AN EXAMINATION OF SOME EXTRACTIVES FROM THE SOLID RESIDUE OBTAINED FROM THE EXPRESSED OIL OF THE PEEL OF CALIFORNIA ORANGES

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Table of Contents

Introduction

The non-volatile residue from the expressed oil of California Oranges has been the subject of several investigations in this laboratory. In 1924-25, Paul Muenzberg Jr. worked upon a small quantity of material obtained through the courtesy of J. A. Hall from the California Fruit Growers Exchange of San Dimas, California. This was undoubtedly, the first precipitate which separated from the oil upon standing. In October, 1925, another and larger quantity of material was received from the same source. It appears that the oil expressed from Valencia Oranges had been stored for about six months after which 10,000 pounds of it was separated from the solid deposit and sold to Fritzsche Brothers, who later separated and returned to the producers about 120 pounds of a second deposit which had formed during the longer period of standing. Of this second deposit, 20 pounds were sent to the University for investigation.

The material consisted of a brownish semi-solid mass with an aromatic odor of orange oil. J. L. Perlman began work upon this material by distilling off the volatile oil from 1250 grams with steam. There remained in the distilling flask:

I. Aqueous solution of the water soluble constituents of the non-volatile residue.

II. The water insoluble constituents of the non-volatile residue.

I.

The Water Soluble Portion. The water soluble portion was evaporated to dryness, yielding a dark brown sticky mass with a sweetish bitter taste. This residue was partly soluble in alcohol. It contained 13.71% of ash. It reduced Fehling's solution, but formed no osazone with phenylhydrazone. Its saponification value was 270. This material weighed 95 grams.

II.

The Portion Insoluble in Water. The portion insoluble in water when dried, weighed 355 grams. It was almost odorless, possessed a slightly bitter taste, and was of a gummy consistency. It appeared to become slightly rancid upon standing. It contained 3.29% of ash, it reduced Fehling's solution and showed a saponification value of 175-180. Upon extracting with alcohol, it was divided into three parts.

1. Portion soluble in hot alcohol, but insoluble in cold alcohol.
2. Portion soluble in cold alcohol.
3. Portion insoluble in alcohol.

Procedure on above Portions: Sample No. 1

This portion of hot alcohol soluble material, upon cooling, gave a yellowish precipitate. This precipitate was filtered out. Its saponification value was 140.

Extracted with petroleum ether, this was separated into two portions:

a) A brown, bitter, semi-solid substance of a fatty or waxy nature having a saponification value of 139.

b) A brown, hard, brittle solid with a saponification value of 140, and containing 1.89% of ash. Upon extracting with hot alcohol, this gave a yellowish white waxy substance without odor or taste and insoluble in cold alcohol.

Sample No. 2

This portion, which was soluble in cold alcohol, was evaporated to dryness. Its saponification value was 177. Upon extracting with petroleum ether, it gave:

a) A thick oily liquid, dark brown in color and having a bitter taste. Saponification value 152.5

b) A thick, brown, bitter, viscous liquid with a saponification value of 171.

Sample No. 3

The residue insoluble in alcohol was a brown, odorless, tasteless powder, containing 11.3% of ash, and showing a saponification value of 202.

Experimental Part

The various extracts prepared by Perlman were given to the writer for further examination.

I.

The water soluble material which had a sweetish bitter taste and reduced Fehling's solution, but formed no osazone, was suspected of containing glucosides. The reducing action both before and after hydrolysis was accordingly determined.

1. A sample weighing one gram was disolved in exactly 100 cc. of water and titrated against Fehling's solution. Of this solution, 16 cc. were required to completely reduce 6 cc. of Fehling's solution, corresponding to 18.65% of reducing sugars in the sample, when computed as dextrose.

The precipitate obtained in this reaction was of a dirty yellowish color and did not resemble the clean red precipitate of cuprous oxide produced by reducing sugars.

2. A second sample of 1 gram was hydrolized by heating for one half hour with a 5% solution of hydrochloric acid. The excess of acid was carefully neutralized, the solution was diluted to 100 cc. and treated with Fehling's solution as before. Exactly 10.5 cc. of this solution were required to completely reduce 4 cc. of Fehling's solution, corresponding to 18.9 % of reducing sugars, computed as dextrose.

The precipitate in this reaction was the clean red precipitate of cuprous oxide characteristic of sugar reductions of Fehling's solution.

The results reported in both reactions above are the averages of several determinations.

Since the reducing property of the water soluble material is not materially increased by boiling with dilute hydrochloric acid, glucosides are probably not present.

Saponification values were run upon this material. These differed widely from those reported by Perlman, the results of two determinations being 81.33 and 80.99, while Perlman reports a saponfication of 270 for the water soluble extracts.

II

An examination of the petroleum ether extract of the material insoluble in water, but soluble in cold alcohol.

This dark brown oily liquid was chosen for study because there was a considerable quantity on hand and it appeared to be more promising of results.

Upon being hydrolized with alcoholic potassium hydroxide, this fraction gave a saponfication value of approximately 125. Perlman reports around 150 for the same material.

A 25 gram sample of the material was next hydrolized using somewhat more than the requisite quantity of potassium hydroxide calculated from the above saponification value. The greater part of the free alkali was neutralized by the careful addition of dilute hydrochloric acid. The saponified mixture was then shaken out with ether. In this way a water soluble and an ether soluble soap was obtained.

1. The Ether Soluble Portion. After complete evaporation, of the ether, the resulting soapy mass was made acid with dilute hydrochloric acid. A semi-solid mass, dark brown in color with an odor resembling that of fatty acids resulted. About 4 grams of this material was obtained after drying.

A sample of this acid material was dissolved in alcohol, standard potassium hydroxide was added and the excess of alkali was titrated with standard hydrochloric acid. In this way, it was determined that 288 milligrams of potassium hydroxide were required to combine with 1 gram of the acid.

This corresponds to a molecular weight of 191, giving us a molecule of 10 or 11 carbon atoms, providing that the acid is monobasic. This is, of course, only a crude approximation of both the molecular weight and the carbon content.

The remainder of the acid was divided into three parts of approximately 1 gram each. These were treated with slightly more than the computed quantity of Zinc Carbonate, Barium Carbonate, and Sodium Carbonate respectively, forming the Barium, Zinc, and Sodium salts of the acid. These were all insoluble in water. They were filtered out, washed with water and decomposed by treating with dilute hydrochloric acid.

The fatty acids thus liberated were solid. Those obtained from the zinc and barium salts were of a light tan color, while that from the sodium salt was brownish in color. They were dried and the melting points were determined. The acid obtained from the sodium soap melted between 45 and 50 degrees.C. Those from the zinc and barium salts melted between 55 and 60 degrees. The melting point of the acid derived from the zinc and barium salts corresponds roughly with that of saturated acids containing 14 to 16 carbon atoms and of unsaturated acids with a higher carbon content.

2. <u>The Water Soluble Portion</u>. The portion of soap which remained in the aquous solution was acidified with dilute hydrochloric acid. The fatty acid was liberated in the form of an oil. This was removed by shaking out with ether. The oil is brown in color, and carried the odor of the original material; an orange like odor.

Lack of time prevented further work upon this material

III.

Petroleum Ether Extract of Material soluble in hot, but insoluble in cold alcohol.

This material was hydrolized with alcoholic potassium hydroxide, and gave a saponification value of 119. Perlman reports 139 upon this material.

APPROVED BY:

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