insoluble product not being obtained by re-ethanolysis of a *maple* ether-soluble lignin.

As in the case of maple lignin, the water-soluble spruce lignin (G′) could be separated into a petroleum ether-insoluble (J′) and a petroleum ether-soluble (K′) fraction and the latter separated further into a bisulfite (L′), an acid (M′), an alkali (N′) and a neutral (O′) fraction. From the bisulfite and alkali fractions 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione and 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone, respectively, were isolated and identified by the usual methods.[3]

Thus re-ethanolysis of both spruce and maple ethanol lignin fractions yields the same products as isolated by use of the standard wood ethanolysis procedure and there would seem to be no doubt but that the extraction of lignin by the action of ethanolic hydrogen chloride involves the previously-discussed[7] concurrent polymerization-depolymerization changes. The amount of polymerization is evidently greater, and the depolymerization less, in spruce (a gymnosperm) than in maple (an angiosperm). The fact that 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione and 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone from spruce wood and these two derivatives together with their 4-hydroxy-3,5-dimethoxyphenyl homologs from maple wood are the only, as yet, isolable cleavage products of each ethanol lignin fraction indicates that they are either *primary* cleavage products or, as now seems more probable, stabilized end-products formed from much more reactive lignin progenitors or units. Hibbert has recently suggested certain chemical structures for the building units of lignin[2b] and favors a polymeric form of 1-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-2-propanone as best in accordance with the experimental facts, but points out that such structures cannot account for the formation of the 1,2-diketones.

A more satisfactory hypothesis would now seem to consist in the assumption, based on as yet unpublished work, that lignin is made up in greater part of units of the hydroxy- and dihydroxyconiferyl alcohol types united by oxygen linkages.[2b]

Acknowledgment.—The authors gratefully acknowledge the kind financial assistance accorded them by the Canadian Pulp and Paper Association.

Summary

1. Successive re-ethanolyses of ethanol lignins extracted from maple wood under very mild conditions, namely, short-period successive re-ethanolyses, bring about depolymerization to low molecular weight units to a much greater extent than does similar treatment of ethanol lignins isolated by the more drastic conditions hitherto employed by Hibbert and co-workers in ethanolysis extractions of lignin.

2. The results obtained by the re-ethanolysis of maple and spruce ethanol lignins support the theory that the action of ethanolic hydrogen chloride on wood involves both polymerization and depolymerization changes.

3. Depolymerization of isolated ethanol lignins by the action of ethanolic hydrogen chloride yields the same lignin building units as are obtained by use of the customary wood ethanolysis procedure, *viz.*, 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione; 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone and, in addition, for hardwoods only, their 4-hydroxy-3,5-dimethoxyphenyl homologs.

4. A direct relationship between these simple propylphenol units and the more complex ethanol lignins is established by the isolation of the former from the latter by ethanolysis.

Montreal, Canada Received February 23, 1943

[Contribution from the Division of Industrial and Cellulose Chemistry, McGill University]

Studies on Lignin and Related Compounds. LXVI. The Ethanolysis of Maple Wood

By E. West, W. S. MacGregor, T. H. Evans, I. Levi and Harold Hibbert

In previous communications[1,2,3] descriptions were given of methods for the isolation of water-soluble ethanolysis products from spruce and maple woods. These "water-soluble oils" represented a mixture of distillable oils (essentially monomeric) and non-distillable resinous material. The presence of the resins was found to interfere with the fractionation of the oils and to facilitate their decomposition, due to their heat sensitivity, into non-distillable products.[4]

An account is now presented of an improved procedure whereby resin formation is minimized and the monomolecular water-soluble ethanolysis products isolated in a purer state. As a consequence, two new components have been isolated from the bisulfite fraction from maple.[5] In addition new components, representing approximately

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(1) Cramer, Hunter and Hibbert, This Journal, **61**, 509 (1939).

(2) Hunter, Cramer and Hibbert, *ibid.*, **61**, 516 (1939).

(3) Brickman, Pyle, McCarthy and Hibbert, *ibid.*, **61**, 868 (1939).

(4) Levi and Hibbert, unpublished results.

(5) Kulka and Hibbert, This Journal, **65**, 1180 (1943).

TABLE I

SUMMARY OF DATA ON ETHANOLYSIS OF MAPLE WOOD

	Products analyzed		Ethanolysis experiment no. 1		2		3	
			Wt., g.	% IKL[a]	Wt., g.	% IKL[a]	Wt., g.	% IKL[a]
Starting material	Oven dry wt. of wood meal		976.0		908.2		884.2	
	Klason lignin (20.3%)		198.1		184.4		179.5	
Reaction products	Residual wood meal	Oven dry wt.	485.6		444.2		428.4	
		(a) Klason lignin[b]	44.4	22.4	41.3	22.4	37.3	20.8
		(b) Klason lignin removed (calcd.)	153.7	77.6	143.1	77.6	142.2	79.2
	Ethanol lignin[b]		116.5	58.8	103.2	55.9	99	55.1
	Water-soluble ethanolysis products ("crude oils")[b]		76.6	38.6	82.0	44.5	89.5	49.8
Total lignin accounted for				119.8		122.8		125.7

[a] IKL = Initial Klason lignin. [b] The percentages are given on the basis of the weight of Klason lignin in the starting material. Since an alkoxyl group has been added to the lignin left in the wood residue, to the ethanol lignin and to some fractions of the isolated oils[2,8] the percentages given are subject to correction by the factor $L/[L + (OC_2H_5)]$ where L represents the molecular weight of the lignin units.

TABLE II

SUMMARY OF DATA FOR FRACTIONATION OF "CRUDE WATER-SOLUBLE OILS" FROM MAPLE WOOD

Ethanolysis experiment no.		1		2		3	
		Wt., g.	% IKL[a]	Wt., g.	% IKL[a]	Wt., g.	% IKL[a]
Water soluble ethanolysis products ("crude oils")		76.6	38.6	82.0	44.5	89.5	49.8
"Crude Oils"	Petroleum ether-soluble	25.3	12.8	25.0	13.6	29.5	16.4
	Petroleum ether-insoluble	43.3	21.8	53.6	29.1	52.5	29.3
Petroleum ether-soluble oils	Bisulfite-soluble	10.3	5.2	11.5	6.2	10.5	5.8
	Bicarbonate-soluble	0.4	0.2	0.5	0.2	0.5	0.2
	Alkali-soluble	24.7	12.5	28.9	15.7	26.0	14.5
	Neutral	5.4	2.7	6.9	3.7	9.0	5.0

[a] IKL = Initial Klason lignin. The percentages given are based on the weight of Klason lignin in the starting material. Since an alkoxyl group has been added to some of the constituents,[2,8] the percentages given are subject to correction by the factor $M/[M + (OC_2H_5)]$, where M represents the average molecular weights.

12% of the total distillable ethanolysis oils (3.2% of the original Klason lignin), have been isolated from the alkali-soluble fraction from maple[6] and are at present under investigation.

During the protracted period of heating (approximately 100 hours at 50°) formerly involved in the concentration of the aqueous-alcoholic precipitation liquors ((B) Flow Sheet I), part of these heat-sensitive oils polymerized into non-distillable tars, and methoxyl-containing material passed into the distillate.

In the present modified procedure the *total volume* of the *unconcentrated* aqueous ethanolysis liquors was extracted continuously with benzene, in this way eliminating, either fully or to a large extent, the above two drawbacks.

In spite of this precaution the ethanolysis oils still contained a considerable amount of resinous material, which was separated by precipitating an acetone solution of the crude benzene-extracted oil into petroleum ether (b. p. 30–50°). This yielded (a) completely distillable petroleum ether-soluble oils (presumably monomers) (E); and (b) a non-distillable petroleum ether-insoluble tar (consisting presumably of dimers, trimers and higher polymers) (D). The petroleum ether-soluble oils in benzene solution were then separated as described previously[3] into bisulfite-soluble, bicarbonate-soluble, alkali-soluble and neutral fractions.

A further modification introduced was that of back-extraction with benzene of each of the bisulfite-, bicarbonate- and alkali-soluble fractions. This was found necessary in view of the fact that the ethanolysis oils are water-soluble and in consequence there exists a tendency for small amounts of the true alkali-soluble fraction and the true "neutral" fraction to distribute themselves in the preceding extraction media.

The isolation of vanillic acid from the alkali-soluble fraction, as well as from the reaction products of partially methylated alkali-soluble oils,[7] appeared to indicate that its presence might be due to decomposition of these oils during the actual extraction procedure and the extraction time with alkali was therefore reduced to a minimum.

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(6) Levi, Fisher, Baker and Hibbert, unpublished results.

(7) E. West, Ph.D. Thesis, McGill University, 1942.

(8) Patterson, West, Lovell, Hawkins and Hibbert, THIS JOURNAL, 63, 2065 (1941).

Since the ethanolysis oils are extremely sensitive to oxidation, all reactions were carried out in an inert atmosphere (carbon dioxide or nitrogen).

The revised ethanolysis procedure is outlined in Flow Sheet I and the yields from a number of experiments employing this technique are given in Tables I and II.

Experimental

Modified Procedure for the Ethanolysis of Wood.—A typical ethanolysis of maple wood was carried out as follows.

Extraction of the Wood.[3]—Air-dried maple wood meal (40 mesh) was extracted with an ethanol–benzene mixture (1:1 by volume), then with ethanol and finally with hot tap water and dried.

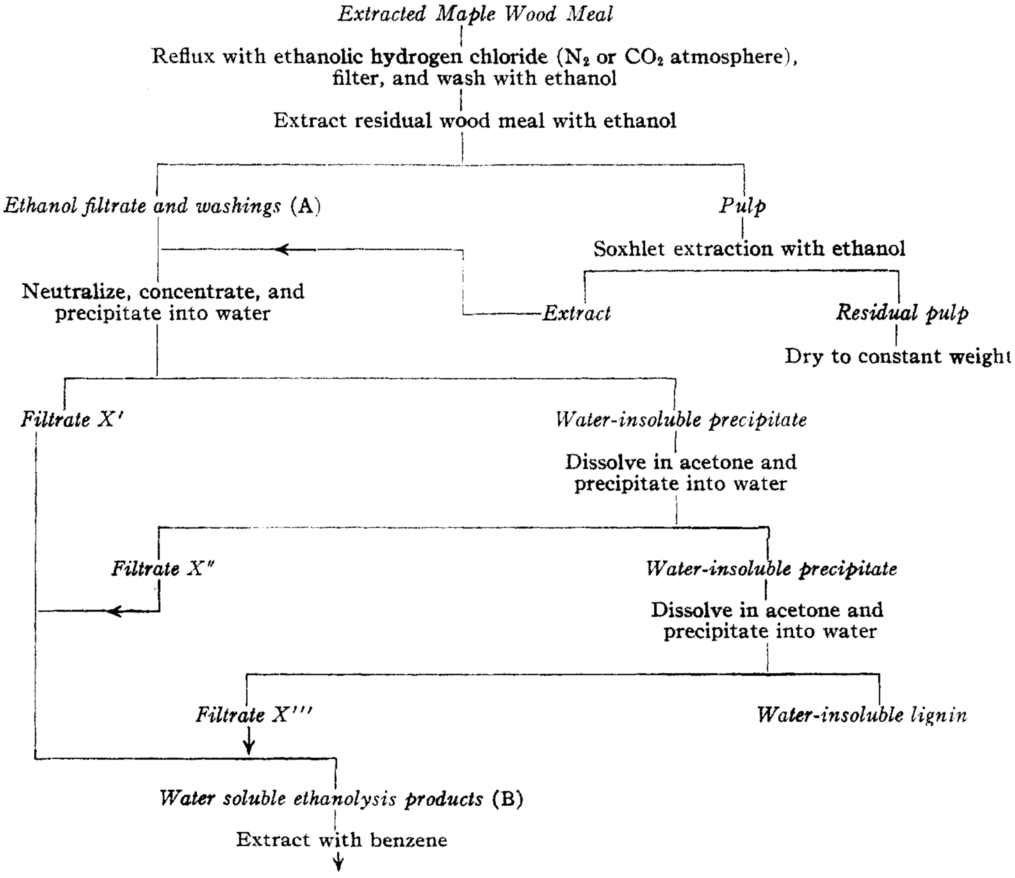
Ethanolysis of the Wood.—The resulting dry wood meal (1000 g., moisture content 2.4%, Klason lignin 20.3%) was refluxed in an inert atmosphere (CO_2 or N_2) with 10 liters of ethanolic hydrogen chloride (2 g. HCl/100 cc. 99% ethanol) for forty-eight hours, filtered with suction and washed thoroughly with hot ethanol (2 liters).[3] The wood residue was exhaustively extracted with ethanol in a Soxhlet extractor and air-dried. Particular attention was paid to the exclusion of atmospheric oxygen throughout. The combined alcoholic extracts, washings and filtrates (A) were neutralized (*p*H 6) by stirring for a considerable time (twelve hours) with solid sodium bicarbonate, filtered and concentrated to about 2 liters (45–50°/20 mm.) in an inert atmosphere (CO_2).

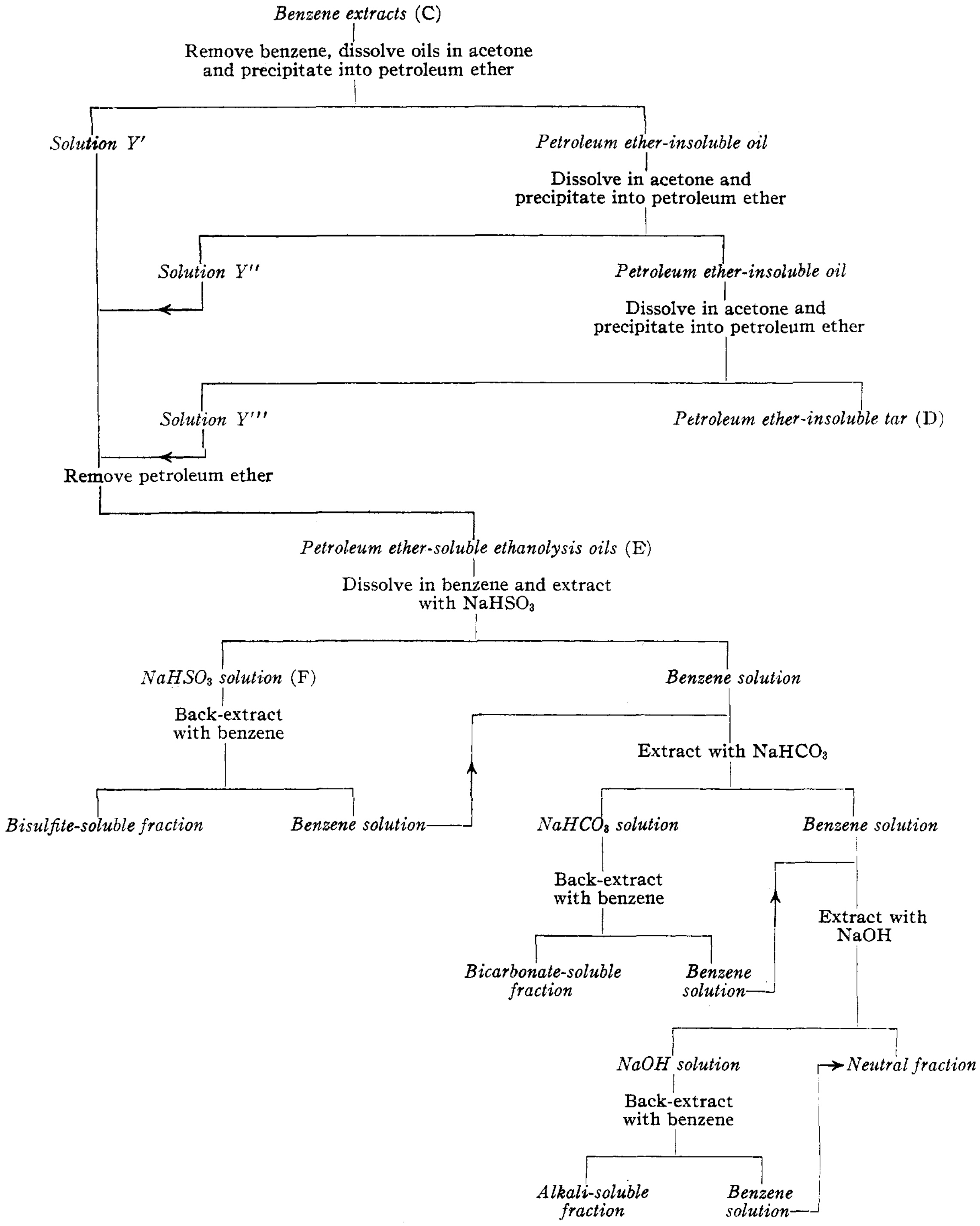
Separation of Ethanol Lignin from the Water-soluble Ethanolysis Oils.—The concentrated alcoholic solution was poured in a fine stream into water (15 liters) with vigorous mechanical stirring. The ethanol lignin which separated was allowed to agglomerate and settle overnight; the clear supernatant liquor was siphoned off and the remaining lignin "sludge" filtered by suction, washed and pressed dry on the Büchner funnel with a rubber dam. The lignin was dissolved in acetone (1200 cc.) and the solution poured into water (12 liters) in a fine stream as described above. The resulting brown, colloidal ethanol lignin was coagulated by stirring with a few cc. of a concentrated sodium chloride solution and the ethanol lignin separated as before. The reprecipitation was repeated using the same conditions to ensure a complete separation of adsorbed oils. The resulting ethanol lignin was air-dried, then vacuum-dried at 25° (weight 116.5 g.).

The combined aqueous liquors containing the ethanolysis oils (B) were made acid to Congo red by the addition of 15% sulfuric acid, and extracted with benzene in a 20-liter continuous extractor similar to that designed by Hoss-

FLOW SHEET I

THE ETHANOLYSIS OF MAPLE WOOD MEAL





field.[9] The extraction was carried out in an atmosphere of carbon dioxide and the benzene was renewed at intervals of about ten hours. After one hundred hours the extraction was essentially complete. The combined benzene extracts (C) were dried with sodium sulfate and the solvent removed under reduced pressure (50°/20 mm.) leaving the crude, water-soluble ethanolysis oils.

Separation of the Resinous Material in the Crude Water-soluble Ethanolysis Oils.—The crude ethanolysis oils (76 g.) were dissolved in acetone (750 cc.) and the solution poured in a fine stream into petroleum ether (b. p. 30–50°) (15 liters) with vigorous stirring. The petroleum ether solution was siphoned off from the residual dark tar. This tar was dissolved in acetone (150 cc.) and reprecipitated into petroleum ether (3 liters). The reprecipitation was

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[9] Hossfield, *Ind. Eng. Chem., Anal. Ed.*, **14**, 118 (1941).

repeated, leaving a viscous tar (D) (25.3 g.). Concentration of the combined petroleum ether solutions (Y', Y'', Y''') (water-bath 50–60°), followed by removal of the last traces of solvent under reduced pressure (50°), left a residue of light-colored petroleum ether-soluble ethanolysis oils (43.3 g.) (E).

Solvent Group Fractionation of the Petroleum Ether-soluble Ethanolysis Oils.—The petroleum ether-soluble oils (43.3 g.) were dissolved in benzene (300 cc.) and the solution extracted successively with (a) eight 30-cc. portions of aqueous sodium bisulfite (20%), and the bisulfite extract (F) back-extracted with two 30-cc. portions of benzene which were then combined with the main benzene solution; (b) three 30-cc. portions of 8% sodium bicarbonate (back-extraction as in (a)); and (c) eight 35-cc. portions of 5% sodium hydroxide (back-extraction as in (a)). (Each of the sodium hydroxide extracts was neutralized *immediately* after extraction.) The oil remaining in the benzene solution was the "neutral fraction."

Each of the extracted fractions (a), (b) and (c) was then acidified (Congo red) with dilute sulfuric acid. In the case of the bisulfite extract the sulfur dioxide was removed after acidification by use of a carbon dioxide bubbler under reduced pressure. The various acidified solutions were extracted with benzene, the benzene solutions dried with sodium sulfate and the solvent removed under reduced pressure yielding a bisulfite-soluble fraction (10.3 g.); bicarbonate-soluble fraction (0.4 g.); alkali-soluble ("phenol") fraction (24.7 g.) and "neutral" fraction (5.4 g.).

Acknowledgments.—The authors wish to thank Mr. M. Kulka, Mr. H. E. Fisher and Mr. S. B. Baker for their assistance in carrying out part of the procedure and to express their appreciation of the financial assistance accorded them by the Canadian Pulp and Paper Association and Canadian Industries Limited.

Summary

An improved method for the extraction and isolation of the water-soluble ethanolysis products from maple wood is given. These are free from resinous materials and represent completely distillable (monomeric) oils, amounting to a total of 29% of the original Klason lignin.

MONTREAL, CANADA RECEIVED FEBRUARY 23, 1943

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

Studies on Lignin and Related Compounds. LXVII. Isolation and Identification of 1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propanone and 1-(4-Hydroxy-3-methoxyphenyl)-2-propanone from Maple Wood Ethanolysis Products. Metabolic Changes in Lower and Higher Plants

BY MARSHALL KULKA AND HAROLD HIBBERT

In a previous communication[1] the isolation of 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione (I) and 1-(4-hydroxy-3,5-dimethoxyphenyl)-1,2-propanedione (II) from the carbonyl components of the water-soluble ethanolysis products of maple wood was reported. It was indicated that about 30% of the bisulfite-soluble fraction of the water-soluble maple ethanolysis oils corresponding to 1.3% of the Klason lignin was still unidentified, and that vanillin and syringaldehyde could not be detected, although their presence had been reported earlier.[2] In a later communication[3] it was shown that the amounts of vanillin and 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione varied in different spruce ethanolysis experiments, the former actually being absent in certain runs.

The purpose of this investigation was to identify the unknown carbonyl components present in the bisulfite fraction of the maple ethanolysis oils, and to settle the question of the presence or absence of vanillin and syringaldehyde. The presence of the two latter compounds has been established definitely and in addition two hitherto unknown carbonyl components, namely, 1-(4-hydroxy-3-methoxyphenyl)-2-propanone (III) and 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone (IV), were isolated and their structures established by direct synthesis.

The ethanolysis procedure used was that described in the preceding communication[4] in which various modifications have been introduced resulting in more complete "group classification" with consequent increase in purity in products. The bisulfite-soluble fraction isolated by this technique was used in this investigation.

Separation and Identification of the Bisulfite-soluble Carbonyl Components.—The dicarbonyl compounds present in the bisulfite fraction were separated quantitatively by precipitation as their

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[1] Kulka, Hawkins and Hibbert, THIS JOURNAL, **63**, 2371 (1941).

[2] Pyle, Brickman and Hibbert, *ibid.*, **61**, 2198 (1939).

[3] Brickman, Hawkins and Hibbert, *ibid.*, **62**, 2149 (1940).

[4] West, MacGregor, Levi, Evans and Hibbert, *ibid.*, **65**, 1176 (1943).