yellow precipitate was secured, the reaction was stopped and the mixture poured into a large quantity of cold water, when the fluoresceïn separates out in a bright yellow, flocculent mass; if a dark precipitate is obtained, the mixture has been heated too long. The fluoresceïn may then be purified by fractional precipitation from an alkaline solution with acid, which gradually removes a tarry impurity probably containing resaceteïn. Another method of purification consists in dissolving the crude fluoresceïn in concentrated sulphuric acid diluted with an equal volume of water and precipitating after filtration by neutralization with sodium hydroxide. That acetic acid is actually given off in the reaction was shown by the odor, by the ferric chloride and the ethyl acetate tests. That the compound formed was actually fluoresceïn was shown by conversion into the diacetate, the dichloride and eosine. The diacetate made either by heating with acetic anhydride or by acetylation with acetyl chloride and pyridine in glacial acetic acid, after purification by crystallization from acetone, melted at 201°, while Baeyer[1] gives 200°.

Calculated for $C_{24}H_{16}O_7$:	C, 69.23; H, 3.88.
Found:	C, 69.04, 69.24; H, 4.03, 4.09.

From this diacetate fluoresceïn was obtained by saponification. The dichloride was made by heating with phosphorus pentachloride at 180°. After crystallization from alcohol it gave a melting-point of 249° (Baeyer, 252°). Calculated for $C_{20}H_{10}O_3Cl_2$: Cl, 19.22; Found, 19.20.

Eosine was made by adding bromine to an alcoholic solution of the fluoresceïn. Calculated for $C_{20}H_8O_5Br$: Br, 49.36; Found, 48.76. Succinyl fluoresceïn was formed with elimination of acetic acid when the condensation was carried on with succinic acid instead of phthalic anhydride.

THE OPTICAL ROTATION OF SPIRITS OF TURPENTINE.

BY CHAS. H. HERTY.

Received February 10, 1908.

Among the physical properties of spirits of turpentine, none has proved of more interest than its optical rotation. In most specimens this property is very marked, and as the liquid is colorless and the determination readily made, many data are found on this subject in chemical literature. Slight variations in the rotation of different samples are to be expected, as spirits of turpentine is not a chemical compound but a mixture of substances, chiefly terpenes. From the results of numerous observations upon commercial samples, the view commonly held previous to 1891 was that French spirits of turpentine, distilled from the oleoresin of *Pinus maritima*, is levo-rotatory and that American spirits of turpen-

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[1] *Ann.*, 183, 1.

tine, distilled in years past, almost wholly from *Pinus palustris*, is dextrorotatory. The difference in the character of the rotation was ascribed, therefore, to the different species from which the spirits of turpentine was produced.

Recognizing the fact that American spirits of turpentine is distilled from more than one species of pine, J. H. Long,[1] in 1891, undertook a study of the volatile oils distilled from oleoresins of well identified individual trees, these trees embracing the several species of pines subjected to turpentining in our southern states. He found that specimens from *Pinus palustris* (Long Leaf Pine)gave dextro-rotatory oils, while those from *Pinus heterophylla* (Cuban or Slash Pine) gave levo-rotatory oils. Since the oleoresins from these two species are indiscriminately mixed, at the time of collection in the woods, the rotation of the oil distilled from such a mixture would naturally vary. *Pinus palustris* is the predominating species and Long attributed to this fact the dextro-rotatory character of American spirits of turpentine. This view has been generally accepted.

The fact that spirits of turpentine is frequently adulterated with optically inactive mineral oil, led A. McGill[2] to make a large number of determinations of the rotation of commercial samples of spirits of turpentine, in the hope of utilizing this property for the detection of adulteration. From the widely varying results obtained he was compelled to declare the method useless.

New evidence upon this point has been obtained from investigations carried on in this laboratory in collaboration with the U. S. Forest Service, the experimental work having been carried out by Messrs. George A. Johnston and W. S. Dickson under the direction of the writer. In order to gain a better knowledge of the oleoresins from the two principal species of pine utilized in the turpentine industry at the present time, fourteen trees were selected on a Florida turpentine farm. One-half of these were *Pinus palustris*, the other half *Pinus heterophylla*. Three trees of each species were tapped for the first time at the beginning of the experiments. In each case a small, young pine, a medium pine, and a large, old pine were selected. In another set four trees were selected, two each *Pinus palustris* and *Pinus heterophylla*. These trees had been subjected to turpentining during the previous year, the chipping, or weekly scarification, on all of them having been unusually shallow, only about one-half as deep as is commonly practiced. In a third set four trees were selected, two each of *Pinus palustris* and *Pinus heterophylla*, which had been turpentined during the previous year, and on each of these the depth of the chipping was the normal cut. The trees in each set were chipped at intervals of seven days.

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[1] *J. Anal. Appl. Chem.*, 6, 1.

[2] *Bulletin No.* 79, *Inland Revenue Dept.*, *Canada*.

Special precautions were taken in the collection of the oleoresins. The cup and gutter system described in *Bulletin No.* 40, *U. S. Bureau of Forestry*, was used. Instead of the clay cup commonly used, oyster pails were substituted. The entire apparatus was covered with black oilcloth fastened securely into the bark of the tree above the chipping surface, thereby protecting the resin from light and avoiding the filling of the pails with rain water. Every four weeks these pails were removed from the tree, tightly stoppered and immediately shipped to this laboratory for examination. The specimens so obtained were extremely pure and free from chips. After removal of the pails, the metal gutters were raised to a point near the chipping surface in order to minimize the amount of oleoresin which might stick to the exposed portion of the trunk above the gutters.

The distillation of the oleoresin was carried out in a 500 cc. Kjeldahl flask, surrounded by a bath of cottonseed oil. Steam from a small boiler was first passed through a small iron pipe in which it could be superheated, then into the distillation flask through a glass tube having on its end a bulb containing a number of openings. By this means strong agitation of the molten oleoresin was obtained. Thermometers were placed both inside the flask and in the oil-bath. The mixed vapors of steam and spirits of turpentine were passed through a Hopkins condensing bulb to prevent the carrying over of solid particles of resin, condensed in an ordinary Liebig condenser and collected in a separatory funnel. After drawing off the lower layer of water, the spirits of turpentine was transferred to a dry flask and allowed to stand over night with calcium chloride. The determinations of the optical rotation of the volatile oils were made with a Schmidt and Haensch half-shadow polariscope, sodium flame, at 20°.

In the following table are given the results from the first collection of the oleoresin in early spring:

TABLE I.

Tree designation.	Species.	Diameter (inches).	Character of chipping.	Optical rotation 100 mm. tube, 20° C.
A1	*P. heterophylla*	7.0	1st year, normal depth	—20°50′
A2	"	14.5	" "	+ 0°15′
A3	"	24.5	" "	—15° 0′
A4	*P. palustris*	7.3	" "	+ 15°40′
A5	"	15.0	" "	+ 8° 9′
A6	"	21.0	" "	+ 18°18′
C1	*P. heterophylla*	12.3	2nd year, shallow	—27°11′
C2	"	8.2	" "	—26°28′
C3	*P. palustris*	13.0	" "	7°26′
C4	"	8.7	" "	+ 7°31′
D1	"	9.0	2nd year, normal depth	+10°50′
D2	"	13.5	" "	+ 1°23′
D3	*P. heterophylla*	13.0	" "	—18°35′
D4	"	9.0	" "	—29°26′

These results show a wide variation in the optical rotation of the volatile oils from the individual trees, even among trees of the same species. In a general way the figures give support to Long's view, namely that the volatile oils from the *Pinus palustris* are dextro-rotatory and those from *Pinus heterophylla* levo-rotatory. That this is not strictly true, however, is evidenced by the dextro-rotation of A2 (*P. heterophylla*) and more especially by the levo-rotation of C3 (*P. palustris*).

With these variations in the first collection from the several trees, the question naturally arose, would the variations change as the season advanced or would the figures prove constant for the individual trees? The rotations for the successive collections follow in Table II:

TABLE II.—OPTICAL ROTATION IN 100 MM. TUBE, 20° C.

Collection.	A1.	A2.	A3.	A4.	A5.	A6.	C1.
1..	—20°50′	+0°15′	—15° 0′	+15°40′	+8° 9′	+18°18′	—27°11′
2..	—22° 5′	—0°30′	—14°26′	+15°22′	+8°50′	+17°43′	—26°48′
3..	—21°45′	+0°15′	—15°55′	+14°15′	+8°27′	+19°30′	—26°25′
4..	—21° 7′	—1°15′	—15°50′	+14°20′	+8°34′	+18°46′	—23°32′
5..	—20°30′	—2° 5′	—15°15′	+14°21′	+8°32′	+19°24′	—21°12′
6..	—20°15′	—3°30′	—15°27′	+14°35′	+8° 4′	+18°16′	—21°46′
7..	—22°15′	—5°45′	—17°52′	+12°49′	+7° 6′	+14°47′	—21°35′

Collection.	C2.	C3.	C4.	D1.	D2.	D3.	D4.
1..	—26°28′	—7°26′	+7°31′	+10°50′	+1°23′	—18°35′	—29°26′
2..	—25°37′	—6°42′	+7°20′	+11°23′	+2°40′	—17° 0′	—27°45′
3..	—26°20′	—4°45′	......	+13° 7′	+2°25′	—15°20′	—28°19′
4..	—26°30′	—4°29′	......	+12°46′	+2°25′	—15° 0′	—27°38′
5..	—26° 7′	—3°55′	......	+13° 0′	+1°13′	—14°38′	—27°48′
6..	—26° 0′	—4° 5′	......	+13° 0′	+1°15′	—14° 7′	—26°11′
7..	—26°28′	—6° 6′	......	+10°48′	—0°55′	—14°19′	—26°12′

NOTE.—The yield of oleoresin from C_4 was so small, after the first and second collections, that not enough volatile oil could be obtained on distillation to fill the 100 mm. tube.

From this table it is seen that the rotation in most cases is quite constant throughout the year. The most marked exception is A2 (*P. heterophylla*). It is evident that some distinct change in the biological activity of this tree has taken place, for while the rotation is reasonably constant during the first half of the year, a steady increase in the levo-character of the oil is apparent during the last half. In the case of C1 (likewise *P. heterophylla*) somewhat the reverse has taken place. A rather marked decrease in the levo-rotation is shown just at the middle of the year, then the rotation remains practically constant during the last half. In the case of C3, another type of change is represented, the levo-rotation decreasing up to the middle of the season and again increasing during the latter half.

With the limited facts at hand, it is impossible to interpret the significance of these changes. That tree which shows the most marked variation, A2, is a healthy, vigorous tree, from which variations would be least expected. Nor can an explanation be offered for the wide variations in the optical rotation of oils from the same species. All of the trees in Series A are located within 20 yards of each other and have, therefore, the same general conditions of climate, light and soil. Fractionation of the volatile oils from these show practically the same rise in boiling-point for the same volume of distillate. It would seem, therefore, that these volatile oils, consisting so largely of pinene, are mixtures principally of dextro- and levo-pinene, the preponderance of the one or the other determining the optical rotation.

UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, N. C., February 2, 1908.

A METHOD OF ANALYZING SHELLAC.[1]

BY PARKER C. MCILHINEY.

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The method of analysis which is in most common use at the present time, both in England and in the U. S., for the determination of the amount of rosin in shellac, is an indirect method depending upon the different powers of a shellac and of rosin to absorb iodine from a suitable solution. Different operators prefer different methods of making this test, some preferring to use the old Hubl method, and others the more modern Wijs method, as modified by Langmuir. Either of these methods is capable of giving reasonably satisfactory results, although the Langmuir method is certainly much to be preferred, both on the score of accuracy and of speed. Another method which is in use is that proposed by Parry, depending upon the solubility of the resinate of silver made from common rosin, in ether, while the corresponding resinates from shellac are insoluble. This method labors under several disadvantages and sources of error, of which the two principal ones are the solubility of the unsaponified portion of the shellac in ether, and the danger of a decomposition of the resinate of silver before it can be separated and determined.

A direct method of separating shellac and rosin and recovering the rosin, at least, in a substantially unchanged form, is greatly to be desired and several experimenters have attempted to make such a separation by taking advantage of the solubility of rosin in petroleum ether, a solvent in which shellac is insoluble. No method of extracting from even a finely pulverized sample of shellac the portion soluble in petroleum ether seems to be capable of removing more than a small part of the rosin contained in the sample.

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[1] Read before the New York Section on March 6, 1908.