of blanks for each set of determinations. The high coefficient of expansion of glacial acetic acid, 0.00115 for 1° C., makes an appreciable error if a slight change of temperature takes place, as will be seen from the following table.

TABLE VII.

Temperature. °C.	40 cc. iodine monobromide in N/10 thiosulphate.
16.0	92.05
17.5	91.85
18.5	91.80
21.5	91.35
24.5	91.10
27.0	90.80
11° change	1.25 cc. decrease.

A change of ± 1° C. gives a change of $\mp$ 0.11 cc. in the amount of N/10 thiosulphate necessary to neutralize 40 cc. of the iodine solution, so that a blank titration of the iodine solution could easily vary 1 cc. N/10 thiosulphate in a day, which would completely vitiate the results.

DOES CHOLESTEROL OCCUR IN MAIZE OIL?

BY AUGUSTUS H. GILL AND CHARLES G. TUFTS.

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ACCORDING to Hoppe-Seyler[1] and to Hopkins,[2] cholesterol occurs in maize oil. As there is evidence of the occurrence of this substance in no other vegetable oil, except olive oil, this is interesting, and of possible importance as a means of detecting maize oil in mixtures with other oils. The statement of Hoppe-Seyler was made before this group of bodies was clearly differentiated, however, and the melting-point ascribed by Hopkins to the alcohol found by him in maize oil is not the true melting-point of cholesterol. The difference in the melting-points is shown below. Cholesterol, 146°-147°;[3] "cholesterol" from maize oil, 137°-137.5°.[3] Hopkins used no other means of identification except the color

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[1] *Bull. Soc. Chim* [2], **6**, 342 (1866); *Medicin.-chem. Untersuch.*, **1**, 162.

[2] This Journal, **20**, 948 (1898).

[3] Wislicenus and Moldenhauer: *Ann. Chem.* (Liebig), **146**, 179 (m. p. 147°); Reinitzer: *Monatsh. Chem.*, **9**, 422 (m p. 147.5°); Hesse: *Ann. Chem.* (Liebig), **192**, 177 (1878) (m. p. 145°-146°); Salkowski: *Ztschr. anal. Chem.*, **26**, 567 (m. p. 146°); Bömer: *Ztschr. Untersuch. Nahr. u. Genus.* (1898), p. 81 (average m. p. of fifty-two samples, 146.4°-147.3°).

reactions, which are not reliable. These considerations seemed to offer a field for investigation.

The method employed for isolating the compound was substantially that of Forster and Riechelman,[1] which consists in the extraction of the oil with 95 per cent. alcohol and separation of the substance sought from the saponified alcoholic solution. Four hundred grams of oil were extracted with 300 cc. of alcohol in successive portions of 100 cc. each, the oil being boiled half an hour with each portion in a liter flask provided with a reflux condenser. After cooling, each portion of alcohol was drawn off by a separatory funnel and the combined extracts were saponified by boiling two hours with 40 cc. of alcoholic soda 1 : 3. The greater part of the alcohol was then distilled and the residue, transferred to an evaporating dish, was carried to dryness on a water-bath. The dried and powdered soap was extracted with three portions of ether of 200 cc. each by shaking in a wide-mouthed stoppered bottle; after settling, the ether was decanted through a filter. The filtered extract was distilled and the residue purified by repeated recrystallization from alcohol.

In applying this method to different portions of oil, it was found that while extraction of the dry soap was tedious and attended by loss of ether and, furthermore, gave a product which was quite impure, the extraction of the aqueous solution of the soap was more rapid, more nearly complete and yielded at once a crystalline residue of a fair degree of purity. For a quantity of oil weighing 600 grams, good results were obtained by dissolving the soap in 250 cc. of water and extracting the solution with ether in 100 cc. portions; after four or five extractions the solution was found practically exhausted. It was found advantageous to distil from the alcoholic extract of the oil a considerable portion of the alcohol before saponification and to use alcoholic potash rather than soda. In this way pure characteristic crystals can be obtained without difficulty from 50 grams of oil.

In working with large quantities of oil, from 500 to 1800 grams, the extraction with alcohol was successfully carried out in an ordinary tin (gallon) can heated on a water-bath. A half-inch brass tube was soldered into the cover and connected by a short piece of stiff rubber tubing with a reflux condenser; the rubber

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[1] *Ztschr. für öffent. Chem.*, 3, 10.

tube was used to permit thorough shaking of the can during extraction. The cover was sealed by winding about it before insertion a string smeared with a dextrin paste.

Altogether about 4 kilos of maize oil were examined according to the method outlined above; based on the extraction of one portion of 600 grams, the yield of fully purified crystals was 0.22 per cent. These melted, when dried at 100°, at 138°-138.3°; when dried *in vacuo,* at 137.5°-138°; and after 18 months, at 128°-130°. To the naked eye the crystals from alcohol, appeared to be broad needles; under the microscope they were found made up of thin laminae much longer than broad and pointed at the ends.

From Raoult's method of molecular weight determination, results were obtained increasing with the concentration, showing association in benzene, the solvent used.

The acetate was made by boiling for one hour with an excess of acetic anhydride. The product was washed with water and then with hot alcohol. From the ethereal solution crystals were precipitated by alcohol, which, purified by recrystallization and dried at 100°, melted sharply at 127.1°; they seemed less soluble in alcohol than the corresponding substance obtained from olive oil.

The propionate was made like the acetate and was purified similarly. When dried at 100°, the crystals melted at 108.4°; they were more soluble in alcohol than were those of the acetate.

The benzoate was made by fusion with an excess of benzoic anhydride, the mixture being heated in an open tube to initial boiling. The product was boiled some minutes with alcohol and was then thrown on a filter and washed with boiling alcohol and with small portions of warm ether. The yield was small but there was no attendant discoloration and the crystals seemed pure. On crystallization from ether they formed oblong rectangular plates, often with re-entrant angles. The melting-point was 142°-142.5°.

The color reactions were as follows. In dilute chloroform solution, sulphuric acid produced a rather bluish pink, while the acid layer was yellow. In concentrated solution, the acid layer was yellow and the chloroform a blood-red which became purple on standing. In dilute acetic anhydride solution, sulphuric acid produced a clear green which, on standing, changed to a pure yellow. In concentrated solution the color was a deep bluish green, permanent for twenty-four hours. Though these reactions and those of the high-melting alcohols of wool grease are too much alike to be of value in analysis, the following differences were observed. On standing, the chloroform layer of Salkowski's test is blood-red with a concentrated solution of wool grease alcohol, and purple with the alcohol from maize oil. With Lieberman's test, in dilute solution, wool grease alcohol gives a bluish green which becomes reddish yellow on standing, while maize oil gives a clear green changing, on standing, to a yellow free from red.

The above results seem sufficient to prove that the alcohol of maize oil is not cholesterol. As shown by the following comparative table, the compound studied is undoubtedly identical with the compound found in wheat and rye and described by Burian under the name "Sitosterol."[1] It is also probably identical with the "Hydrocarotin" of Reinitzer.[2]

MELTING-POINTS OF SITOSTEROL AND ITS ESTERS.

Sitosterol.	From wheat.	From maize oil.	Hydrocarotin.
Sitosterol....	137.5°	138°	137.4°
" acetate.....	124.5°–127°[3]	127.1°	127.6°
" benzoate...	145.0°–145.5°	142.0°–142.5°	144°
" propionate .	108.5°	108.4°	....

SITOSTEROL, A POSSIBLE TEST FOR MAIZE OIL.

BY AUGUSTUS H. GILL AND CHARLES G. TUFTS.

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WHILE the presence of cottonseed oil in other oils is easily detected, the recognition of adulteration of cottonseed oil itself is less simple. The addition of many oils would be shown by their effect on the usual analytical constants, but with maize oil these values show so little divergence from those of pure cottonseed oil that detection of admixture is difficult. Since, however, maize oil contains sitosterol[4] while cottonseed oil contains phytosterol, it seemed that a test might be based upon this difference.

In the preceding article it was observed that the acetate of sitosterol from maize oil seemed rather less soluble in alcohol than

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[1] *Monatsh. Chem.*, 18, 551-574 (1897).

[2] *Ibid.*, 7, 597-608.

[3] Softened at 124.5° and melted at 127°.

[4] See the preceding article.