NOTES

Aromatic Aldehydes from Spruce and Maple Woods

By R. H. J. Creighton, Joseph L. McCarthy and Harold Hibbert

It has recently been reported[1] that a yield of 25% of vanillin based on Klason lignin can be obtained by treatment of spruce wood with alkali in the presence of nitrobenzene. Employing the same technique,[1] we have confirmed this result by digesting spruce woodmeal (35.0 g., 28.6% Klason lignin), sodium hydroxide solution (400 cc., 2 *N*), and nitrobenzene (24 cc.) in a stainless steel bomb with good agitation at 160° for three hours. In duplicate experiments, 4.73 and 5.12 g. of crude vanillin *m*-nitrobenzoylhydrazones (m. p. 204–206°) were finally isolated; after recrystallization, m. p. 210–211°; mixed m. p. 210–211°. Yields were 22.8 and 24.7%, respectively, calculated on the Klason lignin.

Application of this method to maple wood (38.5 g., 22.0% Klason lignin) left 13.7 g. of insoluble woody residue containing 0.2% Klason lignin. Neutralization of the alkaline reaction liquors and continuous extraction with benzene removed 4.23 g., of which 3.63 g. was extractable with sodium bisulfite solution. Acidification of the neutralized aqueous liquor to *p*H 3, and benzene extraction, yielded additional benzene-soluble substances (1.21 g.). The benzene-insoluble material precipitated by acidification of the alkaline aqueous reaction liquor weighed 4.1 g.

Vanillin and syringaldehyde were isolated from the bisulfite solution by acidification and benzene extraction. Their separation was effected by solution of the crude extract in 250 cc. of ethanol and fractional precipitation by gradual addition of increasing amounts of ammonia. In this way, by precipitation of the much more insoluble syringaldehyde addition product, crude syringaldehyde (2.7 g.) was isolated; m. p. 105–112°; after recrystallization, m. p. 110.5–112°; mixed m. p. gave no depression. The ammoniacal ethanol solution remaining after removal of the syringaldehyde component was evaporated to remove the ammonia and ethanol and the residue dissolved in about 125 cc. of dry ether. Addition of ammonia precipitated the crude addition product from which 0.55 g. of crude vanillin-containing material was isolated. A preliminary purification by sublimation[2] at 61° (1 mm.) yielded 0.29 g. crude vanillin (m. p. 75–80°), recrystallized m. p. 80–82°, mixed m. p. no depression. Vanillin was also isolated by direct fractional sublimation[2] of the bisulfite soluble material (3.56 g.) to yield 0.60 g. of crude vanillin (m. p. 77–81°). Precipitation of the total aldehydes in 3.63 g. of the bisulfite soluble extract yielded 7.01 g. of mixed *m*-nitrobenzoylhydrazones.

Based on the Klason lignin content of maple wood, the yield of syringaldehyde isolated by treatment with ammoniacal ethanol amounted to 31.8%; that of vanillin 3.4%. By sublimation 7.1% vanillin was obtained. By weight, the total yield of bisulfite soluble material was 42.9%, while the yield of total carbonyl-containing constituents of the bisulfite soluble fraction was 43.0% (calculated from the mixed *m*-nitrobenzoylhydrazones on the assumption of a syringaldehyde–vanillin ratio of 3:1). A duplicate experiment gave very similar yields.

(1) Freudenberg, Lautsch and Engler, *Ber.*, **73**, 167 (1940).

(2) Hawkins, Wright and Hibbert, This Journal, **59**, 2447 (1937).

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α-Hydroxy-β,β-dimethyl-γ-butyrolactone

By Herbert E. Carter and Luman F. Ney

In the course of work on analogs of pantothenic acid, it was discovered that α-hydroxy-β,β-dimethyl-γ-butyrolactone is obtained readily in a single step by treating an aqueous solution of α,α-dimethyl-β-hydroxypropionaldehyde with potassium cyanide and calcium chloride. The intermediate cyanohydrin is smoothly hydrolyzed at room temperature by the calcium hydroxide produced in the reaction.[1] Shortly after the completion of this work, Reichstein and Grüssner[2] reported a somewhat similar procedure for preparing the lactone. Since our method has certain

(1) This method has been used in the sugar field by Haworth, *et al.* [*J. Chem. Soc.*, 1419 (1933)] and by Hudson, *et al.* [This Journal, **56**, 1248 (1934)].

(2) Reichstein and Grüssner, *Helv. Chim. Acta*, **23**, 650 (1940).

advantages over that of Reichstein and Grüssner[2] and over the two step procedure of Köhn and Neustädter[3] as modified by Stiller, *et al.*,[4] it seemed desirable to publish the details.

Experimental

α,α-Dimethyl-β-hydroxypropionaldehyde.—This compound was prepared by the method of Wesseley,[5] with the exception that the reaction flask was cooled in an ice-bath during the initial vigorous stage of the reaction.

α-Hydroxy-β,β-dimethyl-γ-butyrolactone.—Crude α,α-dimethyl-β-hydroxypropionaldehyde (102 g., 1 mole) was dissolved in 1 liter of water at 60–70°. The solution was cooled under the tap and a cold solution of 133 g. of calcium chloride and 98 g. of potassium cyanide was added rapidly. The flask was stoppered (to exclude carbon dioxide) and was allowed to stand at room temperature with occasional shaking for eighteen hours. The solution was then heated on the steam cone to 70–80° and 151 g. of oxalic acid dihydrate was added. The calcium oxalate was removed by filtration and the filtrate was concentrated to a gum under reduced pressure. It is essential that as much water as possible be removed at this point. The residue was extracted with 1 liter of dry acetone and the insoluble material was removed by filtration. The filtrate was concentrated to a viscous oil under reduced pressure. The oil was taken up in dry acetone and the solution was filtered. The acetone was removed and the residue was fractionated under reduced pressure. The lactone distilled at 125–130° (18 mm.) as an oil which immediately solidified to a glass in the receiver. The yield of lactone, melting at 75–80°, was 100–105 g. (77–81% of the theoretical amount). The *p*-nitrobenzoate of the lactone melted at 137–138° as reported by Stiller, *et al.*[4]

The unusual ease of hydrolysis of the nitrile is interesting in view of the lability of the amide group in pantothenic acid.

(3) Köhn and Neustädter, *Monatsh.*, **25**, 46 (1904).
(4) Stiller, *et al.*, THIS JOURNAL, **62**, 1785 (1940).
(5) Wesseley, *Monatsh.*, **21**, 231 (1930).

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URBANA, ILLINOIS RECEIVED NOVEMBER 1, 1940

Note on the Absorption Spectra of Some Alkyl Chrysenes

BY R. NORMAN JONES

The absorption spectra of 5-methyl,[1] 4,5-dimethyl,[1] 5,6-dimethyl[1] and 4,5-methylenechrysene[2] recently have been determined in these laboratories. The wave lengths and intensities of the various maxima are summarized in Table I and the curves are given in Figs. 1, 2. The experimental technique has been described previously.[3]

The spectra of 5-methyl and 5,6-dimethylchrysene resemble that of the unsubstituted hydrocarbon[4] apart from the usual shift to longer wave lengths and some loss of fine structure. 4,5-Dimethylchrysene differs somewhat from the other two methyl derivatives, the most intense maximum showing some resolution while at longer wave lengths the intensity of absorption is greater and the resolution less.

TABLE I

WAVE LENGTHS (Å.) OF THE MAXIMA AND CORRESPONDING INTENSITIES (LOG E_{molar}) OF THE SPECTRA OF SOME ALKYL AND ALKYLENE-CHRYSENE DERIVATIVES (SOLVENT ETHANOL)

	Max.	Intensity
5-Methylchrysene	2705	4.98
	2865	3.99
	3005	3.98
	3125	4.06
	3265	4.06
	3505	2.89
	3680	2.90
5,6-Dimethylchrysene	2740	4.95
	3040	3.96
	3225	4.08
	3330	4.05
	3550	2.94
	3745	2.84
4,5-Dimethylchrysene	2740	5.10
	2815	5.05
	3120	4.15
	3300	4.34
	3450	4.34
	3800	2.87
4,5-Methylenechrysene	(2590)	4.83
	2655	4.99
	2690	5.04
	3010	4.09
	3130	4.07
	3265	4.09
	3420	2.98
	3465	2.82
	3525	2.65
	3606	2.89

The spectrum of 4,5-methylenechrysene (1) is particularly interesting as in the 1,2-benzanthracene series such a bridge methylene group has been observed to produce a considerable change in the spectrum including an increase in the amount of fine structure resolved.[5] The spectrum of 4,5-methylenechrysene also shows an increase in the amount of fine structure, particularly if comparison is made with 4,5-dimethylchrysene, substituted at the same position (Fig. 2). A corresponding comparison between the dimethyl and the methylene derivative is not possible in the

(1) Compounds kindly supplied by Dr. M. S. Newman: see THIS JOURNAL, **62**, 870 (1940); **62**, 2295 (1940).
(2) Fieser and Cason, *ibid.*, **62**, 1293 (1940).
(3) Jones, *ibid.*, **62**, 148 (1940).
(4) Mayneord and Roe, *Proc. Roy. Soc.* (London), **A152**, 299 (1935).
(5) Jones, THIS JOURNAL, **63**,151 (1941).

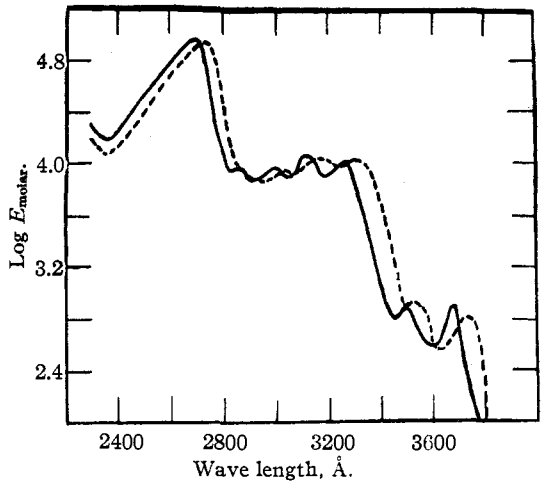


Fig. 1.— ———, 5-Methylchrysene; - - -, 5,6-dimethylchrysene.

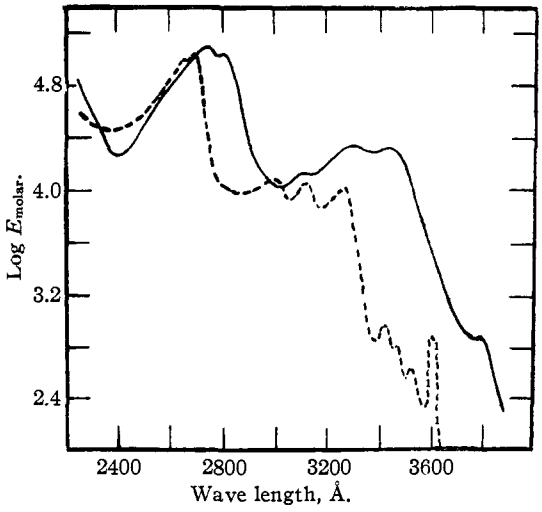
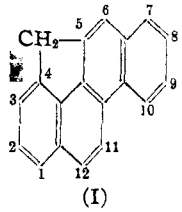


Fig. 2.— ———, 4,5-Dimethylchrysene; - - -, 4,5-methylenechrysene.

1,2-benzanthracene series as all attempts so far made to synthesize 1',9-dimethyl-1,2-benzanthracene have failed.

These variations in structural detail among the spectra, while significant, are not sufficiently great to prejudice the use of absorption spectrophotometry as a means of characterizing the chrysene ring structure.



(I)

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS. RECEIVED OCTOBER 19, 1940

The Preparation of N-Allylnormorphine

BY ELTON L. MCCAWLEY, E. ROSS HART AND DAVID FIELDING MARSH

In the course of a biochemorphic survey of morphine derivatives, N-allylnormorphine has been prepared. Using von Braun's method[1] morphine is acetylated with acetic anhydride to protect the hydroxyl groups. The nitrogen-methyl group is removed by the action of cyanogen bromide and decomposition to normorphine. The normorphine base reacts with allyl bromide at 70° to form N-allylnormorphine hydrobromide, m. p. 126°, soluble in water, sl. sol. in alcohol and insoluble in ether; N-allylnormorphine free base melts at 92–93°.

Anal. Calcd. for $C_{19}H_{21}O_3N$: C, 73.3; H, 7.0; mol. wt., 311.2. Found: C, 74.6; H, 7.5 (Kirk); mol. wt., 313 (Rast).

An iodoxybenzoate test indicates a free phenolic hydroxyl group.

The preparation of normorphine by evolution of formaldehyde from morphine oxide and chromic acid and also the decomposition of N-nitrosonormorphine by alcoholic potash are unsatisfactory due to excessive breakdown of the ring structure. These procedures[2] are unsuitable for the preparation of norcodeine, for the same reason.

N-allylnormorphine appears to have a stronger antagonistic action toward the depression of respiration evoked by morphine than N-allylnorcodeine.[3]

(1) Von Braun, *Ber.*, **47**, 2312 (1914).
(2) Diels and Fischer, *ibid.*, **49**, 1721 (1916); Speyer and Walther, *ibid.*, **63**, 852 (1930).
(3) Pohl, *Z. exp. Path. Therap.*, **17**, 370 (1915).

PHARMACOLOGICAL LABORATORIES
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Thioanilides of Malonic Acids

BY AVERY A. MORTON, A. R. OLSON AND J. W. BLATTENBERGER

Phenyl isothiocyanate has been used[1] as a test for organometallic compounds. If reactions of this reagent with amyl- or benzylsodium parallel those observed[2] with carbon dioxide it should be possible to prepare directly the thioanilides of the corresponding malonic acid according to the se-

(1) Sach and Loevy, *Ber.*, **36**, 585 (1903); Schlenk, Bergmann and co-workers, *Ann.*, **463**, 1; **464**, 1 (1928); Gilman and Breuer, THIS JOURNAL, **55**, 1262 (1933).
(2) Morton and Fallwell, Jr., *ibid.*, **60**, 1426 (1938).

quence of reactions shown below. Small quantities of the expected products were indeed obtained.

$$C_5H_{11}Na \xrightarrow{C_6H_5NCS} C_4H_9CH_2C(=NC_6H_5)SNa \xrightarrow{C_5H_{11}Na}$$

$$C_4H_9CH(Na)C(=NC_6H_5)SNa \xrightarrow{C_6H_5NCS}$$

$$C_4H_9CH[C(=NC_6H_5)SNa]_2 \xrightarrow{HX} C_4H_9CH[CSNHC_6H_5]_2$$

A peculiarity in this preparation was the repeated failure to obtain isolable quantities of either product when a creased flask[3] was used as the reaction vessel. In such cases the product was a material which has not yet been characterized. Increases in yield of 50 to 100% in preparation of certain Grignard reagents and improvement in other reactions have been noted in this Laboratory when the experiments have been carried out in flasks of this special design but this is the first instance where the products appeared different.

Reactions of amylsodium with carbon disulfide, sulfur dioxide, and sulfur trioxide in hope of obtaining various sulfur-containing acids gave mixtures which were not separated readily.

Experiments

Butyldithiomalon Dianilide.—Amylsodium was prepared from 37 g. of *n*-amyl chloride with 20 g. of fine sodium sand in petroleum ether at 0° in an ordinary 3-neck flask arranged in the conventional manner,[4] described before. Phenyl isothiocyanate, 47 g. (0.35 mole) was added dropwise over a period of ten minutes. After stirring for thirty minutes, the mixture was decomposed with 30 ml. of alcohol followed by 150 ml. of water. The two latter were then separated. The aqueous layer was acidified and extracted with ethyl ether and with ethyl acetate. The combined extracts were evaporated to a dark brown non-crystalline solid, and the latter extracted with petroleum ether and with ligroin. Crystals melting from 67 to 68° were obtained.

The organic layer in turn yielded a heavy residual oil on evaporation which was distilled in a Hickman alembic at 5 to 10 microns. The fraction boiling from 100 to 135° slowly crystallized yielding a product identical with the crystals obtained by extraction of the aqueous layer. The combined product was recrystallized from alcohol giving 1.2 g. (2% based on the amyl chloride used) of material melting at 67–68°.

Anal. Calcd. for $C_{19}H_{22}N_2S_2$: S, 18.71; N, 8.19. Found: S, 18.3; N, 8.10.

Upon saponification with excess alkali aniline was evolved and the alkali consumed was equivalent to the above formula. Saponification equivalent calcd., 171; found, 169.

Phenyldithiomalon Dianilide.—Preparation of *n*-amylsodium was carried out as before. Toluene, 33 g., was then added and the mixture refluxed for one hour, after which phenyl isothiocyanate, 47 g., was added dropwise. Decomposition and separation were carried out in the same manner as before. Crystals from the aqueous layer were identical with those obtained from the organic layer by distillation at 2 to 3 microns at 120 to 150°. The combined product was carefully sublimed at 60–80° and 2 microns giving a clean white material melting 66 to 67°; yield 1.5 g. or 2.4% based on the amyl chloride used.

Anal. Calcd. for $C_{21}H_{18}N_2S_2$: S, 17.68; N, 7.74. Found: S, 17.1; N, 7.70. Aniline was detected upon hydrolysis with alkali. Saponification equivalent. Calcd., 181; found, 184.

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(3) Morton, *Ind. Eng. Chem., Anal. Ed.*, **11**, 170 (1939).

(4) Morton and Richardson, THIS JOURNAL, **62**, 123 (1940).

The Identity of α- and β-Earleine with Betaine and Choline, Respectively

BY ARTHUR STEMPEL AND ROBERT C. ELDERFIELD

In a previous communication from this Laboratory[1] the isolation of two non-toxic, nitrogenous bases from *Astragalus earlei*, or Big Bend loco weed, was described. These were assigned the empirical formulas $(C_{16}H_{37}N_3O_7)_x$ and $(C_{16}H_{37}N_3O_4)_x$ on the basis of analytical data on their salts and were named α- and β-earleine, respectively. With the limited amount of material at hand it was not possible to characterize the bases further at that time. In the meantime we have secured additional amounts of the weed and have identified the bases as betaine and choline, respectively. A study of the thermal decomposition of "β-earleine" provided the clue for the correct interpretation of its nature, from which the identity of "α-earleine" with betaine was surmised. From the decomposition products of "β-earleine" we have identified trimethylamine and acetaldehyde. A sample of "β-earleine" produced a typical choline effect on white mice when tested in the Parke, Davis laboratories through the kind coöperation of Dr. Oliver Kamm. The names α- and β-earleine should, therefore, be stricken from the literature.

Experimental

Identification of Betaine.—The isolation was carried out as previously described.[1] The picrate melted at 184° and gave no depression in melting point when mixed with betaine picrate.

Anal. Calcd. for $C_5H_{11}O_2N \cdot C_6H_3O_7N_3$: C, 38.2; H, 4.1; N, 16.2. Found: C, 38.3; H, 4.1; N, 15.6.

The styphnate melted at 186–188° (dec.).

(1) Pease and Elderfield, *J. Org. Chem.*, **5**, 192 (1940).

Anal. Calcd. for $C_5H_{11}O_2N \cdot C_6H_3O_8N_3$: C, 36.5; H, 3.9; N, 15.5. Found: C, 36.8; H, 4.1; N, 15.0.

The hydrobromide melted at 225°.

Anal. Calcd. for $C_5H_{11}O_2N \cdot HBr$: C, 30.3; H, 6.1; N, 7.0; Br, 40.4. Found: C, 30.8; H, 6.2; N, 7.0; Br, 40.1.

Identification of Choline.—When "β-earleine" was decomposed by heating in a stream of nitrogen, trimethylamine was isolated from the products by means of its picrate, which melted at 228–229°, and gave no depression of melting point when mixed with a known sample. Acetaldehyde was also isolated as the 2,4-dinitrophenylhydrazone which melted at 164°.

Anal. Calcd. for $C_8H_8O_4N_4$: C, 42.9; H, 3.6; N, 25.0. Found: C, 43.1; H, 3.4; N, 24.8.

The picrate melted at 247° and no depression was observed when it was mixed with choline picrate.

Anal. Calcd. for $C_5H_{14}ON \cdot C_6H_3O_7N_3$: C, 39.8; H, 4.8; N, 16.9. Found: C, 39.8; H, 4.7; N, 16.9.

The picrate of the acetate, prepared with acetic anhydride, melted at 111.5–112.5° and gave no depression in melting point with acetylcholine picrate.

Anal. Calcd. for $C_7H_{15}O_2N \cdot C_6H_3O_7N_3$: C, 41.7; H, 4.8; N, 15.0. Found: C, 42.0; H, 4.9; N, 15.1.

The micro analyses reported were performed by Mr. Saul Gottlieb of these laboratories.

We wish to acknowledge our appreciation for the kind coöperation of S. B. Penick and Co., of New York City, and of Parke, Davis and Co., of Detroit, Michigan, in carrying out preliminary extraction of the weed which was secured with the aid of Dr. Frank P. Mathews, of the Loco Weed Laboratory, Alpine, Texas. Our thanks are also due the American Academy of Arts and Sciences for a grant for technical help in this investigation.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, N. Y. RECEIVED NOVEMBER 20, 1940

NEW BOOKS

The Chemical Composition of Foods. By R. A. MCCANCE and E. M. WIDDOWSON, Department of Medicine, University of Cambridge. Chemical Publishing Co., Inc., 148 Lafayette St., New York, N. Y., 1940. 150 pp. 14.5 × 22.5 cm. Price, $2.50.

The data recorded in this book were accumulated as the result of the chemical analyses of foods supported by the Medical Research Council (England) in the laboratory of the senior author. Accordingly, they do not represent a compilation of the data recorded in the literature. This, at least, implies that the analytical methods employed were uniform and that the results are strictly comparable. In the introduction reference is made to certain difficulties involved in the choice of analytical procedures, particularly in the instance of the fat determination, where the Soxhlet method gives much lower results than the Liebermann method with certain foods. The authors also discuss the doubtful propriety of recording phytin (or phytic acid) phosphorus as "non-available," and of classifying as "available" that portion of the iron which reacts with α,α′-dipyridyl, as has been done in two special tables in the closing portion of the book. The occasions for substantial gains in certain elements during the processing for consumption are also presented. Since particular attention is given to cooked dishes ready for the table, the recipes and methods of preparation are given in some detail, so that one section of the volume reads like a veritable cookbook. For the American reader this is desirable, since numerous of the dishes are not well known on this side of the Atlantic, particularly in the instance of the puddings and meat pies.

About four-fifths of the book is occupied by the tabulated data of analyses. The first series of tables includes the proximate analysis (excluding crude fiber), Na, K, Ca, Mg, Fe, Cu, P, S and Cl content, calories per 100 g. and acid-base balance of 541 foods classified as (1) cereals and cereal products, (2) dairy products, (3) meat, poultry and game, (4) fish, (5) fruit, (6) nuts, (7) vegetables, (8) sugar, preserves and sweetmeats, (9) beverages, (10) beers, (11) condiments, (12) vegetable fats, (13) cakes and pastries, (14) puddings, (15) meat and fish dishes, (16) egg and cheese dishes, (17) sauces and soups. Beginning with (3) the method of cooking, if any, nature of the edible material, and grams of edible matter as eaten, from each 100 grams of purchased food are also recorded and this continues through (7). In the instance of (8), (13), (14), (15), (16) and (17) there are cross references to the recipes appearing earlier in the book.

In the next block of tables the same data are set over into terms of *grams or milligrams per ounce*, presumably for the convenience of dietitians and others who are more accustomed to dealing with portions scaled in the common or avoirdupois system. The one exception to the system is in the instance of beers, which is based upon the pint.

An advantage in the organization of these data lies in the fact that they include food as served. One cannot but wonder if the English culinary practices are so uniform as to permit of accepting these data as representative of each item, however; also whether or not the average of only two preparations (p. 11, line 23) is sufficient to compensate for the variability in raw materials and technical skills.

The reviewer has tried the volume out on several dietitians, who have reacted rather favorably, and it seems probable that they, rather than the food chemist or tech-