purification. After standing overnight, the precipitate was collected, washed well with water, and air-dried; yield, 116 g. (83%), m.p. 80–86°. Recrystallization from methanol (charcoal) gave the colorless 4-methylcatechol dimethanesulfonate, m.p. 88–90°.

Anal. Calcd. for $C_9H_{12}O_6S_2$: C, 38.56; H, 4.32; S, 22.87. Found: C, 38.60; H, 4.35; S, 22.83.

Dimesyl protocatechuic acid (II). A 28-g. (0.1 mole) quantity of 4-methylcatechol dimethanesulfonate was dissolved in 160 ml. of 88% sulfuric acid. Chromium trioxide (20 g. of chromium trioxide in 80 ml. of water) was added over 20 min. The temperature rose rapidly and was kept below 110° by controlling rate of addition of chromic acid and cooling with water. The reaction mixture was poured immediately into ice water. After standing overnight, the separated solid was collected, washed well with water, and air-dried; yield, 26 g. The crude product was suspended in 500 ml. of 5% sodium bicarbonate and then covered with 150 ml. of ethyl acetate with vigorous stirring. After phase separation, the ethyl acetate layer was extracted three times with 50-ml. portions of 5% sodium bicarbonate. The combined bicarbonate solution and extracts were acidified with concentrated hydrochloric acid, cooled in ice for 3 hr., and the dimesyl protocatechuic acid collected and air-dried; yield, 18 g. (58%), m.p. 207–209°. Recrystallization from ethanol-ethyl acetate (charcoal) gave a white solid, m.p. 208–209° (lit.[1] m.p. 208–210°).

Dimesyl protocatechuyl chloride (III). A 15.8-g. (0.051 mole) quantity of dimesyl protocatechuic acid, m.p. 206–209°, was heated under reflux with 50 ml. of thionyl chloride for 1 hr. After excess thionyl chloride was removed, petroleum ether (b.p. 30–60°) was added. After cooling 2 hr., the solid present was collected and washed with petroleum ether; yield, 16.5 g. (98.5%), m.p. 138–143°. Recrystallization from toluene gave 14 g. of the crystalline acid chloride, m.p. 140–141°.

Anal. Calcd. for $C_9H_9ClO_7S_2$: C, 32.89; H, 2.76; S, 19.51; Cl, 10.79. Found: C, 33.45; H, 3.23; S, 19.11; Cl, 10.59.

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(3) Mesyl (methanesulfonyl or methylsulfonyl) denotes the CH_3SO_2— group; mesyloxy (methane- or methylsulfonoxy, or methane- or methylsulfonyloxy), the CH_3SO_3 group; and mesylation, a reaction with mesyl (methanesulfonyl) chloride. For more detailed nomenclature, see R. S. Tipson, *Advances in Carbohydrate Chem.*, 8, 109 (1953).

(4) J. H. Looker, C. H. Hayes, and D. N. Thatcher, *J. Am. Chem. Soc.*, 79, 741 (1957).

(5) J. H. Looker and D. N. Thatcher, *J. Org. Chem.*, 19, 784 (1954).

The Action of Alkali on 4-Methyl-4-dichloromethyl-2,5-cyclohexadien-1-one

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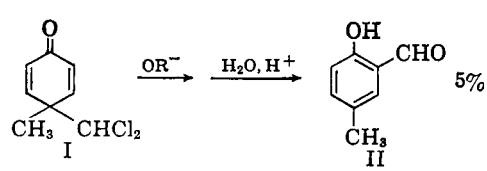
In connection with the work of Dodson *et al.*[1] on the transformations of 1-methyl-1-dichloromethyl-2(1*H*)-naphthalenone in basic medium, it may be of interest to note the corresponding behavior of 4-methyl-4-dichloromethyl-2,5-cyclohexadien-1-one (I), well known by-product of the Reimer-Tiemann synthesis when applied to *p*-cresol.[2] I, when treated with aqueous or alcoholic potassium hydroxide or sodium methoxide in methanol, gives, along with large amounts of dark tars, small yields of 2-hydroxy-5-methylbenzaldehyde (II).



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(2) K. v. Auwers and G. Keil, *Ber.*, 35, 4207 (1902).