

place, it was allowed to crystallize. On recrystallization from 95% alcohol the product was obtained in the form of long, double wedge-shaped yellowish red crystals with thin, pointed ends. It contains some water of hydration, the amount of which was not determined, and on complete dehydration it forms a dark grayish brown, amorphous powder, which is quite soluble in water, giving a deep red solution. Analysis of the dehydrated product for sodium gave figures that agree with formula below.

Subs., 0.2970: Na_2SO_4 , 0.0800.

Calc. for $(\text{SO}_3\text{NaC}_6\text{H}_4\text{Cl}_2)_2\text{N}_2$: Na, 8.77. Found: 8.72.

Summary.

1. The details of a method for obtaining practically a quantitative yield of *p*-dichloro-nitrobenzene have been worked out on a laboratory scale.

2. The results obtained by Holleman and Van der Linden in the sulfonation of *p*-dichlorobenzene have been confirmed, and the details of a convenient method for purification of the resulting sulfonic acid have been described.

3. A new tetrachloro-diphenylsulfonè, separating as a by-product in the sulfonation of *p*-dichlorobenzene, has been isolated and its composition determined.

4. One of the nitrosulfonic acids of *p*-dichlorobenzene, the 2,5-dichloro-4-nitrobenzene-sulfonic acid, has been prepared and its structure established.

IOWA CITY, IOWA.

[CONTRIBUTION FROM THE OIL, FAT AND WAX LABORATORY OF THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE COMPOSITION OF HUBBARD SQUASH SEED OIL.

BY WALTER F. BAUGHMAN AND GEORGE S. JAMIESON.

Received November 3, 1919.

Hubbard squash (*Cucurbita maxima*) belongs to the same family in which pumpkin and watermelon are classified. Extensive examinations have been made of both pumpkin seed oil and watermelon seed oil by Power and Salway.¹ However, no report of an examination of squash seed oil has been found in the literature. The object of the investigation, reported in this paper, was to determine the constituents of a specimen of the expressed oil of Hubbard squash seed.

Seeds.—The seeds were examined with the following results:²

| | |
|--------------------|-------|
| | % |
| Moisture..... | 5.72 |
| Ether extract..... | 36.66 |

¹ THIS JOURNAL, 32, 347, 360 (1910).

² Analysis made by J. M. Johnson, formerly of This Laboratory.

Preparation of the Oil.—The oil was expressed in January, 1918, by means of an oil expeller, under the supervision of Mr. H. S. Bailey, formerly in charge of this laboratory, who also refined a portion. The oil was stored at room temperature until May, 1919, before an opportunity was found for making an examination of it.

Physical and Chemical Examination.—The crude oil has a yellow color in thin layers and a brownish red color in layers of moderate thickness, while the refined oil is yellow with a red tinge. Both crude and refined oils have a bland, fatty taste and a fatty odor. The physical and chemical characteristics are given in Table I. The percentages of saturated and unsaturated acids were determined on the refined oil. For all other determinations reported in Col. I crude oil was used. The low Reichert-Meissl and Polenske numbers indicate the almost complete absence of glycerides of volatile acids. Only 0.33% of acids soluble in water was found. The acetyl value, 27.8, indicates a small amount of glycerides of hydroxylated acids. The keeping quality of the oil is very good as shown by the low acid value, and also by the absence of a rancid taste or odor. The percentage of insoluble acids, 94.66, has been corrected for unsaponifiable matter and represents the actual amount of insoluble acids and not insoluble acids + unsaponifiable matter (Henner number), which is sometimes reported.

TABLE I.—HUBBARD SQUASH SEED OIL.
Physical and Chemical Characteristics.

| | Oil. | Insoluble acids. | Liquid acids. | Solid acids. |
|-------------------------------|--------|------------------|---------------|--------------|
| Specific gravity 25°/25°..... | 0.9179 | ... | ... | ... |
| Refractive index 25°..... | 1.4714 | ... | ... | ... |
| Iodine number (Hanus)..... | 121.0 | ... | 151.2 | 3.8 |
| Saponification value..... | 191.5 | 201.8 | 201.7 | 210.3 |
| Mean molecular weight..... | ... | 278.0 | 278.1 | 266.8 |
| Reichert-Meissl number..... | 0.37 | ... | ... | ... |
| Polenske number..... | 0.39 | ... | ... | ... |
| Acetyl value..... | 27.8 | ... | ... | ... |
| Acid value..... | 0.50 | ... | ... | ... |
| Unsaponifiable matter, %..... | 1.06 | ... | ... | ... |
| Soluble acids, %..... | 0.33 | ... | ... | ... |
| Insoluble acids, %..... | 94.66 | ... | ... | ... |
| Unsaturated acids, %..... | 76.45 | ... | ... | ... |
| Saturated acids, %..... | 18.37 | ... | ... | ... |
| Titer..... | ... | 29.8° to 29.85° | | ... |

Since the percentages of saturated and unsaturated acids were determined on the refined oil the influence of the unsaponifiable matter was to some extent eliminated. The mean molecular weight of the saturated acids, 266.8, indicates a mixture of palmitic acid (m. w. 256.3) and stearic acid (m. w. 284.4). The mean molecular weight of the unsaturated acids, 278.1, is slightly lower than either oleic acid (m. w. 282.4) or linolic acid (m. w. 280.3).

The Renard test for arachidic acid gave a precipitate, the weight of which was equivalent to 5.6% of the oil. However, after several recrystallizations from 95% alcohol the melting point of this precipitate was found to be 68.5–69°, indicating stearic and not arachidic acid.

Examination of the Unsaturated Acids.—The unsaturated acids were separated by the lead salt-ether method and dried in a current of carbon dioxide. The bromine addition derivatives were then made and separated according to the method of Eibner and Muggenthaler.¹ To the unsaturated acids dissolved in dry ether and cooled to -10° bromine was slowly added. The mixture was then allowed to stand for two hours at -10° . The ethereal solution contained no precipitate, showing the absence of linolenic acid since linolenic hexabromide is insoluble in ether. The excess bromine was then removed by washing in a separatory funnel with an aqueous solution of sodium thiosulfate. The ethereal solution was dried with anhydrous sodium sulfate, filtered into a flask and the ether distilled off, after which the residue was boiled with petroleum ether. Oleic dibromide is very soluble in petroleum ether while linolic tetrabromide is soluble with difficulty. After standing in the ice-chest overnight the insoluble tetrabromide was filtered off. The filtrate was evaporated to dryness, dried in a vacuum oven and weighed. The bromine content was then determined by boiling a small sample of the residue with conc. nitric acid and solid silver nitrate. Oleic dibromide contains 36.18% of bromine and linolic tetrabromide contains 53.33%. Therefore, knowing the bromine content of the residue, it is possible to calculate the proportions of dibromide and tetrabromide present. The data obtained upon examining the unsaturated acids are given below:

| | |
|---|-----------|
| Sample of unsaturated acids..... | 3.7335 g. |
| Linolic tetrabromide insoluble in petroleum ether, m. p. 113–114° | 4.4076 g. |
| Residue (dibromide and tetrabromide)..... | 4.8237 g. |
| Bromine content of residue..... | 43.65% |
| Dibromide in residue 56.44% or..... | 2.7225 g. |
| Tetrabromide in residue 43.56% or..... | 2.1012 g. |
| Total tetrabromide found..... | 6.5088 g. |
| Linolic acid equivalent to tetrabromide 2.0368 g. or..... | 55.09% |
| Oleic acid equivalent to dibromide 1.7370 g. or..... | 46.49% |

The percentages of linolic and oleic acids in the unsaturated acids are converted into percentages of glycerides in the original oil as follows:

| | Found. % | Calculated to basis of 100%. | Original oil. %. | Glycerides in original oil. %. |
|-------------------|-------------|------------------------------------|------------------------|--------------------------------------|
| Oleic acid..... | 46.49 | 45.77 | 34.99 | 36.56 |
| Linolic acid..... | 55.09 | 54.23 | 41.46 | 43.34 |
| Total..... | 101.58 | 100.00 | 76.45 | 79.90 |

¹ Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 1, 5th Ed., 568–578.

Examination of Saturated Acids.—The saturated acids were separated from the unsaturated acids by the lead salt ether method. The methyl esters were prepared and subjected to fractional distillation under diminished pressure. The temperatures and pressures during distillation and the weights of the fractions are given in Table II. The iodine numbers and saponification values of the various fractions were determined and the mean molecular weights calculated, using 56.1 as the molecular weight of potassium hydroxide. These results are contained in Table III. The molecular weight of methyl palmitate is 270.3 and of methyl stearate 298.4. The molecular weights of the 5 fractions lie between these two values and indicate mixtures of palmitate and stearate. The molecular weight of the residue is greater than that of methyl stearate and indicates, therefore, an ester of an acid of greater molecular weight than stearic.

TABLE II.
Fractional Distillation in Vacuum of Methyl Esters of Saturated Acids,
46.8 g. Ester Subjected to Distillation.

| Fractions. | Temperature, Degrees. | Pressure, Mm. | Weight of fraction. G. |
|--------------|----------------------------------|------------------|---------------------------|
| 1..... | 178-181 | 7 | 22.6 |
| 2..... | 182-184 | 6.5 | 10.2 |
| 3..... | 185 rose quickly to 187, 187-189 | 6.5 | 6.05 |
| 4..... | 189-195 | 5.5 | 5.85 |
| 5..... | 196 rose quickly to 210, 210-224 | 6.0 | 1.15 |
| Residue..... | | ... | 0.80 |
| Total..... | | ... | 46.65 |

TABLE III.
Results of Analyses of Fractions Obtained by Distilling Methyl Esters of Saturated
Acids.

| Frac- tion. | Iodine No. | Saponifi- cation value. | Mean molecular weight. | Palmitic acid. | | Stearic acid. | | Arachidic acid. | | Unsat'd acids. | |
|----------------|---------------|-------------------------------|------------------------------|----------------|-------|---------------|-------|-----------------|------|----------------|------|
| | | | | %. | G. | %. | G. | %. | G. | %. | G. |
| 1..... | 1.6 | 206.0 | 272.3 | 87.76 | 19.82 | 6.04 | 1.36 | .. | .. | 1.06 | 0.24 |
| 2..... | 2.7 | 199.9 | 280.6 | 59.60 | 6.08 | 33.60 | 3.43 | .. | .. | 1.79 | 0.18 |
| 3..... | 3.8 | 195.3 | 287.2 | 36.79 | 2.23 | 55.82 | 3.38 | .. | .. | 2.50 | 0.15 |
| 4..... | 4.7 | 191.6 | 292.8 | 17.63 | 1.03 | 74.49 | 4.38 | .. | .. | 3.10 | 0.18 |
| 5..... | 6.3 | 189.1 | 296.6 | 5.80 | 0.07 | 85.30 | 0.98 | .. | .. | 4.17 | 0.05 |
| Residue | 19.7 | 187.5 | 299.2 | ... | ... | 75.94 | 0.60 | 6.36 | 0.05 | 13.02 | 0.10 |
| Total. | | | | | 29.23 | | 14.13 | | 0.05 | | 0.90 |

The free acids recovered from Fraction 5 and from the residue, were fractionally crystallized from 95% alcohol, and the melting points determined with the following results:

| Fraction 5. | M. p. |
|---------------------------------------|--------|
| 1st crystallization from alcohol..... | 64-65° |
| 2nd crystallization from alcohol..... | 65-67° |
| 3rd crystallization from alcohol..... | 67-68° |

The last crop of crystals was too small for further recrystallization. Since stearic acid melts at 69° this fraction apparently did not contain an acid higher than stearic.

| Residue. | M. p. |
|---------------------------------------|--------|
| 1st crystallization from alcohol..... | 70-71° |
| 2nd crystallization from alcohol..... | 76-77° |

The melting point of arachidic acid is 77°. This last crop of crystals after drying, weighed 0.1047 g. It was subjected to combustion analysis with the following results:

Calc. for arachidic acid: C, 76.85; H, 12.91. Found:¹ C, 76.71; H, 13.22.

This is conclusive evidence of the presence of arachidic acid.

The percentages and weights of unsaturated, palmitic, stearic and arachidic acids present in the various fractions and in the residue have been calculated with the results given in Table III. The various steps in the calculation of Fraction 1 are given below in order to illustrate the method.

278.1 = mean molecular weight of unsaturated acids.

278.1 + 14 = 292.1 mean molecular weight of methyl esters of unsaturated acids.

56.1 = molecular weight of potassium hydroxide.

$\frac{56.1}{292.1} \times 1000 = 192.1 =$ saponification value of methyl esters of unsaturated acids.

151.2 = iodine number of unsaturated acids.

$\frac{278.1}{292.1} = \frac{x}{151.2} \therefore x = 144.0 =$ iodine number of esters of unsaturated acids.

$\frac{1.6 \times 100}{144.0} = 1.11 =$ percentage of esters of unsaturated acids.

100-1.11 = 98.89 = percentage of esters of saturated acids.

0.0111 × 192.1 = 2.1 mg. = potassium hydroxide required to saponify unsaturated esters in one gram of fraction.

206.0-2.1 = 203.9 mg. potassium hydroxide required to saponify saturated esters in one gram of fraction.

203.9 ÷ .9889 = 206.2 saponification value of saturated esters.

56.1 ÷ .2062 = 272.1 mean molecular weight of saturated esters.

Using the molecular weights of methyl palmitate (270.3) and methyl stearate (298.4) the data below are calculated.

| | % of saturated acids. | % of fraction. | % of free acids in fraction |
|---------------------------------------|-----------------------|----------------|-----------------------------|
| Methyl palmitate..... | 93.59 | 92.55 | 87.76 |
| Methyl stearate..... | 6.41 | 6.34 | 6.04 |
| Methyl esters of unsaturated acids... | .. | 1.11 | 1.06 |
| Total..... | 100.00 | 100.00 | 94.86 |

The data in Table III are summed up in Table IV and the percentages of glycerides in the original oil calculated. It will be noted that the calculated amount of arachidic acid in the residue is only 0.05 g., whereas we were able to crystallize out 0.1047 g. The residue was very highly

¹ Analysis by Chas. E. F. Gersdorff.

colored and this interfered with the accuracy of the determination of the saponification value. There was at least, therefore, 0.1047 g. of arachidic acid in the residue and this is equivalent to 0.04% of the glyceride in the original oil.

TABLE IV.
Composition of Saturated Acids.

| | G. | %. | % of original oil. | % of glycerides in original oil. |
|---------------------|-------|--------|--------------------|----------------------------------|
| Palmitic acid..... | 29.23 | 65.97 | 12.12 | 12.73 |
| Stearic acid..... | 14.13 | 31.89 | 5.86 | 6.12 |
| Arachidic acid..... | 0.05 | 0.11 | 0.02 | 0.02 |
| Oleic acid..... | 0.90 | 2.03 | 0.17 | 0.18 |
| Linolic acid..... | | | 0.20 | 0.21 |
| Total..... | 44.31 | 100.00 | 18.37 | 19.26 |

Summary.

The chemical and physical characteristics of a sample of cold pressed Hubbard squash seed oil have been determined. An exhaustive study has been made of the composition of the oil, the results of which are given in the following table:

| | %. |
|------------------------------------|------|
| Glycerides of { Palmitic acid..... | 13 |
| { Stearic acid..... | 6 |
| { Arachidic acid, trace about..... | 0.04 |
| { Oleic acid..... | 37 |
| { Linolic acid..... | 44 |
| Unsapnifiable matter..... | 1 |

WASHINGTON, D. C.

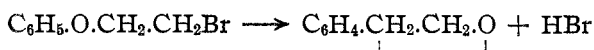
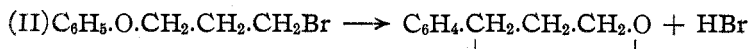
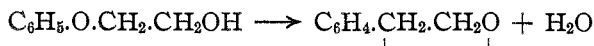
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

SYNTHESES OF CHROMANES AND COUMARANES. II.

By R. E. RINDFUSZ, P. M. GINNINGS AND V. L. HARNACK.

Received November 4, 1919.

In a previous article¹ it was shown that chromane and coumarane may be easily prepared by either of two methods:



The procedure in each case is to heat the hydroxy or bromo ether with zinc chloride. The same products may also be obtained by heating free

¹ THIS JOURNAL, 41, 665 (1919).