Anal. Calcd. for $C_{16}H_{22}Cl_2N_4O_3$: C, 49.36; H, 5.70. Found: C, 48.95; H, 6.58.

1,4-[2,2'-Di(5,5'-nitrolepidyl)]-piperazine.—Two grams of 5-nitro-2-chlorolepidine was heated with 2 g. of piperazine hexahydrate at 140–150° for three hours. The solid orange reaction product was extracted with dilute hydrochloric acid, the filtered solution was made ammoniacal, and the orange precipitate filtered. Recrystallization from 10 cc. of boiling pyridine gave orange needles, m. p. 320° (dec.).

Anal. Calcd. for $C_{24}H_{22}N_6O_4$: C, 62.87; H, 4.84. Found: C, 62.93; H, 5.26.

Summary

The nitration of 2-chlorolepidine has been studied, and the structures of the resulting derivatives have been established as 5-nitro- and 6-nitro-2-chlorolepidine, respectively. A route to lepidine derivatives substituted in position-5 has thereby been opened.

2-Chlorolepidine and its nitro derivatives have been condensed with piperazine and N-β-aminoethylmorpholine, and some of the condensation products have been tested for their antimalarial action.

2-Hydroxylepidine-5-diazonium chloride has been found to cyclize with the formation of 5-hydroxy-3-pyrido[4,3,2,-*de*]-cinnoline.

A simplified preparation of lepidine from 2-hydroxylepidine has been reported.

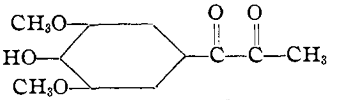
CHARLOTTESVILLE, VIRGINIA RECEIVED JULY 3, 1941

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

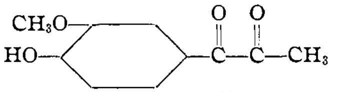
Studies on Lignin and Related Compounds. LIII. Isolation of Vanilloyl and Syringoyl Methyl Ketones from Ethanolysis Products of Maple Wood

BY MARSHALL KULKA, W. LINCOLN HAWKINS AND HAROLD HIBBERT

In a preliminary communication[1] it was indicated that the syringyl dicarbonyl component, obtained from the bisulfite-soluble fraction of maple ethanolysis oils, was syringoyl methyl ketone (I), its identity being established through its mono- and disemicarbazones. The analogous guaiacyl derivative, vanilloyl methyl ketone (II), also was isolated in the form of the same derivatives, along with vanillin, from the bisulfite-soluble fraction of spruce ethanolysis oils.[2]



I



II

In this latter communication, it was shown that the amounts of vanillin and vanilloyl methyl ketone varied in different ethanolysis experiments, the former actually being absent in certain runs, and this fact led to the belief that vanillin might be a secondary product of the ethanolysis reaction, probably resulting from an oxidative cleavage.

In an earlier investigation of the bisulfite-soluble fraction of maple ethanolysis oils, Pyle, Brickman and Hibbert[3] isolated, in addition to derivatives of the diketones (I and II), also vanillin and syringaldehyde. While these aldehydic components were identified by comparison with authentic samples, and were present as relatively large amounts (*ca.* 20%) of the distilled bisulfite-soluble fraction, the results were based on a single ethanolysis extraction.

The bisulfite-soluble ethanolysis oils from maple wood have now been reinvestigated in order to effect the quantitative separation and isolation of the diketones as such, to establish the identity of syringoyl methyl ketone, and to determine possible variations in the amounts of aldehydic components present.

Separation of the Diketones.—A quantitative separation of the two diketone components in the distilled bisulfite-soluble fraction of crude oils has been accomplished by conversion into their nickel glyoxime salts (III), through treatment with hydroxylamine sulfate in the presence of nickel chloride, as applied previously to analogous compounds.[4]

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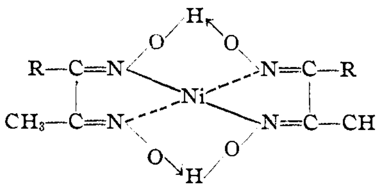
[1] Brickman, Pyle, Hawkins and Hibbert, THIS JOURNAL, **62**, 986 (1940).

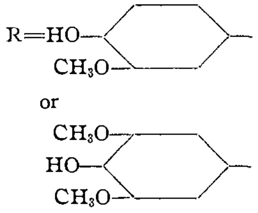
[2] Brickman, Hawkins and Hibbert, *ibid.*, **62**, 2149 (1940).

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

[4] Diehl, "The Applications of the Dioximes to Analytical Chemistry," the G. Frederick Smith Chemical Co., Columbus, Ohio, 1940; Prill, Fabricius and Hammer, Iowa State College of Agriculture Research Bulletin 268, Dec., 1939; Johlin, THIS JOURNAL, **37**, 892 (1915).



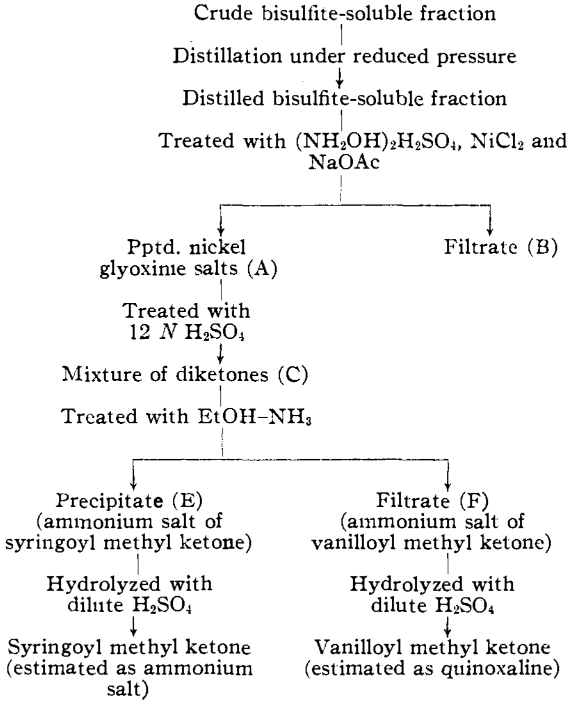
III



Precipitation took place slowly, requiring from four to five days for completion, the diketones (as confirmed by control experiments) being precipitated to the extent of 90–95%. These were regenerated from their nickel salts by the action of hot mineral acid and the syringoyl separated from vanilloyl methyl ketone by precipitation of the former from ethanol solution as its ammonium salt.[3,5]

CHART I

SEPARATION OF SYRINGOYL AND VANILLOYL METHYL KETONES



The isolation and separation of the diketones are summarized in Chart I and the results of several ethanolysis runs shown in Table I.

TABLE I

ANALYSIS OF BISULFITE-SOLUBLE FRACTIONS

Amount of dry maple wood taken for each experiment was 1000 g. containing 220 g. of Klason lignin

	Ethanolysis experiments 1 Duplicate runs		2	3
Total bisulfite-sol. oils, g.	13.0		17.5	9.0
Total recovered distilled oils, g.	10.6		10.0	7.3
Bisulfite-sol. fraction used, g.	1.030	1.730	5.258	3.253
Nickel glyoxime salts found, g.	0.425	0.691	3.544	1.732
Ammonia salt of syringoyl methyl ketone, g.	0.193	0.280	1.627	0.911
Syringoyl methyl ketone in distilled fraction				
(a) Found, %	17	15	29	26
(b) Corrected, %[a]	22	20	38	34
Quinoxaline of vanilloyl methyl ketone, g.	0.062	0.079	0.659	0.172
Vanilloyl methyl ketone in distilled fraction				
(a) Found, %	4	4	9	4
(b) Corrected, %[a]	6	5	13	6
Total diketone in distilled fraction				
(a) Found, %	21	19	38	30
(b) Corrected, %[a]	28	25	51	40

[a] Control runs showed that 76% of syringoyl methyl ketone and 70% of vanilloyl methyl ketone could be recovered from a mixture of the synthetic diketones. The "correction factors" are thus 1.3 and 1.4, respectively.

In Experiment I the results are given of two duplicate runs in both of which the ethanolysis procedure was varied from that normally employed in that ethyl orthoformate was added to the ethanol–hydrochloric acid extraction medium with the object of "fixing" free, possibly very reactive, carbonyl groups. The yields obtained, however, were considerably lower than in the case where the normal procedure was employed (Expts. 2 and 3); no explanation for this can be given. The average value found for the total isolated diketones (Expts. 2 and 3), based on the Klason lignin content of the original wood, was 2%, and that of the corresponding "corrected" values 2.5%. Both vanillin and syringaldehyde were absent in each case. These aldehydic components, if present, would be found in the filtrate (B) left after removal of the precipitated nickel glyoxime salts and would be removable by extraction with organic solvents. Runs made on a control mixture of approximately equal amounts of the two diketones, vanillin and syringaldehyde,

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(5) Hunter and Hibbert, THIS JOURNAL, **61**, 2190 (1939).

showed that each of the components could be recovered to the extent of at least 70%. Absence of aldehydic components in the bisulfite-soluble fraction may be due to (1) slight variations in the ethanolysis reaction, or (2) a difference in the wood due to climatic or soil factors. In place of the aldehydic components a new constituent, amounting to about 30% of the total distilled bisulfite-soluble fraction, has been isolated and is under investigation.

Isolation and Identification of Syringoyl Methyl Ketone.—Syringoyl methyl ketone was liberated from its ammonium salt by acids, and isolated in crystalline form as were also its quinoxaline and monosemicarbazone derivatives. Comparison of the naturally-occurring diketone with the pure synthetic product, obtained by oxidation of α-hydroxypropiosyringone,[2] established its identity. The relative ease with which α-hydroxypropiosyringone is oxidized to syringoyl methyl ketone suggested that this change might actually take place during the ethanolysis reaction. It has been found,[6] however, that while α-hydroxypropiosyringone undergoes *partial* polymerization to lignin-like substances under conditions of ethanolysis, the principal reaction product is α-ethoxypropiosyringone, no diketone apparently being formed.

Both syringoyl and vanilloyl methyl ketones are therefore to be regarded as primary products of the ethanolysis reaction and as true building units. The possible role of such diketones in plant respiration has been pointed out in a recent communication.[7]

Experimental Part

Ethanolysis of Maple Wood.—A detailed account of the ethanolysis procedure and fractionation of the water soluble oils is given in a recent communication,[8] and this was followed in the present investigation (particular attention being paid to the exclusion of atmospheric oxygen). The resulting bisulfite-soluble fraction of the ethanolysis oils was distilled at a bath temperature of 150–200° (0.2 mm.).

Investigation of the Distilled Bisulfite-soluble Fraction

(a) Isolation of the Diketones.—An aliquot portion of the bisulfite-soluble fraction (3.253 g.) was dissolved in water (900 cc.), and hydroxylamine sulfate (2 g.), 5% nickel chloride solution (12 cc.) and crystalline sodium acetate (15 g.) added. The reaction mixture was refluxed gently in an atmosphere of carbon dioxide for twenty-four hours. The precipitated nickel glyoxime salts were removed by filtration through a sintered glass filter, more hydroxylamine sulfate (0.3 g.) and nickel chloride solution (3 cc.) added to the filtrate, and the refluxing continued for an additional twenty-four hours. This process was continued until there was no further precipitation (four to five days). The combined precipitated salts were washed with cold water and dried at 100°; yield 1.732 g. They were now mixed with 12 *N* sulfuric acid (400 cc.), the solution allowed to stand at room temperature for twenty-four hours and then maintained at 40° for four hours. After cooling it was extracted with benzene, the benzene extract dried over sodium sulfate and sodium bicarbonate to neutralize any sulfuric acid, and the benzene removed at atmospheric pressure leaving a mixture of the crude diketones (C).

(b) Separation of the Diketones.—The mixture (C) (1.2 g.) was dissolved in absolute ethanol (40 cc.), cooled to 0° and 4 cc. of a cold (0°) 9% solution of ammonia in absolute ethanol added. After standing at 0° for a few hours, the precipitated ammonium salt of syringoyl methyl ketone (E) was filtered, and washed with a cold (0°) 1% solution of ammonia in ethanol (10 cc.). The filtrate (F) was neutralized immediately with dilute sulfuric acid and extracted with benzene. On removal of the solvent, vanilloyl methyl ketone separated out as a yellow oil which crystallized on standing; yield, 0.21 g. The crude product, after one crystallization from water, melted at 68–69° and gave no depression when mixed with an authentic sample of vanilloyl methyl ketone. The quinoxaline prepared from this product melted at 160–161° and showed no depression when mixed with a pure synthetic product.

The ammonium salt of syringoyl methyl ketone (E) was purified by dissolving in hot ethanol, cooling and adding an excess of a 9% solution of ammonia in ethanol. The reprecipitated ammonium salt (0.911 g.) was filtered, washed as before, dried (vacuum), dissolved in hot water, and an equivalent amount of dilute sulfuric acid added. On standing, syringoyl methyl ketone separated out in the form of yellow needles (0.7 g.); it was recrystallized first from water and then from petroleum ether (b. p. 100–110°); m. p. 80–81°; no depression when mixed with a pure synthetic syringoyl methyl ketone. *Anal.* Calcd. for $C_{11}H_{12}O_5$: C, 58.9; H, 5.4; OCH_3, 27.7. Found: C, 59.1; H, 5.7; OCH_3, 27.6.

Monosemicarbazone of Syringoyl Methyl Ketone.—Fine, white, needle-like crystals; m. p. 210–211° (with decomposition); no mixed melting point depression. *Anal.* Calcd. for $C_{12}H_{15}O_5N_3$: C, 51.2; H, 5.4; N, 14.9; OCH_3, 22.1. Found: C, 51.0; H, 5.6; N, 15.0; OCH_3, 21.9.

Quinoxaline of Syringoyl Methyl Ketone.—Light yellow needles; m. p. 160.5–161.5°; no mixed melting point depression. *Anal.* Calcd. for $C_{17}H_{16}O_3N_2$: C, 68.9; H, 5.5; N, 9.5; OCH_3, 20.9. Found: C, 69.1; H, 6.0; N, 9.5; OCH_3, 20.8.

Separation of a Mixture of Vanillin, Syringaldehyde, Vanilloyl Methyl Ketone and Syringoyl Methyl Ketone.—Amounts taken were 0.159, 0.144, 0.237, and 0.158 g., respectively. Separation was accomplished using the same method (section b). The mixture of vanillin and syringaldehyde, obtained by benzene extraction of the fil-

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(6) West, Hawkins, and Hibbert, unpublished results.

(7) Hibbert, This Journal, **62**, 984 (1940); for comprehensive review, see *Paper Trade J.*, **112**, No. 4, 35 (1941).

(8) Brickman, Pyle, McCarthy and Hibbert, This Journal, **61**, 868 (1939).

trate from the precipitated nickel salts and removal of the solvent under atmospheric pressure, was dissolved in absolute ethanol (10 cc. per 0.2 g. mixture) and treated with a cold 9% solution of ammonia in ethanol (1 cc.) at 0°. The precipitated ammonium salt of syringaldehyde was removed by filtration, washed with a 1% solution of ammonia in absolute ethanol (5 cc.) and converted to the *m*-nitrobenzoylhydrazone[9] of syringaldehyde. Vanillin was recovered from the acidified filtrate by extraction with benzene and also converted to its *m*-nitrobenzoylhydrazone. Yields obtained were vanillin hydrazone, 0.226 g.; syringaldehyde hydrazone, 0.190 g.; quinoxaline of vanilloyl methyl ketone, 0.225 g., and ammonium salt of syringoyl methyl ketone, 0.131 g.; equivalent to 70, 69, 70 and 76% of the free carbonyl derivatives, respectively.

Synthesis of Syringoyl Methyl Ketone.—α-Hydroxypropiosyringone[5] (5 g.) was added to a hot solution of copper sulfate (14.4 g.), pyridine (24 cc.) and water (12 cc.), the mixture heated for two hours on a steam-bath, and, after cooling, poured into a slight excess of dilute hydrochloric acid. The aqueous solution was extracted with ether, and the latter removed, leaving 3.5 g. of an oily residue distilling at 147° (0.04 mm.). This distillate (2.9 g.) was recrystallized, first from hot water, and then from petroleum ether (b. p. 100–110°); light orange-colored needle-shaped crystals; m. p. 80–81°. *Anal.* Calcd. for $C_{11}H_{12}O_5$: C, 58.9; H, 5.4; OCH_3, 27.7. Found: C, 58.7; H, 5.7; OCH_3, 27.7.

Monosemicarbazone.—Fine, white, needle-like crystals; m. p. 210–211° (with decomposition). *Anal.* Calcd. for $C_{12}H_{15}O_5N_3$: C, 51.2; H, 5.4; N, 14.9; OCH_3, 22.1. Found: C, 51.4; H, 5.7; N, 14.7; OCH_3, 22.0.

Quinoxaline.—The quinoxaline was prepared by dissolving the syringoyl methyl ketone (0.2 g.) in water (20 cc.) at 70° and adding to this a hot solution (70°) of *o*-phenylenediamine (0.12 g.) in water (10 cc.). After standing overnight, the precipitate (0.24 g.) was filtered and recrystallized first from water, then from dilute ethanol (1:6); light yellow-colored crystals, m. p. 161–161.5°. *Anal.* Calcd. for $C_{17}H_{16}O_3N_2$: C, 68.9; H, 5.5; N, 9.5; OCH_3, 20.9. Found: C, 69.0; H, 5.6; N, 9.4; OCH_3, 20.9.

Summary

1. The syringoyl and vanilloyl methyl ketones present in the bisulfite-soluble fraction obtained from the ethanolysis of maple wood have now been isolated in the pure crystalline state.
2. Their quantitative separation has been effected by conversion into the insoluble nickel glyoxime salts.
3. The total diketone fraction amounts to approximately 2 to 3% of the Klason lignin in the original maple wood.

MONTREAL, CANADA RECEIVED JUNE 30, 1941

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[9] Tomlinson and Hibbert, THIS JOURNAL, 58, 345 (1936).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE UNIVERSITY OF IDAHO]

The Action of Sodium on 2,2'-Dichlorodiethylamine[1]

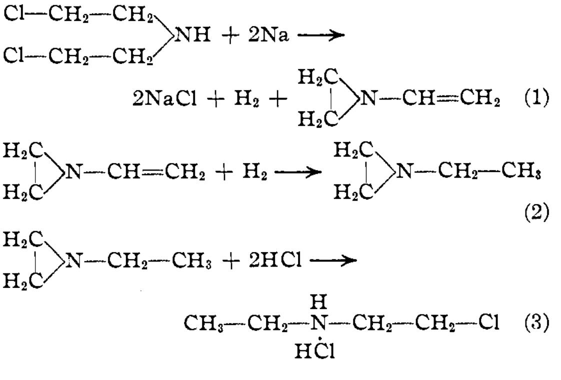
BY PERCY A. LASSELLE AND S. A. SUNDET

In an attempt to prepare pyrrolidine by the treatment of 2,2'-dichlorodiethylamine with metallic sodium no pyrrolidine was obtained. Ring closure or possibly chain formation was expected to take place.

It was in an attempt to prepare N-vinylethyleneimine that the action of other alkaline reagents on 2,2'-dichlorodiethylamine was studied. The instability of the free dichloroalkylamine, resulting in decomposition and polymerization, apparently made these attempts fruitless.

The fractionation of the toluene solution resulting from the reaction with sodium yielded an amine mixture. The hydrogenation of this mixture resulted in N-ethylethyleneimine which upon evaporation with an excess of hydrochloric acid gives the hydrochloride of 2-chlorethylethylamine. This hydrochloride was prepared by another method for purposes of comparison.

The rapid, although partial, hydrogenation and the properties of the amine mixture indicate the presence of N-ethylethyleneimine and some less saturated compound. The following reaction of 2,2'-dichlorodiethylamine with sodium was suggested as taking place



The N-vinylethyleneimine (1, as yet unknown) would be hydrogenated in part by the hydrogen

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[1] This paper was presented at the Northwest Scientific Association meeting at Spokane, Washington, December 28, 1940.