

rosin and glycerine having an acid number as low as 6 or 7, which were as a rule darker in color than the rosin employed. Esters were prepared whose acid numbers lay between 13 and 13.5 which were good in color.

2—Ethyl alcohol, phenol, cresol, aniline, alpha and beta naphthylamine, sugar, starch and dextrose did not combine with the rosin to form neutral substances under ordinary conditions. Aromatic amino compounds did not combine with the rosin in presence of dehydrating agents even under considerable pressure.

3—Bone-black, fuller's earth and sulfur dioxide had no beneficial effect on the color of rosin esters.

4—A qualitative and quantitative method for determining rosin anhydrides in the presence of rosin acids and rosin esters was studied.

5—Congo gum, pontianak gum and dammar gum were esterified with glycerine to a greater or lesser degree. Copal gums which had been cracked and rendered soluble in varnish makers' solvents were found to esterify readily.

MONTCLAIR, NEW JERSEY

CEANOTHUS VELUTINUS (SNOW BRUSH) AS A SOURCE OF WAX AND TANNIN

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Received November 4, 1915

The study of this shrub was undertaken with the hope of being able to utilize a material that at present is both a fire menace and a nuisance in California forests. This study, though not complete, will show that this plant contains easily available products of high commercial value.

BOTANICAL

Ceanothus velutinus (Douglas),¹ commonly known as "Snow Brush," is a widely branching shrub, two to six feet, and sometimes more, in height. The leaves are alternately petioled, roundish or broadly ovate, about three inches in length and have polished resinous upper surfaces, but are somewhat pubescent beneath.

The area inhabited by this plant is bounded roughly by the Coast Range of California on the west, the Columbia river on the north, Colorado on the east, and San Francisco Bay on the south. It is especially plentiful in the Shasta National Forest in the neighborhood of Sisson, California, where it has been estimated² that 30,000 tons could be gathered within 5 miles of the railroad and three times this amount could be gathered within 15 miles.

We are indebted to the United States Forest Service for 500 lbs. of leaves and twig ends used in this investigation. This material was gathered at Sisson, California, and shipped to Berkeley.

EXAMINATION FOR ESSENTIAL OILS

An attempt was made to distill about 50 lbs. of leaves and twigs for essential oils. The distillate was slightly opalescent and by redistillation and extrac-

tion of the distillate a minute quantity of a pungent-smelling oil was isolated. This quantity was not sufficient for examination. Probably if the leaves had been distilled as soon as cut, sufficient oil would have been isolated to study, but the yield would not be of commercial importance.

EXTRACTION OF WAX

The remainder of the twig ends, after drying on a steam radiator, were separated from the leaves by threshing. The leaves were ground in a coffee mill and sifted through a twenty-mesh screen. They were next thoroughly extracted with dry 86° Bé. gasoline in a specially designed Soxhlet extractor of 10 lb. capacity. The average yield of wax was 7.3 per cent of the weight of leaves.

The wax had a greenish appearance, due to a little chlorophyll. At first it was of pasty-like consistency,

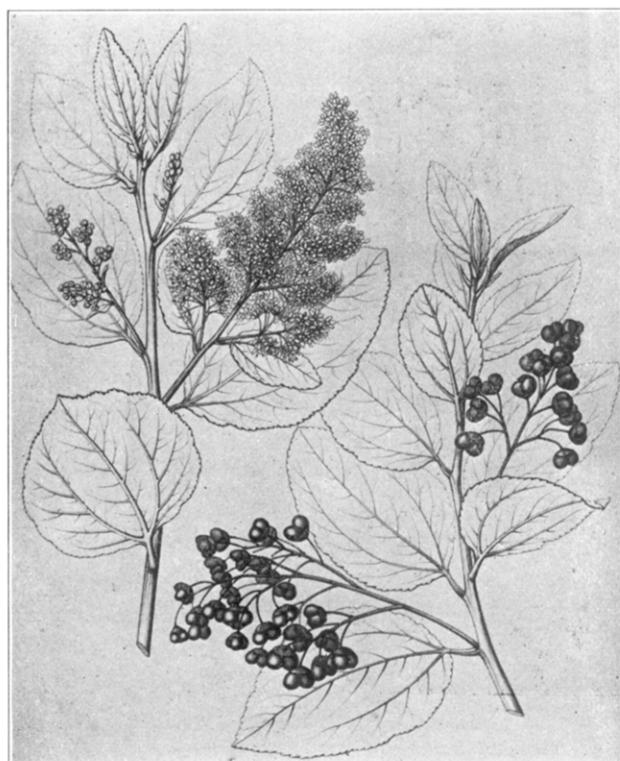


FIG. 1

but on standing on the steam bath and driving off more solvent it became brittle, breaking with a conchoidal fracture. The crude wax had the following constants:

Free acid.....	20.3	Reichert-Meissl No. .	7.5
Saponification number.....	93.4	Sp. gr. at 15°.....	0.988
Iodine value.....	19.5	Melting point.....	78-79° C.

CHEMICAL EXAMINATION OF WAX

In order to separate the wax into some of its components, a well-dried portion was extracted with alcohol in a Soxhlet extractor. The material remaining in the cartridge when dried was a dark brown paraffin-like mass. When boiled with alcoholic potash a portion saponified. The unsaponified material was separated from the soap liquors. On examination, this portion proved to be a hydrocarbon. It could not

¹ Parson's "Wild Flowers of California"

² Personal communication from Acting Forester of Fifth District.

be obtained in a purified state and appeared to be composed of a number of homologous hydrocarbons, having a melting point between $50-57^{\circ}\text{C}$. Upon cooling, the potash soap became a mucilaginous mass. On acidifying, filtering and recrystallizing from alcohol solution, an acid crystallizing in straight needles, having a melting point of $76-76.5^{\circ}$, was isolated. Creotic acid melts at 77.8° . When titrated in an alcoholic solution with caustic potash its acid number was 140.5. The acid number of creotic acid ranges from 136-146.¹

On cooling, crystals separated out of the original alcoholic extract. Water was added to this alcoholic extract and the fats separating out were filtered. They were washed entirely free of chlorophyll with dilute alcohol solution. The fats were saponified in fairly concentrated potash solution, the solution diluted and the unsaponified portion filtered off. The soap liquids were evaporated to a small volume on the steam bath and acidified. The fatty acids separating out were filtered, washed and dried. They melted at $65-67^{\circ}$.

A fractional crystallization was made of these fatty acids with magnesium acetate in hot alcohol.² This fractionation was repeated three times and two acids of fair purity were isolated. One melted at $61-62^{\circ}$, the other at $68-69^{\circ}$. The silver salt of the former when ignited yielded 28.85 per cent of silver, the latter 27.56 per cent of silver. Palmitic acid melts at 62° and combines with 29.55 per cent silver. Stearic acid melts at $71-72^{\circ}$ and combines with 27.43 per cent silver. The alcohols liberated in the saponification

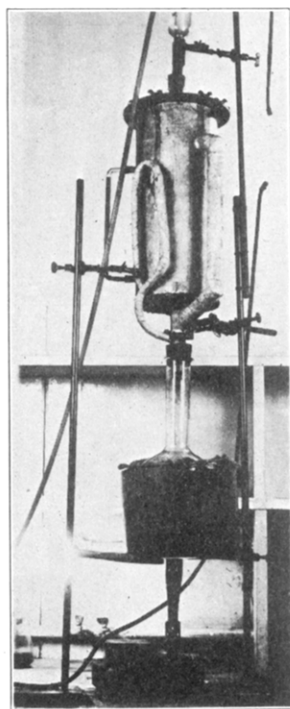


FIG. 11

of the palmitic and stearic acids were washed with dilute ethyl alcohol and dried. The melting point was between 78 and 80° . When heated with soda lime³ and the resulting acids separated, an acid showing the properties of creotic acid as previously described was isolated. This would indicate ceryl alcohol. A higher acid with properties corresponding to melissic acid was isolated, indicating myricyl alcohol. Some traces of a lower acid were present but not sufficient to identify it. The original wax is probably composed of creotic acid in the free condition, a hydrocarbon, and palmitic and stearic acids in combination with ceryl and myricyl alcohols. A faint acrolein test seemed to point to the presence of a small quantity of glycerides.

¹ Lewkowitsch's "Oils, Fats and Waxes," 1898, 51.

² Leathe's "Monograph on Fats," p. 79.

³ Lewkowitsch's "Oils, Fats and Waxes," p. 74.

EXAMINATION OF LEAVES

TANNING—The extract from these leaves responded to the following qualitative tests for tannins: hydrogen ion gave a brown precipitate; salt gelatine solution, a heavy white precipitate; iron alum, a green coloration; and bromine water, an immediate precipitation. These tests would indicate the presence of catechol tannins.

An examination for mixed tannins was made as directed by Procter.¹ [The separation of the catechol from the other tannins by this method depending on the insolubility of the catecholic tannin compound with formaldehyde in the presence of hydrochloric acid.] In this case it was found that the tannins were exclusively of the catecholic variety, for on filtering the precipitate and testing the filtrate with salt-gelatine solution, no more tannins were detected.

A portion of the tannin that had been separated by adding dilute acid² was thoroughly dried, and distilled in a retort. The distillate recrystallized from alcohol had a melting point of 110° , was soluble in water and ether and with iron alum gave a deep green coloration. An empirical formula calculated from combustion and molecular weight data could be represented as $\text{C}_6\text{H}_4(\text{OH})_2$. This corresponds to catechol.³

Glucose was identified partially free but to a greater extent combined, as a glucoside. A water extract of the leaves was taken and divided into two samples. The first sample was treated with lead subacetate and polarized. The second sample was treated with dilute hydrochloric acid, clarified and polarized. The polarization was dextro in both cases, but in the second sample was greatly increased. The presence of glucose was confirmed by preparing the glucosazone and microscopically studying the crystal form and determining the melting point.

A weighed sample of leaves was extracted with a Procter sand filter. The extract analyzed by the official method of the American Leather Chemists' Association⁴ showed 17.3 per cent tannins.⁵

INORGANIC ELEMENTS—In order to determine whether or not these leaves contained inorganic salts that in any way would injure hides in tanning, an ash determination was made with the following results:

	Per cent
Moisture in leaves.....	11.2
Total ash.....	5.53
SiO_2	0.65
CaO	1.30
FeO	0.15

TANNERY TESTS

Through the courtesy of Mr. David Bloom, of Samuel Bloom & Sons, tanners in San Francisco, a practical test of ceanothus leaves was conducted on hides under tannery conditions.

Samples of hides from the "lime," "pickle" and "bate" were treated in water with these leaves ground

¹ Procter's "Leather Chemists' Pocketbook," p. 51.

² Trimbell's "Tannins."

³ Trottman's "Leather Trades Chemistry," p. 98.

⁴ Procter's "Leather Chemists' Handbook," pp. 94-96.

⁵ This material compares very favorably with other sources of leaf tans. According to Trottman pistacia contains 14-16 per cent tannins; tammari, 9-10 per cent; quebracho, 17-20 per cent; oak bark, 12 per cent; sumac (crude), 19 per cent.

to pass a twenty-mesh screen. The hides tanned quickly, the grain being completely struck through in a short time. It was found that this material did not plump the hides properly. The hides were in all three cases completely tanned without harmful discoloration. A side of hide that had been prepared for the one-bath chrome, one-bath vegetable tan, was submitted to these leaves for the vegetable tan. Here, too, the hide was well tanned but not properly plumped. Another objection raised was the bulkiness of the leaf residue in the tanning vats. To do away with this nuisance it would be necessary to make this material up into an extract. To this extract suitable plumping organic acids could be added.

The preliminary data above described would indicate that these leaves are an extremely satisfactory source of tannin for tannery purposes. Work along this line is progressing in the tannery.

SUMMARY

Ceanothus velutinus, a widely distributed plant, has been found to contain 7.3 per cent and 17.3 per cent tannins. The wax was composed of free hydrocarbons, free creotic acid and in a great part of palmitic and stearic acids in combination with ceryl and myricyl alcohols. A trace of glycerides appeared to be present.

The tannin was found to be of the catecholic variety. Tests in the tannery have led the authors to believe that a suitable extract for tanning purposes could be made from these leaves. From the quantity of this shrub available, its objectionable presence in the forests and the value of the products obtainable from it, this material should become of considerable economic importance.

In concluding, we would wish to thank Mr. Carl A. Kupper and Mr. C. S. Smith, of the United States Forest Service, for obtaining the material for the investigation and for the survey of its occurrence; Professors W. C. Blasdale and H. C. Biddle, of the Chemistry Department of the University of California, for valuable suggestions given during the progress of the work; and Mr. David Bloom, for permitting the experimental work in the tannery.

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SOME QUALITATIVE TESTS FOR GUM ARABIC AND ITS QUANTITATIVE DETERMINATION¹

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Received December 16, 1915

INTRODUCTION

The group of polysaccharides includes such diverse substances as the starches, cellulose, the dextrans, the true gums and the plant mucilages. They possess in common the property of being decomposable hydrolytically into one or more sugars, usually pentoses or hexoses. By oxidation the acids corresponding to these sugars are formed, but the first step toward this reaction appears to be hydrolysis.

The true gums, of which gum arabic is typical, dissolve in cold water, yielding clear solutions which,

¹ Published by permission of the Director of the Bureau of Standards. Copies of the complete paper, from which this is abridged, can be obtained by application to the Director, Bureau of Standards, Washington, D. C.

though viscous and adhesive, can be filtered. The closely related and quite similar mucilages, such as gum tragacanth and cherry-tree gum, simply swell up and form more or less homogeneous suspensions that cannot be filtered. Perhaps most of the so-called gums are mixtures of one or more representatives of the above classes.

As might be expected from their chemical nature, the gums do not readily lend themselves to reactions of a definite qualitative or quantitative value. One of us learned how unsatisfactory some of the qualitative tests are when samples of mucilage first came to the Bureau of Standards for examination. This led to an extended study of the literature and of the various qualitative reactions that have been published, and finally to a comparatively accurate quantitative method. In the last part of this work the two of us joined forces, hoping to carry on a much more extended investigation than was found later to be possible.

The object of this paper is to discuss briefly some of the more important qualitative and quantitative methods and give references showing, as far as possible, what other methods have been published.

QUALITATIVE TESTS

In nearly all cases a 2 per cent solution of gum arabic was used. Similar solutions of dextrin and of gum ghatti, a substitute for arabic, were subjected to the same tests.

(1) FERRIC CHLORIDE AND ALCOHOL—A mixture of 2.5 volumes of 50 per cent alcohol and 1 volume of neutral ferric chloride solution containing 25 g. of the salt in 100 cc., precipitates gum arabic, though often only on long standing.¹ Gum ghatti gives no precipitate, and dextrin a very slight one.

(2) POTASSIUM HYDROXIDE—According to Liebermann,² solutions of gum arabic and of dextrin become amber-yellow when warmed with potassium hydroxide, while the closely related gum senegal gives at most a faint yellow color. Sollman³ stated that dextrin when so treated turns more or less brown, while some sugars and gums other than arabic, behave similarly. Rideal and Youle⁴ came to the conclusion that this test is of no value. Two samples of gum arabic, among a number tested by them, gave a green color; a solution of ghatti turned pink, and dextrin a very dark red or almost black. Nevertheless this test is among those recommended in the latest edition of "Lunge."⁵ Our own experiments amply confirm the statements that this test is of no value.

(3) COLOR REACTIONS WITH PHENOLS—Reiche⁶ found that gum arabic gives a flocculent blue precipitate when boiled with orcinol and concentrated hydrochloric acid. Other carbohydrates gave yellow or brown colors. Other investigators obtained reactions

¹ Roussin, *J. Pharm. Chim.*, [4] 7 (1868), 251. See also Allen's "Com. Org. Anal.," 4th Ed., Vol. III, p. 443.

² *Chem.-Ztg.*, 14 (1890), 665.

³ *Am. J. Pharm.*, 83, 176; *Chem. Zentr.*, 82, I (1911), 1560.

⁴ *J. Soc. Chem. Ind.*, 10 (1891), 610.

⁵ "Chem.-Tech. Untersuchungsmeth.," 6th Ed., Vol. III (1911), pp. 167-8.

⁶ *Ber. Ges. Förder. Chem. Ind.*, 1879, 74; *Chem.-Ztg.*, 4 (1880), 191.