minations[5] except for the water-soluble material and for unsaponifiable matter in the oil.[6]

The water-soluble material was determined as follows. A sample of crushed seeds was agitated at room temperature with water for one hour. The foaming, soap-like emulsion was allowed to stand, filtered, evaporated, dried and weighed. The soluble matter amounted to 17.5% of the total sample of seeds rendered.

Calculated on the basis of the original sample, a protein determination on the soluble matter showed 2.3%. The dissolved protein readily coagulates on addition of acid.

Negative tests for sugar and starch were obtained from the soluble material, but after hydrolysis 3.6% of the original sample was present as sugar (calculated as dextrose) and a highly colored substance, red in acid and blue in base, was produced.

The chemical composition of the crushed seeds is presented in Table I.

Some characteristics of the crude oil, as extracted with ether, are presented in Table II.

TABLE I

COMPOSITION OF SEEDS

Determ.	Per cent.
Moisture	11.7
Protein	21.2
Fat	3.8
Starch	27.9
Fiber	17.7
Ash	2.8
Non-protein water-sol. matter	15.2

TABLE II

CHARACTERISTICS OF CRUDE OIL

Determ.	Result
Sp. gr. 25°/25°	0.9209
n^{25}D	1.4730
Iod. no. (Hanus)	97.3
Sap. V.	194.2
Acid V.	4.5
Satd. acids, %	13.8
Unsatd. acids (Iod. no. 120.6 (Hanus), %	78.4
Unsap. matter, %	3.0
Acetyl value	6.9

The values given in the tables are mostly self-explanatory. The starch content as given in Table I represents all water insoluble substances that will hydrolyze, under the conditions of the experiment, to give sugar.

The vegetable oil would necessarily be classified as a non-drying oil.[7]

GOOSE CREEK, TEXAS RECEIVED MARCH 19, 1937

The Direct Demonstration of the Sucrose Linkage in the Oligosaccharides

BY HARRY W. RAYBIN

The writer has previously reported an apparently specific reaction given only by sucrose (and raffinose, the trisaccharide containing sucrose in the molecule) out of a large number of sugar compounds tested.[1] To date there has been no report in the literature of any other sugar giving a similar reaction. On the other hand Purves and Hudson have reported a gamma-methyl fructoside which was hydrolyzed by the enzyme invertase, but which did not give the reaction with diazouracil. They concluded that this "reaction was therefore more specific for the sucrose linking than the action of invertase."[2] Isosucrose does not give this reaction.[3] Sucrose octaacetate does not give the reaction until after deacetylation.

The glucose-fructose linkage of sucrose is also present in the trisaccharides raffinose and gentianose, and in the tetrasaccharide stachyose. These sugars may be represented as follows.[4]

Sucrose: Fructofuranose-glucose
$2 \longleftrightarrow 1$
Raffinose: Fructofuranose-glucose-galactose
$2 \longleftrightarrow 1 \quad 6 \longleftrightarrow 1$
Gentianose: Fructofuranose-glucose-glucose
$2 \longleftrightarrow 1 \quad 6 \longleftrightarrow 1$
Stachyose: Fructofuranose-glucose-galactose-galactose
$2 \longleftrightarrow 1 \quad 6 \longleftrightarrow 1 \quad 6 \longleftrightarrow 1$

A direct test for the sucrose linkage in these sugars has hitherto not been possible without hydrolysis. The reaction of raffinose with diazouracil[1] is believed to be the first demonstration of this kind. It was of interest therefore to extend this reaction to the two other rarer sugars, but they have not been available from either commercial or academic sources in this country.

A sample of gentianose has finally been obtained through the kindness of Prof. Henri Hérissey of the University of Paris, and has now been found to give typical blue-green color, similar to sucrose and raffinose.

Stachyose is still unavailable, but in view of the results at hand may be predicted to respond similarly.[5]

After this note was submitted for publication, a sample

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(5) Credit for the protein determination and for gathering and preparing some of the material is due C. Smalling, J. R. Martin, C. Crawford and W. Ruez.

(6) Andés, "Vegetable Fats and Oils," D. Van Nostrand Company, Inc., New York, 1925, p. 385.

(7) Jamieson, "Vegetable Fats and Oils," The Chemical Catalog Co., Inc., New York, 1932, p. 341.

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(1) H. W. Raybin, THIS JOURNAL, **55**, 2603 (1933).

(2) C. B. Purves and C. S. Hudson, *ibid.*, **56**, 711 (1934).

(3) Professor Sir James C. Irvine (private communication).

(4) E. F. Armstrong, "The Carbohydrates," 1934.

(5) The use of this reaction is not always applicable to unknown mixtures as other sugars sometimes prevent or obscure the test.

of stachyose was received through the further kindness of Prof. Hérissey, and was found to react as expected.

A contribution from the Chemical Laboratory of the Bureau of Food and Drugs of the New York City Department of Health, 125 Worth St., New York City.

NEW YORK, N. Y. RECEIVED APRIL 24, 1937

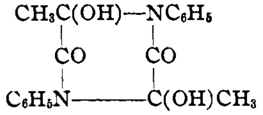
The Dimerization of Pyruvic Anilide

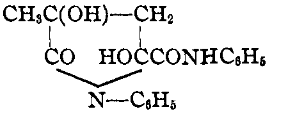
BY JOHN V. SCUDI

Continuing a study[1] of condensation reactions of alpha ketoamides it was observed that pyruvic anilide did not condense with a series of active methylene compounds or substituted benzaldehydes under Knoevenagel[2] conditions. Quantitative yields of dimeric pyruvic anilide[3] were precipitated. This preferential condensation of pyruvic anilide with itself directed attention toward the structure of the dimer.

Wohl and Lips[4] revised the structure of Bischoff and Walden[5] and suggested a diketopiperidine (I). They demonstrated that the anilide hydrogens were involved in the dimerization, since n-methylpyruvic anilide did not dimerize. Their structure was based largely upon the stability of the compound to hydrolysis.

Since benzoylformanilide does not dimerize, one of the methyl hydrogen atoms is involved in the dimerization, and while the dimer is stable to acid hydrolysis, it shows the lability characteristic of aldols in alkaline media. The dimer dissolved in cold 10% sodium hydroxide with regeneration of the monomeric pyruvic anilide. This was demonstrated by oxime formation. The alkaline solution was boiled for five minutes. Two molecules of aniline were obtained and the pyruvic acid was isolated as the hydrazone. For these reasons, and the extensive analogies reported,[1,6] structure II seemed more probable.


I


II

The dimer, treated with dry hydrogen chloride in alcohol, lost a molecule of water, and a single ethoxyl group was introduced into the compound (III). Upon treatment with concentrated sulfuric acid in boiling acetic anhydride, two molecules of water were lost, and a single acetyl group was introduced (IV). This is evidence of an unsymmetrical structure of the dimer.

In analogy with condensation products of benzoylformanilide[1,6a] the structure of III is probably 1 - phenyl - 2 - ethoxyl - 2 - formanilide - 4 - hydroxy-4-methylpyrrolidone-5. The structure of IV may be either the 1-phenyl-2-formanilide-4-acetyl-4-methylpyrrolin-2-one-5, or the 2-acetyl derivative with the appropriate double bond shift. These structures have not been definitely established but since the problem is being discontinued, it was decided to report these data.

Experimental

Pyruvic Anilide.—Lactanilide was prepared in excellent yields according to the method of Bischoff and Walden[5] and the crude product used directly. To 165 g. of crude lactanilide dissolved in one liter of 20% acetic acid, 88 g. of sodium bichromate, and 89 ml. of concentrated sulfuric acid were added. The reaction mixture was allowed to stand for thirty minutes at room temperature, was quenched to 0° and diluted to 3 liters. The product,[3] recrystallized from slightly acidulated water, was obtained in 30–45% yields: m. p. 104°; the phenylhydrazone[3] melted at 170–171°, and the oxime[7] at 143°.

Anal. Calcd. for $C_9H_9O_2N$: N, 8.59. Found: N, 8.46, 8.66.

Dimeric Pyruvic Anilide (II).—Five drops of diethylamine was added to 5 g. of pyruvic anilide in 20 ml. of acetone. Solidification occurred within thirty minutes. The product was filtered off, washed with dilute acetone and recrystallized from 50% aqueous alcohol: white needles, m. p. 208–209°. The product was identical with that obtained by the methods of Nef[3] or Wohl and Lips.[4] The yields averaged 90–95% and became quantitative upon working up filtrates. No other condensation product could be isolated. Dimerization occurred in the presence of molecular amounts of the following active methylene compounds and benzaldehydes: acetophenone, ethyl cyanoacetate, ethyl acetoacetate, nitromethane, diethyl malonate, benzaldehyde, p-hydroxybenzaldehyde, and anisaldehyde.

Anal. Calcd. for $C_{18}H_{18}O_4N_2$: N, 8.59. Found: N, 8.31.

Alkaline Hydrolysis of II.—Treatment of II in cold 10% sodium hydroxide with hydroxylamine hydrochloride gave the oxime of pyruvic anilide. The identity of this substance was confirmed by comparison with an authentic sample.[7]

One gram of II was warmed carefully to a boil in 15 ml. of 10% sodium hydroxide under a reflux condenser, and

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(1) Scudi and Lindwall, THIS JOURNAL, **57**, 1646, 2302 (1935).

(2) Knoevenagel, *Ann.*, **281**, 25 (1894); **288**, 321 (1895); *Ber.*, **31**, 2588 (1898); **37**, 4464 (1904).

(3) Nef, *Ann.*, **270**, 267 (1892).

(4) Wohl and Lips, *Ber.*, **40**, 2313 (1907).

(5) Bischoff and Walden, *Ann.*, **279**, 79 (1894).

(6) (a) De Jong, *Rec. trav. chim.*, **20**, 91 (1901); (b) Bashour and Lindwall, THIS JOURNAL, **57**, 178 (1935).

(7) Ponzio and de Paolini, *Gazz. chim. ital.*, **57**, 653 (1927).