

## THE DIBASIC ACIDS OF JAPAN WAX\*

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Japan wax from the berries of *Rhus succedanea* L. (Anacardiaceae) is available commercially and has been the subject of many chemical studies. Tsujimoto (1935) has shown that it consists of glycerides in which the glycerol is esterified with palmitic acid (77%); stearic and arachidic acid (5%); oleic acid (12%); linoleic acid (1%); and dibasic acids (6%). An unusual feature of the wax is the presence of dibasic acids which belong to the normal series  $\text{HOOC}(\text{CH}_2)_n\text{COOH}$  and confer toughness and plasticity on the wax.

The dibasic acids, "japanic acid", were first reported (Eberhardt 1888) to be  $\text{C}_{18}\text{H}_{36}(\text{COOH})_2$  and later by Geitel and van der Want (1900) as  $\text{C}_{20}\text{H}_{40}(\text{COOH})_2$ . Tsujimoto (1931*a*, 1931*b*) considered them to be a mixture of the homologues  $\text{C}_{21}\text{H}_{42}(\text{COOH})_2$  and  $\text{C}_{20}\text{H}_{40}(\text{COOH})_2$ . Ruzicka, Stoll, and Schinz (1928) accepted the formula  $\text{C}_{19}\text{H}_{38}(\text{COOH})_2$  for "japanic acid" and described the cyclic ketone obtained by heating its thallium salt as cycloeicosanone. More recent work suggested that the dibasic acids are of even-carbon number; by fractionation Siina (1940) isolated a component which he identified as *n*-eicosanedicarboxylic acid,  $\text{HOOC}(\text{CH}_2)_{20}\text{COOH}$ , and inferred that other fractions consisted of this acid and *n*-octadecanedicarboxylic acid. Similar conclusions were reached by Kurita and Kato (1952), who reported that after fractional crystallization the dibasic acids consist mostly of  $\text{C}_{22}\text{H}_{42}\text{O}_4$ , and that a dibasic acid of lower molecular weight is also present.

In the present investigation the dibasic acids isolated from a commercial sample of Japan wax were converted into a mixture of hydrocarbons by the reaction sequence: acids  $\rightarrow$  dimethyl esters  $\rightarrow$  diols  $\rightarrow$  di-iodides  $\rightarrow$  hydrocarbons. A gas chromatographic examination of the hydrocarbons obtained in this way shows conclusively that the dibasic acids are a mixture in which the  $\text{C}_{20}$  and  $\text{C}_{22}$  acids predominate, but that the  $\text{C}_{16}$ ,  $\text{C}_{18}$ ,  $\text{C}_{24}$ , and  $\text{C}_{26}$  acids also occur together with traces of  $\text{C}_{19}$ ,  $\text{C}_{21}$ , and  $\text{C}_{23}$ . These results suggest that the japanic acid of the earlier literature was essentially a mixture of  $\text{C}_{20}$  and  $\text{C}_{22}$  dibasic acids, the relative proportions of which might be expected to vary according to the amount of purification to which it had been subjected. It seems certain that the supposed  $\text{C}_{21}$  acid of Ruzicka, Stoll, and Schinz (1928) was such a mixture, and that the cyclic ketone prepared from its thallium salt was a mixture of the  $\text{C}_{19}$  and  $\text{C}_{21}$  ketones. The percentage composition of the dibasic acids is shown in Table 1.

### Experimental

The dibasic acids, melting over the range from 102–110 °C, were separated from a commercial sample of Japan wax in 5.8% yield using the procedure described by Tsujimoto (1931*a*, 1931*b*). They were only very sparingly soluble in light petroleum and consequently were twice heated

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with this solvent and filtered at room temperature to ensure complete removal of palmitic and other fatty acids. The dibasic acids were converted into their dimethyl esters (m.p. 50–53 °C) by refluxing with methanol–benzene (1 : 1) containing H<sub>2</sub>SO<sub>4</sub> (1%). Reduction of the dimethyl esters with lithium aluminium hydride gave diols, m.p. 95–97 °C, which were converted into hydrocarbons by methods which have been described previously (Downing, Kranz, and Murray

TABLE I  
PERCENTAGE COMPOSITION OF THE DIBASIC ACIDS HOOC.(CH<sub>2</sub>)<sub>n</sub>.COOH

| Carbon Number<br>of Chain<br>(n + 2) | Weight<br>(%) | Carbon Number<br>of Chain<br>(n + 2) | Weight<br>(%) |
|--------------------------------------|---------------|--------------------------------------|---------------|
| 16                                   | 1.2           | 22                                   | 53.5          |
| 18                                   | 4.0           | 23                                   | 0.4           |
| 19                                   | Trace         | 24                                   | 3.5           |
| 20                                   | 35.5          | 25                                   | Not detected  |
| 21                                   | 0.7           | 26                                   | 1.2           |

1960; Kranz *et al.* 1960). The conditions used in the gas chromatographic separations and the basis for identification of the hydrocarbons have been fully described in the papers cited immediately above. Gas chromatograms were run with pure C<sub>22</sub> and C<sub>24</sub> *n*-hydrocarbons for comparison, and when the retention times of the members listed in Table I were plotted on a log scale against the carbon number a straight line resulted, consistent with the behaviour of members of an homologous series.

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