ON THE DIBASIC ACIDS IN JAPAN WAX.

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Japan wax is obtained in Japan exclusively from the berries (mesocarps) of "Hazé-noki," *Rhus succedanea L.* (Anacardiaceae). The statement often mentioned in foreign books that the wax is prepared from many species of the genus Rhus is erroneous. *Rhus succedanea* grows chiefly in the southwestern parts of the country, and so the wax industry is conducted in Kiushiu and Shikoku. Formerly in more northern parts of the country, "Urushi" wax was prepared from the berries of *Rhus vernicifera L.*, but this industry has now nearly ceased to exist. The production of Japan wax has appreciably diminished than in former times; nevertheless it is one of the most important fats produced in Japan.

It is strange to note that the chemical examination of Japan wax has but rarely been undertaken by native chemists; in 1911 the author(1) reported experiments on the general properties and chemical composition of the wax, and recently I. Sakuma(2) made an extensive investigation on the colouring matter and the bleaching of the wax.

The discovery of a dibasic acid in Japan wax is due to L. E. Eberhardt,(3) who observed the occurrence of an acid (m.p. 117.5°C.) belonging to the oxalic acid series and assigned to it the chemical formula $C_{18}H_{36}(CO_2H)_2$. In 1900 A. C. Geitel and G. van der Want(4) made a closer study on the chemical composition of Japan wax. On dissolving the insoluble fatty acids in alcohol, and fractionally precipitating the acids with magnesium acetate in hot solution, they obtained an acid of m.p. 117°C., palmitic acid, and impure oleic acid. They named the high melting acid "japanic acid" ("Japansäure"), and by the determination of neutralisation value, etc., confirmed its formula to be $C_{20}H_{40}(CO_2H)_2$. Further they described the separation of the acid as potassium salt, the formation of a ketone $C_{20}H_{40}CO$ (m.p. 82–83°C.) from it on strong heating, and also the probable occurrence of the acid as a mixed glyceride with palmitic acid in the wax. R. Schaal(5) fractionated the Japan wax fatty acids under diminished pressure and obtained

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(1) *J. Soc. Chem. Ind. Japan,* **14** (1911), 321.

(2) Scientific Report of Kiriu Higher Technical School, No. 3 (1929).

(3) Diss. Strasburg, 1888.

(4) *Z. prakt. Chem.,* **61** (1900), 151.

(5) *Ber.,* **40** (1907), 4784.

homologues of higher dibasic acids. The chief acid was $C_{19}H_{38}(CO_2H)_2$ (m.p. 117–117.5°C.), but $C_{18}H_{36}(CO_2H)_2$ and $C_{17}H_{34}(CO_2H)_2$ were also present. E. Tassily⁽¹⁾ also fractionated the methyl esters of Japan wax fatty acids and identified japanic acid, $C_{21}H_{40}O_4$, and two lower homologues.

The present author⁽²⁾ isolated high melting acids (m.p. 119–121°C.), which he considered to consist mainly of japanic acid, and calculated its amount in the wax as ca. 2%. It should be noted that the melting points of these acids were far higher than those mentioned in the literature, but at that time no further experiment was performed as to their chemical composition. At present even in the standard works on fats and oils, the formula for so-called japanic acid is somewhat indefinite, either $C_{21}H_{40}O_4$ or $C_{22}H_{42}O_4$ being adopted.

The experiments described in this paper are the continuation of the investigation made some twenty years ago. The result shows that the main constituent of the dibasic acids in Japan wax is heneicosane dicarboxylic acid. $C_{23}H_{44}O_4$, accompanied probably by eicosane dicarboxylic acid, $C_{22}H_{42}O_4$.⁽³⁾ Further a peculiar property of Japan wax dibasic acids is mentioned.

Experimental Part.

(I) Matetial. The samples of Japan wax were procured from Higo Seirô Kaisha (Higo Wax Manufacturing Company) of Kumamoto, Kiushiu. Nine samples of raw or fresh wax (Ki-rô)⁽⁴⁾ and one sample of bleached wax (Sarashi-rô) were used. Among others the following three samples were chiefly used.

(1) No. 1. New berry wax; pale brownish yellow colour.
(2) No. 2. Old berry wax; colour nearly the same as No. 1.
(3) No. 3. New berry wax; brownish yellow colour.

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(1) *Bull. Soc. Chim.*, Bd. **9–10** (1911), 608.

(2) Loc. cit.

(3) After the present paper (in Japanese) had been published in the Report of Tokyo Imperial Industrial Laboratory, Vol. 25, No. 4 (1930), I have noticed the investigation of B. Flaschenträger and F. Hall (*Chem. Zentr.*, 1930, Bd. II, 2761). The result obtained by them agrees in many respects with that of my experiments.

(4) "Ki-rô" is the name given to an unbleached, raw or fresh Japan wax. When the berries of *Rhus succedanea* are stored, the colouring matter in them become gradually insoluble in the wax in the preparation. The wax obtained from new or fresh berries has usually a dark brown colour, and is called "Shinmi-rô" (new berry wax). The wax from the berries stored beyond the next rainy season in this country (June to July) is called "Komi-rô" (old berry wax), and has a far lighter colour. Notwithstanding many disadvantages, it is customary for the wax manufacturers to keep the berries until they become "Komi" (old berry). Sometimes they are stored for several years. Then they are called "Ô-komi" (literally "great" old berry, "Ô" is used here in the sense of "very"); the wax from them, "Ô-komi-rô", has the lightest brownish or greenish yellow colour.

Characteristics, etc. of the Waxes.

	No. 1.	No. 2.	No. 3.
d_4^{100}	0.8626	0.8627	0.8620
M.p.	52–52.5°	49.5–50°	50–50.5°
Acid value	4.5	7.8	3.1
Saponif. value	205.7	207.5	206.7
Iodine value (Wijs)	18.8	17.5	20.2
Hehner value	94.56	94.64	95.14
Unsaponif. matter	0.60%	0.60%	0.51%

The fatty acids⑴ gave the following numbers:

	No. 1.	No. 2.	No. 3.
M.p.	59–59.5°	60.5–61.5°	60–61°
Neutralisation value	213.2	212.3	210.5
Iodine value (Wijs)	19.5	17.8	19.9

The comparatively high iodine values are due to the admixture of the kernel oil of the berry. The iodine values of many samples of the wax formerly determined by me ranged 10.3–13.8. The characteristics of Japan wax cited in foreign books are usually those which were determined on the bleached wax. As by bleaching process (insolation), fairly profound changes of the composition occur, the numbers are quite different from that of the genuine wax.

(II) Approximate Quantitative Determination of the Dibasic Acids. As japanic acid appears not the only dibasic acid in Japan wax, this name is reserved for a while, and "Japan wax dibasic acids" or simply "dibasic acids" are used in the following description. To investigate the dibasic acids, it is firstly most important to know at least their rough amount in the wax. By utilizing their difficult solubility in petroleum ether, the author has devised the following procedure as the approximate determination of these acids.

About 1 gr. of the Japan wax fatty acids is accurately weighed in a small flask, and 50 c.c. of petroleum ether (b.p. until 80°C.) are added. The flask is repeatedly immersed in a water bath at 40–50°C., and shaken to dissolve the acids.⑵ It is necessary to cork the flask to prevent the evaporation of petroleum ether, but the cork is often removed to diminish the internal pressure caused by the expansion of the solvent. The main part of the dibasic acids remains as a fine precipitate. The flask is next cooled in ice-water for 30 minutes, thereby the dibasic acids are completely

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(1) In this report, the "fatty acids" mean the insoluble acids plus unsaponifiable matter.

(2) This warming is necessary in order to disintegrate the mass of the acids. By direct treatment of the acids with petroleum ether at 25°C, there is some possibility that a part of palmitic acid remains enveloped in the dibasic acids.

precipitated together with palmitic acid. Then the flask is put in water at 25°C. for one hour with frequent shaking. By this treatment the precipitated palmitic acid is again dissolved in petroleum ether leaving the dibasic acids. The solution is filtered through a tared Gooch crucible(1) kept at about 25°C. by suitable arrangement. As the dibasic acids are deposited as a colloid-like state, the filtration presents some difficulty. The liquid is finally sucked with a pump, and the precipitate washed three times with each 5 c.c. of petroleum ether. The crucible with the precipitate is dried at 90°C. to a constant weight. As it is difficult to transfer all the precipitate to the crucible, a portion of the dibasic acids adhering to the flask is weighed separately, and its weight is added to that of the main part.

The dibasic acids are slightly soluble in petroleum ether; for example, 100 c.c. of the latter (b.p. until 80°C., d_4^{25} 0.6493) dissolve 0.0045 gr. of the acids (refined specimen) at 25°C. As the above method has been proposed only as a rough determination, no correction is made for the loss caused by this solubility. Moreover, oxidised acids, colouring matter, and other impurities are also precipitated, and these would make the apparent weight of the dibasic acids rather higher.

By the above mentioned concentration, palmitic acid does not deposit even when the solution is cooled to 20°C., so that more or less lowering of temperature on filtering is of no consequence. Also sterol in the unsaponifiable matter does not precipitate by this treatment.

In a test made with a sample of a known composition (palmitic acid 80%, oleic acid 15%, dibasic acids 5%), it was found that the dibasic acids can be determined with an error of about within 0.5%. So the method is sufficient satisfactory for the approximate determination of these acids. The results obtained on a number of commercial unbleached Japan wax are given in the following table:

Waxes	Data	Percentage of the dibasic acids in the fatty acids
No. 1	Samples mentioned above	5.6
,, 2		5.9
,, 3		5.2
,, 4	Kumamoto; old berry	6.0
,, 5	Saga; new berry	6.1
,, 6	Nagasaki; new berry	5.7
,, 7	Kagoshima; "Ô-komi"	5.9
,, 8	,, ; new berry	5.3

N. B. No. 7 is free from the kernel oil; it had the iodine value 12.5.

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(1) As filtering materials, a filter paper (its circumferential part pasted to the bottom of the crucible) and asbestos fibres are used.

Besides the above samples, a wax from the Prefecture of Kumamoto was found to contain 7.2% of the dibasic acids. This rather abnormally high content is probably due to the difference of the variety of "Haze" tree. To determine the acid content in genuine wax prepared in the laboratory, a sample of the wax was extracted from the mesocarps of new berries from a district of Kiushu, and it was treated with animal charcoal. The fatty acids from this wax contained 5.2% of the dibasic acids. The latter melted at 107–108°C and had the neutralisation value 288. So they consisted of nearly pure compounds.

By calculating from the Hehner value (mean 94.7), the contents of the dibasic acids in the Japan waxes mentioned in the above table amount to 4.9–5.8%. It will be seen from the above that the amount of the dibasic acids in Japan wax is far greater than hitherto considered.

In the case of bleached wax, the method could not be recommended, since oxidised acids produced by insolation are difficultly soluble in petroleum ether. An experiment gave the number 6.5%, which appeared to be somewhat high.

(III) Preparative Separation of the Dibasic Acids. Geitel and van der Want separated so-called japanic acid by utilizing the difficult solubility of its potassium salt in alcohol.(1) The mixed fatty acids are dissolved in 95% alcohol so as to form 10% solution, and the solution is neutralised with alcoholic potash. The potassium salt of the dibasic acid separates as a precipitate. The solution is then filtered in a hot funnel at 50–62°C., thereby the salt remains on the filter. This is finally decomposed with hydrochloric acid. The drawbacks of this method are the necessity of neutralising the total acids, the difficulty of filtration owing to colloidal nature of the precipitate, and bad yield.

It is clear that the dibasic acids may be prepared in some quantity by applying the procedure of the above mentioned determination on a large scale, but obviously a very large amount of the solvent is required. However, on extracting the mixed fatty acids in a Soxhlet apparatus, about 2% of the crude dibasic acids may be obtained as an insoluble residue. After several trials, the author recommends the following methods as preparative separation in laboratory.

(1) Separation by means of Lead Salt. The dibasic acids are fractionally precipitated with a calculated quantity of lead acetate in alcoholic solution.

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(1) The salt is readily soluble in dilute alcohol.

10 Gr. of Japan wax fatty acids are dissolved in 100 c.c. of 95% alcohol. To this solution is added a solution of 0.6 gr. of lead acetate (which corresponds to about 7% of the dibasic acids) in 10 c.c. of the alcohol. The mixed solution is warmed on a water bath to above 70°C., and then rapidly filtered on a hot funnel kept a little above 70°C. The precipitate on the filter is returned to the flask, and treated with 20 c.c. of the alcohol and filtered as before. The precipitate is then decomposed with hydrochloric acid.

The lead salt of palmitic acid is soluble in 95% alcohol at 70°C. The repetition of the treatment is to remove palmitic acid as completely as possible from the precipitate. By this method, about 5.6% of the crude dibasic acids were obtained from the fatty acids of the wax No. 3.

Instead of lead, the salts of alkaline earths, magnesium, or zinc may probably be used. Indeed, Geitel and van der Want used magnesium acetate for such purpose. Sodium salt was found to be unsuitable.

(2) *Separation by means of the Distillation of Esters.* This is of course not novel, since it was already applied by Tassily, but the method is most convenient for preparative purpose. The following is an example.

1000 Gr. of Japan wax are heated with 1000 gr. of methanol containing 2.5% of HCl on a water bath for 12 hours to ensure methanolysis. The methyl esters are liquid in summer season. They are distilled under 5–5.5 mm. pressure until the temperature rises to 185°C. (bath temperature 230°C.) thereby more than 80% of the esters distil over. The residue which contains the dibasic acids is saponified, and the free acids are extracted in a Soxhlet apparatus with petroleum ether to dissolve admixed palmitic and oleic acids. An experiment by this method gave 50 gr. or 5% of the crude dibasic acids.

The reason why the distillation is interrupted at 185°C., is to avoid the decomposition of the acids by overheating. But in the experiments made recently, the distillation was carried out up to 205°C/3 mm. without apparent defect, so that more than 90% of the distillate were obtained. It seems also that the distillation may even be continued up to higher temperatures, until the esters of the dibasic acids themselves distil over. In this case, however, there is much fear for decomposition, especially if the esterification is not complete, and the quantity is large.

Technically it will be most simple to distil the free fatty acids, but particular care should be necessary, since if we accept the statement of Geitel and van der Want, japanic acid forms a ketone at high temperature.

(IV) On the Chemical Composition of the Dibasic Acids. It has been described in the introductory remark that the chemical formula of japanic acid is somewhat indefinite, either C_{21} or C_{22} formula being adopted. It is rather doubtful too whether there occur in reality the homologues of japanic acid in Japan wax. It should also be noted that the samples of the foreign investigators appear to have been bleached waxes, which certainly must have contained many impurities formed by bleaching process. In view to obtain the dibasic acids more easily free from such impurities, the author made experiments on raw or fresh, unbleached waxes.

(*1*) *Experiment 1.* Firstly the dibasic acids were separated according to the classic method of Geitel and van dar Want. The temperature of filtration was kept at 55–60°C. It has been observed that the potassium salt remains dissolved at above 70°C., but the solution becomes turbid at 65°C., and an appreciable precipitate is formed already at 62°C.

About 3 gr. of the salt were obtained from 100 gr. of the fatty acids of the wax No. 1. After thrice recrystallisation, the free acids melted at 119–120°C., and had the neutralisation value 294.4⁽¹⁾

Anal. Subst. = 0.1082; CO_2 = 0.2854; H_2O = 0.1126 gr. Found: C = 71.94; H = 11.65%.

The substance corresponded, therefore, mainly to $C_{23}H_{44}O_4$. The m.p. was higher than those recorded in the literature.

The calculated numbers for the high members of the dibasic acids are as follows:

	Mol. wt.	Neutr. value	C (%)	H (%)
$C_{21}H_{40}O_4$	356.3	315.0	70.72	11.31
$C_{22}H_{42}O_4$	370.3	303.0	71.29	11.43
$C_{23}H_{44}O_4$	384.3	292.0	71.81	11.54

(*2*) *Experiment 2.* 50 Gr. of the fatty acids of the wax No. 3 were treated by the lead salt separation method, and the crude dibasic acids were decolourised with animal charcoal; yield, 2.8 gr. After thrice recrystallisation from alcohol, the purified acids (0.8 gr.) formed white crystals of m.p. 119–120°C. and the neutralisation value 288.9.

Anal. Subst. = 0.1287; CO_2 = 0.3385; H_2O = 0.1350 gr. Found: C = 71.73; H = 11.74%.

The mother liquor gave on concentration 0.9 gr. of white crystals; on washing with petroleum ether, they melted at 111–112°C., and had the neutralisation value 287.3.

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(1) In alcoholic solution, the potassium salt separates out as a precipitate. In order to observe the accurate end of titration, the addition of a little water to dissolve it is necessary.

So the result of the analysis and the neutralisation values of these substances corresponded to those of $C_{23}H_{44}O_4$.

(*3*) *Experiment 3.* By the procedure mentioned in the ester distillation method (until 185°C./5 mm.), 48.5 gr. of the crude product were obtained from 1000 gr. of the methyl esters of the wax No. 2. This was dissolved in 95% alcohol, treated with animal charcoal, and then recrystallised from about 10 times of its quantity of the alcohol. The crystals were separated into two parts : first crop (A), 20 gr., m.p. 114–115°C., and second crop (B), 19 gr., m.p. 112–113°C. The crystals were very fine, and presented difficulty on filtration.

(a) Purification by Recrystallisation. The crude acids were purified by repeated recrystallisation from 95% alcohol.

(1) Purification of the Part A. At the beginning, 5 gr. of it were crystallised from 100 c.c. of the alcohol. The recrystallisation was repeated six times, using about 20 times of alcohol for each crop of crystals.

	M.p.	Neutr. value⁽¹⁾
1st recrystallisation	115°	—
2nd ,,	116–120°	285
3rd ,,	117–120°	286
4th ,,	121–122°	290
5th ,,	122–123°	288
6th ,,	122–123.5°	289

After 3rd recrystallisation, the m.p. became almost constant. The neutralisation values corresponded nearly to that (292.0) of $C_{23}H_{44}O_4$.

Two analyses of the last (6th) substance were as follows :

Subst. = 0.1190 and 0.1282; CO_2 = 0.3107 and 0.3343; H_2O = 0.1226 and 0.1353 gr.
Found: C = 71.21 and 71.12; H = 11.53 and 11.81%.

The results corresponded to $C_{22}H_{42}O_4$ rather than $C_{23}H_{44}O_4$. But judging from the neutralisation value, the substance has been considered to consist mainly of $C_{23}H_{44}O_4$.

(2) Purification of the Part B. 5 Gr. of the substance were recrystallised.

	M.p.	Neutr. value
2nd recrystallisation	109–109.5°	288
3rd ,,	112–113.5°	290

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(1) The saponification values of these compounds were usually a little higher, but as errors may more likely be involved in the determination, they were omitted in this paper.

Although the m.p. was low, the neutralisation value corresponded to $C_{23}H_{44}O_4$.

(b) Purification by the Fractional Distillation of the Esters. As by the purification by crystallisation, there may be some doubt as to the individuality of the compound obtained, the substance was esterified and fractionally distilled under diminished pressure. The methyl ester was prepared by heating the substance with an excess of methanol (containing HCl) for 3 hours on a water bath.

(1) Distillation of the Ester of the Part A. 14.8 Gr. were distilled under 5 mm. pressure. The distillation began at the temperature 270°C. (last temp. 280°C.). The distillates formed white crystalline solids.

Dist. temp.	Yield (gr.)	M.p.	Solidif. p.	Saponif. value
(1) Until 240°	2.9	54.5°	—	269
(2) 240–250°	7.7	56.3°	ca. 55°	274
(3) 250–252°	2.1	57.8°	ca. 56.5°	275
(4) Residue	1.7	—	—	—

The following are the calculated numbers for the methyl esters of C_{21} to C_{23} dibasic acids:

	Mol. wt.	Saponif. value
$C_{21}H_{38}O_4(CH_3)_2$	384.3	292.0
$C_{22}H_{40}O_4(CH_3)_2$	398.4	281.7
$C_{23}H_{42}O_4(CH_3)_2$	412.4	272.1

The saponification values of the above distillates nearly corresponded to that of the C_{23} formula.

The free acids obtained by saponification from the distillates had the following properties:

	M.p.	Solidif. p.	Neutr. value
Acid from fraction (1) (Once recrystallisation from alcohol)	113–114°	—	293
Acid from fraction (2) (Twice recrystallisations from alcohol)	Mainly liquid at 118°; became clear at 121°	Became turbid at 111°; solidified at 109°	292
Acid from fraction (3) (Twice recrystallisations from alcohol)	Liquid at 122; clear at 123.5°	Deposited crystals at 116°; solidified at 114°	293

Anal. of the acid from (3). Subst. = 0.1348; CO_2 = 0.3516; H_2O = 0.1390 gr.
Found: C = 71.14; H = 11.54%.

All the neutralisation values corresponded to that of $C_{23}H_{44}O_4$, but the result of the analysis approached rather to the C_{22} formula.

The free acid from the distillation residue melted after purification at 117°C., and showed the neutralisation value 265. This value nearly corresponded to that (263.2) of $C_{26}H_{50}O_4$. The actual occurrence of such an acid in the wax is, however, very doubtful.

(2) Distillation of the Ester of the Part B. 14.5 Gr. were used. The distillation (5mm.) began at the bath temperature 258°C. (last temp. 280°C). The distillates were white crystals.

Dist. temp.	Yield (gr.)	M.p.	Solidif. p.	Saponif. value
(1) Until 240°	5.8	50.8°	—	260
(2) 240–251°	7.1	56°	ca. 54°	275
(3) Residue	1.0	—	—	—

The fraction (1) seemed fairly impure. The saponification value of (2) nearly corresponded to that of the C_{23} formula.

The properties of the free acids obtained from the distillates were examined:

	M.p.	Solidif. p.	Neutr. value
Acid from fraction (1) (Once recrystallisation)	115–116°	—	286
Acid from fraction (2) (Once recrystallisation)	113–113.5°	—	299
Acid from fraction (2) (Twice recrystallisations)	114°	ca. 104°	303

The acid from the fraction (1) had unexpectedly higher m.p. than that from (2). In spite of the fact that the saponification value of the latter fraction nearly corresponded to that of the C_{23} formula, the neutralisation value of its free acid coincided to that (303.0) of $C_{22}H_{42}O_4$.

From the results of the distillation, it appeared that the acids in the part A mainly consisted of $C_{23}H_{44}O_4$, while those of the part B contained an appreciable amount of $C_{22}H_{42}O_4$.

Summarising the results of the experiments made on the composition of the dibasic acids, it has been concluded that the main constituent of the acids is $C_{23}H_{44}O_4$, but probably the acid $C_{22}H_{42}O_4$ also occurs in a fair proportion. It seems rather doubtful that the acids of consecutive even and odd numbers occur in one and same wax, but actually no proof has been obtained to negate it, inasmuch as there is no sufficient ground to consider $C_{22}H_{42}O_4$ to be a mixture of $C_{21}H_{40}O_4$ and $C_{23}H_{44}O_4$, and still less to presume $C_{23}H_{44}O_4$ as a mixture of $C_{22}H_{42}O_4$ and $C_{24}H_{46}O_4$.(1)

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(1) The dibasic acids in Urushi wax appears to consist chiefly of $C_{22}H_{42}O_4$.

(V) On a Peculiar Property of the Dibasic Acids. In the experiments on the dibasic acids, the author has observed the following interesting facts:

1. The structure of the solidified Japan wax fatty acids is very fine, and in spite of its brittleness, it has still a peculiar coherency and tenacity.

2. When freed from the dibasic acids, the crystals of the fatty acids became large and coarse, and nearly lose the coherency and tenacity.

As a matter of fact, by adding the dibasic acids, the fatty acids regained their original properties. To observe more closely the effect of the addition on various fatty and waxy substances, the following experiments were performed. The dibasic acids used in these experiments melted at 118–119°C., and had the neutralisation value 294; the structure was observed after well cooling of the melted mass.

(1) Japan wax fatty acids freed from the dibasic acids. M.p. 56.5°C.; markedly crystalline with various speckled structure. To them were added:

(a) Dibasic acids 1%. Crystals became finer, but still pretty crystalline.

(b) Dibasic acids 2%. Very fine crystals; became totally homogeneous mass; whiteness (opacity) increased. M.p. 60°C.(1)

(2) Palmitic acid. Coarse, needle-shaped crystalline mass (markedly on the surface).

(a) 2% Addition. Crystals became fairly fine, and the surface smoother.

(b) 5% Addition. Became fine, white crystalline mass with a waxy smooth surface.

(3) Stearic acid. The effect was greater than in the case of palmitic acid.

(4) Hardened herring oil. M.p. 54°C.; this had originally a fine crystalline structure, but the 2% addition made its appearance more waxy.

(5) Fatty acids from the hardened herring oil. M.p. 53.-54°C.; also a fine crystalline structure; the 2% addition had a pretty effect, but not so marked.

(6) Hardened sperm oil. M.p. 54°C.; coarse, beautiful crystalline structure.

(a) 1% Addition. Crystals became finer, and opacity increased.

(b) 2 %Addition. A marked effect; became a very fine crystalline, homogeneous structure.

(7) Paraffin. M.p. 52°C.; had a marked transparency.

(a) 2% Addition. Crystals became finer, and opacity (whiteness) increased.

(b) 4% Addition. Became a markedly white, homogeneous structure.

Thus it may be observed that the dibasic acids have a peculiar property to make the crystalline structure of fatty and waxy substances finer and more opaque; they also give to the substances a certain coherency and tenacity. Nor do the added acids separate out from the mass on long keeping.

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(1) The addition did not materially raised the m.p.; so in the following the description of the m.p. of the mixtures is omitted.

In the literature on fats, we find as the "hardening agent" ("Härtungsmittel") for candle materials, such substances as sebacic acid and stearic anilide. According to the author's experiments, they are, however, far less effective than the Japan wax dibasic acids. The same is true for dihydroxystearic acid.

A characteristic property of Japan wax that it may be kneaded between fingers to a "mochi" (rice-cake)-like mass without adhering, is due to the presence of the dibasic acids as glycerides. Many other solid fats, for instance, hardened fish oils, are usually brittle, and at the same time become very sticky and unpleasantly adhere to the fingers.

The fact that the glycerides of the dibasic acids are really responsible for this property, has been experimentally proved by the author by synthesizing two fats from the following fatty acid compositions by heating them with the equivalent parts of glycerol in sealed tubes to 200–205°C.:

(a) Palmitic acid 80; oleic acid 15 parts.

(b) ,, ,, ,,; ,, ,, ,,; dibasic acids 5 parts.

Whereas the fat from (a) was brittle and sticky, that from (b) exhibited nearly the same property as Japan wax.(1)

This peculiar property could not be considered to be specific to the dibasic acids of Japan wax, but probably it will be common to the higher members of the dibasic acids. Possibly this property of the dibasic acids may find applications in industry.

Summary.

(1) As "japanic acid" of Geitel and van der Want appears not the only dibasic acid in Japan wax, this name has been reserved for a while, and the expression of the "Japan wax dibasic acids" or more simply the "dibasic acids" is used in this paper.

(2) Basing on the difficult solubility of the dibasic acids in petroleum ether, a method for their approximate determination has been proposed. The results obtained by this method show that the content of the dibasic acids in the mixed fatty acids of Japan wax amounts to 5–6%, which are far greater than hitherto considered.

(3) For the preparative separation of the dibasic acids, the lead salt precipitation method and the ester distillation method have been found to be most convenient.

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(1) The synthesized fats appeared to consist chiefly of diglycerides, but the effect of the dibasic acids as glycerides may be recognized as proved.

(4) As the results of the chemical examination of the dibasic acids, it has been concluded that the main constituent of the acids is heneicosane dicarboxylic acid, $C_{23}H_{44}O_4$, but probably eicosane dicarboxylic acid, $C_{22}H_{42}O_4$, also occurs in a fair proportion.

(5) As a peculiar property of the dibasic acids, it has been found that the comparatively small addition of them to fatty and waxy substances makes the crystalline structure of these substances finer and more opaque, and at the same time gives certain coherency and tenacity.

(6) The characteristic property of Japan wax that it may be kneaded to a "mochi"-like mass without adhering to the fingers is due to the presence of the glycerides of the dibasic acids.

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