

only at higher temperatures. The monofluorides are inferior anesthetic agents while the difluorides have no such effect. These behaviors are in good agreement with the facts recently demonstrated that the atomic distances between the C and F atoms is 1.41 Å. in the monofluorides, while it is only 1.36 Å. in the difluorides.²

	B. p., °C.	Per cent. F		Per cent. Cl	
		Calcd.	Found	Calcd.	Found
CHCl ₂ F	8.9 to 9.0	18.4	18.1	68.0	68.2
CHClF ₂	-40.8 to -40.6	43.9	43.5	40.1	40.4
CH ₂ ClF	-9.0 to -9.1	27.7	27.4	51.8	51.8
CH ₂ F ₂	-51.6	74.1	74.1

The analyses were carried out as described previously.³

(2) Brockway, *J. Phys. Chem.*, **41**, 185 (1937).

(3) Henne and Hubbard, *THIS JOURNAL*, **58**, 406 (1936), and **56**, 1078 (1934).

DEPARTMENT OF CHEMISTRY
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Standardization of Ceric Sulfate with Potassium Iodide by the Acetone Method

BY DAVID LEWIS

That ceric sulfate can be substituted for potassium permanganate in oxidimetry has been established by many investigators. Among the reactions which take place quantitatively with both reagents is the oxidation of iodides. In a recent paper Kolthoff, Laitinen and Lingane¹ have shown that pure potassium iodide can be used as a primary standard for permanganate.

One of the indicator titration methods studied by them was the acetone method of Berg.² They report poor reproducibility and low results by this method. The writer's experience with this titration using ceric sulfate as oxidant is of interest in this connection. As previously demonstrated³ the titer varies with the acid concentration. Within the range 0.9-2.7 *N* sulfuric acid the results are accurate to 0.1%. Below this range low results, above it high results, are obtained. With potassium iodate Berg recommends that the solution be 2-2.5 *N* in sulfuric acid. The low results of Kolthoff, *et al.*, were obtained in solutions initially 0.9 *N*. Since the reaction between acetone and iodine is acid catalyzed, these low results are attributed to a low rate of reaction. As the end-

point of this titration seldom lasts more than three minutes under the best conditions of acidity, it is not the low rate of reaction but probably the concomitant production of new reducing substances which causes too much oxidant to be used. The most suitable acidity seems to vary with the oxidant.

In the routine standardization of ceric sulfate solutions with sodium oxalate, the writer has included a comparison with potassium iodide by the acetone method and potentiometrically. All three agree to $\pm 0.1-0.2\%$. The potassium iodide was analytical reagent (Mallinckrodt) and was dried at 125-130° for three hours before use. For the accuracy indicated this treatment is sufficient, since titrations of aliquots by the acetone method and potentiometrically check to 0.1%.

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The Siene Bean. The Composition of Siene Beans. Some Characteristics of Siene Bean Oil

BY TOM S. PERRIN

The sturdy growth and abundance of fruit exhibited by the siene bean plant attracted the writer's attention. This investigation was undertaken with the idea that a knowledge of the composition of the seeds might reveal a use for them, as was the case with soy beans.¹

The siene bean plant (*Daubentonio longifolia*), sometimes called "coffee bean" or "rattle box," grows abundantly both inland and along the Gulf Coast of Texas and Florida as a wild plant.² It is a perennial plant that may grow as large as the average peach tree. The tree produces a seed similar to that of the soy bean, the pod containing from four to eight seeds. Siene beans are very hardy and bear prolifically, producing fruit even the first year. Three pounds of shelled beans were gathered from one tree. The seeds are extremely toxic to sheep³ and, as found in this Laboratory, to guinea pigs.

Standard procedures⁴ were used in all deter-

(1) Burlison, *Ind. Eng. Chem.*, **28**, 772 (1936).

(2) Schultz, "Texas Wild Flowers," Laidlaw Brothers, New York, 1928, p. 154.

(3) Marsh and Clawson, *J. Agr. Research*, **20**, 507-513 (1922); *Analyst*, **46**, 145.

(4) "Methods of Analysis of A. O. A. C.," Assoc. Agr. Chem. Washington, D. C., 1935, pp. 335-352, pp. 404-429.

(1) Kolthoff, Laitinen and Lingane, *THIS JOURNAL*, **59**, 429 (1937).

(2) Berg, *Z. anal. Chem.*, **69**, 369 (1926).

(3) D. Lewis, *Ind. Eng. Chem., Anal. Ed.*, **8**, 100 (1936).

minations⁵ 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		TABLE II CHARACTERISTICS OF CRUDE OIL	
Determ.	Per cent.	Determ.	Result
Moisture	11.7	Sp. gr. 25°/25°	0.9209
Protein	21.2	<i>n</i> _D ²⁰	1.4730
Fat	3.8	Iod. no. (Hanus)	97.3
Starch	27.9	Sap. V.	194.2
Fiber	17.7	Acid V.	4.5
Ash	2.8	Satd. acids, %	13.8
Non-protein water-sol. matter	15.2	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

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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.

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 fructose 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 ↔ 1

Raffinose: Fructofuranose-glucose-galactose
2 ↔ 1 6 ↔ 1

Gentianose: Fructofuranose-glucose-glucose
2 ↔ 1 6 ↔ 1

Stachyose: Fructofuranose-glucose-galactose-galactose
2 ↔ 1 6 ↔ 1 6 ↔ 1

A direct test for the sucrose linkage in these sugars has hitherto not been possible without hydrolysis. The reaction of raffinose with diazouracil¹ 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

(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.