with naphthazarin. The analysis showed a deficiency of 1.4% of chlorine. We were unable to purify the product further.

We hereby wish to thank the Badische Anilin und Soda-Fabrik of Ludwigshaven on the Rhine for a very generous supply of sublimed naphthazarin.

Summary

1. Recent work shows that the hydroxyl groups in naphthazarin are para to each other and not ortho.

2. The following new derivatives of naphthazarin were prepared: 2,3,6,7-tetrabromonaphthazarin, its diacetate and dianilide; 2,3,6,7-tetrabromodiquinone and its dianilide.

3. The known dichloride of naphthazarin was also made from diquinol and likewise the known dibromonaphthazarin.

4. Certain unsuccessful reactions are noted.

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THE LOWER FATTY ACIDS OF COCONUT OIL

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The analysis of coconut oil has been carried out in a variety of ways, each of which has led to a widely different result. A full discussion of the subject is to be found in the paper of Armstrong, Allan and Moore,[1] in which it was clearly shown by these authors that fractionation of the esters of the acids can yield significant results only when the separation of the various components has been so complete as to yield these in substantially pure form, so that the saponification values of the intermediate fractions may legitimately be employed for the estimation of their composition. These authors conducted their fractionation on the ethyl esters obtained from not more than one kilo of coconut oil, and were unable to detect any acid lower than caprylic acid.

We have carried out a systematic fractionation on approximately 130 kilos of methyl esters obtained from commercial coconut oil[2] by a modification of the method of Haller and Youssoufian.[3] The fractionation was carried out repeatedly and systematically until the total amount of fractions intermediate between those of the pure components amounted to

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[1] Armstrong, Allan and Moore, *J. Soc. Chem. Ind.*, **44**, 63T (1925).

[2] This material was stated by its manufacturers (the Procter and Gamble Company) to have been prepared from copra of mixed origin but to be of representative quality.

[3] Haller and Youssoufian, *Compt. rend.*, **143**, 803 (1906).

less than 5% of the entire amount. No attempt was made to separate the esters of acids higher than myristic.

Distributing the components of the intermediate fractions pro rata according to the weights and boiling ranges of these, the results indicate the following composition: methyl caproate, 0.48%; methyl caprylate, 8.9%; methyl caprate, 5.7%; methyl laurate, 45.2%; methyl myristate, 16.5%; higher esters, 23.4%. The value for methyl myristate should be slightly higher than is indicated since its separation from the higher esters was not carried to completion. The above percentages are based on the final total weight, which was about 3% lower than that of the weight of the crude ester. The losses, which may be partially accounted for by the presence of alcohol, have thus been distributed through the series.

The purity of the individual esters was checked by determining the melting points of the acids prepared by hydrolysis of the appropriate fractions; in all cases satisfactory agreement with recorded values was obtained.

Attention is drawn to the presence of methyl caproate. Its identity was established by conversion of the free acid through its chloride into the amide, which possessed the same melting point as the amide prepared from synthetic caproic acid and showed no change of melting point on mixing with an authentic sample. The anilide also possessed the melting point recorded in the literature.

Since only 3 g. of distillate passed over below 151° (corr.), it may confidently be asserted that butyric acid is not present in detectable amounts in coconut oil.

Experimental

In 22-liter flasks were placed 8 kg. of coconut oil, 9600 g. of methyl alcohol and 500 g. of sulfuric acid. The mixture was refluxed for forty-eight hours on the steam-bath, allowed to cool to room temperature and the top layer of esters separated. The mixture of esters was placed in a 15 gal. crock and made just neutral to methyl orange with sodium carbonate solution, when 6 liters of a saturated salt solution was stirred into the mixture and allowed to settle. The bottom layer was siphoned off and discarded.

The crude ester (130 kg. from 136 kg. of coconut oil) was distilled under reduced pressure in 7–8 liter portions from a 12-liter flask fitted with a 24cm. column, dividing the distillate into five fractions. Fractionation of these was systematically carried out until the distribution of the various fractions shown in the table was reached. The final distillations of the lowest fractions were carried out under atmospheric pressure.

Samples of the esters were saponified; the resulting free acids showed the following constants: caproic acid, b. p. 204–206° (corr.); caprylic acid, m. p. 14–15°; capric acid, m. p. 30–31°; lauric acid, m. p. 42–43°; myristic

B. p., (corr.) °C.	Product, g.
To 151	3
151–153	534 (methyl caproate)
153–162	41
162–178	49
178–189	25
189–194	75
195–196	10800 (methyl caprylate)
196–199	171
199–204	76
204–210	83
210–215	76
215–220	96
220–226	116
226–232	164
232–234	6320 (methyl caprate)
234–242	170
242–249	254
249–260	164
260–	597

B. p. (corr.), °C. 7 mm.	Product, g.
121–124	344
124–126	55,153 (methyl laurate)
126–129	596
129–133	132
133–138	799
138–146	485
146–155	213
155–157	18,763 (methyl myristate, m. p. 16–17°)
157–162	786
162–167	895
167–	29,545

acid, m. p. 53–54°. A sample of the caproic acid was converted by means of thionyl chloride into the acid chloride and the crude product so obtained was added with stirring to concentrated ammonia held below 0° by the addition of ice. The precipitated amide, after washing with dilute ammonia and drying in air, melted at 93–95° and possessed a distinct odor of caproic acid. On recrystallization from toluene the odor was removed and the melting point rose to 98–99°. A sample of authentic caproic acid (prepared from *n*-butyl bromide by the malonic ester synthesis) yielded an amide which also melted at 98–99°.[4] A mixture of these two amides showed no change in melting point. Another portion of the chloride was converted into the anilide by adding it to a benzene solution of aniline. The benzene solution was washed with dilute acid and dilute alkali and concentrated, when it deposited crystals of the anilide which melted at 94.5–95.5°.[5]

Summary

Systematic fractionation of about 130 kilos of methyl esters of coconut oil acids has been carried out; the results give definite information as to the quantitative distribution of the various lower acids in the original oil. The following acids have been isolated: caproic acid (0.46%), caprylic acid (8.7%), capric acid (5.6%), lauric acid (45.0%), myristic acid (16.5–18%).

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[4] (a) Kelbe, *Ber.*, **16**, 1200 (1883), and (b) Hofmann, *Ber.*, **17**, 1411 (1884), give m. p. 100°; (c) Autenrieth, *Ber.*, **34**, 183 (1901), quotes 98°; (d) Robertson, *J. Chem. Soc.*, **115**, 1220 (1919), quotes 101°.

[5] Kelbe (ref. 4 a) gives m. p. 95°; Robertson (ref. 4 d) quotes 92°.