

## Solvation Properties of Maleopimaric Acid and Related Substances

**LEON H. ZALKOW and MARVIN L. CORSER<sup>1</sup>, Department of  
Chemistry, Oklahoma State University, Stillwater**

Abo (1960) recently reported that attempts to hydrolyze maleopimaric acid, I (see Fig. 1), to the tricarboxylic acid lead instead to a hydrated anhydride,  $C_{24}H_{32}O_5 \cdot H_2O$ . During the course of another investigation, we noticed that I tenaciously held solvent of crystallization even when subjected to low pressures (1 mm). This investigation was undertaken in an attempt to find means of removing the solvent of crystallization and to determine if the solvent of crystallization was involved in a stoichiometric ratio. The study also included abietic acid, II, and the fumaric acid adduct of abietic acid, III.

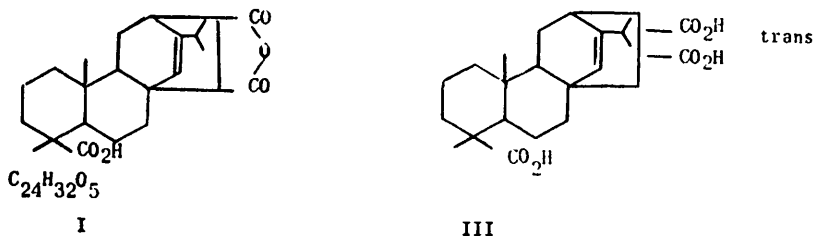


Figure 1

When I and III were crystallized from acetic acid and dried at low temperatures and 1 mm pressure, they were each found to undergo a transition before melting; however, if they were first heated at this transition point or above at reduced pressure and then resubmitted to melting, no transition was observed (see Table I). The final melting point was the same in either case. In order to determine the amount of acetic acid

TABLE I MELTING POINT OBSERVATIONS

| Compound | Transition Point | M. P.      |
|----------|------------------|------------|
| I        | 110 - 135°       | 233 - 234° |
| III      | 190 - 210°       | 252 - 253° |

of crystallization present, the various samples were titrated with standard base after being crystallized from acetic acid and dried both below (case 2) and above (case 1) their transition points at 1 mm. The molecular weights were calculated using the equation:

$$M.W. = (\text{gms. of compound}) (\text{no. of carboxyl groups}) (1000) / (\text{ml. of base}) (N \text{ of base})$$

and the samples were titrated both with standard aqueous sodium hydroxide (~ 0.1 N) and with standard methanolic sodium hydroxide (~ 0.1 N). Using both bases, the presence of the anhydride moiety in I was detectable since in aqueous base an anhydride titrates as a dibasic acid and in

<sup>1</sup>The experimental work described in this paper was performed by M. L. C. while a participant in the National Science Foundation Undergraduate Research Program (Summer, 1961). We wish to thank the National Science Foundation for this financial support.

methanolic base it titrates as a monobasic acid. In the latter case, the anhydride gives the half acid ester.

The results obtained are shown in Table II. The observed molecular weights are average values of four to six determinations. It can be seen that I and III when dried below their transition points (case 2) crystallize with acetic acid in a 1:1 molar ratio whereas drying above the transition point (case 1) removes the attached acetic acid. However, abietic acid, II, does not retain acetic acid under these conditions. In the literature (Simonsen, 1952), there are several reports that abietic acid and

TABLE II MOLECULAR WEIGHTS BY NEUTRALIZATION

| Compound     | Theoretical M.W. |               | Observed M.W. |                 |
|--------------|------------------|---------------|---------------|-----------------|
|              | No Solvation     | 1:1 Solvation | Aqueous Base  | Methanolic Base |
| I (case 1)   | 401              | 461           | 401           | 402             |
| I (case 2)   | 401              | 461           | 465           | 458             |
| III (case 1) | 418              | 479           | 417           | 420             |
| III (case 2) | 418              | 479           | 474           | 478             |
| II (case 2)  | 302              | 362           | 299           | 303             |

related compounds crystallize with solvent of crystallization. Our crystalline samples (case 2) were dried at approximately room temperature and 1 mm pressure. Under these conditions abietic acid does not retain acetic acid.

Table III lists the molecular weights obtained after crystallizing I from the solvents shown and drying the crystalline material at room temperature and 1 mm pressure. We repeated the attempted hydrolysis of I to give the tricarboxylic acid (first line of Table III) and our results are consistent with those reported by Abo. The molecular weights observed are close to the theoretical value of 419 and the product titrated as

TABLE III MOLECULAR WEIGHTS OF MALEOPIMARIC ACID CRYSTALLIZED FROM VARIOUS SOLVENTS

| Solvent                         | Observed M.W. |                 |
|---------------------------------|---------------|-----------------|
|                                 | Aqueous Base  | Methanolic Base |
| Acetone-H <sub>2</sub> O        | 423           | 420             |
| 80% Acetic Acid                 | 463           | 459             |
| 75% Acetic Acid                 | 463           | 460             |
| 67% Acetic Acid                 | 462           | 462             |
| 50% Acetic Acid                 | 418           | 419             |
| 88% Formic Acid                 | 397           | 406             |
| 70% Formic Acid                 | 400           | 395             |
| 66% Formic Acid                 | 397           | 392             |
| CCl <sub>4</sub> -Benzene (3:1) | 410           | 398             |

a dicarboxylic acid in methanolic base. In addition the infrared spectrum of the hydrolysis product (see Table IV) showed the presence of the anhydride moiety. From Table III, it can be seen that crystallization of I from 80%, 75% or 67% aqueous acetic acid still yields solvated I containing a molar equivalent of acetic acid whereas crystallization of I from 50% aqueous acetic acid gives I solvated with water. Surprisingly, the results indicate that crystallization of I from aqueous formic acid gives solvent-free I. The last line in Table III gives the results of crystallization

of I from  $\text{CCl}_4$ -benzene and the value obtained with aqueous base appears too high. Since this value is an average of only two runs, its accuracy is questionable.

Table IV lists some of the significant peaks in the infrared spectra of the compounds discussed.

TABLE IV INFRARED SPECTRA

## Significant Absorption Peaks in Microns

| Compound             | Anhydride Carbonyls | Acid Carbonyls | Other Bands                       |
|----------------------|---------------------|----------------|-----------------------------------|
| I                    | 5.60, 5.40          | 5.88S, 5.77W   | 7.68VW, 7.77M, 8.09S              |
| I · HOAc             | 5.60, 5.40          | 5.88S, 5.83S   | 6.95W, 7.05M, 7.64S, 7.72S, 8.09S |
| I · H <sub>2</sub> O | 5.67, 5.45          | 5.88M, 5.80S   | 2.82M, 2.68M, 6.10M, 8.05S, 8.14S |
| II                   | — —                 | 5.90S          | 7.80S                             |
| III                  | — —                 | 5.85S, 5.88S   | 7.75-7.85 (broad)                 |
| III · HOAc           | — —                 | 5.85S, 5.88S   | 8.25-8.35 (broad)                 |
|                      |                     |                | 7.75-7.85 (broad)                 |
|                      |                     |                | 8.25-8.35 (broad)                 |

S=strong; M=medium; W=weak; VW=very weak.

It can be seen from Table IV that water of solvation shifts the anhydride carbonyl absorption of I whereas acetic acid of solvation does not affect the anhydride carbonyl absorption. The strong band at  $5.83\mu$  in I · HOAc is probably due to the carbonyl group of acetic acid and this band masks the weaker band at  $5.77\mu$  in I. This is probably also true in I · H<sub>2</sub>O except the acetic acid carbonyl group appears at  $5.80\mu$  in this case. It is not possible to see the acetic acid of solvation in the spectrum of III · HOAc. The infrared spectra suggest that acetic acid and water may not be bound to the molecules discussed in the same manner.

The data presented in this paper show that maleopimaric acid and the fumaric acid adduct of abietic acid crystallize with acetic acid in a 1:1 molar ratio. The solvent of crystallization is removed by heating the solvated molecules above the temperature at which they undergo a crystalline modification at reduced pressures. Under these conditions, abietic acid does not crystallize with solvent of crystallization. Maleopimaric acid crystallizes from some aqueous solutions as a hydrated anhydride (1:1). The water of crystallization shifts the carbonyl absorption in the infrared of the anhydride group in maleopimaric acid to higher wavelengths whereas acetic acid of crystallization does not affect this absorption peak. The 1:1 maleopimaric acid-acetic acid complex can be recrystallized from aqueous acetic acid (> 50% acetic acid) without loss of the solvated acetic acid.

## LITERATURE CITED

- Abo, Masahiro, 1960. Hydrolysis Products of Abietic Acid - Maleic Anhydride Adduct. *Bull. Chem. Soc. Japan* 33, 798.
- Simonsen, Sir John, 1952. *The Terpenes*, Vol. 3, Cambridge, p. 374.