ON ABIETIC ACID AND SOME OF ITS SALTS.

By Emil Oscar Ellingson.

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One of the first investigators who succeeded in isolating a crystalline substance from colophony was Baup.[1] To the crystalline material obtained from the colophony of the *Pinus Abies* tree he gave the name abietic acid. Since the time of Baup many experimental results have been contributed to the study of this acid, but in several instances they do not agree. For example, the melting point of the substance on record varies to such an extent that one may be inclined to question the purity of the acid studied.

Although the subject of this paper deals, in general, with the preparation of abietic acid and its salts, the chief object of the investigation was to isolate the acid in the purest obtainable condition and to compare the product with that described in the literature.

Abietic Acid.

The abietic acid prepared by the writer was obtained from commercial colophony, the method of preparation being similar to that employed by Maly.[2] His method consists mainly in extracting the rosin by means of 70% alcohol at about 50°, after which the undissolved residue is recrystallized several times from about 85% hot alcohol by adding some water to the solution to make the acid crystallize out more rapidly.

The acid described in this paper was prepared in the following manner: To 1500 grams of 70% alcohol about 800 grams of rosin are added and the mixture heated on a boiling water bath for thirty minutes. A five-liter Jena flask may be used as a container. Part of the rosin dissolves, coloring the alcohol yellow, and the remainder forms a reddish yellow liquid immiscible with the alcoholic solution. When the container is shaken vigorously the mixture assumes the appearance of a white emulsion. On standing in a cool place, the emulsion separates into two distinct liquid layers, of which the lower one solidifies after a few hours to a yellow, granular mass. The supernatant liquid is poured off from the hardened layer and the latter again extracted in a fresh quantity of 70% alcohol and otherwise treated in the same way. This procedure is repeated once more, after which the final residue is recrystallized about seven times from hot 95% alcohol without the addition of water. A few cubic centimeters of acetic acid, added to the solution when recrystallizing the first time, seemed to aid the process of crystallization. Emmerling[3] allowed the acid to crystallize from concentrated acetic acid before attempting to recrystallize it from alcohol.

If water be added to start the precipitation of the acid, the latter crys-

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[1] *Ann. chim. phys.*, **31**, 108 (1826).

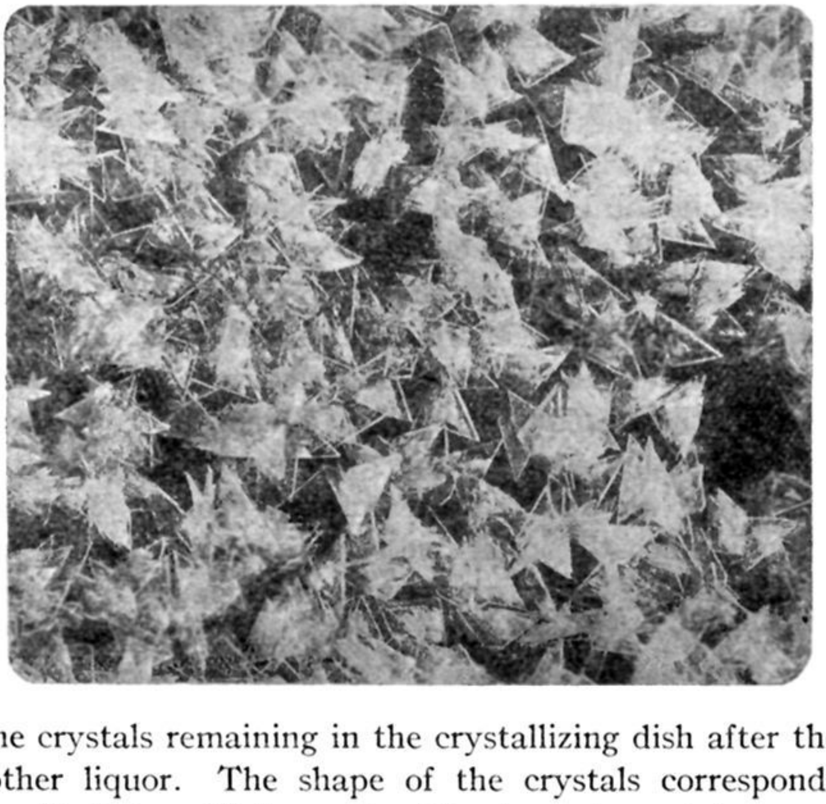
[2] *J. prakt. Chem.*, **86**, 111 (1862).

[3] *Ber.*, **12**, 1442 (1879).

tallizes fairly rapidly but the compound is not pure, the crystals occluding an appreciable quantity of other resinous materials from the solution. It was found that some of these impurities clung to the acid even when no water was added. The complete separation of the acid from this admixture of resinous substance constitutes the main difficulty in securing the pure compound.

To obtain pure abietic acid it should be allowed to crystallize slowly from a hot solution of 95% alcohol, in which from 10% to 15% of the acid has been dissolved, repeating the process until the compound shows a definite melting point. The alcoholic solution is placed in a large crystallizing dish and about one-third or one-half of the solvent allowed to evaporate spontaneously at room temperature. The crystals are then drained free from the remaining mother liquor.

As the recrystallization proceeds, the crystals gradually become larger and more distinct and, finally, the acid appears in the shape of transparent, colorless, triangular plates. The accompanying photograph was taken of the crystals remaining in the crystallizing dish after the removal of the mother liquor. The shape of the crystals corresponds to that usually described for abietic acid. The largest crystals measured one centimeter on an edge, which is somewhat more than the usual size heretofore obtained.



Ordinarily, abietic acid is said to be a crystalline compound of a light yellow color, but the crystals obtained by the writer were perfectly colorless. While this is evidence of the high purity of the compound, the crystals were, nevertheless, observed to be coated with a very thin, sticky material. To eliminate this impurity, the crystals were further recrystallized several times from 95% alcohol, but it was impossible to get rid, entirely, of the final traces of the foreign substance. Whether the contamination is due to a resinous impurity not properly removed, or to a slight decomposition of the crystalline acid to non-crystalline substances was not ascertained. It is possible that a gradual oxidation or some other chemical change takes place when the acid is in contact with alcohol and atmospheric oxygen.

The melting point was determined in the usual way, beginning with the sample obtained from the first recrystallization of the extracted residue. With each successive crystallization the melting point rose gradually from 120°, for the less pure material, to 152° for the pure acid. Since the latter invariably appeared to be melted at 152°, this temperature was taken as the melting point of the pure compound.

It should be mentioned in this connection that the rate at which the acid is heated has a marked influence on the observed melting point. If the rate of rise in temperature be about one degree per three or four minutes, the crystals begin to soften at 142°–146°, whereas if the rate be about two degrees per minute they do not melt below 152° and are sometimes not wholly melted until a temperature of 155° has been registered. However, when the rate is regulated to about one degree per minute the compound starts to melt at or near 150° and is entirely melted at 152°. By thus moderating the rate any decomposition due to prolonged heating is reduced, and any possible discrepancy existing between the thermometer reading and the actual temperature of the melting acid, due to too rapid heating, is minimized.

From these observations it seems that the acid is not characterized by a sharp melting point. According to Schwalbe,[1] abietic acid decomposes on heating above 120°, giving off carbon dioxide. That rosin and abietic acid give off vapors when melting is a well known fact. These fumes contain hydrocarbons. Such a behavior would naturally result in a somewhat variable melting point in the acid.

In the literature one finds the melting point given by different investigators varying all the way from 120° to 182°. Thus, Maly[2] found it to be 165°, Emmerling[3] 139°, Flückiger[4] from 120° to 135°, Mead and Kremers[5] from 150° to 156°, Levy[6] 182°, Loos[7] from 149° to 161°, and Frankforter[8] 130°. This wide discrepancy cannot be due to the impurity of the

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[1] *Z. angew. Chem.*, **18**, 1852 (1905).

[2] *J. prakt. Chem.*, **92**, 2 (1864).

[3] *Ber.*, **12**, 1442 (1879).

[4] *J. prakt. Chem.*, **101**, 239 (1867).

[5] *Proc. Am. Pharm. Assoc.*, **41**, 204 (1893).

[6] *Z. angew. Chem.*, **18**, 1739 (1905).

[7] *Dissert.*, **1900**, published by the Chemical Publishing Co., Easton, Pa.

[8] THIS JOURNAL, **31**, 536 (1909).

acid under consideration but rather to the formation of isomerides whose properties may differ greatly. The variation of about two degrees in the melting point of the acid examined by the writer is therefore very satisfactory. It is well known that resinous compounds do not, as a rule, exhibit a perfectly sharp melting point.

In the process of melting, the colorless acid became reddish brown. The coloration is probably caused by a chemical action going on in the compound at higher temperatures. That a change has taken place is further shown by the appreciable non-crystalline, resinous residue that remains after evaporating the mother liquor taken from a recrystallization of the melted acid in alcohol.

Another proof that a chemical change occurs in the acid during melting is that the heat of combustion of the melted acid is a little lower than that of the unmelted compound. Since the heat of combustion is less for the melted than for the unmelted acid the change seems to be one of oxidation. It is, therefore, evident that this slight alteration in the composition of abietic acid, near its melting temperature, accounts for the fact that the melting point is not a sharp one.

The yield of abietic acid obtained from the colophony at hand was only about 10%. According to some experimenters yields as high as 83% have been reached. The low percentage realized by the writer refers strictly to the pure acid. Undoubtedly some of it remained in the mother liquors, mixed with the resinous substances, from which it would be difficult to isolate the acid in the pure condition by fractional crystallization. No attempts were made to recover the part which may have been lost in this way.

The formula of abietic acid is either $C_{19}H_{28}O_2$ or $C_{20}H_{30}O_2$, preferably the latter. The corresponding molecular weights are 288 and 302, respectively. Experiments on the molecular weight of the acid prepared as just described were made according to both the freezing- and boiling-point methods. The boiling was done by electrical heating. The results of these determinations are shown in Tables I and II.

The results obtained in a given solvent by the cryoscopic method are fairly concordant. There is, however, a marked disagreement in the data for the *different* solvents. The results in benzene (Table I) indicate that the acid molecules are associated in this solvent.

Abietic acid is readily soluble in most organic liquids, the solutions formed being non-electrolytes. Attempts were made to pass an electric current through 1% solutions of the acid in pyridine, acetic acid, alcohol, benzene, and phenol, at temperatures ranging from 25° to 75°. A conductance slightly above that of the pure solvent was noticed only in the pyridine solution. This solution was, therefore, investigated further to ascertain if the acid and pyridine had combined to form an abietate of pyridine in solution. About five grams of the acid were dissolved in twenty grams of pyridine and the solution carefully distilled under reduced pressure to separate the product of the interaction of the acid and the base. No such compound could be isolated in this way, for the base distilled off pure and the acid remained in the retort as a brown rosin-like mass. Solutions of the acid in aniline, dimethylaniline, and amylamine were similarly treated and with the same results. Mach[1] succeeded in preparing a crystalline, water-soluble compound, by allowing the much stronger base, tetramethyl ammonium hydroxide, to act on the acid. The product, however, decomposed rapidly on exposure to the air.

Molecular Weight.

Table I.—Freezing Point Method.

Solvent used.	Grams of acid in 100 grams of solvent.	Lowering of the F. P. Degrees.	Corresponding mol. wt.
Acetic acid. Mol. depression, 3880	0.9924	0.141	272
	1.1422	0.168	263
	1.6272	0.236	267
	2.2720	0.319	275
Benzene. Mol. depression, 5000	1.1488	0.113	507
	1.3414	0.130	516
	2.0599	0.193	533
	2.2219	0.209	532
Phenol. Mol. depression, 7500	1.2793	0.337	284
	2.3011	0.608	283
	2.7735	0.744	279

Table II.—Boiling Point Method.

Solvent used.	Grams of acid in 100 grams of solvent.	Rise of the B. P. Degrees.	Corresponding mol. wt.
Pyridine. Mol. elevation, 3010	1.1055	0.157	212
	1.2006	0.195	185
	1.6625	0.238	210
Acetic acid. Mol. elevation, 3900	0.8154	0.138	230
	1.5846	0.270	229
Benzene. Mol. elevation, 2670	0.5137	0.041	341
	1.0284	0.077	356
	2.0824	0.147	378
Alcohol. Mol. elevation, 1150	1.1202	0.038	336
	2.2649	0.074	360

Having thus failed in the production of salts of this nature, the preparation and analysis of the abietates of the metals was next taken up, a description of which follows.

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[1] *Monatsh.*, 15, 636 (1894).

Salts of Abietic Acid.

Assuming that abietic acid, whose composition may be expressed by the formula $C_{20}H_{30}O_2$, is a monobasic acid, the abietates ought to occur as compounds of the type $M(C_{20}H_{29}O_2)n$, where M represents the metal having a valence of *n*. While the latter formula has generally been assigned to the salts, it appears from the following work that the normal salt, $M(C_{20}H_{29}O_2)n$, is rarely formed. On the contrary, acid salts or salts expressed by the general formula, $M(C_{20}H_{29}O_2)n.XC_{20}H_{30}O_2$, are most frequently obtained.

The abietates of sodium, potassium, silver, copper, calcium, barium, strontium, cobalt, nickel, iron, zinc, chromium, aluminum, manganese, cadmium and tin were prepared as described below. The sodium and potassium salts were first made by neutralizing the acid with a slight excess of alkali in a moderately dilute aqueous solution. The reaction took place in a flask provided with a reflux condenser, the contents being heated until complete solution of the acid had been effected. The two salts were also obtained by neutralization of the acid in alcoholic potash or soda solution. Sodium abietate crystallized in long, needle-shaped crystals from the alcoholic solution on cooling.

The abietates of the heavy metals were then prepared from sodium abietate by double decomposition in the following manner: A dilute aqueous solution of sodium abietate was added in small portions to a dilute solution of some salt, usually the chloride or sulphate of the metal whose abietate was desired. By this treatment the abietate is completely precipitated. The latter was then thoroughly washed with water, filtered, and dried in a vacuum at about 80°. To make certain that no hydroxide of the metal present is mixed with the abietate, the dry precipitate was redissolved in pure benzene, filtered, the solvent evaporated, and the residue dried as before. The hydroxide referred to may be formed by the interaction of the inorganic salt and the slight excess of sodium hydroxide present in the sodium abietate solution.

Tin abietate was prepared by double decomposition in a non-aqueous solution. Thus, on adding a benzene solution of stannic chloride to a dilute solution of copper abietate in the same solvent, until no further precipitation of cupric chloride was observed, the abietate of tin remained in solution. After the cupric chloride had settled, the clear, supernatant liquid was filtered and evaporated in a vacuum at about 80°. The residue obtained was redissolved in benzene, filtered, the filtrate evaporated to dryness, and the yellow residue powdered and further dried as before.

It should be stated that the precipitation of the cupric chloride from the reaction between the stannic chloride and copper abietate was *instantaneous*. Reactions of a similar nature were carefully studied several years ago by Kahlenberg,[1] who found that certain salts were precipitated instantaneously and completely in non-aqueous solvents.

Of the salts prepared, the sodium abietate was the only one obtained in a crystalline condition when it was made in an alcoholic solution. The alkali and ammonium abietates have all been isolated in a crystalline form by several investigators, such as Maly,[2] Mach,[3] Levy,[4] Loos,[5] and others.

Since the abietates of the heavy metals, prepared as described, were not crystallizable from solution, their state of purity is doubtful. Although the abietates of the heavy metals have been obtained both as normal and acid salts by Maly,[6] Mach,[7] and others, the results of the analysis given below show that these salts contain an excess of abietic acid in nearly every case.

The analysis of the abietates consisted in finding the percentage of metal present. The substance was carefully ignited in a porcelain crucible until the acid had been burned off. The basic residue was then treated with nitric or sulfuric acid, dried, ignited to constant weight, and weighed as the oxide or sulfate of the metal in question. The following table contains the results of the analyses conducted in this manner, accompanied by the calculated formula in each case:

Tin abietate gave an average of 6.10% tin, which corresponds to $Sn(C_{20}H_{29}O_2)_2.4C_{20}H_{30}O_2$.

Column I contains the results obtained by analyzing abietates which had been prepared by precipitation from aqueous solutions without subsequent solution in benzene. The sodium abietate from which the abietates were made contained a very slight excess of alkali. Column II shows the results from portions of the same samples of abietates as in Column I, with the only difference that they were first dissolved in benzene, the solution filtered and evaporated to dryness, and the powdered residue dried in the usual way before the analysis. As already stated, the benzene treatment was applied in order to remove from the abietate any metallic hydroxide which may have been formed during the precipitation. Hence, the figures in Column II should show a smaller percentage of metal than those in Column I. This is also the case throughout.

The abietates whose analysis is given in Column III were obtained by precipitation from a freshly prepared aqueous solution of sodium abie-

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[1] *J. Phys. Chem.*, **6**, 1 (1902).

[2] *Ann. Chem.*, **129**, 97 (1864).

[3] *Monatsh.*, **15**, 633 (1894).

[4] *Z. angew. Chem.*, **18**, 1739 (1905).

[5] *Dissert.*, 1900.

[6] *Ann. Chem.*, **129**, 98 (1864).

[7] *Monatsh.*, **15**, 633 (1894).

TABLE III.

Salt.	I.		II.		III.	
	% metal.	Corresponding formula.	% metal.	Corresponding formula.	% metal.	Corresponding formula.
Chromium abietate	3.38	$Cr(C_{20}H_{29}O_2)_3.2C_{20}H_{30}O_2$	2.83	$Cr(C_{20}H_{29}O_2)_3.3C_{20}H_{30}O_2$	4.50	$[Cr(C_{20}H_{29}O_2)_3]_3.2C_{20}H_{30}O_2$
	3.20		2.78		4.27	
	3.25		....		....	
Manganese abietate	4.85	$[Mn(C_{20}H_{29}O_2)_2]_2.3C_{20}H_{30}O_2$	4.20	$Mn(C_{20}H_{29}O_2)_2.2C_{20}H_{30}O_2$	6.87	$[Mn(C_{20}H_{29}O_2)_2]_2.C_{20}H_{30}O_2$
	4.94		4.62		6.83	
	4.96		....		....	
Nickel abietate	5.80	$[Ni(C_{20}H_{29}O_2)_2]_6.7C_{20}H_{30}O_2$	5.30	$[Ni(C_{20}H_{29}O_2)_2]_2.3C_{20}H_{29}O_2$	6.94	$[Ni(C_{20}H_{29}O_2)_2]_2.C_{20}H_{29}O_2$
	5.77		5.27		6.98	
	5.75		....		....	
Iron abietate	4.98	$[Fe(C_{20}H_{29}O_2)_3]_2.C_{20}H_{30}O_2$	4.44	$Fe(C_{20}H_{29}O_2)_3.C_{20}H_{30}O_2$	7.45	Basic iron abietate
	5.00		4.44		7.39	
	5.02		....		....	
Cadmium abietate	8.37	$Cd(C_{20}H_{29}O_2)_2.2C_{20}H_{30}O_2$	7.73	$[Cd(C_{20}H_{29}O_2)_2]_2.5C_{20}H_{30}O_2$	10.43	$Cd(C_{20}H_{29}O_2)_2.C_{20}H_{30}O_2$
	8.36		....		11.04	
	8.41		....		....	
Cobalt abietate	6.18	$Co(C_{20}H_{29}O_2)_2.C_{20}H_{30}O_2$	5.80	$[Co(C_{20}H_{29}O_2)_2]_5.6C_{20}H_{30}O_2$	6.38	$Co(C_{20}H_{29}O_2)_2.C_{20}H_{30}O_2$
	6.31		5.73		6.30	
	6.25		....		....	
Strontium abietate	8.26	$[Sr(C_{20}H_{29}O_2)_2]_4.5C_{20}H_{30}O_2$	7.62	$[Sr(C_{20}H_{29}O_2)_2]_2.3C_{20}H_{30}O_2$	6.93	$Sr(C_{20}H_{29}O_2)_2.2C_{20}H_{30}O_2$
	8.21		7.59		7.12	
	8.32		....		....	
Aluminum abietate	3.36	Basic aluminum abietate	2.93	$Al(C_{20}H_{29}O_2)_3$	....	
	3.33		2.97		....	
Copper abietate	8.56	$[Cu(C_{20}H_{29}O_2)_2]_4.C_{20}H_{30}O_2$	6.67	$Cu(C_{20}H_{29}O_2)_2.C_{20}H_{30}O_2$	....	
	8.51		6.78			

tate which contained a considerable excess of alkali, followed by the usual benzene treatment. Consequently, the results in Column III should be about equal to those in Column II. From the table it is seen that this is not the case. Instead of being equal they run higher, and even above those in Column I.

The results of these analyses, Table III, show that the abietates examined were not the pure normal or acid salts but probably normal or acid salts combined with varying amounts of abietic acid. The amount of the acid adhering to the salt may perhaps depend upon the concentration and degree of alkalinity of the sodium abietate solution from which the abietates are precipitated. On the whole, the salts are rich in abietic acid, but the analyses of the iron abietate given in Column III and of the aluminum abietate found in Column I indicate basic salts in these two cases. Furthermore, the results on aluminum abietate given in Column II correspond to the normal salt.

Some of the abietates possess characteristic colors resembling those of the corresponding inorganic salts. In the dry state the abietates given below are colored as follows:

Nickel abietate	greenish yellow
Chromium abietate	greenish yellow
Copper abietate	light blue
Cobalt abietate	lavender
Manganese abietate	pinkish white
Iron abietate	light brown
Silver abietate	white at first

turning brown on exposure to light.

The solubility of fourteen abietates in non-aqueous solvents and in water was investigated. The results are given in Table IV. The capital

TABLE IV.—SOLUBILITY.

	Abietate of													
Solvent.	Ba.	Ca.	Sr.	Cu.	Cd.	Zn.	Cr.	Al.	Co.	Ni.	Mn.	Ag.	Fe.	Na.
Pyridine	S	S	S	S	S	S	S	S	S	S	S	S	S	s
Aniline	S	S	S	S	S	S	S	S	S	S	S	S	S	I
Methyl alcohol	s	s	s	s	S	s	s	I	s	s	s	I	I	S
Ethyl alcohol	s	S	s	s	S	s	s	I	s	s	s	I	s	S
Amyl alcohol	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Benzene	S	S	S	S	S	S	S	S	S	S	S	S	S	I
Turpentine	S	S	S	S	S	S	S	S	S	S	S	S	S	I
Heptane	I	S	S	s	S	S	s	S	s	s	S	I	I	I
Kerosene	I	s	s	S	S	S	s	S	S	S	S	s	I	I
Carbon bisulfide	S	S	S	S	S	S	S	S	S	S	S	S	S	I
Ether	s	S	S	S	S	S	S	S	S	S	S	s	s	s
Acetone	I	s	I	S	S	S	S	I	S	S	S	s	s	I
Carbon tetrachloride	S	S	S	S	S	S	S	S	S	S	S	S	s	I
Chloroform	S	S	S	S	S	S	S	S	S	S	S	S	s	I
Ethyl acetate	S	S	S	S	S	S	S	S	S	S	S	S	s	I
Water	I	I	I	I	I	I	I	I	I	I	I	I	I	S

letter S indicates a fairly copious solubility, namely, that about 4% of the salts are present in solution, while small s represents a very slight solubility. Likewise, the capital letter I means that the salt is practically insoluble. Although these results are only qualitative, they may be of interest to those working with resins.

Based on this table, the following summary concerning the solubility of the salts is added. The abietates of the heavy metals are insoluble in water and but slightly soluble in methyl alcohol. In general, they are quite soluble in the ordinary non-aqueous liquids. Sodium abietate, on the contrary, dissolves readily in water and the alcohols but not in other solvents. Of the three alcohols used, amyl alcohol is the best solvent and methyl alcohol the poorest. Amyl alcohol dissolves all the abietates given in Table IV. Aluminum abietate is insoluble and chromium abietate soluble in acetone. Benzene, turpentine, pyridine, aniline, and carbon bisulfide dissolve all the abietates except that of sodium. Cadmium abietate dissolves in all the non-aqueous solvents tried. Methyl alcohol and heptane are the poorest organic solvents for the abietates.

In this paper it has been shown that abietic acid can be prepared sufficiently pure to give a fairly constant, though not a sharp melting point; that the formation of well defined crystals of the acid is good reason for regarding it as pure; that the production of pure salts of the acid is more difficult than the isolation of the pure acid itself.

Summary.

1. Pure abietic acid was isolated from commercial colophony by alcoholic extraction and recrystallization.

2. The molecular weight of the acid was determined by the freezing- and boiling-point methods. According to the cryoscopic method the molecular weight varied from 263 to 275, from 507 to 533, and from 279 to 284 in acetic acid, benzene, and phenol, respectively. Similarly, for the ebullioscopic method, it varied from 185 to 212, from 229 to 230, from 341 to 378, and from 336 to 360 in pyridine, acetic acid, benzene, and alcohol, respectively.

3. The heat of combustion of the melted acid was observed to be less than that for the unmelted, which indicates that the compound is probably oxidized at temperatures near its melting point. This accounts for the lack of sharpness in the melting point of the acid. The melting point was found to lie between 150° and 152°.

4. The abietates of sodium and potassium were made by neutralizing the acid with the corresponding alkali. From the sodium abietate solution the abietates of the heavy metals were precipitated.

5. Most of the abietates prepared were analyzed and nearly all of them were found to contain an excess of abietic acid.

6. It was observed that the abietates of the heavy metals were quite soluble in non-aqueous solvents and insoluble in water.

In conclusion, the writer takes this opportunity to thank Professor Kahlenberg for his valuable suggestions offered during the progress of the work.

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THE USE OF PYRIDINE AS A SOLVENT IN THE ESTIMATION OF HYDROXYL GROUPS BY MEANS OF ALKYL MAGNESIUM HALIDES.

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During the past eight or nine years there have been published a number of articles dealing with a method for the determination of hydroxyl groups in organic compounds by means of the Grignard reagent. The reaction involved, discovered by Grignard and Tissier,[1] and first developed qualitatively by Tschugaeff,[2] is as follows:

$$R.MgX + R'.OH = R.H + R'.OMgX.$$

In the methods proposed for the quantitative estimation of hydroxyl groups, the substance is dissolved in some solvent and the solution mixed with a solution of CH_3MgI in amyl ether, with a resultant evolution of methane, the volume of which is measured. From this volume can be readily calculated the number of hydroxyl groups in the molecule.

It is necessary, in carrying out a determination, to avoid all traces of moisture in the apparatus and in the reagents used. A more troublesome difficulty arises in connection with the use of a suitable solvent. The requirements in this direction call for, first, low vapor pressure; second, ease of purification; and third, general applicability.

Ethyl ether, the solvent used by Tschugaeff,[3] is useless for quantitative purposes on account of its very high vapor pressure. The first investigators to apply the method to quantitative purposes were Hibbert and Sudborough, who used amyl ether and phenetole with partial success.[4] These two solvents met admirably the first two requirements named above, but their application was not sufficiently wide, and it was shown that while very accurate results were obtained in many determinations, amyl ether solutions of the aliphatic amines and the lower fatty alcohols gave abnormal results, while phenetole solutions of almost all hydroxyl compounds and amines gave low results.

[1] *Compt. rend.*, **132**, 835 (1900).

[2] *Ber.*, **35**, 3912 (1902).

[3] *Loc. cit.*

[4] Hibbert and Sudborough, *J. Chem. Soc.*, **85**, 933 (1904); Sudborough, *Ibid.*, **95**, 477 (1909); Hibbert, *Ibid.*, **101**, 328 (1912).