On the Hydrolysis Products of Abietic Acid-Maleic Anhydride Adduct

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(Received November 26, 1959)

In 1932 Ruzicka and his coworkers[1] found that the saponification product of methyl abietate-maleic anhydride adduct could not be isolated as tricarboxylic acid but identified with the anhydride adduct directly obtained from the reaction between colophony and maleic anhydride, and they stated that the tricarboxylic acid, which was produced at the beginning of the saponification, had a tendency to convert easily into the anhydride acid in the course of acidification or recrystallization.

It was also reported that *cis*-9, 10-dihydroanthracene-9, 10-endo-α, β-succinic acid[2] and alkyl-1, 4-dihydronaphthalene-1, 4-endo-α, β-succinic acid[3] had similar tendencies. These dibasic acids could not be successfully purified by recrystallization, even from the low-boiling solvents, because of their partial or complete conversion to the corresponding anhydrides. It may be seen that these tendencies are common characteristics of these structural homologues.

In the present work an attempt has been made to isolate the hypothetical tricarboxylic acid which might be directly produced by means of the hydrolysis of the abietic acid-maleic anhydride adduct. Some properties of those hydrolysis products which were obtained in a few ways were compared with those of maleic anhydride- or fumaric acid- adducts with abietic acid and discussion was offered as to their chemical structures.

Experimental

Maleic Anhydride Adduct with Abietic Acid.—60 g. of abietic acid (so-called Steele's acid which was produced by refluxing Chinese gum rosin with acetic acid) and 20 g. of maleic anhydride were heated at 170~180°C with stirring under a slow stream of carbon dioxide for two hours. The reaction mixture was dissolved in 100 ml. of glacial acetic acid, and this was poured into a large amount of water with stirring. The separated yellowish resinous product was refluxed with a small amount of carbon tetrachloride to remove the unreacted abietic acid, and recrystallized from glacial acetic acid. Further recrystallization was carried out from benzene-carbon tetrachloride according to the procedure of Ruzicka and his coworkers[1]. Thirty-two grams of fibrous white needles melting at 226~228°C were obtained.

Found: C, 71.63; H, 7.82. Calcd. for $C_{24}H_{32}O_5$: C, 71.96; H, 8.06%. $[\alpha]_D^{15}$ −31.0° (10% in chloroform).

Besides the above, the most refined sample could be obtained by purification with the aid of sublimation of the above crystal under reduced pressure of 1 mmHg at 190~210°C. Its analytical data are shown in Table I with other properties.

Fumaric Acid Adduct with Abietic Acid.—50 g. of abietic acid and 20 g. of fumaric acid were heated at 195~200°C with the same procedure as the above for two hours. The reaction mixture was dissolved in 150 ml. of glacial acetic acid, and this was poured into a large amount of hot water with stirring and filtered through a hot funnel. This procedure was repeated twice. The unreacted abietic acid was removed from the yellowish powder by refluxing in benzene, filtered and the filtrate was recrystallized from glacial acetic acid. An analytical sample was obtained by repeated recrystallization from dioxane. Its properties and analytical results are shown in Table I with others. Purification by the vacuum sublimation method was unsuccessful owing to its thermal decomposition.

Hydrolysis of Maleic Anhydride Adduct.—It was carried out in two ways. (1) 30 g. of purified maleic anhydride adduct was dissolved in 100 ml. of acetone and added 30 ml. of water. The flask was immersed in a water bath kept at 60~70°C, and boiled gently under a reflux condenser for two hours. On cooling at room temperature, white crystals began to precipitate. After the crystallizations from acetone-water were repeated, they were filtered and ground into fine powder and then dried at room temperature under reduced pressure (2~5 mmHg). They reached the constant weight after about two hours. The analytical data are shown in Table I with others. (2) Ten grams of purified maleic anhydride adduct was dissolved in excess of 10%, aqueous sodium hydroxide solution and precipitated by acidification with 2 N hydrochloric acid. The precipitate was collected, washed with water repeatedly and recrystallized from acetone. All the procedures after hydrolysis were carried out at room temperature, in order to prevent the reversion to the original anhydride. Drying was carried out under the same condition as above. The analytical data are shown in Table I with others.

Measurement of Acid Number[4].—*Total Number.*—0.2~0.3 g. of the sample in about 50 ml. of the

1) L. Ruzicka, P. J. Ankersmit and B. Frank, *Helv. Chim. Acta*, **15**, 1289 (1932).

2) W. E. Bechmann and L. B. Scott, *J. Am. Chem. Soc.*, **60**, 481 (1938); **70**, 1458 (1948).

3) M. C. Kloetzel and H. L. Herzog, ibid., **72**, 1991 (1950).

4) E. F. Siegel and M. K. Moran, ibid., **69**, 1457 (1947); W. Klausch, *Farbe u. Lack*, **63**, 119 (1957).

TABLE I. PROPERTIES AND ANALYSES OF TWO KINDS OF ABIETIC ACID ADDUCT AND HYDROLYSIS PRODUCTS OF MALEIC ANHYDRIDE ADDUCT

	Adduct of fumaric acid	Adduct of maleic anhydride	Hydrolysis products of maleic anhydride adduct (1)[a]	(2)[b]
Melt. pt., °C	249~252	226~228	226~228 (187~210[c])	
Analyses, %:				
Calcd., C	68.87	71.97	68.87[d]	
Calcd., H	8.19	8.05	8.19[d]	
Found, C	68.96	71.69	68.70	68.73
Found, H	8.10	7.89	8.01	8.05
Acid number:				
Calcd., Apparent	393	280	393[d]	
Calcd., Total	393	420	393[d]	
Found, Apparent	387	280	270	273
Found, Total	395	417	395	397
$[\alpha]_D^{15}$	+34.0°	−25.2°	−24.0°	−23.6°
(g./100 ml. ethanol)	(2.0)	(5.0)	(2.0)	(2.0)
Solubility at room temp.:				
Chloroform	insol.	sol.	insol.	
Benzene	insol.	sol.	insol.	

a) Refluxed the acetone containing water solution of maleic anhydride adduct for two hours and recrystallized from its solution. b) Precipitated by acidification of the alkali solution of maleic anhydride adduct. c) Measured in a sealed capillary tube. d) Calculated for hypothetical tricarboxylic acid $C_{24}H_{34}O_6$ which may be produced on the hydrolysis process.

mixture of 1 : 3 *tert.*-butyl alcohol and acetone was dissolved, and about 10 ml. of water were added to prevent the turbidity which happened often in titration, and titrated with 0.1 N aqueous sodium hydroxide solution by means of potentiometric titration method. — *Apparent Number.* — 0.2~0.3 g. of the sample was dissolved in about 50 ml. of ethanol and titrated with 0.1 N alcoholic sodium hydroxide.

Thermal Degradation Curves.—An apparatus of Honda's thermal balance[5] was used. About 0.5 g. of fine powdered sample was heated at constant rate of 10°C/5 min. and loss of weight of sample was measured.

Discussion

As was shown in Table I, the elementary analytical data of both hydrolysis products, which were obtained in two ways as mentioned above, were in good agreement with that expected for the aimed tricarboxylic acid $C_{24}H_{34}O_6$ respectively. They were insoluble in benzene or chloroform, similarly to fumaric acid adduct, at room temperature, but soluble at elevated temperature. Their specific rotation was negative like that of the maleic anhydride adduct, and the decrease of the rotation nearly corresponded with the decrease of the concentration of the asymmetric carbons attendant upon the increase of their molecular weights. The melting points which were measured by the ordinary method agreed with that of the maleic anhydride adduct. However, when they were measured in a sealed capillary tube they showed a remarkable depression and were distinct from anhydride.

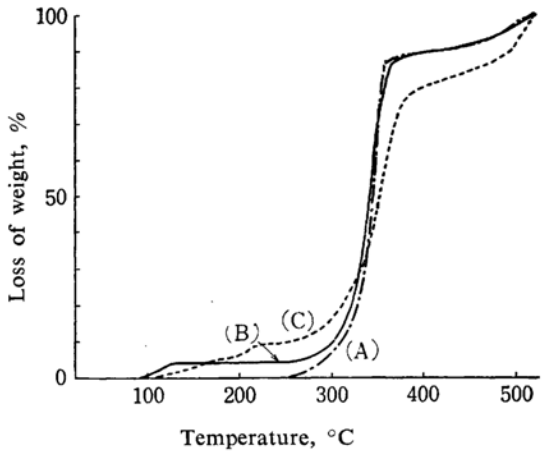


Fig. 1. Thermal degradation curves of (A) abietic acid-maleic anhydride adduct, (B) hydrolysis product of A, and (C) abietic acid-fumaric acid adduct.

Another distinguished difference was observed in the thermal degradation curves of the three kinds of adducts (Fig. 1). The hydrolysis product showed suddenly 4.1 to 4.4% weight loss at about 100 to 120°C (Curve B, Fig. 1), which corresponded approximately to the loss of

5) K. Honda, *Sci. Rep. Tohoku Univ.*, 4, 97 (1915).

one molecule of water from one molecule of the hypothetical tricarboxylic acid. After it was heated at that temperature the weight was kept constant till it began once more to lose the weight nearly along the curve A of anhydride adduct at about 250°C. In the other run, when the heating was stopped at 150°C, it was confirmed that the remaining product was the same one as anhydride adduct by its mixed melting point and infrared spectrum.

Now, if the above mentioned hydrolysis products had the same structure as the hypothetical tricarboxylic acid (I) which corresponded with the abietic acid-maleic acid adduct, it should be expected that there would be no difference in titer between titrations in a primary alcoholic and a tertiary alcoholic medium. Contrary to our expectation, it was found that they titrated only about two thirds of the expected titration in ethanol (Table I).

Incited by this fact, we were led to find more interesting facts: (a) When the titration of above hydrolysis product was carried out in the mixed solution of acetone — *tert.*-butyl alcohol—water, with alcoholic (ethyl) alkali solution as titer, we also obtained only about the apparent acid number, two thirds of the expected one for the tricarboxylic acid I. (b) Even if it was titrated after the solution was kept at its refluxing temperature for two hours, we also found the same result. Under the same condition, ordinary anhydrides, e. g. maleic anhydride and phthalic anhydride etc., were titrated to their own total acid number respectively. (c) Furthermore, it was also confirmed that the maleic anhydride adduct itself showed only an apparent acid number under the same condition as (a) or (b).

From these facts it seems that they have not the expected tricarboxylic acid structure but an anhydride one in spite of their elementary analyses and other evidences mentioned above. And then, it seems that the anhydride adduct cannot be hydrolyzed in a hydrous medium, even at its refluxing temperature, but proceeds readily to monoesterification with primary alcohol included in titer.

On the other hand, the infrared spectra of them, compared with those of maleic anhydride- and fumaric acid- adducts (Fig. 2), supported an existence of five membered ring anhydride structure. And also, it was first revealed by these spectra that there were two forms of products according to their hydrolysis method, (1) or (2). In either case, two characteristic bands due to the carbonyls in five membered anhydride ring appeared near 1770 and 1830 cm^{-1} similar to that found in the anhydride adduct. These results make it possible to explain their anomality in acid number consistently.

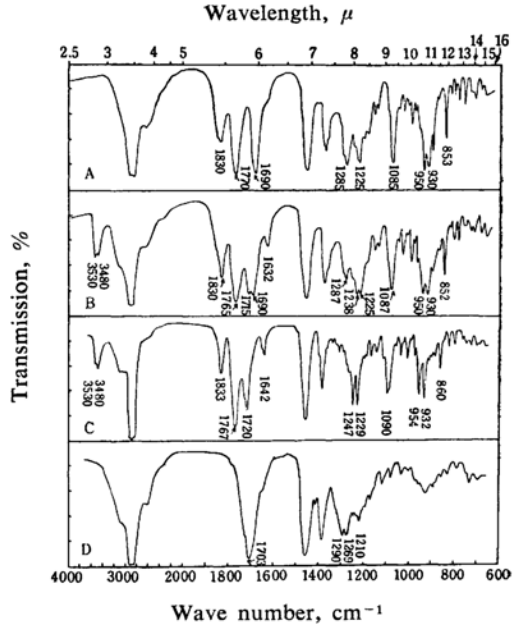
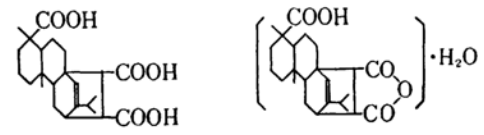


Fig. 2. Infrared spectra in Nujol of (A) abietic acid-maleic anhydride adduct, (B) hydrolysis product (α-form), recrystallized from acetone-water solution of A, (C) hydrolysis product (β-form), precipitated by acidification of the alkali solution of A, (D) abietic acid-fumaric acid adduct.

But if it is so, it becomes difficult to make compatible their elementary analytical data or their thermal degradation curves etc. with an existence of anhydride structure. The only reasonable explanation for this would be that the anhydride adduct had a tendency to form a monohydrate II without opening the anhydride ring in hydrate solution for some reason, e. g. it may be due to the stereochemically unusual approach in positions between the two carbonyl groups belonging to the succinic acid structure added to 6-, 14-carbons of abietic acid.



It was considered that the bands at 3530, 3480 and 1642 cm^{-1} suggested the existence of a hydrated water. Two forms of the hydrolysis products perhaps appeared from the difference in the mode of hydrogen bonding. It is considered that the carbonyl band at 1720 cm^{-1} in β-form is assigned to that of the tertiary carboxyl group under the influence of hydrogen bond caused by the hydrated water. In α-form, it divided in two bands, at 1715 and 1690 cm^{-1}.

It seems that one is under the influence of hydrogen bond and the other is not.

It seems to be almost sure that the hydrated water is stoichiometric component in the hydrolysis products, because those products which were dried to the constant weight at room temperature under reduced pressure always showed the reproducible stepwise loss of weight at the range of about 120 to 250°C in the thermal degradation curves, while abietic acid or its fumaric acid adduct which was recrystallized from acetone-water and dried under the same condition showed neither such a stepwise loss of weight in that curve nor the water bands in its infrared spectrum. It seems probable that the hydrated water is the same sort as the zeolitic water by reason of the fact that the collapse of crystals which should happen near their dehydrating temperature can not be observed in an open capillary. It could be also analyzed by Karl Fischer's method. The water content measured by this method was compared with the loss of weight at 150°C in the thermal degradation curve about the samples which were dried under various conditions in Table II.

Table II. Drying time and water content of hydrolysis products of maleic anhydride adduct

Drying time, hr. (at 2 mmHg/28°C)	Loss of weight at 150°C, %	Water content by means of Karl Fischer's method %
1	4.43	4.20
2	4.32	—
4	4.31	4.10
6	4.15	4.42
11	4.30	3.98

Samples: Hydrolysis products precipitated from acetone containing water solution.

Summary

Hydrolysis of abietic acid-maleic anhydride adduct was carried out in two ways. The elementary analytical data of both resulting products were in good agreement with that calculated for the hypothetical tricarboxylic acid $C_{24}H_{34}O_6$, and at about 100 to 120°C these products lost the weight, which corresponded to the loss of one molecule of water from one molecule of the acid, to revert to the original anhydride adduct. But, they showed only an apparent acid number when the titrations were carried out in ethyl alcohol, similarly to the case of the anhydride adduct. Their infrared spectra suggested an existence of five-membered ring anhydride structure and a hydrated water. On the basis of these facts, we offered an anhydride adduct monohydrate structure II for the above hydrolysis products.

The author wishes to thank Dr. Shiro Tsuruta, Dr. Wataru Koga and Dr. Kiyoshi Sakashita for many stimulating discussions and helpful suggestions.

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