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NEW SOURCES OF INULIN¹

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In spite of the fact that inulin was discovered 125 years ago² and that voluminous literature has appeared since that time,³ both the chemical nature of inulin and its physiological significance are but little understood.

Inulin, prepared originally from elecampane (*Inula helenium*), has been since detected in a great many plants, mostly of the family *Compositae*. For actual preparation of quantities of inulin, only a few plants have been used, among which dahlia (*Dahlia variabilis*), Jerusalem artichoke (*Helianthus tuberosus*), chicory (*Cichorium intybus*) and dandelion (*Taraxacum officinale*) are by far the most important. Dean⁴ prepared inulin from burdock roots (*Lappa minor*) and the roots of goldenrod (*Solidago*).

Although the similarity of inulin prepared from different sources was evident, the identity of products of different origin was averred by some investigators and denied by others. The question was finally settled by Tanret,⁵ who fractionated the inulin from the Jerusalem artichoke into five—as he believed—distinct compounds, varying in their molecular complexity, specific rotation (-17 to -39°), and the degree of solubility in water and dilute alcohol. Some doubt may be felt as to the existence of Tanret's compounds as definite chemical individuals; the existence, however, of a series of complex anhydrides of levulose—by whatever name we may call them—was established beyond doubt. Dean⁴ suggested that the name inulin be limited to the fraction of specific rotation between -33 and -40° , and that the compounds of lower levorotatory power and higher solubility be called levulins. This suggestion, however, does not seem to constitute an improvement over Tanret's classification, since it is apparent that a compound whose specific rotation varies 7° cannot be called a chemical individual. For the time being, until the chemistry of the group

¹ Read at the meeting of the American Association for the Advancement of Science, December 30, 1930, Cleveland, Ohio.

² V. Rose-Gehlen's "*Neues Allgem. J. Chem.*," 3, 217 (1804); also Nicholson's "*J. Nat. Phil. Chem.*," 12, 97 (1805).

³ No attempt will be made in this article to review the literature on the subject. The reader is referred to Dragendorff's "*Materialien zu einer Monographie des Inulins*," 1870; and articles by Kiliani, *Ann.*, 205, 145 (1880); Willaman, *J. Biol. Chem.*, 51, 275 (1922); Harding, *Sugar*, 636 1923; and others, who quote extensively the literature on the subject.

⁴ Dean, *Am. Chem. J.*, 32, 69 (1904).

⁵ Tanret, *Bull. soc. chim.*, 9, 200, 227, 622 (1893); also Colin, *Rev. Gen. Bot.*, 31, 75, 179, 229, 277 (1919).

is better known, we may speak of the inulin group or inulin compounds as comprising all complex anhydrides of levulose.

In view of the fact that the practical sources of inulin are limited in number, we thought it would be advisable to call the attention of investigators in this line to some new sources of inulin, found in the course of systematic investigation of carbohydrates of uncultivated plants indigenous to the United States.

Inulin from Camas Roots.—Camas roots—*Quamasia quamash* (Pursh) Coville (*Camassia esculenta* Lindl.)⁶—were extensively and to a certain extent still are used for food by the North American Indians. The roots were cooked in stone-lined pits in the ground to a sweet, molasses-like sirup, or were roasted and ground into flour. Camas can be found in large quantities in Colorado, Utah, Idaho, Montana, Washington, Oregon and California. It is used as an ornamental plant in France.⁷

Results of analyses of camas roots received from different parts of the country are given in Table I.⁸

TABLE I
ANALYSES OF CAMAS ROOTS

Source and date recd.	Moisture, %	Reducing sugar (calcd. as dextrose)		Non-reducing sugar (calcd. as sucrose)	
		On dry basis		On dry basis	
Utah, August, 1929	50.5	2.8	5.7	22.0	44.4
California, January, 1930	64.3	1.3	3.6	18.7	52.4
Idaho, May, 1930	58.2	2.8	6.7	15.2	36.6
Oregon, May, 1930	66.0	3.0	8.8	11.6	34.1
Washington, June, 1930	68.0	2.2	6.9	13.3	41.6
Idaho, June, 1930	68.3	2.7	8.5	14.2	44.8
Montana, July, 1930	66.9	1.5	4.5	15.0	45.3
Oregon, July, 1930	67.3	3.8	11.6	16.9	51.7

⁶ Lewis and Clark Expedition, by E. Coues, 1893, pp. 952, 999; Pursh, "Flora Americae Septentrionalis," 1814, Vol. I, pp. 226-227; Brown, *Trans. Bot. Soc. Edinburgh*, 9, 378 (1868); Rep. Commiss. Agr. for 1870, p. 404; Palmer, *Am. J. Pharm.*, 50, 539 (1878); Newberry, *Pop. Sci. Monthly*, 32, 31 (1887); Havard, *Bull. Torrey Bot. Club*, 22, 98 (1895); Coville, *Contrib. U. S. Nat. Herbarium*, Vol. 5, No. 2 (1897); Blankinship, *Mont. Agr. Coll. Exp. Sta. Bull.*, 56 (1905); Spinden, *Mem. Am. Anthropol. Assn.*, Vol. II, pt. 3, 200 (1908); Chamberlin, *Proc. Acad. Nat. Sci. Phila.*, 63, 24 (1911), also *Mem. Am. Anthropol. Assn.*, Vol. II, pt. 5 (1911); Stout, *J. N. Y. Bot. Gard.*, 15, 50 (1914); Wilson, *Ottawa Naturalist*, 30, 17 (1916); McClintock, "Old Indian Trails," 1923, appendix; Anderson, "Trees and Shrubs of Brit. Col.," 1925.

⁷ Bois, "Les plantes alimentaires chez tous les peuples," Paris, 1927.

⁸ We wish to acknowledge our indebtedness for furnishing us with roots to Professor H. St. John, at the time with State College of Washington, Pullman, Wash., and to the following members of the U. S. Forest Service: R. H. Rutledge, Regional Forester, Ogden, Utah; S. W. Stoddard, Supervisor, Targhee National Forest, St. Anthony, Idaho; E. N. Kavanagh, Asst. Regional Forester, Portland, Ore.; G. D. Brown, Supervisor, Fremont National Forest, Lakeview, Ore.; Evan W. Kelley, Regional Forester, Missoula, Mont.; and K. D. Flock, Chief of Party, G-Surveys, Monarch, Mont.

An extract of camas root prepared for sugar analysis showed a rotation of -2.75° V. in a 2-dm. tube. After hydrolysis, the rotation was -6.7° . The rotation of other solutions taken from different samples of roots was as follows

Before hydrolysis.....	-2.0°	-2.6°	-2.4°	-2.4°
After hydrolysis.....	-5.6°	-6.1°	-6.5°	-6.5°

When it is taken into consideration that the specific rotation of inulin is about -35° and the specific rotation of levulose is -92° , the figures given above indicate that most (if not all) of the "non-reducing sugar" in camas roots is present in the form of inulin. Both the root and its extract give a positive Seliwanoff's reaction.

Owing to the presence of pectin-like gum in camas roots, the usual extraction of inulin with water is inconvenient, and the following method was used.

Two hundred grams of bulbs, put through a meat chopper, was extracted by heating with 1 liter of 50% alcohol and a little calcium carbonate. It was then made up to 2 liters with 95% alcohol and filtered. Eighteen hundred cubic centimeters of the filtrate was evaporated to about 400 cc. The solution was treated with neutral lead acetate and, after filtering, deleaded either with hydrogen sulfide or sodium carbonate. It was then evaporated to a thin sirup, and several volumes of 95% alcohol was added. After a few hours the alcohol was poured off the precipitated gummy material and some absolute alcohol added. After the gum had hardened it was dried in vacuo at about 70° . The spongy material obtained was easily ground to a white powder. The yield was 30-31 g. Various preparations of the material thus obtained had a specific rotation of -23.0 to -29.0° ; 80 to 90% of it was non-reducing sugar (inulin); 2 to 3% reducing sugar was present, and the rest was mostly moisture and ash. On dissolving the inulin in a very small amount of water and reprecipitating it with a large volume of alcohol, a product of specific rotation of -33.0° was obtained. It had no trace of reducing sugar. The inulin thus obtained was *soluble in cold water and 60% alcohol*. The latter dissolves about 5% inulin at room temperature. It resembled somewhat the inulin from asphodel, described by Colin and Neyron de Méons,⁹ although the asphodel inulin had a considerably lower specific rotation.

Inulin from *Allium nuttallii* S. Wats.—This variety of wild onion was used for food by various Indian tribes. The Cheyennes boiled it with meat.¹⁰ A sample received from Nebraska (April, 1930) showed the following content of reducing and non-reducing sugars.

⁹ Colin and Neyron de Méons, *Compt. rend.*, **185**, 1604 (1927).

¹⁰ Grinnell, "The Cheyenne Indians," 1923, Vol. II, p. 171.

	%	On dry basis, %
Moisture.....	69.8	..
Reducing sugar.....	1.7	5.6
Non-reducing sugar.....	18.1	59.9

A solution of sugars prepared from the bulbs had a rotation of -5.5° V. in a 2-dm. tube. On hydrolysis the rotation changed to -12.5° . Seliwanoff's reaction was positive.

Two hundred grams of bulbs, put through a meat chopper, was extracted with about 2 liters of cold water. After filtering and washing the pulp, the solution was treated with neutral lead acetate. The excess of lead was removed with hydrogen sulfide. Excess hydrogen sulfide was removed by a stream of air. The solution was filtered with decolorizing carbon and evaporated in vacuo to a thin, colorless sirup. Several volumes of 95% alcohol was added. The amorphous precipitate was dried in vacuo. The yield was 25 g. of white powder. Without further purification the specific rotation was $[\alpha]_D^{20} -31^{\circ}$. The inulin thus obtained was *soluble* in cold water and 70% alcohol (5% solution).

Both camas roots and wild onions belong to the family of *Liliaceae*, which has been little investigated for its inulin contents.¹¹

The third source of inulin we came across—*Balsamorhiza sagittata* (Pursh) Nutt—belongs to the family *Compositae*, known to contain many inulin-bearing plants. Although, at certain stages of growth, balsam root apparently contains a great deal of inulin,¹² it cannot be considered a very good practical source of inulin on account of the heavy bark and the woody structure of the root itself. The root, however, has been used for food and medicinal purposes by the Indians.¹³

The decorticated root had the following content of reducing and non-reducing sugars

Source and date recd.	Moisture, %	Reducing sugar (calcd. as dextrose)		Non-reducing sugar (calcd. as sucrose)	
		On dry basis		On dry basis	
Utah, July, 1929	7.0	10.6	11.4	9.3	10.1
Wyoming, August, 1929	9.0	12.4	13.6	9.0	9.9
Utah, May, 1930	8.8	2.1	2.3	6.2	6.8

A solution of sugars prepared from the root had the optical rotation -1.2° V. in a 2-dm. tube. After hydrolysis the rotation was -3.3° .

¹¹ Chevastelon [Dissertation, Paris, 1894, quoted through four-page abstract, *J. Pharm. Chim.*, 2, 83 (1895)] prepared from garlic inulin of sp. rot. -39° , very soluble in cold water and 70% alcohol. Similar preparations were made from hyacinth and other representatives of the Lily family.

¹² Inulin crystals were found by V. A. Pease, Associate Microscopist, Bureau of Chemistry and Soils, and George L. Keenan, Microanalyst, Food and Drug Administration, U. S. Department of Agriculture, in the course of histological and microchemical study of this plant (unpublished records).

¹³ Yanovsky, *THIS JOURNAL*, 52, 3446 (1930).

Seliwanoff's reaction was positive. One hundred grams of powdered root was treated in the way described for *Allium nuttallii*. The inulin obtained was redissolved in water and reprecipitated with alcohol. The yield was 3.2 g. The specific rotation was -27.7° . The product was soluble in water, but less soluble in dilute alcohol than the inulin from camas or wild onions; 40% alcohol dissolved 5% of inulin.

Summary

1. Three new sources of inulin are described, two plants of the family of *Liliaceae* and one of the *Compositae*.
2. The specific rotation of inulin from these sources ranged from -28 to -33° . All products were soluble in water and dilute alcohol.
3. In the light of this work and that of Chevastelon, it appears that there is no correlation between the specific rotation and the solubility of inulin.
4. No claim is made that any of the products described was a definite chemical individual.

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IDENTIFICATION OF ALCOHOLS. PARA-NITROPHENYL URETHANS

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The common reagents used for the preparation of solid derivatives of the alcohols are 3,5-dinitrobenzoyl chloride, phenyl isocyanate and α -naphthyl isocyanate. Since the melting points of many of these derivatives of the common aliphatic alcohols are rather low, which makes them difficult to purify, and since the differences in the melting points of certain pairs of compounds are rather small, it was thought that a series of higher-melting derivatives would be of value. The present communication presents the data obtained on *p*-nitrophenyl urethans of the common aliphatic alcohols. Table I summarizes the properties of the new derivatives and also lists the melting points of the 3,5-dinitrobenzoates, phenyl urethans and α -naphthyl urethans for comparison.

From the above table it is evident that the *p*-nitrophenyl urethans possess a few advantages over the other derivatives. The general melting point range is higher, which makes them easier to recrystallize. In two instances the melting point difference does not permit absolute identification, namely, *n*-propyl and isopropyl alcohols and hexyl and heptyl alcohols.

Para-nitrophenyl urethans may be prepared by the reaction between an alcohol and either *p*-nitrophenyl isocyanate or *p*-nitrophenylcarbonyl