

**Salicyl Aldehyde to Saligenin.**—A solution is made of 30 g. of salicyl aldehyde in 60 cc. of alcohol and 0.25 g. of catalyst is added. The reduction is complete in about 75 minutes and practically a quantitative yield is obtained.

**Nicotinic Acid Hydrochloride to Nipocotinic Acid Hydrochloride.**—A solution is made of 10 g. of nicotinic acid hydrochloride in 150 cc. of water and 1.0 g. of catalyst is added. The reduction is complete in about 2 hours. The product may be isolated by vacuum evaporation of the solution.

### Summary

1. Since experiments indicate that the oxygen which must always be present in platinum black if it is to be an active catalyst, is present in the form of an oxide of platinum, it was concluded that the oxides of platinum should be excellent catalysts. These are being studied.

2. An oxide of platinum has been formed by the fusion of chloroplatinic acid with sodium nitrate and has proved to be an excellent catalyst.

3. Various types of organic compounds such as phenols, pyridine derivatives, aromatic and aliphatic aldehydes and heterocyclic compounds have been reduced. The speed of reduction with this catalyst is greater than when ordinary platinum black is used.

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### NOTE

**Vanillin Glyceride.**—The attention of the writer was recently called to a deposit which had formed in a flavoring mixture consisting essentially of alcohol, glycerin, and vanillin. The precipitate was easily purified by filtration and washing with water and, thus isolated, was a white, almost odorless, micro-crystalline powder, slightly soluble in water and ether. It was moderately soluble in cold alcohol, easily on heating, separating from solution on cooling in distinct crystalline plates. It was also easily soluble in 0.5 *N* potassium hydroxide solution, without, however, showing any definite neutralization, and was precipitated in crystals on the addition of acid, behaving thus like a phenol.

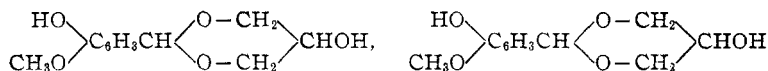
On warming the crystals with water, they dissolved slowly and the odor of vanillin became apparent. After a few hours' heating, vanillin alone crystallized from the cooled solution, and in the mother liquor glycerin was found by the usual tests. The hydrolysis was greatly hastened by acid catalysts, and an approximate analysis of the compound was made as follows.

2.0795 g. of substance was mixed with 20 cc. of warm water, and 1 cc. of 0.5 *N* hydrochloric acid added. The crystals dissolved immediately, and vanillin separated. To insure a complete hydrolysis, the mixture was heated for 1 hour at 90–100°. On cooling, the solution was extracted 4 times with ether, in 10cc. portions. The ether extract, evaporated to constant weight at 50°, was nearly pure vanillin; the aqueous solution similarly evaporated left a residue of slightly discolored glycerin.

Calc. for vanillin: (1 mol.) 67.25%. Found: 1.405 g., or 67.5%.

Calc. for glycerin: (1 mol.) 40.71%. Found: 0.818 g., or 39.3%.

The substance is evidently the result of a combination of vanillin and glycerin in molecular proportions, with elimination of one molecule of water, and has probably one of the following two structural formulas.



It would thus be analogous to the acetals and glucosides and, in fact, a quite similar compound from benzaldehyde and glycerin has been described by Fischer.<sup>1</sup> The free phenol group accounts for the acidic nature and, at the same time, the absence of a free aldehyde group explains why the acid properties are less marked than in the case of vanillin.

Experiments on the preparation of the compound from its constituents showed that the reaction between vanillin and glycerin was much accelerated by the presence of mineral acid, but the latter was a very disturbing factor during the isolation of the product. Working in the cold and as rapidly as possible, it was found impossible to free the crystals from mother liquor before a very considerable hydrolysis had occurred, and any trace of acid left in the preparation caused its complete decomposition in a short time. To secure a stable product, it was found advisable to dissolve the crude crystals in a slight excess of 0.5 N alkali, and reprecipitate by somewhat less than the equivalent amount of acid, thus leaving the mother liquor slightly alkaline. After washing free from alkali, the crystals thus obtained appear to be permanent. Where time is no object, the preparation without acid is perhaps simpler.

For example, a mixture of 5 g. of vanillin, 25 g. of glycerin, 15 g. of alcohol, and 2 g. of 30% hydrochloric acid was allowed to stand at ordinary temperature. After 3 days the formation of crystals was noticed. After 10 days the crystals were filtered, washed with cold water, and dried in a desiccator. Five days later the preparation, amounting to 2.45 g., was found to be entirely decomposed into vanillin and glycerin.

A similar mixture with 1.5 g. of 90% sulfuric acid in place of the hydrochloric acid yielded after 3 weeks 2.95 g., or 59% of the vanillin used, which after careful purification as described proved to be stable. The same mixture without any acid yielded after 11 weeks 1.83 g., or 36.6%.

Vanillin glyceride melts, not very sharply, at 160–162°. On adding a little acid to a dilute (about 0.2 N) alkaline solution, it crystallizes slowly in distinct plates which, under the microscope, in convergent polarized light, show an orthorhombic interference figure. Axial angle,  $2E = 90-100^\circ$ . Birefringence, positive: dispersion,  $r < v$ .

When the crystals are touched with a drop of dil. hydrochloric acid they quickly disappear and on standing, or on slow evaporation, the characteristic monoclinic needles of vanillin are observed.

<sup>1</sup> Fischer, *Ber.*, 27, 1536 (1894).

The writer hopes to be able to report later on the reaction of glycerin with other aromatic aldehydes.

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**The Carbohydrate Content of Navy Beans.**<sup>1</sup>—In a recent paper, Peterson and Churchill<sup>2</sup> have reported upon the carbohydrate content of the navy bean (*Phaseolus vulgaris*). Closely similar figures were obtained in work done by the writer several years ago.

The methods used in the two investigations were much the same—including separation of the carbohydrates by successive alcohol and cold water extraction, and enzyme digestion. Thus, closely agreeing figures were obtained in the two pieces of work for total sugars, dextrins, starch, pentosans and crude fibre.

Among the differences, in methods and results, it should be stated that Peterson and Churchill determined pentosans in several different fractions, the writer only on the whole bean. It is possible therefore that the figures in the later method for dextrin and starch really include a small amount of pentosans.

In the method under discussion the carbohydrate obtained by enzyme hydrolysis was subtracted from the carbohydrate obtained by acid hydrolysis of the residue—from the cold water extraction and the result called "insoluble hemicellulose," giving a figure considerably higher than that obtained by the Wisconsin Investigators by boiling their malt extract residue with 1% hydrochloric acid. Unlike the other workers the writer was never able to obtain mucic acid when attempting to determine galactans. It was not known whether this failure was due to the absence of galactans or to the method used.

A table comparing most of Peterson and Churchill's results with those of the writer is given below.

It was noted with interest that some of the difficulties encountered in manipulation were much the same. This was especially true with reference to fineness of grinding, filtering, time and completeness of digestion. In the present work it was found that bean flour passing a 100-mesh sieve gave more satisfactory results than flour passing a larger mesh sieve. The fat, for instance, was more easily and completely extracted with the fine flour than with the coarse flour. This complete extraction of the fat decreased the difficulties encountered in filtering the later extracts.

<sup>1</sup> The work reported in this article was conducted at the Nutrition Laboratory, Department of Home Economics, University of Chicago. It formed part of a thesis submitted in partial fulfilment of the requirements for the degree of Master of Science in the University of Chicago, June, 1919.

<sup>2</sup> Peterson and Churchill, *THIS JOURNAL*, **43**, 1180 (1921).

Composition of navy beans ( <i>Phaseolus vulgaris</i> )		
	Peterson and Churchill	Eichelberger
Moisture.....	12.96	10.08
Ash.....	3.88	3.43
Ether extract.....	1.83	2.36
Protein ( $N \times 6.25$ ).....	18.42	22.69
Alcohol soluble carbohydrate as dextrose (total sugar).....	1.59	2.61
Dextrins.....	3.71	3.23
Starch.....	35.20	35.22
Insoluble hemicelluloses, by difference....	....	8.90
Hemicelluloses.....	(.83) <sup>a</sup>	....
Pentosans.....	8.37	(8.08) <sup>a</sup>
Galactans.....	1.33	....
Crude fibre.....	3.94	3.62
Organic acids, waxes, etc., by difference...	8.77	7.86
	100.00	100.00

<sup>a</sup> Not included in summation, since it is included with the item above.

Here, as in Peterson's work, the blue coloration with iodine during enzyme digestion disappeared very slowly. However, the author found that after 17 hours' digestion with commercial pancreatin, under a layer of toluol, the coloration completely disappeared and constant results for enzyme digestion were obtained.

In conclusion, I wish to express my sincere thanks to Dr. Katherine Blunt, of the University of Chicago, for her personal interest and careful supervision of this work.

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## NEW BOOKS

**An Introduction to the Analytical Chemistry of the Rarer Elements.** By LOUIS J. CURTMAN, Assistant Professor of Chemistry, Chief of the Division of Qualitative Analysis, College of the City of New York. Privately printed, New York, 1921. 64 pp. 21 × 14.5 cm. Price \$1.25.

This small book, according to the preface, "is designed to lay a sound foundation for the analytical study of the rarer elements" and the author has made a careful selection of experiments to accomplish this result. It is a source of satisfaction to know that "every experiment was personally performed by the author." It is undoubtedly of advantage to have all reagents and test solutions of known strength, although in practice with natural and industrial products the problem may not be so conveniently arranged for us.