CRYSTALLINE *d*-FRUCTOSE PENTACETATE

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Progress in the investigation of fructose has always been impeded by the difficulty of crystallizing its derivatives. According to the accepted view of the constitution of fructose, its molecule contains five hydroxyl groups and therefore a pentacetate or two isomeric pentacetates, in case alpha and beta forms of fructose are postulated, should exist. Winter[2] acetylated fructose according to the Liebermann method with acetic anhydride and anhydrous sodium acetate, but did not obtain a crystalline product. Erwig and Koenigs[3] also prepared an amorphous resin by the action of acetic anhydride and zinc chloride on fructose. They obtained analytical data which agree with the formula of a pentacetyl fructose, but since the substance was amorphous, its chemical individuality is doubtful. It would appear probable from the method of preparation that it was a mixture of isomeric pentacetates of fructose. Panormov[4] prepared from fructose by a modification of Baumann's method of benzoylation an amorphous product which had the composition of a pentabenzoylfructose, but its failure to crystallize prevented in this case also the establishment of convincing direct proof that five hydroxyl groups are present in fructose. Several years ago, one of us[5] prepared a crystalline tetracetate of fructose, but the expected pentacetate was not obtained. Recently we have succeeded in preparing a pentacetate of *d*-fructose which crystallizes very readily, as is the case with fructose tetracetate.

Forty grams of very pure recrystallized *d*-fructose are added in the form of fine powder to a mixture of 240 cc. acetic anhydride and 10 cc. concentrated sulfuric acid, which is cooled by an ice and salt bath and vigorously stirred by a motor driven glass paddle. When the fructose is dissolved, which requires about an hour, the mixture is shaken with about 500 cc. of ice water, neutralized in a large dish with sodium bicarbonate, separated from the excess of solid bicarbonate by filtration, and the residue on the filter is washed with chloroform to dissolve the adhering acetylated sugar. The filtrate is extracted with chloroform for the same purpose. The chloroform solutions are mixed, dried with calcium chloride and distilled *in vacuo* to a small volume, 30–50 cc. This solution is then spread in a thin layer on a flat crystallizing dish and a strong current of air is passed over the yellowish fluid until the odor of chloroform disappears, and that of acetic anhydride becomes noticeable.

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[1] Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture.

[2] *Ann.*, **244**, 295 (1888).

[3] *Ber.*, **23**, 672 (1890).

[4] *J. Russ. Phys. Chem. Soc.*, **1**, 375 (1891).

[5] Brauns, *Verslag v. d. Koninkl. Akad. v. Wetensch.*, Amsterdam, **1908**, 577.

The sirup is then placed in a vacuum desiccator near potassium hydroxide and on stirring at intervals, it soon crystallizes to a solid mass. This is stirred in a mortar with some ether and filtered by suction, yielding about 16 g., or 20% of the theoretical, of pure *d*-fructose pentacetate of correct melting point and specific rotation. The substance may be easily recrystallized from ether and by slow evaporation brilliant, clear crystals may be obtained, measuring about 1 cm. in length and several mm. in width.

Fructose pentacetate melts at 108–109°. It is colorless, odorless and has a bitter taste. It is slightly soluble in cold water, insoluble in petroleum ether and readily soluble in benzene, chloroform, ether and alcohol. In comparison with fructose tetracetate, its solubility in ether and in alcohol is greater.

0.2919 and 0.2302 g. gave 0.5267 and 0.4147 g. CO_2 and 0.1515 and 0.1195 g. H_2O, corresponding to 49.21 and 49.13% C and 5.81 and 5.81% H; calc. for $C_6H_7O(C_2H_3O_2)_5$: 49.21% C, and 5.68% H.

The quantitative saponification of fructose pentacetate requires care, because the liberated fructose is so readily attacked by acid or alkali. Erwig and Koenigs[1] found the sugar to be slightly attacked by three hours' boiling with 0.1 *N* sulfuric acid. We observed a similar action and after trying various modifications, discarded the method of acid hydrolysis. It was found, however, that fructose pentacetate may be saponified readily by shaking at 0° with 0.1 *N* sodium hydroxide, a reagent which does not produce from fructose, under the same conditions, detectable amounts of acid, according to control experiments.

By shaking 0.4000 g. powdered fructose pentacetate with 75 cc. 0.1 *N* sodium hydroxide during two hours at 0° and titrating with 0.1 *N* sulfuric acid and phenolphthalein, the amount of acetic acid produced was found to be 73.99%. In a similar experiment of 3$^1/_2$ hours' duration, the value 77.20% was found, and in a third, lasting 5 hours, the value was 76.87%. The theoretical quantity for a fructose pentacetate is 76.93%. Evidently the saponification is complete after 3$^1/_2$ hours. The solution was levorotatory after saponification, indicating the regeneration of fructose.

The molecular weight of the fructose pentacetate was determined by the lowering of the freezing point of benzene. In three experiments, 1.789, 1.928 and 3.359 g. fructose pentacetate per 100 g. benzene gave the respective depressions, 0.226°, 0.242° and 0.415°, from which the values 396, 398 and 404 are calculated for the molecular weight in comparison with the theoretical value 390.

Fructose pentacetate can be obtained from benzene solution with one molecule of benzene of crystallization. This substance melts at 90° and on standing in the air readily loses benzene, which was recognized by its odor. On drying at ordinary temperature during one week, the substance lost 14.1% in reaching constant weight. Further drying at 70° did not decrease its weight. The formula $C_{16}H_{22}O_{11}.C_6H_6$ corresponds to 16.6% benzene.

The specific rotation of the fructose pentacetate was measured in chloro-

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[1] *Loc. cit.*

form and in benzene solution. 2.500 g. fructose pentacetate without recrystallization were made up to 50 cc. with chloroform (*chloroformum purificatum*, U. S. P.), and the solution polarized in a 2 dcm. tube at 20° with sodium light 12.04 circular degrees to the left, hence $[\alpha]_D^{20}$ = —120.4°. After one recrystallization from ether 2.500 g. fructose pentacetate made up in the same manner rotated 12.09 circular degrees to the left, hence $[\alpha]_D^{20}$ = —120.9°. After a second recrystallization from ether, the material still rotated —120.9°, which is taken as the specific rotation of the pure substance. 1.000 g. of pure fructose pentacetate made up to 50 cc. with benzene rotated, under the above mentioned conditions, 4.22 circular degrees to the left, hence $[\alpha]_D^{20}$ = —105.5 for its solution in benzene.

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THE VOLATILE OILS OF THE GENUS SOLIDAGO.

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The genus Solidago, commonly known as Golden-rod, is one of the larger genera of the plant family Compositae. It is quite widely and favorably known for the beauty which the golden-yellow flowers lend to late summer and early autumn, but is more or less unpopular as an alleged cause of hay fever.

Although a very large genus, numbering about seventy-five species in the United States alone, it has been of comparatively little practical value and consequently has received little attention at the hands of the phytochemist.

Of the four or five species which have been distilled, two, *Solidago canadensis* and *S. odora*, give a very fair yield of volatile oil and may, possibly, become of some economic importance. Only two of the oils thus far distilled, those of *Solidago canadensis*[1] and *S. nemoralis*[2] have received anything like a thorough chemical investigation.

The Volatile Oil of Solidago Rugosa.

Solidago rugosa Mill. is an American species found in damp thickets and on the borders of fields from Newfoundland to Ontario and southwestward to the Gulf of Mexico. It grows from one to six feet high.

In 1893 Oberhauser[3] made a chemical examination of the flowering plant and reported, among other things, a volatile oil present to the extent of 0.996%. The flowers and leaves were separately distilled with water. From the flowers he obtained a colorless oil having d_{15° 0.8486; from the leaves a straw-colored oil having d_{15° 0.8502. Both oils had an

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[1] *Report of Schimmel & Co.*, April, 1894, p. 57.

[2] THIS JOURNAL, **36**, 2538 (1914).

[3] *Am. J. Pharm.*, **65**, 122 (1893).