

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 $[\alpha]_D^{20} = -120.4^\circ$. 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 $[\alpha]_D^{20} = -120.9^\circ$. 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 southward to the Gulf of Mexico. It grows from one to six feet high.

In 1893 Oberhauser³ 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

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

² THIS JOURNAL, 36, 2538 (1914).

³ Am. J. Pharm., 65, 122 (1893).

odor resembling origanum. Reactions with iodine and bromine indicated the presence of large amounts of terpenes. "On careful heating each began to boil at 130°."

From plants of this species collected near Auburn, Ala., we obtained by steam distillation of the fresh material a small amount of a light yellow oil, the yield being about 0.4%. The plants were in full bloom and were on the average three to four feet high. The material was carefully examined and was known to be free from other plants. Our determination of the plants was confirmed by comparison with specimens in the herbarium of the Alabama Polytechnic Institute.

The following physical and chemical properties were determined: d_{25}^{25} , 0.8620; α_D , -12.8° ; n_D^{23} , 1.4813; saponification number, 4.22; saponification number after acetylation, 10.97. These values correspond to 1.47% of ester calculated as bornyl acetate and 1.67% of free alcohol calculated as borneol.

After saponification the oil was fractionated under diminished pressure, then under atmospheric pressure. The results are given in Table I.

TABLE I.

No. of fraction.	Boiling temperature.	d_{25}^{25} .	α_D (100 mm. tube.)	n_D^{28} .
1.....	Below 165°	0.8520	- 3.78°	1.4688
2.....	165-170°	0.8560	+ 8.32°	1.4700
3.....	170-175°	0.8530	+24.04°	1.4725
4.....	175-180°	0.8510	1.4745
5.....	180	0.9200	1.4764
6.....	Residue			

From Fraction 1, which formed the greater part of the oil, there was prepared a nitrosyl chloride, m. p. 103°. As will be seen the boiling temperature, specific gravity, and index of refraction of this portion of the oil all agree closely with those of α -pinene and there can scarcely be any doubt that the oil is composed mainly of that terpene. For similar reasons it may be said that Fraction 4 is most probably composed mainly of limonene. The higher specific gravity of the two intervening fractions shows conclusively that a third compound, probably β -pinene, is present. Fraction 5 contained the alcohol resulting from saponification. That a saponification number of 10.97 was obtained after acetylation is, however, not absolute proof that a free alcohol was present, since it has been shown by Bouchardat and Lafont¹ and by Sievers² that unsaturated hydrocarbons may be acetylated.

The Volatile Oil of *Solidago Odora*.

Solidago odora Ait., commonly known as Sweet Scented Golden-rod or Blue Mountain Tea, is a native of the United States, growing in dry

¹ *Compt. rend.*, 102, 171 (1886).

² University of Wisconsin, Science Series, *Bull.* 434 (1911).

or sandy soil on the borders of thickets and in open woods from New Hampshire to Florida, westward to Missouri and Texas. The stem is $1\frac{1}{2}$ to $3\frac{1}{2}$ feet high. The whole plant is strongly aromatic, having a pleasant odor resembling that of anise and a sweetish aromatic taste.

The leaves and flowering tops of this plant were official in the United States Pharmacopoeia from 1820 to 1870, being placed in the secondary list of the *Materia Medica*. At times it has occupied a rather important place among medicinal plants, having been used to cover the taste and odor of disagreeable medicines, also as a stimulant, carminative and stomachic. It has been much used as a domestic remedy to produce diaphoresis, allay colic and promote menstruation.

Golden-rod oil has been an article of commerce, in a small way, for many years, although it has probably been nothing more than a nondescript oil distilled from a mixture of weeds without any attempt at selection. "While a little true, scented golden-rod oil has probably been distilled here and there in an experimental way, we have never seen more than a few ounces at a time purporting to be such."¹

In 1891 Schimmel & Co.² obtained from *Solidago odora* by steam distillation a sample of oil which they described as strongly aromatic but not especially pleasant; density, 0.963.

In 1906 the same firm³ obtained from the United States two volatile oils, one of which they considered to be oil of *Solidago odora* and was described as follows: light yellow color, pleasant refreshing aroma; d_{15}° , 0.8904; α_D , $-15^{\circ} 14'$; ester number 34.2, after acetylation 59.9; did not dissolve to a clear solution in 10 volumes of 90% alcohol. By using 95% alcohol the solution was clear at first only. Turbidity was produced by addition of more than 1.5 volumes of 95% alcohol. Judging from the odor of the oil they considered the ester content to be composed mainly of bornyl acetate, the ester number found corresponding to about 12% of that ester.

Making all due allowance for variations known to occur in oils from the same source, the marked differences between the physical and chemical constants of the oil described by Schimmel & Co. and the oil distilled by us make it evident that the two were not obtained from plants of the same species.

The oil used in our investigation was obtained by steam distillation from fresh material consisting of the greater part of the flowering plant carefully examined and known to be free from other plants. The plant is easily distinguished from the other species of this genus by its linear-lanceolate, entire, shining leaves and their anise-like odor.

¹ Private communication from Dodge & Olcott Co.

² *Report*, Oct., 1891, p. 40.

³ *Ibid.*, April, 1906, p. 64.

TABLE II.

No. of sample.	When distilled.	Yield. %.	Rotation 100 mm. tube.	No. of sample.	When distilled.	Yield. %.	Rotation 100 mm. tube.
1.....	Sept. 20	0.64	+10.75°	6.....	Sept. 30	1.32	+11.75°
2.....	Sept. 21	1.14	+10.75°	7.....	Oct. 1	1.14	+12.02°
3.....	Sept. 21	1.09	+15.75°	8.....	Oct. 2	1.13	+20.12°
4.....	Sept. 25	1.18	+11.80°	9.....	Oct. 4	1.19	+16.75°
5.....	Sept. 27	1.53	+13.80°	10.....	Sept. 12	0.65	+ 9.33°

The results obtained on this oil are given in Table II. By reference to the table it is seen that the yield was above 1% in every case but two. Botanists describe a variety of *Solidago odora* characterized by having odorless leaves. We found a few plants of this kind, but it seems hardly probable that they were present in sufficient quantity to account for this low yield.

In the case of Sample 5, where the yield was unusually high, the material was collected mainly in open fields which had been cultivated. These plants were decidedly more branched and consequently possessed a much larger quantity of leaves and flowers in proportion to stem. As there is very little oil in the stem this would, of course, give a larger percentage of oil. Sample 10 was obtained from plants which had been transplanted and cultivated in an open field. The plants were harvested about the 12th of September and after drying were shipped to Madison, Wisconsin, where they were distilled about three months later. The yield would undoubtedly have been considerably higher if the plants had been collected two weeks later and distilled in the fresh condition.

The greater part of the oil used in this investigation consisted of the first nine samples which were mixed after the optical rotation of each had been determined. The color of the oil was slightly yellowish, the odor somewhat like that of anise and at the same time somewhat suggestive of safrol. The taste was warm and sweetish, very noticeably less sweet than oil of anise. The following constants were determined: d_{25}^{25} , 0.9310°; α_D , +13.72°; n_{D28} , 1.5065; saponification number, 7.9; acid number, 0.63; % of OCH_3 , 15.9. These saponification values correspond to 3.11% of ester calculated as bornyl acetate and 2.96% of free alcohol calculated as borneol. Considering the methoxy compound to be methyl chavicol, this value for OCH_3 would indicate that 75.89% of the oil consists of methyl chavicol.

For Sample 10, the oil from cultivated plants, the following constants were found: d_{15}^{25} , 0.9450°; α_D , +9.33°; n_{D24} , 1.5140; saponification number, 8.9; after acetylation, 19.4. One cc. of the oil with two drops of 90% alcohol gave a turbid mixture. One volume of the oil with 0.4 volume of 90% alcohol produced a clear mixture. One volume of the oil gave a turbid mixture after the addition of 15 volumes of the alcohol.

Action of Reagents on the Oil.—With a drop of conc. nitric acid the oil

gives a bright green color which soon changes to reddish brown. With an excess of acid a bright red color is produced. With conc. sulfuric acid a brownish purple soon becoming rose colored on the edges is produced. Conc. hydrochloric acid causes a dull red color. Glacial acetic acid dissolves it without change of color. Conc. formic acid causes a purplish color which soon changes to reddish brown. Conc. aqueous solution of potassium hydroxide produces no visible change, but when boiled with 0.5 *N* alcoholic potassium hydroxide the oil becomes very dark colored.

Test for Phenol.—5 cc. of the oil were shaken in a cassia flask with an excess of 5% aqueous solution of potassium hydroxide and the oil then brought into the graduated neck of the flask. No diminution in the volume of the oil was observed, showing the absence of phenols, or the presence of not more than traces.

Test for Aldehydes and Ketones.—With Schiff's reagent for aldehydes no color was produced within two minutes. With sodium bisulfite and hydroxylamine negative results were obtained, showing that aldehydes and ketones are either absent or present only in traces.

Test for Anethol.—Since the odor of the oil suggested the possible presence of anethol, some of the oil was kept in a freezing mixture of ice and salt for several hours, the sides of the container being repeatedly rubbed with a glass rod. No solid separated. Information obtained by fractionation of the oil also showed that anethol is either absent or present in very small amount.

Test for Methoxy Compounds. Quantitative Determination of the Methoxy Group.—The only substance known to have an odor similar to that of anethol is its isomer methyl chavicol. If this substance were the bearer of the characteristic odor the oil should give a positive result when treated according to the method of Zeisel.¹ In order to throw light on this question an estimation was made, following Perkin's² modification of the Zeisel method. The amount of silver iodide obtained corresponded to 15.9% of methoxyl. To determine whether the alkoxyl present was methoxyl or ethoxyl or possibly both, the alkyl halide formed by the action of boiling hydriodic acid on the oil was conducted into an alcoholic solution of dimethyl aniline. A beautiful, white, crystalline substance was obtained having the melting point 212–213°. The melting point given for trimethyl phenyl ammonium iodide is 212–214°, and for dimethyl ethyl phenyl ammonium iodide is 124°. Consequently the alkoxyl group in the oil must be the methoxyl group.

Saponification and Fractionation of the Oil.—The oil was heated one hour on a boiling water bath with an excess of potassium hydroxide

¹ *Monatsh.*, **6**, 989 (1885).

² *J. Chem. Soc.*, **83**, 1367 (1903).

in alcoholic solution, and the greater part of the alcohol removed by distillation. The liquid remaining in the distilling flask was mixed with a large volume of water, the oil which separated was removed, washed till neutral, dried with anhydrous sodium sulfate and fractionated under a pressure of 20 mm. The five fractions thus obtained were refractionated three times under atmospheric pressure. The results are given in Table III.

TABLE III.

No. of fraction.	Boiling temperature.	d_{25}^{25} .	α_D	$n_D^{18.9}$.
1.....	165-180°	0.8440	+68.56
2.....	180-210°	0.8930	+48.34
3.....	210-212°	0.9640	+ 0.25	1.5240
4.....	212-225°	0.9680	+ 0.20
5.....	225-240°

The constants given for Fraction 3 are for that fraction after it was again repeatedly redistilled. From fraction 225-240° there was obtained a fraction boiling at 236-240°. $n_D^{18.9}$ for this fraction was 1.5295.

Test for Pinene.—From Fraction No. 1 a nitrosyl chloride, m. p. 103° was prepared by the method of Wallach¹ and also by the method of Ehestaedt.² From this compound both a nitrol-piperidide and a nitrol-benzylamine were prepared, but their behavior in regard to melting point was such as to make the presence of pinene doubtful.

From the alcohol distilled from the saponification mixture there was obtained, by dilution with water, a small amount of a hydrocarbon having the odor of pinene. From it also a nitrosyl chloride was prepared having the m. p. 103°.

Test for Phellandrene.—Fractions Nos. 1 and 2 were tested for phellandrene by the method of Wallach and Gildemeister³ for preparing phellandrene nitrosite but with negative results in both cases.

Identification of Methyl Chavicol.—The odor of the oil is generally described as being anise like, but the odor of Fraction No. 3 suggests both anethol and safrol. Indeed, the odor of safrol is so pronounced that several persons familiar with volatile oils mistook this fraction for oil of sassafras.

Although the odor of this fraction may be considered as somewhat anise-like the absence of anethol is shown in several ways, as follows: (1) Its taste is only moderately sweet while that of anethol is decidedly sweet; (2) its boiling point is too low by 10-12°; (3) when subjected to a freezing mixture it could not be made to solidify or deposit any crystals, whereas anethol is readily crystallized when subjected to cold. On the

¹ *Ann.*, 245, 251 (1888).

² *Report of Schimmel & Co.*, April, 1910, p. 104.

³ *Ann.*, 246, 282 (1888).

other hand its odor, taste, boiling point, density, index of refraction and its being almost optically inactive all agree in suggesting methyl chavicol.

Preparation of Anisic Acid.¹—In order to obtain further knowledge of the chemical nature of this fraction, 25 g. were shaken with three liters of a warm 3% solution of potassium permanganate, the MnO_2 filtered off, the filtrate evaporated to a small volume and acidified with dilute sulfuric acid. A white solid separated, which, after recrystallization from alcohol, was obtained in brilliant needles having the melting point 184° . The melting point of anisic acid is given as 184.2° . A methoxyl estimation of the compound obtained in this experiment gave 19.95% of

methoxyl; calculated for $C_8H_8 \begin{cases} OCH_3 (1) \\ COOH (4) \end{cases}$, $OCH_3 = 20.39\%$. The com-

compound resulting from the oxidation of this fraction of the oil is, therefore; anisic acid and the experiment proves that that part of the oil which boils at $210-212^\circ$ consists mainly of anethol or of methyl chavicol.

Preparation of Homoanisic Acid.¹—30 g. of this fraction were shaken in the cold with 20 g. each of potassium permanganate and acetic acid in two liters of water. On completion of the reaction the liquid was made alkaline by the addition of sodium carbonate, filtered, the filtrate evaporated to a small volume, acidified with dilute sulfuric acid and extracted with ether. On evaporation of the ether there was obtained a white solid. When crystallized from hot water it was obtained in beautiful, shining plates having the melting point $85-86^\circ$. The melting point of homoanisic acid is given at 86° .

Since methyl chavicol on oxidation yields homoanisic acid and anethol does not, this experiment proves that the methoxy compound contained in this fraction of the oil is methyl chavicol.

Further Examination of the Fraction Boiling at $210-212^\circ$.—That this fraction is not composed wholly of methyl chavicol was shown in several ways. An estimation of methoxyl gave 16.98% (OCH_3); calculated for

methyl chavicol, $C_8H_8 \begin{cases} CH_2-CH=CH_2 (1) \\ OCH_3 (4) \end{cases}$, $(OCH_3) = 20.94\%$. Al-

though the original oil was saponified before it was fractionated this fraction showed an ester number of 9.12, corresponding to 3.19% of ester calculated as bornyl acetate and 2.51% of combined alcohol calculated as borneol. After acetylation an ester number of 46.85 was obtained, corresponding to 13.35% of total alcohol and 10.84% of free alcohol, calculated as borneol.

Test for Camphor.—The fractions boiling at $195-210^\circ$ and $210-212^\circ$ were separately examined for camphor by the usual method of preparing

¹ Bertram and Walbaum, *Arch. Pharm.*, **235**, 179, 182 (1897).

camphor oxime, but from neither fraction could any camphor oxime be separated. The experiment was repeated with both fractions but the results were also negative. This shows, therefore, that practically no camphor exists in the oil.

Identification of Borneol.—Although Schimmel & Co. expressed the view that bornyl acetate was a constituent of an American golden-rod oil which they considered to be oil of *Solidago odora*, there is nothing whatever in the odor of the genuine oil that suggests either bornyl acetate or free borneol. In fact, the amount of methyl chavicol present is so large that the odor of a considerable quantity of either the acetate or the free alcohol would be completely masked. However, since acetylation indicated the presence of a considerable amount of free alcohol in this fraction and since the boiling point is practically that of borneol, the fraction boiling at 210–212° was treated as follows: 35 cc. were shaken one hour with 20 g. of potassium dichromate and 25 g. of conc. sulfuric acid in 200 cc. of water. The mixture was then made slightly alkaline with sodium carbonate and distilled with steam. 31 cc. of oil were recovered. This was boiled one hour on a water bath with 20 g. of hydroxylamine hydrochloride and 30 g. of sodium hydroxide in 250 cc. of alcohol. The mixture was then diluted with water, the oil which separated was removed and the alkaline liquid shaken out with ether. The mixture was then acidified slightly with acetic acid and again shaken out with ether. On evaporation of the ether there was obtained a thick, syrupy, brown mass, from which a small amount of a crystallized substance separated on standing. This was obtained almost colorless by pressing between porous plates. An attempt was made to recrystallize it from dilute alcohol, but, unlike camphor oxime, it was quite readily soluble. From its solution in diluted alcohol it was recovered by extraction with ether. On evaporation of the ether a syrupy liquid remained, which on standing a short time solidified to a white, crystalline mass. After drying between filter paper and then in a desiccator it melted at 45°.

Since borneol could not be identified in this way, recourse was had to the method of Haller¹ for the separation of borneol and camphor by conversion of the former into acid bornyl succinate, using, however, phthalic anhydride instead of succinic acid. 100 cc. of the fraction were heated with 15 g. of phthalic anhydride in a flask in a glycerin bath at 150–160° for about fifty hours. On cooling, the oil was poured off from the phthalic anhydride which had crystallized out, then dissolved in ether and the ethereal solution shaken several times with a 5% solution of sodium carbonate. This solution was treated with sodium hydroxide and then distilled. A small amount of a white solid collected in the condensing tube. This product was crystallized from petroleum ether, sublimed

¹ *Compt. rend.*, 108, 1308 (1889).

and again crystallized from petroleum ether. It was obtained in hexagonal plates, melting point $203-204^{\circ}$. From this compound a phenyl urethane was prepared having the melting point $138-139^{\circ}$. This experiment proves that borneol is a constituent of the oil.

The bornyl phenyl urethane was crystallized from hot petroleum ether, but before it separated a few larger crystals were formed which melted at $149-150^{\circ}$. The formation of this compound seems to indicate the presence of a second alcohol in the oil.

Fractionation of the Oil from Cultivated Plants.—Sample No. 10.—After saponification this sample was fractionated under ordinary pressure. In Table IV physical constants are given for these fractions.

TABLE IV.

No. of fraction.	Boiling temperature.	$n_{D20.6}^{\circ}$.	α_D .	$d_{25}^{25^{\circ}}$.
1.....	$170-176^{\circ}$	1.4735	$+62.6^{\circ}$	0.8408
2.....	$176-180^{\circ}$	1.4769	$+71.0^{\circ}$
3.....	$180-195^{\circ}$	1.4880	$+57.4^{\circ}$
4.....	$195-210^{\circ}$	1.5118	$+15.4^{\circ}$
5.....	$210-212^{\circ}$	1.5210	$+0.7^{\circ}$
6.....	$212-222^{\circ}$	1.5221	$+0.1^{\circ}$
7.....	$222-236^{\circ}$	1.5260	-0.2°	0.9840
8.....	Residue	1.5505

A nitrosyl chloride was prepared from Fraction 1 by the method of Wallach.¹ After filtering out the crystals which first separated two further quantities of the nitrosyl chloride were obtained in succession by the addition of alcohol to the filtrate. The melting points, in order, of these products were 103° , $101-102^{\circ}$, $99-101^{\circ}$. A nitrol-piperidide was apparently formed but not in sufficient quantity to permit of purification and melting-point determination.

Fractions 2 to 7 inclusive were treated with concentrated formic acid. A pronounced purplish color was produced with Fraction 2. A similar color was formed with the next four fractions, but with gradually diminished intensity. With Fraction 7 no color was produced. These tests are of some importance as they show that the substance which produces the characteristic purplish color when the oil is treated with conc. formic acid is found among the lowest boiling constituents of the oil, but whether it is a terpene or not remains to be proved. We are not aware that this reaction has been reported for any terpene. With conc. nitric acid Fraction 4 gave a green color.

Although the data obtained are not sufficient to establish the identity of a low boiling compound, the physical constants of Fraction 1 may be considered proof of the presence of at least one terpene. It will also be seen that these constants are in better agreement with those of sabinene

¹ *Ann.*, 245, 251 (1888); 253, 251 (1889).

or sylvestrene than with those of α -pinene. The optical rotation of Fraction 2 shows that at least two compounds are present which have a lower boiling point than that of methyl chavicol. While the physical constants given for Fraction 2 may be considered as an indication of the presence of limonene, mixed with one or more other terpenes of lower optical rotation, there was nothing in the odor to suggest this.

Examination for Acids. Volatile Acids.—The aqueous alkaline liquid resulting from the saponification of the oil was concentrated on the water bath, filtered and acidified with dil. H_2SO_4 and then steam distilled. The distillation was continued until the distillate was only faintly acid. The distillate was collected in four fractions. Each fraction was made slightly alkaline with sodium hydroxide and concentrated on a water bath. Although there was an excess of alkali there was decomposition and loss of acid as indicated by the odor. The solutions were then treated with silver nitrate solution, drop by drop, until the sodium hydroxide was removed. The remaining precipitate was collected, dried and ignited. The percentage of metallic silver obtained was as follows: Fraction 1, 33.67%; Fraction 2, 39.8%; Fraction 3, 69.45%; Fraction 4, 73.9%. The silver salts were all quite dark in color. Whether the reduction was due to the presence of formic acid could not be satisfactorily established. From the data obtained it can not be stated what acids are present though there must be at least three volatile acids present.

Nonvolatile Acids.—The residue remaining in the flask after steam distillation was heated with barium carbonate and water, filtered and the filtrate treated with silver nitrate solution. A light yellowish precipitate was obtained, which, after drying and ignition, yielded 25.22% metallic silver.

Summary.

The oil of *Solidago rugosa* is composed mainly of terpenes, of which, at least, three are present. That α -pinene is one of these is highly probable. In addition there also appears to be present at least one ester and one free alcohol, 1.47% of ester calculated as bornyl acetate and 1.67% of alcohol calculated as borneol.

The oil of *Solidago odora* contains the following:

1. Terpenes, 10–15%.
2. Esters, about 3%, calculated as bornyl acetate.
3. Borneol and possibly another alcohol, the total percentage of free alcohol being about 3% calculated as borneol.
4. Methyl chavicol, forming about 75% of the oil.
5. A small amount of volatile fatty acids, at least three.
6. A small amount of nonvolatile acid.