ON THE DIBASIC ACIDS IN A FEW SUMACH BERRY WAXES.

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Received October 3rd, 1931. Published December 28th, 1931.

In the preceding paper the author has reported the investigation made on the dibasic acids in Japan wax ("hazé" wax), which is obtained in this country exclusively from the berries of "hazé" tree, *Rhus succedanea L.* It will be then natural to consider that whether such acids also occur in the waxes from other species of sumach trees. This is important and interesting from genetic relation of the trees, when we recollect that same or similar substances are often produced in plants of closely allied species. To contribute to this question, the author has tried experiments on the waxes (correctly, fats) from the berries of the following four species of Japanese sumach trees:[1]

(1) Besides the waxes from these four species, the fat from the berries of "nurudé", *Rhus semialata Murr., var. Osbeckii DC.* was also examined. The fat formed a brownish green-yellow semi-solid of the saponification value 199.2 and the iodine value 83.3. The petroleum ether insoluble substance in the fatty acids from this fat amounted only to 0.77%, and the dibasic acids appeared not to be present.

1. "Urushi-noki," *Rhus vernicifera DC.* This tree gives the well-known Japanese lacquer ("urushi") as the excretion of the stem. It chiefly grows in the northern part of Japan, and reaches to a height of 20–30 feet.

2. "Yama-hazé," *Rhus sylvestris S. et Z.* This is widely distributed in the country, and reaches to a height of more than 20 feet. Its berries resemble those of hazé, but are smaller.

3. "Yama-urushi," *Rhus trichocarpa Miq.* Chiefly grows in mountainous districts, and reaches to about 10 feet. The berries are far smaller than hazé berries.

4. "Tsuta-urushi," *Rhus toxicodendron L., var. vulgaris Pursh., f. radicans Engl.* This is a viny shrub growing in mountainous districts. The size of the berries resembles to that of yama-urushi.

Excepting yama-urushi wax, the occurrence of the dibasic acids has been confirmed in the other three waxes.

Experimental Part.

(I) **The Sumach Berries.** The berries of urushi and yama-urushi were procured from Fukushima Prefecture, while those of yama-hazé and tsuta-urushi were purchased from Kiso district of Nagano Prefecture. Although different in sizes, the berries somewhat resembled each other and also to hazé berries, and formed fairly flat, irregular ellipsoidal shapes with more or less pointed ends. The sizes, weights and analyses, etc., of the berries are given in the following table:

		Urushi	Yama-hazé	Yama-urushi	Tsuta-uruchi
Size (mm.)	Length	7–9	7–8	3–5	3.5–4
	Width	6–9	7–8	4–6	4–5
	Thickness	ca. 4	3–3.5	ca. 3	2.5–3
Weight of 100 berries (gr.)		7.76	7.34	2.17	2.61
Ratio of shell(1) to kernel		46.2 : 53.8	27.6 : 72.5	20.5 : 79.5	39.5 : 60.5
Analysis of shell					
Moisture (%)		5.22	4.06	5.52	3.18
Crude wax (%)		41.23	47.61	51.54	67.81

(1) Shell means exocarp and mesocarp. But in the cases of the berries of yama-hazé, yama-urushi and tsuta-urushi, the exocarps were for the most part lost during transportation.

(II) Properties of the Sumach Berry Waxes. The waxes were obtained by extracting the shells (chiefly mesocarps) of the berries with ether.

Properties of the Waxes.

	Urushi	Yama-hazé	Yama-urushi	Tsuta-urushi
Colour	Brownish yellow	Brownish black	Dark brown	Brownish black
d_4^{100}	0.8653	0.8679	0.8639	0.8895
M.p.	52.5–53°	51–52°	49–50°	38–39°
Acid value	3.1	6.2	14.1	—
Saponif. value	209.5	202.9	205.2	208 (?)
Iodine value (Wijs)	12.9	24.9	16.8	82 (?)
Unsaponif. matter (%)	0.62	—	0.78	—

Properties of the Fatty Acids.[1]

	Urushi	Yama-hazé	Yama-urushi	Tsuta-urushi
M.p.	62°	56–57°	54–55°	ca. 51–52°
Neutralisation value	212.9	214.1	212.6	212 (?)
Iodine value (Wijs)	12.8	14.6	17.1	26
Petroleum ether insoluble substance (crude dibasic acids) (%)	6.3	1.6	1.9	6.3

The crude tsuta-urushi wax contained the Japanese lacquer in appreciable proportion, so that only ambiguous results were obtained in the determination of the characteristics.

(III) Examination of the Occurrence of the Dibasic Acids.

(*1*) *Urushi wax.* By the lead salt precipitation method, 3.17 gr. of the crude dibasic acids (animal charcoal treated) were obtained from 50 gr. of the fatty acids. After fourth recrystallisation from 95% alcohol, the substance (0.8 gr.) melted at 117–118°C., and had the neutralisation value 301.3.

Anal. Subst. = 0.1148; CO_2 = 0.2980; H_2O = 0.1175 gr. Found: C = 70.96; H = 11.45%. Calc. for $C_{22}H_{42}O_4$: C = 71.29; H = 11.43%.

The further recrystallisations gave the following results:

	M.p.	Neutr, value
5th recrystallisation	119–120°	300.4
6th ,,	120–121°	299.1

So the substance appeared to consist chiefly of $C_{22}H_{42}O_4$.

(1) The fatty acids of yama-hazé and tsuta-urushi waxes were treated with animal charcoal before determination.

The mother liquors up to 4th recrystallisation were united, which on concentration gave 0.83 gr. of crystals of m.p. 116–117°C. and the neutralisation value 301.8. This neutralisation value also corresponded to that of the C_{22} formula.

(2) *Yama-hazé wax.* 50 Gr. of the methyl esters of the fatty acids were distilled under 6 mm. pressure until the temperature rose to 190°C. (bath temperature 225°C.), thereby 82.6% of the esters distilled over. The residue (6.4 gr.) was saponified, and the free acids (4.8 gr.) were dissolved in 250 c.c. of petroleum ether. After standing over-night the insoluble part (1.8 gr.) was dissolved in alcohol, treated with animal charcoal, and crystallised from alcohol. The refined substance (0.37 gr.) formed a grayish white powder of m.p. ca. 111°C. and the neutralisation value 280.6. After further decolourisation and recrystallisation, the substance (0.26 gr.) showed the m.p. 111–112°C. and the neutralisation value 290.1. The mixed test with the Japan wax dibasic acids (m.p. 123.5°C.) was 114–115°C.

From the above results, it appears that the chief constituent of the dibasic acids in yama-hazé wax is $C_{23}H_{44}O_4$.

(3) *Yama-urushi wax.* 10 Gr. of the fatty acids were treated with petroleum ether, and 0.2344 gr. of the insoluble substance was obtained. After decolourisation and recrystallisation it melted at 102°C., and had the neutralisation value 223.4. Although the want of the material prevented further investigation, the occurrence of a substance, which was difficultly soluble in petroleum ether and had the m.p. above 100°C., has been confirmed. Whether this consisted of dibasic acids or not, was, however, undecided.

(4) *Tsuta-urushi wax.* 100 Gr. of the methyl esters of the fatty acids[1] were distilled under 5 mm. pressure in the like manner as in the case of yama-hazé wax until the temperature rose to 180°C. (bath temp. 225°C.). By this operation 62% of the esters distilled over, and the residue (37 gr.) formed a brownish black, viscous liquid. The free acids obtained by saponification from the residue were dissolved in 500 c.c. of petroleum ether, and standing overnight, the insoluble substance (7 gr.) was separated from almost black mother liquor. By crystallising this substance from 100 c.c. of 95% alcohol, about 1.6 gr. of blackish brown crystals was obtained. These were treated with animal charcoal, and twice recrystallised from alcohol. The final refined product (0.7 gr.) melted at 117–118°C., and had the neutralisation value 286.7; the mixed test with the dibasic acids of Japan wax was 121–121.5°C. So the substance was confirmed to be $C_{23}H_{44}O_4$.

(1) The distillate consisted chiefly of the methyl ester of myristic acid.

Summary.

(1) The crude dibasic acids in urushi wax amounted to about 6.3% of the fatty acids. Their chief constituent appeared to be eicosane dicarboxylic acid, $C_{22}H_{42}O_4$.

(2) Yama-hazé and tsuta-urushi waxes also contained the dibasic acids, which amounted respectively to about 1.6 and 6.3% of the fatty acids. They consisted mainly of heneicosane dicarboxylic acid, $C_{23}H_{44}O_4$.

(3) The fatty acids of yama-urushi wax gave a small amount of a substance of m.p. 102°C. Whether this consisted of the dibasic acids or not, was, however, undecided.

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