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A Chemical Study of Rhus glabra

A. W. Martin
A CHEMICAL STUDY OF RHUS GLABRA.

BY A. W. MARTIN.

The Anacardiaceae, or Sumach family, numbers about four hundred species.

Most of these, however, are tropical; only a few grow in the northern states. Rhus glabra, the one under investigation, is abundant and is one of the hardy species. It grows from two to twenty feet high. The flowers are small and of a greenish-red color. They grow in clusters from three to eight inches long. The fruit consists of red berries subglobular in shape and about 3 m.m. in diameter. They consist of the seed proper within a coating of felt-like husk which contains all of the coloring matter and nearly all of the acid present in the seed.

A water extract of the seed and of the leaves is used for dyeing. The leaves and bark have been used for tanning purposes on account of the large amount of tannic acid present. In a few cases, decoction of the seed has been used medicinally although its real value is questionable.

The seed used in the following experiments was gathered the latter part of September after the full growth had been reached and the seed partly matured. The first work done was on a mixture of two different species, Rhus glabra and Rhus hirta. An examination showed the two species were different and hence the work proper was done on the Rhus glabra.

In beginning the general analysis, the whole seed was used while later it was found advisable to separate the seed from the husk before making the examination.

(171)
MOISTURE IN THE WHOLE SEED.

100 grams of the powdered seed, dried at 102 degrees to 110 degrees lost 6.862 grams, 6.8 per cent. The above represents the loss when dried to constant weight at 110° C.

ASH IN THE SEED.

Ten grams of the powdered seed gave 0.2655 gram of ash, or 2.65 per cent of ash.

DETERMINATION OF FREE ACID IN THE SEED.

An examination of the acid properties of the seed showed the free acid to be wholly tannic or gallo-tannic acid. An examination was made by means of a standard solution of sodium hydroxide in which 1 c.c. was equivalent to .01 per cent acid. Five grams of the seed required 52 c.c. of the standard solution, or 10.5 per cent of acid. The above determination was made by simply extracting the seed for some time without grinding it. A second determination was made by first grinding the seed and then extracting as before. In this case 5 grams of the powder required 59 c.c. of standard solution or 12.03 per cent of acid. These determinations with others prove that nearly all of the acid exists in the husk and not in the seed proper.

EXAMINATION OF THE HUSKED SEED.

Some difficulty was experienced in removing the husk from the seed. By adjusting a mill very loosely, it was found that the husk could be removed easily without injuring the seed. Several determinations gave an average of 60 per cent seed, 40 per cent husk.

A determination of the moisture and ash in the hulled seed gave 4.93 per cent of moisture; 2.08 per cent of ash.

DETERMINATION OF OIL IN THE SEED.

The whole seed of the Rhus glabra contains two distinct oils, one in the husk and the other in the seed
proper. The oil in the seed was more carefully studied. Five determinations gave the following:

1. 100 grams of seed gave 9.8 grams of oil.
2. 100 grams of seed gave 8.5 grams of oil.
3. 100 grams of seed gave 9.0 grams of oil.
4. 100 grams of seed gave 9.1 grams of oil.
5. 100 grams of seed gave 9.1 grams of oil.

The average of these determinations is 9.1 per cent of oil.

PROPERTIES OF THE OIL.

The oil is a light colored liquid at the ordinary temperature. At 18 degrees below zero, it changes to a semi-solid.

- Its specific gravity at 8° C is 0.931
- Its specific gravity at 15° C is 0.9532
- Its specific gravity at 18° C is 0.9227
- Its specific gravity at 20° C is 0.92

It is readily soluble in ether, chloroform, benzole, carbon-disulphide, and readily so in acetone. It is not a drying oil, as is shown by the following comparison with wheat and linseed oils:

<table>
<thead>
<tr>
<th>Oil Type</th>
<th>5 days</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linseed Oil</td>
<td>.037</td>
<td>.130</td>
<td>.28</td>
<td>1.74</td>
<td>4.82</td>
<td>7.55</td>
</tr>
<tr>
<td>Wheat Oil</td>
<td>.037</td>
<td>.077</td>
<td>.15</td>
<td>.24</td>
<td>.30</td>
<td>.37</td>
</tr>
<tr>
<td>Rhus Oil</td>
<td>.005</td>
<td>.027</td>
<td>.054</td>
<td>.071</td>
<td>.104</td>
<td>.QRW</td>
</tr>
</tbody>
</table>

The index of refraction was taken with a Pulfrich refractometer at different temperatures with the following readings:

- Index of refraction at 0° C: 1.48821
- Index of refraction at 15° C: 1.48228
- Index of refraction at 27° C: 1.47779

The absorption spectrum of the oil was peculiar. With a film of oil 4 m.m. thick, the whole violet end of the spectrum was cut off and a sharp black band appeared directly over the lithium band. With thicker films, the light was completely cut off.
The saponification value was made by the well known Kottstorfer method. Three determinations gave the following results:

(I) 2.0005 grams of oil required ...... 0.3908 grams of KOH.
(II) 1.8923 grams of oil required ...... 0.3681 grams of KOH.
(III) 1.9096 grams of oil required ...... 0.3707 grams of KOH.

Calculated milligrams of KOH per gram of oil:

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<thead>
<tr>
<th></th>
<th>(I)</th>
<th>(II)</th>
<th>(III)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>milligrams</td>
<td>195.3</td>
<td>194.9</td>
<td>194.13</td>
<td>194.7</td>
</tr>
</tbody>
</table>

In making the iodine value determination, Hubl's method was followed, results of which were as follows:

1. 0.1611 gram of oil required ...... 0.014155 gram iodine.
2. 0.1668 gram of oil required ...... 0.014339 gram iodine.
3. 0.1737 gram of oil required ...... 0.014848 gram iodine.

Per cent of iodine found:

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<thead>
<tr>
<th></th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>per cent</td>
<td>87.86</td>
<td>85.96</td>
<td>86.48</td>
<td>86.4</td>
</tr>
</tbody>
</table>

The acid value was determined by the regular method of titrating with standard potassium hydroxide solution. Two determinations gave the following results:

1. 8.5585 grams of oil required ...... 0.02285 gram of KOH.
2. 7.6232 grams of oil required ...... 0.02146 gram of KOH.

Calculated acid value:

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<thead>
<tr>
<th></th>
<th>(1)</th>
<th>(2)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>2.67</td>
<td>2.81</td>
</tr>
</tbody>
</table>

Glycerole was determined by the Benedict Zsigmondy method, that is the oxidation of glycerole to oxalic acid by means of potassium permanganate. Two determinations gave an average of 8.81 per cent of glycerole.
In determining the unsaponifiable matter, the method used for the determination of cholesterol was used with the hope of finding one of the known forms of that substance. The method was slightly modified, using a methyl alcoholic solution of potassium hydroxide instead of the common alcoholic solution. The ether extract of the soap thus formed gave about one per cent of a white crystalline substance which had a melting point of 59° to 60° C. The substance has been preserved for future study. It's melting point and general properties exclude it from the list of known cholesterols.

An Examination of the Husk.

One of the characteristic properties of the husk of the sumach seed, is its strong acid property. An examination showed the presence of both tannic and malic acids. An examination of the two acids was made as follows:

100 grams of the dried husk were extracted with hot water and clarified as far as possible by filtration. The filtrate then concentrated by evaporation, a little lime water added and allowed to stand for some time. A reddish granular deposit was formed which on examination, was found to be the calcium salt of malic acid. By filtering and again evaporating, all of the malic acid was separated from the tannic acid. The two lots of the malate were purified and weighed. The tannic acid was determined in the filtrate with the following results:

100 grams of the husk gave 7.32 grams of tannic acid or 7.32 per cent.
100 grams of the husk gave 1.35 grams of the malate or 1.35 per cent.

The Oil in the Husk.

By extracting the husk with ether, an oil was obtained with different properties from the oil in the seed proper. It appeared almost black when first extracted, had an entirely different odor and solidified at 0° C. At 35° C, it
became a thin liquid and had a specific gravity of .933. It resembles the Rhus oil in some of its properties. It is essentially a non-drying oil.

An average of three determinations of the iodine value gave the following:

1. .1815 gram of the oil gave or required 0.01584 gram of iodine.
2. .1560 gram of the oil gave or required 0.01364 gram of iodine.
3. .1638 gram of the oil gave or required 0.01422 gram of iodine.

Per cent of iodine:

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<thead>
<tr>
<th></th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>87.1</td>
<td>87.4</td>
<td>86.74</td>
<td>87.2</td>
</tr>
</tbody>
</table>

The saponification and acid values were, allowing for the difference in the amount of tannic and malic acids, the same as in the Rhus oil proper.

THE UNSAPONIFIABLE SUBSTANCE IN BETA OIL.

By the ordinary method, a large amount of unsaponifiable matter was determined. Several analyses were made, an average of which was 2.26 per cent of the oil. Upon examining the oil, it was found to be of complex nature. The body of the oil seemed to have the same composition as the alpha oil but the substances appearing as impurities were different. The chief substance, however, was the compound which belongs to the so-called unsaponifiable substance group.

During the past few years, several of these compounds have been isolated and some of them analyzed. This work has led us to believe that these substances which are now labelled "Unsaponifiable matter" will be found to be a distinct class of organic substances.

SEPARATION OF THE ALCOHOL FROM THE OIL.

It was found in studying the oil that acetone dissolved about 80 per cent of the oil, leaving behind the remainder as a black, tar-looking oil which contained nearly all of the alcohol. Upon standing, the alcohol precipitated out almost quantitatively. The substance thus obtained, was saponified with alcoholic potassium hydrate and extracted with ether. On evaporating the ether the substance was
obtained as a semi-crystalline mass. The substance is insoluble in water, acids and alkalies. Insoluble in cold alcohol but quite soluble in hot. It is insoluble in acetone but soluble in benzole and ether. Melting point of the pure substance is 63.5 to 65° C.

Analyses of the substance gave the following results:

I. 1006 gram of the substance gave .306 gram CO₂ and .127 gram H₂O
II. 1003 gram of the substance gave .304 gram CO₂ and .1237 gram H₂O
III. 1522 gram of the substance gave .4621 gram CO₂ and .1845 gram H₂O

<table>
<thead>
<tr>
<th></th>
<th>Found</th>
<th></th>
<th>(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>83.104</td>
<td>82.75</td>
<td>82.78</td>
</tr>
<tr>
<td>H</td>
<td>14.104</td>
<td>13.74</td>
<td>13.47</td>
</tr>
</tbody>
</table>

Calculated for the formula C₃₀H₅₇OH.

At this point the material which had been prepared was nearly exhausted and the work still to be completed. An attempt was made, however, to form esters with both acetyl chloride and benzoyl chloride. These would be expected to form readily in the case of a monatomic alcohol. No compound was obtained. The substance, after several hours treatment with either of these chlorides, now melted sharply at 61 degrees C, seemingly due to the removal of slight impurities by this treatment which had still persisted despite repeated purifications by other methods.

It is not possible with the work so far done to conclude that this is or is not an alcohol, especially as it has been found difficult to form esters with the glyesterol of wheat oil by these methods. If the substance should ultimately prove to be only a paraffin, it would be interesting to have found that present in so large an amount in the vegetable kingdom.
Four rock fragments showing specimens of *Nileus vigilans* in the position in which they were found in the undisturbed stratum.