possess, when administered in substance for the purpose indicated, would therefore appear to be attributable to a mechanical action. In any case, the remedial value of pumpkin seeds cannot be considered such as to justify their recognition by a national pharmacopoeia.

[CONTRIBUTION FROM THE WELLCOME CHEMICAL RESEARCH LABORATORIES, LONDON.]

CHEMICAL EXAMINATION OF WATERMELON SEED.

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The seeds of the watermelon (*Cucurbita citrullus*, Linné) have been employed to some extent medicinally on account of their diuretic properties, but chiefly as a domestic remedy. So far as known to us, they have never been examined chemically. Lewkowitsch[1] has briefly noted the physical and chemical constants of the fatty oil, and of the mixed fatty acids obtained therefrom, but makes no statement regarding the composition of the oil, and no further information concerning this product appears to be available.

As many of the plants belonging to the family of *Cucurbitaceae* contain in some of their parts substances which possess a considerable degree of physiological activity, it was deemed desirable to submit the seeds of the watermelon to a complete chemical examination. Such an investigation appeared, furthermore, of interest from the point of view of comparing the constituents of these seeds with those of the common pumpkin (*Cucurbita pepo*, Linné), which have recently been completely examined by us.[2]

EXPERIMENTAL.

The material employed was obtained from the United States and consisted of fresh watermelon seeds of good quality.

A portion of the crushed seed was first tested for the presence of an alkaloid by means of Prollius' fluid, but with a negative result.

For the purpose of a complete investigation, 22.5 kilograms of the seed were crushed and the shells separated as completely as possible from the kernels. The shells amounted to 10.95 kilograms, thus corresponding to 48.7 per cent. of the weight of the seed. The ground kernels were then subjected to strong hydraulic pressure, when 1665 grams of fatty oil were obtained, corresponding to 7.4 per cent. of the weight of the entire seed. The so-called "press-cake" remaining after the removal of the oil amounted to 8.88 kilograms. These operations, connected with the expression of the oil, were carefully conducted for us by Messrs. Stafford, Allen & Sons, of London, to whom our thanks are due.

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[1] "Chemical Technology and Analysis of Oils, Fats and Waxes," 3rd Edit., Vol II, p. 511.

[2] THIS JOURNAL, 32, 346.

A portion of the entire seed, when ground and extracted in a Soxhlet apparatus with light petroleum (b. p. 30–45°), yielded 19.0 per cent. of fatty oil.

I. Examination of the Expressed Oil.

The expressed oil of watermelon seed has a light yellow color and, unlike that from pumpkin seed, is completely devoid of fluorescence. The constants of the oil were determined with the following results:

	Expressed oil.	Oil extracted by petroleum.
Specific gravity 20°/20°	0.9233	0.9219
Acid value	3.9	3.6
Saponification value	191.8	189.9
Iodine value	121.1	121.8

For a complete chemical examination of the oil, 250 grams of it were employed. It was first subjected to distillation with steam, but the distillate contained no volatile oil nor any acid.

Hydrolysis of the Oil.

The oil which had been subjected to distillation with steam, as above described, was separated from the water, the latter then extracted with ether to recover a small amount of suspended oil, and, after adding this to the main portion, the whole was hydrolyzed by heating with an alcoholic solution of 70 grams of potassium hydroxide. The greater portion of the alcohol was then removed, water added, and the alkaline liquid repeatedly extracted with ether. The ethereal liquids were united, washed with a little water, dried with anhydrous sodium sulphate, and the ether removed, when about 0.5 gram of a light yellow oil was obtained, which soon solidified. The solid product, after three crystallizations from a mixture of ethyl acetate and alcohol, separated in pearly leaflets, melting at 163–164°. After drying at 105° it was analyzed:

0.0881 gave 0.2667 CO_2 and 0.0905 H_2O. C = 82.6; H = 11.4.
$C_{20}H_{34}O$ requires C = 82.8; H = 11.7 per cent.

This substance, when dissolved in chloroform with a little acetic anhydride, and a drop of sulphuric acid subsequently added, gave a blue coloration, rapidly changing to green, and finally to brown. It is evidently a phytosterol.

The Fatty Acids.

The alkaline, aqueous solution of potassium salts, which had been extracted with ether as above described, was acidified with sulphuric acid and the mixture distilled with steam. The distillate, however, contained no volatile acid. The fatty acids remaining in the distillation flask were taken up with ether, the ethereal solution being washed, dried, and the solvent removed. For the purpose of determining the constants of the mixed fatty acids, a portion was heated for some time at 100° under diminished pressure, in order to remove the last traces of ether, after which the following results were obtained: M. p. (complete fusion), 35°; d 50°/50° = 0.8894; neutralization value, 198.2; iodine value, 118.2. Optically inactive. A determination of the acetyl value indicated the absence of hydroxy acids.

The mixed fatty acids, which consisted of a liquid and a solid portion, were first partially separated by filtration with the aid of a pump. The solid acids were then fractionally crystallized from alcohol until no further separation could be effected by this means. The least soluble fraction melted at 66–68°, and was considerable in amount. In order to ascertain whether this fraction was homogeneous, it was dissolved in hot alcohol and a measured portion of concentrated, aqueous barium acetate added, drop by drop, with constant stirring. The mixture was then filtered, while still hot, with the aid of a pump, and the precipitate washed with a little hot alcohol. The whole operation was then repeated, and in this manner four successive fractions of barium salt were obtained. The acids liberated from each of these fractions were crystallized once from alcohol, when they had the following melting points: 69–70°, 69–70°, 67–69°, 65–67°. The acid melting at 69–70° separated in glistening, pearly leaflets and was analyzed:

0.1267 gave 0.3522 CO_2 and 0.1448 H_2O. C = 75.8; H = 12.7.

0.5155 neutralized 18.1 cc. 0.1 *N* KOH. Neutralization value = 197.0°.

$C_{18}H_{36}O_2$ requires C = 76.1; H = 12.7 per cent. Neutralization value = 197.5.

It is thus evident that the substance melting at 69–70° was stearic acid, and that no acid of higher carbon content was present.

All the portions of acid obtained in the course of the original fractionation which melted below 66–68° were united and fractionally precipitated with barium acetate in the manner previously described. Six fractions of barium salt were thus obtained, from which the acids were subsequently liberated. The last of these fractions of acid was oily, and to a large extent unsaturated, while the remaining five fractions, after being once crystallized from alcohol, melted at 66–68°, 65–67°, 65–67°, 64–66°, and 57–58°, respectively. Each of these fractions was titrated, with the following results:

Fraction 1 (m. p. 66–68°), 0.2661 neutralized 9.5 cc. 0.1 *N* KOH. N. V. = 200.3.

Fraction 2 (m. p. 65–67°), 0.1356 neutralized 4.8 cc. 0.1 *N* KOH. N. V. = 198.6.

Fraction 3 (m. p. 65–67°), 0.1828 neutralized 6.5 cc. 0.1 *N* KOH. N. V. = 199.5.

Fraction 4 (m. p. 64–66°), 0.0876 neutralized 3.15 cc. 0.1 *N* KOH. N. V. = 201.8.

Fraction 5 (m. p. 57–58°), 0.1707 neutralized 6.35 cc. 0.1 *N* KOH. N. V. = 208.7.

$C_{18}H_{36}O_2$ requires a neutralization value of 197.5.
$C_{16}H_{32}O_2$ requires a neutralization value of 219.1.

From the above results it was evident that fractions 1–4, inclusive, consisted, to a large extent, of stearic acid, while fraction 5 would appear to have contained about equal parts of stearic and palmitic acids.

It may therefore be concluded that the solid fatty acids of watermelon seed oil consist only of palmitic and stearic acids, the latter being present in the larger proportion.

The liquid acids, which had been separated from the solid portion as previously described, constituted the larger proportion of the total fatty acids. In order to separate the small amount of saturated acids still contained in the liquid portion, the whole was converted into a lead salt and this extracted with ether. The portion of lead salt soluble in ether yielded 145 grams of liquid acid, which possessed the following constants: *d* 20°/20° = 0.9027; b. p. 233–240°/20 mm.; neutralization value, 200.1; iodine value, 142.1.

0.1230 gave 0.3433 CO_2 and 0.1293 H_2O. C = 76.1; H = 11.7.
$C_{18}H_{34}O_2$ requires C = 76.6; H = 12.1 per cent.
$C_{18}H_{32}O_2$ requires C = 77.1; H = 11.4 per cent.

The above results indicated that the liquid acid consisted of a mixture of unsaturated acids, and with the endeavor to effect their separation a method was employed which depended on the fractional precipitation of their barium salts. Five fractions of barium salt were thus obtained, each of which was shaken with hydrochloric acid in the presence of ether, the ethereal solution being subsequently washed, dried, and the solvent removed. After heating for a time at 100° under diminished pressure, in order to remove the last traces of ether, the iodine value of the several fractions of acid was determined:

Fraction I. 0.1035 of acid absorbed 0.1455 I. Iodine value = 140.6.
Fraction II. 0.1573 of acid absorbed 0.2249 I. Iodine value = 143.0.
Fraction III. 0.1436 of acid absorbed 0.2073 I. Iodine value = 144.4.
Fraction IV. 0.0983 of acid absorbed 0.1417 I. Iodine value = 144.2.
Fraction V. 0.0987 of acid absorbed 0.1417 I. Iodine value = 143.6.
$C_{18}H_{34}O_2$ requires an iodine value of 90.1.
$C_{18}H_{32}O_2$ requires an iodine value of 181.4.

The first fraction still contained a small amount of saturated acid, while the iodine values of the remaining four fractions indicated that the latter were practically identical in composition. It was, however, also apparent that a separation of the acids had not been effected by the above-described method.

From the iodine values above noted it could be concluded that the mixture of unsaturated acids consisted of oleic and linoleic acids in approximately equal proportions. In order to confirm this assumption, 30 grams of the mixture were oxidized in alkaline solution with an equal weight of potassium permanganate. The product of oxidation was digested with large quantities of ether, which extracted a substance melting at 126–128° and which, after crystallization from alcohol, separated in small, glistening leaflets melting at 128°.

0.1039 gave 0.2594 CO_2 and 0.1075 H_2O. C = 68.1; H = 11.5.

$C_{18}H_{36}O_4$ requires C = 68.4; H = 11.4 per cent.

This substance was evidently dihydroxystearic acid, and its formation established the presence of oleic acid in the mixture of liquid acids.

The oxidation product, after extraction with ether, was heated with large quantities of water, and the liquid filtered while hot. These deposited a pure white, crystalline substance, melting at 154–155°, which, after crystallization from alcohol, separated in small, thin needles, melting at the same temperature.

0.1138 gave 0.2574 CO_2 and 0.1068 H_2O. C = 61.7; H = 10.4.

$C_{18}H_{36}O_6$ requires C = 62.1; H = 10.3 per cent.

This substance was thus identified as tetrahydroxystearic acid (sativic acid), and its formation established the presence of linoleic acid in the mixture of liquid acids. As no hexahydroxystearic acid could be isolated from the product of oxidation, it may be concluded that linolenic acid is not a constituent of the oil.

II. Examination of the Press-cake.

The so-called "press-cake" resulting from the expression of 22.5 kilograms of watermelon seeds, deprived as completely as possible of the shells, amounted, as previously noted, to 8.88 kilograms. This was completely extracted with hot alcohol, when, after the removal of the greater portion of the alcohol, a thin, dark brown, oily extract was obtained, amounting to 1644 grams. It evidently contained a considerable quantity of fatty oil which had escaped expression from the seed, and which was removed by treating the extract with light petroleum (b. p. 30–45°). The amount of fatty oil obtained in this way was 1340 grams, thus corresponding to 81.5 per cent. of the total alcoholic extract. Its constants were as follows: *d* 20°/20° = 0.9328; saponification value, 191.4; iodine value, 112.7.

The fatty oil obtained from the press-cake, as above described, would naturally be expected to be similar in composition to that obtained from the seed by expression, and its examination proved this to be the case. It was found to contain a very small amount of a phytosterol, melting at 160°, and the mixed fatty acids obtained on hydrolysis possessed the following constants: m. p., 34°; *d* 50°/50° = 0.8916; neutralization value, 197.6; iodine value, 129.5. These acids, like those obtained from the expressed oil, consisted of a mixture of palmitic, stearic, oleic and linolic acids.

The portion of the alcoholic extract which remained undissolved by treatment with light petroleum was subjected to distillation with steam, but no volatile product was obtained. The contents of the distillation flask then consisted of a dark colored aqueous liquid (*A*) and a quantity of a black resin (*B*), which were separated by filtration and the resin well washed with water.

The Aqueous Liquid (*A*).

The aqueous liquid was repeatedly extracted with ether, the ethereal liquids being washed, dried, and the solvent removed. About 0.5 gram of a viscid, brown oil was thus obtained, which deposited nothing in the cold, and which, in alcoholic solution, gave with ferric chloride a green coloration. The oily product was digested with a large volume of light petroleum, but no crystalline substance could be isolated from it. It was thus ascertained that the seed of the watermelon, unlike those of the pumpkin, do not contain salicylic acid.

Treatment with Basic Lead Acetate.

The aqueous liquid, which had been extracted with ether as above described, was subsequently treated with basic lead acetate, which yielded a yellowish brown precipitate. The latter was collected on a filter, thoroughly washed, and then suspended in water and decomposed by hydrogen sulphide. On filtering the mixture and concentrating the filtrate under diminished pressure, a reddish brown liquid was obtained, which gave a bluish black coloration with ferric chloride, thus indicating the presence of tannin. As the liquid deposited only a little amorphous material on standing, it was finally mixed with purified sawdust and the dried mixture extracted successively in a Soxhlet apparatus with ether, ethyl acetate and alcohol. These solvents, however, did not effect the separation of any crystalline substance.

The filtrate from the basic lead acetate precipitate was treated with hydrogen sulphide for the removal of the excess of lead, filtered, and this filtrate concentrated under diminished pressure. A reddish brown, sirupy liquid was thus obtained, which contained a large amount of sugar, since it readily yielded *d*-phenylglucosazone, melting at 210°. The liquid gave a precipitate with potassium-mercuric iodide, and on heating with alkalies evolved ammonia, but these reactions were evidently due to protein products and not to the presence of an alkaloid, since the entire seed, when tested for substances of this class by means of Prollius' fluid, gave a perfectly negative result.

A portion of the aqueous liquid which had been purified by treatment with basic lead acetate, as above described, was heated for some time in a reflux apparatus with such an amount of sulphuric acid that the latter represented 5 per cent. by weight of the mixture. During the operation a quantity of resinous material separated, which was quite insoluble in the usual organic solvents. On subsequently passing steam through the liquid a slightly acid distillate was obtained, in which the presence of formic and acetic acids was determined. The acid, aqueous liquid which remained in the distillation flask was repeatedly extracted with ether, which, however, removed only traces of brown, amorphous material. No evidence was thus obtained of the presence in the aqueous liquid of any definite substance of a glucosidic nature.

The Resin (B).

The resin from the "press-cake" amounted to 70 grams. The greater portion of this material (68 grams) was digested with hot alcohol, then mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 30–45°)	extracted	27.0	grams	= 39.7	per cent.
Ether	"	3.8	"	= 5.6	"
Chloroform	"	3.0	"	= 4.4	"
Ethyl acetate	"	2.2	"	= 3.2	"
Alcohol	"	15.5	"	= 22.8	"
Total,		51.5	"	= 75.7	"

By this process of extraction a considerable portion of the resin had evidently been rendered insoluble.

Petroleum Extract of the Resin.

This was a dark-colored, viscid product. It was heated in a reflux apparatus with an excess of an alcoholic solution of potassium hydroxide, the greater portion of the alcohol then removed, water added, and the alkaline mixture extracted with ether. The ethereal liquid was washed, dried, and the solvent removed, when a very small quantity (0.2 gram) of a light yellow solid was obtained. This was crystallized from a mixture of ethyl acetate and alcohol, when it melted at 158–159°. It was a phytosterol and apparently identical with that previously isolated from the expressed oil of the seed.

The alkaline, aqueous liquid, from which the above-mentioned phytosterol had been separated, was acidified with sulphuric acid and extracted with ether. During the extraction a small quantity of resinous matter separated, which was removed by filtration. This was dried on a porous tile, and then dissolved in pyridine, when it yielded a crystalline substance which, after a few crystallizations from the same solvent, separated in colorless, prismatic needles, melting and decomposing at about 260°. It was found to be identical with a new substance, $C_{24}H_{40}O_4$, which was subsequently isolated from the ether extract of the resin, as described below.

The ethereal liquid, as above obtained, was washed, dried, and the solvent removed, when it yielded a mixture of fatty acids. This was distilled under diminished pressure, when it passed over between 230 and 245°/25 mm., leaving only a small amount of resin. The distilled product, on cooling, became partially solid. The solid portion was therefore separated by filtration, with the aid of the pump, and crystallized from alcohol, when it was obtained in glistening plates, melting at 60–62°.

0.3561 neutralized 32.2 cc. 0.1 *N* KOH. Neutralization value = 208.0.
$C_{18}H_{36}O_2$ requires a neutralization value of 197.5.
$C_{16}H_{32}O_2$ requires a neutralization value of 219.1.

The product evidently consisted of a mixture of palmitic and stearic acids in about equal proportions.

The liquid acids which had been separated from the solid portion by filtration were for the most part unsaturated, since they readily absorbed bromine, and the presence of oleic acid was also indicated by the behavior towards nitric acid.

The fatty acids contained in the petroleum extract of the resin were therefore the same as those obtained from the expressed oil of watermelon seeds.

Ether Extract of the Resin.

Isolation of a New Alcohol, Cucurbitol, $C_{24}H_{40}O_4$.—The ether extract of the resin was a dark brown, soft mass, and amounted to only 3.8 grams. It was digested with cold alcohol, which removed the coloring matter, while the greater portion of the material remained as a yellowish brown powder. This was collected on a filter and washed with a little cold alcohol, after which it was dissolved in warm pyridine. From this solution a substance separated in the form of radiating clusters of colorless needles, which, when slowly heated, melted and decomposed at 260°. The substance, after drying at 110°, was analyzed:

0.0626 gave 0.1680 CO_2 and 0.0587 H_2O. C = 73.2; H = 10.4.
$C_{24}H_{40}O_4$ requires C = 73.5; H = 10.2 per cent.

The substance is thus seen to agree in composition with the formula $C_{24}H_{40}O_4$. When dissolved in chloroform with a little acetic anhydride, and a drop of concentrated sulphuric acid subsequently added, a blue coloration is produced, which slowly becomes greenish, and finally dull brown. When heated with acetic anhydride it yielded an acetyl derivative which crystallized in radiating clusters of fine needles, melting at 150°. The acetyl derivative is very soluble in ethyl acetate and moderately so in alcohol, but the amount available was not sufficient for analysis.

No substance of the formula $C_{24}H_{40}O_4$, possessing properties similar to those above described, has hitherto been recorded. With consideration, therefore, of the source and alcoholic nature of the new compound, it is proposed to designate it *cucurbitol.*

It is of interest to note, in this connection, that two substances of alcoholic nature, which appear to be closely related to cucurbitol, have recently been isolated in these laboratories. One of these was obtained from the resin of *Grindelia camporum*, Greene, and agrees in composition with the formula $C_{23}H_{38}O_4$. It melts at 256–257°, and yields an acetyl derivative melting at 161°.[1] This compound, which was not previously named, may now be conveniently designated *grindelol.* The other substance was obtained from jalap resin and possesses the formula $C_{21}H_{34}O_4$.[2] The latter compound, designated *ipurganol,* melts at 222–225° and yields an acetyl derivative melting at 166–167°. The three substances, cucurbitol, grindelol, and ipurganol, show slight differences in their color reactions when subjected to the above-mentioned test in chloroform solution with acetic anhydride and concentrated sulphuric acid. Thus ipurganol gives at first a purplish pink coloration, changing to blue, then becoming bright green, and finally brown, while grindelol gives at first a blue color, which changes to a duller green than the preceding, and finally becomes brown, and in the case of cucurbitol the intermediate greenish tint is still less pronounced. In view of the composition and character of these three new compounds, it is evident that they are members of a homologous series, which is represented by the general formula $C_nH_{2n-8}O_4$.

Chloroform, Ethyl Acetate and Alcohol Extracts of the Resin.

The chloroform and ethyl acetate extracts were both very small in amount (3.0 and 2.2 grams respectively), and, like the alcohol extract of the resin, formed brittle, black solids. They were all carefully examined, but nothing definite could be isolated from them.

III. Examination of the Shells.

The shells from 22.5 kilograms of watermelon seeds amounted to 10.95 kilograms, thus corresponding to 48.7 per cent. of the weight of the seed. This material was ground and extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol, a dark-colored, oily product was obtained, which contained some resin in suspension. The entire amount of extract (907 grams) was first mixed with a large volume of light petroleum, in order to effect the separation of the fatty oil (*A*). The portion of extract remaining undissolved by the petroleum may be designated as (*B*).

The Fatty Oil (*A*).

The petroleum solution of the fatty oil was filtered, dried with anhy-

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[1] Compare *Proc. Am. Pharm. Assoc.*, **55**, 342 (1907).

[2] THIS JOURNAL, **32,** 89.

drous sodium sulphate, and the solvent removed. A dark green, opaque oil was thus obtained, which amounted to 750 grams, or 82.7 per cent. of the total alcoholic extract. It possessed the following constants: *d* 20°/20° = 0.9351; saponification value, 191.3; iodine value, 114.6.

For the examination of the fatty oil 150 grams of it were employed. This was brought into a flask with a little water and steam passed through the mixture, but the distillate contained only traces of volatile acid.

Hydrolysis of the Oil.

The fatty oil remaining in the distillation flask after the above-mentioned treatment with steam was separated from the water and hydrolyzed by heating with an alcoholic solution of 40 grams of potassium hydroxide. The greater portion of the alcohol was then removed, water added, and the alkaline solution extracted repeatedly with ether. The ethereal liquids were united, washed with water, dried with anhydrous sodium sulphate, and the solvent removed. About 0.5 gram of a solid substance was thus obtained, which crystallized readily from a mixture of ethyl acetate and alcohol. It first melted at 140°, and after a second crystallization separated in pearly leaflets, melting at 141–142°. After drying at 105° it was analyzed:

0.0970 gave 0.2930 CO_2 and 0.1012 H_2O. C = 82.4; H = 11.6.
$C_{20}H_{34}O$ requires C = 82.8; H = 11.7 per cent.

This substance is thus seen to be a phytosterol, and its identity was further confirmed by the characteristic color reactions.

The Fatty Acids.

The alkaline, aqueous solution of potassium salts, which had been extracted with ether as above described, was acidified with sulphuric acid and again extracted with ether, the ethereal solution being washed, dried, and the solvent removed. A dark brown, semi-solid mass of fatty acids was thus obtained, which possessed the following constants: M. p., 32°; *d* 50°/50° = 0.8968; neutralization value, 200.2; iodine value, 115.8.

The acid, aqueous liquid which had been extracted with ether was distilled with steam, but the distillate contained only traces of volatile acid.

The mixed fatty acids were first separated into a solid and a liquid portion by filtration with the aid of a pump. The solid portion was then fractionally crystallized from alcohol, when the least soluble fraction, on further crystallization, melted successively at 63–66°, 66–68°, 68–69°, and finally at 71°. It was thus evident that some acid of higher carbon content than stearic acid was present, and the substance melting at 71° was analyzed:

0.1060 gave 0.2968 CO_2 and 0.1201 H_2O. C = 76.4; H = 12.6.
$C_{18}H_{36}O_2$ requires C = 76.1; H = 12.7 per cent.
$C_{20}H_{40}O_2$ requires C = 76.9; H = 12.8 per cent.

This substance thus appeared to consist of a mixture of stearic and arachidic acids, and the separation of the latter in a pure state was subsequently accomplished by the fractional distillation of the solid portion of mixed fatty acids. On distilling the solid acids under diminished pressure, they began to boil at 230°/18 mm., but nearly the entire amount passed over between 233 and 240°/18 mm., while a small final fraction was collected at 240–250°/18 mm. The last-mentioned fraction readily solidified on cooling, and was then crystallized twice from ethyl acetate, from which it separated in rosettes of glistening leaflets, melting at 76–78°.

0.0935 gave 0.2633 CO_2 and 0.1077 H_2O. C = 76.8; H = 12.8.
$C_{20}H_{40}O_2$ requires C = 76.9; H = 12.8 per cent.

The identity of this substance as arachidic acid was thus established.

The fraction of acid distilling at 230–233°/18 mm. melted at 59–60°, while that collected between 233 and 240°/18 mm. melted at 62–64°. Both of these fractions consisted of mixtures of palmitic and stearic acids.

The liquid portion of the mixed fatty acids was highly unsaturated, and, like the corresponding product from the expressed oil of the seed, evidently consisted of a mixture of oleic and linoleic acids.

Portion of Alcoholic Extract Insoluble in Petroleum (B).

This portion of the original extract of the shells formed a black, resinous mass, amounting to 150 grams. It was mixed with water and distilled with steam, but the distillate contained only traces of volatile acid. The contents of the distillation flask then consisted of a light yellow, aqueous liquid and a quantity of a black resin. These were separated by filtration and the resin well washed with water.

The Aqueous Liquids.

The above-mentioned, yellow, aqueous liquid was repeatedly extracted with ether, which removed about 1 gram of a brownish yellow oil. On digesting this product with water, the resulting liquid gave a greenish coloration with ferric chloride. The oily product was practically insoluble in water and only partially soluble in sodium carbonate, but dissolved completely in a solution of sodium hydroxide, and was therefore phenolic in character. It was distilled under diminished pressure, whereby some resinous material was removed, and then benzoylated. A crystalline solid melting at 205–210° was thus obtained, but the amount was much too small for further examination.

The aqueous liquid was subsequently treated with a slight excess of basic lead acetate, which yielded a relatively small amount of a yellowish precipitate. This was collected, washed, suspended in water, and decomposed by hydrogen sulphide. On filtering the mixture a liquid was obtained which gave a bluish black coloration with ferric chloride, indicating the presence of tannin, but no definite compound could be isolated from it.

The filtrate from the basic lead acetate precipitate possessed a light green color. This was due to the presence of a very small amount of copper, which, by a special test, was subsequently found to be contained in the original watermelon seed.[1] After treatment with hydrogen sulphide for the removal of the excess of lead, and filtering, the liquid was concentrated under diminished pressure. A light yellow sirup was thus obtained, which deposited nothing crystalline on standing. It contained a quantity of sugar, since it readily reduced Fehling's solution, and yielded *d*-phenylglucosazone, melting at 212–213°.

The aqueous liquid, when heated with alkalies, developed ammonia, which was evidently due to the presence of soluble protein compounds, but it was observed that a peculiar basic odor was also produced. In order to ascertain whether by this treatment any volatile base other than ammonia was formed, a portion of the liquid was heated with baryta in a current of steam, the volatile product being collected in hydrochloric acid. The salt thus obtained, which was small in amount, was converted into the platinum compound, and the latter, after drying in a vacuum over sulphuric acid, was analyzed:

0.0785 of the salt gave, on ignition, 0.0340 Pt. Pt = 43.3.
$(NH_4)_2PtCl_6$ requires Pt = 43.9 per cent.

This salt, therefore, was practically pure ammonium chloroplatinate.

Another portion of the aqueous liquid was heated in a reflux apparatus with such an amount of sulphuric acid that the latter represented 5 per cent. of the weight of the mixture. On distilling the product with steam, only small quantities of formic and acetic acid were obtained, and the contents of the distillation flask, when subsequently extracted with ether, likewise yielded nothing which would indicate the presence of a glucoside in the original aqueous liquid.

A portion of the aqueous liquid was finally mixed with purified sawdust and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with ether, ethyl acetate and alcohol, but no definite substance could be isolated by means of these solvents.

The Resin.

The black, resinous material contained in the portion of alcoholic extract which was insoluble in petroleum, and which had been separated from the aqueous liquid, as above described, amounted to 68 grams. The greater part (66 grams) of this material was digested with alcohol, then mixed with purified sawdust, and the thoroughly dried mixture

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[1] An account of the wide distribution of copper, in both the vegetable and animal kingdoms, is recorded in the *Am. J. Pharm.*, **77**, 274 (1905).

extracted successively in a Soxhlet apparatus with various solvents. The results were as follows:

Petroleum (b. p. 30–45°)	extracted	25.6	grams	= 38.8	per cent.
Ether	"	3.2	"	= 4.8	"
Chloroform	"	9.2	"	= 13.9	"
Ethyl acetate	"	3.4	"	= 5.2	"
Alcohol	"	7.4	"	= 11.2	"
Total,		48.8	"	= 73.9	"

Petroleum Extract of the Resin.

This extract was a dark, viscid liquid. On the addition of ether a small quantity of a gelatinous substance separated, which was removed by filtration. This substance was very sparingly soluble in alcohol, but readily soluble in hot acetic acid, and also in pyridine, from both of which solvents it was again deposited in a gelatinous form.

The portion of the extract which was soluble in ether was heated with an alcoholic solution of potassium hydroxide. After removing the alcohol, water was added and the alkaline liquid extracted with ether. The ethereal liquid, after the removal of the solvent, yielded about 0.5 gram of a light yellow solid, which, when crystallized from a mixture of ethyl acetate and alcohol, separated in glistening leaflets, melting at 138–140°. The melting point and color reactions of this substance indicated that it was identical with the phytosterol, $C_{20}H_{34}O$ (m. p. 141–142°), obtained from the fatty oil of the shells of watermelon seeds.

The alkaline solution of potassium salts, after extraction with ether, was acidified with sulphuric acid and again treated with ether, the ethereal liquid being washed, dried and the solvent removed. The fatty acids thus obtained were distilled under diminished pressure, when the greater portion passed over between 235 and 240°/20 mm., a small fraction having also been collected at 240–260°/20 mm. The fraction 235–240°/20 mm. became partially solid on cooling. The solid portion was therefore removed and crystallized from alcohol, when, after the first crystallization, it melted at 55–58°.

0.3334 neutralized 12.05 cc. 0.1 N KOH. Neutralization value = 202.8.

$C_{18}H_{36}O_2$ requires a neutralization value of 197.5.

$C_{16}H_{32}O_2$ requires a neutralization value of 219.1.

It was thus evident that the above portion of solid acid consisted of a mixture of palmitic and stearic acids, the former predominating.

The liquid portion of fatty acids from the fraction 235–240°/20 mm., when tested with nitric acid, was found to contain some oleic acid.

0.2331 absorbed 0.3301 iodine. Iodine value = 141.6.

These liquid fatty acids, therefore, like those contained in the expressed oil of watermelon seeds, evidently consisted of a mixture of oleic and linoleic acids.

The small fraction of acid collected at 240–260°/20 mm. solidified in the receiver. After two crystallizations from alcohol it separated in glistening leaflets, melting at 76–77°. This substance was identified as arachidic acid.

Ether Extract of the Resin.

This extract was a dark brown solid and very small in amount (3.2 grams). It was digested with cold alcohol, which removed the coloring matter, leaving a light brown, amorphous powder. On treating the latter with pyridine a few needle-shaped crystals were deposited, together with some amorphous, brown material. The crystalline substance, which was mechanically separated, melted and decomposed at 260°, and yielded an acetyl derivative melting at 150°. It gave the characteristic color reaction of *cucurbitol*, $C_{24}H_{40}O_4$, and was identical in every respect with the latter compound, as isolated from the "press-cake" of watermelon seeds.

Chloroform, Ethyl Acetate and Alcohol Extracts of the Resin.

These were all dark colored, brittle solids, from which no crystalline substance could be obtained.

Summary.

The results of the present investigation of watermelon seeds may be summarized as follows:

The seeds contain no alkaloid, and no evidence was obtained of the presence of a glucoside.

I. *The Fatty Oil.*—The amount of oil obtained from the kernels by expression corresponded to 7.4 per cent. of the weight of the entire seed. The entire seed, when ground and extracted with light petroleum, yielded 19.0 per cent. of fatty oil. The amount of the latter is, therefore, very much less than was obtained by us from pumpkin seed.[1] The expressed oil, which was optically inactive, possessed the following constants: Specific gravity, 20°/20° = 0.9233; acid value, 3.9; saponification value, 191.8; iodine value, 121.1. The composition of the oil was approximately as follows:

Linoleic acid, as glycerides,	45	per cent.
Oleic acid, as glyceride,	25	"
Palmitic acid Stearic acid } as glycerides,	30	"
	100	"

Of the two solid acids, the stearic acid is in predominating amount. The oil contains, furthermore, a very small amount of a phytosterol, $C_{20}H_{34}O$ (m. p. 163–164°). It is thus seen that this oil agrees very closely

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[1] THIS JOURNAL, 32, 351.

in composition with the expressed oil of pumpkin seed examined by us.[1]

II. *The "Press-cake."*—This material was extracted with hot alcohol, and in the resulting extract the presence of the following constituents was determined: (1) A quantity of fatty oil, corresponding to about 6 per cent. of the weight of the entire seed, and agreeing closely in character with that obtained by expression; (2) soluble protein products; (3) a quantity of sugar; (4) resinous material, amounting to about 0.3 per cent. of the weight of the entire seed. From the resin there were isolated a very small amount of a phytosterol (m. p. 158–159°), and a new alcohol, designated *cucurbitol*, $C_{24}H_{40}O_4$ (m. p. 260°), which yields an acetyl derivative melting at 150°. Cucurbitol appears to be closely related to two other crystalline alcohols recently isolated in these laboratories, namely, *grindelol*, $C_{23}H_{38}O_4$ (m. p. 256–257°), from *Grindelia camporum*, which yields an acetyl derivative melting at 161°, and *ipurganol*, $C_{21}H_{31}O_4$ (m. p. 222–225°), from jalap resin, which yields an acetyl derivative melting at 166–167°. These three alcohols are evidently members of a homologous series, which is represented by the general formula $C_nH_{2n-8}O_4$.

III. *The Shells.*—These amounted to 48.7 per cent. of the weight of the entire seed. They contained a quantity of fatty oil, which was similar in character to that obtained from the kernels by expression, but, in addition to the fatty acids obtained from the latter, a small amount of arachidic acid was isolated. The resinous material contained in the shells corresponded to about 0.3 per cent. of the weight of the entire seed, and from it, besides a mixture of fatty acids, very small quantities of a phytosterol (m. p. 138–140°) and *cucurbitol*, $C_{24}H_{40}O_4$, were separated. It was observed that these shells, like those of the pumpkin seed, contain traces of copper.

In order to ascertain whether the resin obtained from watermelon seed possesses any physiological activity, some tests were kindly conducted for us by Dr. H. H. Dale, Director of the Wellcome Physiological Research Laboratories. The resin, both from the kernels and the shells of the seed, was administered to a dog in amounts of one gram each, but no obvious effect was produced, and it may therefore be considered quite innocuous.

THE CONSTITUTION OF RETENE AND ITS DERIVATIVES.

By John E. Bucher.

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In the early part of the work in this laboratory on the condensation of aromatic propiolic acids to derivatives of 1-phenyl-2,3-naphthalene-

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[1] This Journal, 32, 358.