

DIBASIC ACID GLYCERIDES OF JAPAN WAX

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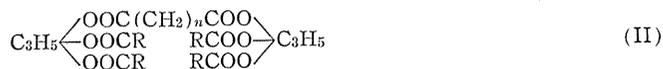
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Dibasic acid glycerides or glycerides containing dibasic acid group were formerly studied by A.C. Geitel and G. van der Want¹⁾ who separated a glyceride containing dibasic acid (Japanic acid) and palmitic acid groups in an equimolecular proportion. Afterwards, Lewkowitsch²⁾ assigned a formula of monomeric type (I) to this glyceride.



Tsujimoto³⁾ separated Japan wax glycerides by fractional adsorption on Japanese acid clay into various glyceride fractions including a fraction containing as high as 38.5% of dibasic acid in its total fatty acids, and indicated that dibasic acid glycerides of Japan wax appear not to be of the monomeric type (I), although the formula of dimeric type (II) can not be accepted in some respects.



where $\text{HOOC}(\text{CH}_2)_n\text{COOH}$ is dibasic acid; RCOOH is monobasic acid.

Kato and Nagano⁴⁾ fractionated Japan wax glycerides by fractional adsorption on activated charcoal and came to a conclusion that the dibasic acid glycerides of Japan wax are of the dimeric type (II), in which, however, a part of monobasic acid group has undergone hydrolysis resulting in the formation of free hydroxyl group in the glyceride molecule. On the other hand, Fujita⁵⁾ separated by fractional crystallization of Japan wax a dibasic acid glyceride containing dibasic acid ($\text{C}_{20}\text{H}_{38}\text{O}_4$) and palmitic acid groups in an equimolecular proportion and having M.P. $54^\circ\text{--}55^\circ\text{C}$ and saponification value 264.7 (calculated, 264.4). However, he did not touch upon the type of this glyceride—whether it is of the type (I) or of the type (II).

The present paper describes the results of our experiments relating to dibasic acid glycerides of Japan wax.

Experimental

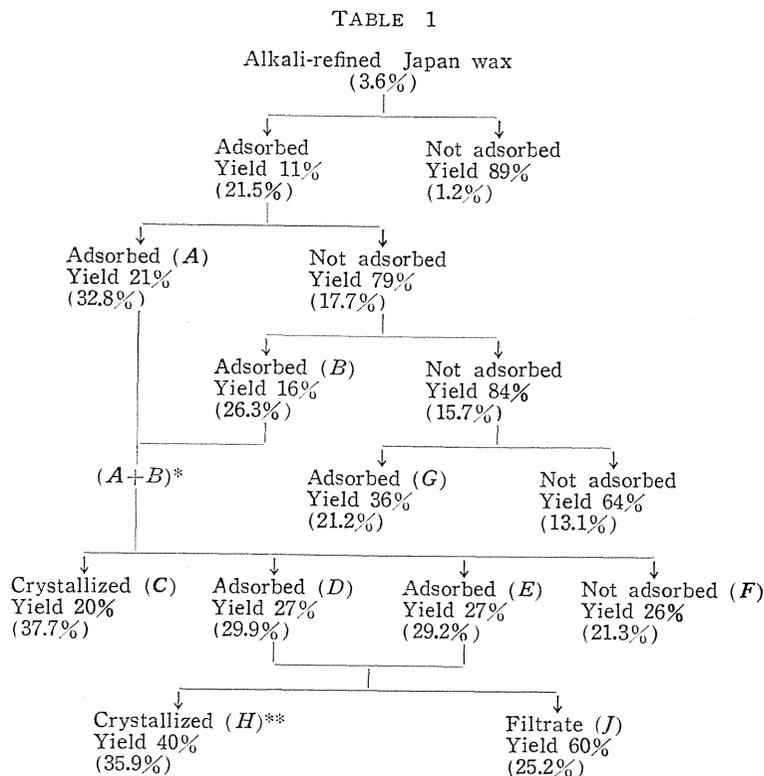
Bleached Japan wax of acid value 33.4 was used in these experiments. A mixture of 500 g of wax and one liter of 90% alcohol was neutralized with 1 N alcoholic potash at about 70°C , and then allowed to stand at about 60°C . The alcoholic layer separated was removed. The alcohol-insoluble portion was washed

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repeatedly with one liter of 90% alcohol, and finally freed from alcohol and water by heating on a water bath under vacuum. The alkali-refined wax thus obtained had the following constants. The dibasic acid was determined by the method of Tsujimoto⁶⁾ and expressed in percentage on the basis of the total fatty acids (not freed from unsaponifiable matter).

M.P. 56° C, A.V. 0.55, S.V. 210.1, I.V. 3.8, acetyl V. 9.6, Unsaponif. M. 0.76%, dibasic acid 3.6%.

Ten g of alkali-refined wax was dissolved in 200 cc of benzene, and the solution was allowed to pass slowly into a glass tube of 2 cm in diameter and 25 cm in length uniformly filled with 60 g of activated clay. One hundred cc of benzene was subsequently passed into the tube in order to wash the activated clay. The benzene solution and the benzene washing coming out from the bottom of the tube were



*: Two parts of the fraction (A) and one part of the fraction (B) were united, and the mixture was recrystallized from petroleum ether giving the fraction (C). The portion recovered from the mother liquor of recrystallization was dissolved in benzene and subjected to fractional adsorption on alumina. The fractions (D) and (E) were obtained from the upper and lower portions of alumina column, respectively, and the fraction (F) from the benzene solution coming out from the bottom of the alumina column. Molecular weights determined by the Rast method were found to be about 1,100 for both the fractions (D) and (E) and about 950 for the fraction (F).

** : The fractions (D) and (E) were combined, and recrystallized from petroleum ether, giving the fractions (H) and (J).

united and the material remaining dissolved in the solution was recovered by distilling off benzene. The activated clay in the tube was dried and extracted with ether. The ether solution was washed first with a solution of sodium carbonate and then with water, and the ether was distilled off. On repeating these operations on each 10 g batch, 290 g of alkali-refined wax in total was separated into the portion adsorbed on activated clay and the portion not adsorbed. The portion adsorbed was subjected further to fractional adsorption and fractional crystallization as shown in Table 1. The figures in the parentheses in Table 1 denote the content of dibasic acid in each fraction.

On recrystallizing the combined fractions of (*C*) and (*H*) ten times from petroleum ether and acetone, there was eventually obtained a fraction (*K*) of M.P. 55° C, S.V. 224.4, acetyl V. 90.5, Unsaponif. M. 1.9%, dibasic acid 37.7% and Mol. Wt. (Rast) about 1,400. Thus the content of dibasic acid was not noticeably raised even after repeated recrystallizations.

Recrystallization of the combined fractions of (*F*) and (*G*) from petroleum ether yielded a fraction (*L*) of M.P. 51° C, S.V. 221.4 and dibasic acid 26.8%. A comparative determination of the viscosities (expressed in numbers of second) of this fraction and several kinds of solid fats by the capillary method gave 1,386 for this fraction, 356 for hydrogenated fish oil, 377 for hydrogenated cotton seed oil and 366 for alkali-refined Japan wax, indicating that this fraction has a very high viscosity as compared with ordinary solid fats.

Discussion of Results

Taking the dibasic acid component of the dibasic acid glycerides of Japan wax as docosanedioic acid $C_{20}H_{40}(COOH)_2$, and the monobasic acid component as palmitic acid $C_{15}H_{31}COOH$, molecular weights, saponification values, acetyl values, and contents of dibasic acid in the total fatty acids for several members of dibasic acid glycerides are given in Table 2.

TABLE 2

Dibasic acid glyceride	Mol. Wt.	S.V.	Acetyl V.	Dibasic acid (%)
(1) Dimeric; 1 dibasic acid and 4 palmitic acid groups	1,472	228.6	0	26.5
(2) Dimeric; 2 dibasic acid and 2 palmitic acid groups	1,330	253.1	0	59.1
(3) Monomeric; 1 dibasic acid and 1 palmitic acid groups	665	253.1	0	59.1
(4) Dimeric; 1 dibasic acid and 3 palmitic acid groups; 1 free hydroxyl group	1,234	227.3	44.0	32.5
(5) Dimeric; 1 dibasic acid and 2 palmitic acid groups; 2 free hydroxyl group	996	225.4	103.9	41.9

The fraction (*K*), if based on the content of dibasic acid, corresponds to a mixture of the glycerides (1) and either (2) or (3), but its saponification value is a little lower than that of the glyceride (1). Even if the presence of unsaponifiable matter in the fraction (*K*) is taken into consideration, the saponification value of the glyceride constituting the fraction (*K*) appears to be too low to regard the fraction (*K*) as a mixture of the glycerides (1) and either (2) or (3). Furthermore,

the molecular weight of the fraction (K) appears scarcely to permit the occurrence of the glyceride (3) in the fraction (K). As noted by Kato and Nagano⁴⁾ on the dibasic acid glyceride separated by them, it is reasonably concluded from a remarkably large acetyl value of the fraction (K) that the fraction (K) consists mainly of the glycerides (4) and (5) having free hydroxyl group in their molecules.

Referring to the fraction (L), it is difficult to draw a definite conclusion on its composition because of the lack of data on its acetyl value and unsaponifiable matter. However, a remarkably high viscosity of this fraction as compared with those of ordinary solid fats seems to indicate that this fraction also consists chiefly of glycerides of dimeric type.

The glycerides reported by Geitel and van der Want¹⁾ and Fujita⁵⁾ which contains dibasic acid and palmitic acid groups in an equimolecular proportion without having free hydroxyl group may naturally occur in Japan wax, but it was not separated in our experiments. The glyceride of this type is inferred to be of dimeric type from the fact that many of the glyceride fractions obtained in our experiments containing relatively large proportions of dibasic acid group showed high molecular weights.

Summary

Glycerides of Japan wax were fractionated by fractional adsorption and fractional crystallization. On examining fractions consisting of dibasic acid glycerides, it was concluded that the dibasic acid glycerides of Japan wax consist mainly of the glycerides of dimeric type which have free hydroxyl group in their molecule and are formed by a partial hydrolysis of monobasic acid group from the glycerides of dimeric type containing one dibasic acid group and four monobasic acid groups. Dibasic acid glycerides which are not hydrolyzed at all may naturally occur in Japan wax, but such glycerides are also considered to be of dimeric type.

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