PURIFICATION OF ABIETIC ACID FROM ROSIN AND PREPARATION OF SOME OF ITS DERIVATIVES[1]

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Received August 3, 1927 Published November 5, 1927

Rosin has not received as much scientific study as its importance in the industrial arts warrants. The annual value of rosin produced, of which somewhat less than sixty per cent. is exported, is approximately forty million dollars.

Rosin consists principally of organic acids commonly called abietic acid of the empirical formula $C_{20}H_{30}O_2$, and of a small per cent. of neutral material termed "resene." The resene seems to exert a decided influence on the reactivity of abietic acid. This is evidenced in a number of ways, but it has been especially noted in the esterification of the acid. No reaction or only a very small yield is at times obtainable when rosin is employed, but a satisfactory yield results when pure abietic acid is used. One of the chief difficulties encountered in research on this material has been obtaining a pure abietic acid.

The sodium complex salt method[2,3,4,5] was employed in securing abietic acid from which the other derivatives were prepared. It is of interest to note that abietic acid and the normal sodium salt are soluble in alcohol, whereas the sodium complex salt ($C_{19}H_{29}COONa.3C_{20}H_{30}O_2$) is insoluble. Advantage is taken of this fact to effect purification, the resene remaining in solution being thereby separated from the abietic acid. This method, it is believed, has decided advantages over methods previously used that involve long and tedious crystallizations. Yields of 80% may be secured and the time required for the purification is greatly shortened. It has been noted that when abietic acid or its salts are in contact with the resene, oxidation is greatly facilitated. This has been definitely shown by preparing rosin soaps and noting the resulting changes in the presence and absence of resene. Extended crystallizations, especially in the presence of resene, give ideal opportunity for such oxidation.

Isomerization of rosin is essential for the formation of the complex

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[1] The research described in this paper was carried out while Dr. Kesler was the incumbent of the Rosin Fellowship sustained in Mellon Institute by the Pine Institute of America (1924–1926), to which organization the authors are grateful for this support and also for the release of the work for publication. The present contribution is an abstract of a thesis presented by Dr. Kesler to the Graduate School of the University of Pittsburgh in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Aschan, *Ann.*, **424**, 117–33 (1921).

[3] Maly, *Ann.*, **129**, 96 (1864).

[4] Fremy and Sievert, *Zeitschrift für die gesammten Naturwissenschaften*, **14**, 311 (1849).

[5] *Bulletin de L'Institut du Pin*, March 15, **1926**, p. 350.

salts as commercial amorphous rosin gives no such precipitate. The isomerization can be followed by the change in optical rotation. The original acid rotates light to the right, while the isomerized products give a negative rotation. Mineral acids effect this change. Aqueous or gaseous hydrochloric acid proves to be an effective isomerizing agent. The same result may be accomplished by heating to 250°.

As only a few esters of abietic acid are noted in the literature,[6,7,8,9,10] a number of esters were prepared in order that the properties of these interesting neutral derivatives of rosin might be investigated. The use of dry hydrogen chloride as a catalytic agent was unsuccessful, so more energetic methods were sought. A number of methods have been used, and in the case of phenols the very reactive material phosgene was employed. The type reaction is $RCOONa + R'ONa + COCl_2 \longrightarrow RCOOR' + 2NaCl + CO_2$.

Hahn[11] gives a method for preparing esters of benzenesulfonic and *p*-toluenesulfonic acids. Gilman and Beaber[12] have also prepared a number of esters of *p*-toluenesulfonic acid. The alkyl *p*-toluenesulfonates obtained by this method, when mixed and heated with equimolecular quantities of sodium abietate dissolved in water, give the desired esters of abietic acid and sodium *p*-toluenesulfonate, which is water-soluble and may be recovered. The reaction proceeds very smoothly and often gives 95% yields. The type reaction is

$$CH_3C_6H_4SO_2Cl + ROH + NaOH \longrightarrow CH_3C_6H_4SO_3R + NaCl + H_2O$$
$$CH_3C_6H_4SO_3R + C_{19}H_{29}COONa \longrightarrow CH_3C_6H_4SO_3Na + C_{19}H_{29}COOR$$

The cost of reagents is not at all prohibitive to commercial production. It is possible to prepare not only aliphatic esters by this method but certain terpene esters as well.

The lower aliphatic esters are heavy, viscous oils of increasing boiling points with increasing weights. The specific gravities decrease as the series is ascended. The refractive indices check quite closely with the specific gravities and indicate that two double bonds are present in the molecule. The esters of the normal alcohols have higher boiling points than the corresponding *iso* compounds. A similar relation is also true in the case of specific gravities. The esters were all distilled at reduced pressures without decomposition.

Esters prepared with phenols could not be secured by any of the usual

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[6] Houben-Weyl, "Die Methoden der organischen Chemie," Georg Thieme, Leipzig, **1922**, II, p. 494.

[7] Virtanen, *Ann.*, **424**, 189 (1921).

[8] Ruzicka and Meyer, *Helv. Chim. Acta*, **6**, 1077 (1923).

[9] Ellis and Rabinovitz, *J. Ind. Eng. Chem.*, **8**, 406 (1916).

[10] Kaufman and Friedebach, *Ber.*, **55**, 1508 (1922).

[11] Hahn, *Ber.*, **54**, 1531 (1921).

[12] Gilman and Beaber, THIS JOURNAL, **47**, 518 (1925).

methods of esterification. As a result, a new method was developed which involves the action of phosgene upon dry sodium phenolates and sodium abietate with the formation of sodium chloride and carbon dioxide. It is quite essential that the materials be finely powdered, well mixed and thoroughly dried. Pressure increased the yields. The method works very well for all phenols employed and is believed to be a general reaction. Esters prepared with phenols are semi-solids at room temperature and are darker in color than the aliphatic esters. This method also gives fair results with certain of the terpene alcohols, such as are found in pine oil. Both rosin and pine oil are commercial products and their union gives esters which should be of considerable practical value. The pine oil alcohols are quite difficult to esterify as certain of them, such as terpineol, are tertiary alcohols. The esters are insoluble in water, but soluble in the usual organic solvents. However, they are only slightly soluble in cold alcohol but more so when heated. The insolubility in alcohol decreases as the series is ascended.

The plasticizers or softeners used in the manufacture of nitrocellulose lacquers are an important industrial commodity. The amount of plasticizer varies from 40 to 60% of the nitrocellulose employed. Its purpose is to remain in the film, keeping it soft and pliable without greatly diminishing its strength. The softener should be non-volatile and neutral in character; it should be miscible with lacquer solvents and a solvent for nitrocellulose; it should be stable on aging in lacquer films. Some of the esters of abietic acid appear to have application in this industry.

Experimental

One kilogram of "G" grade rosin containing 91% abietic acid was isomerized either by passing a current of dry hydrogen chloride gas through the melted rosin with constant stirring for twenty minutes, or by adding 1% of hydrogen chloride in the form of commercial aqueous hydrochloric acid to a hot 33% alcoholic solution of rosin. This was boiled for fifteen minutes. Aqueous or alcoholic sodium hydroxide was added to neutralize completely the hydrochloric acid and enough more to neutralize one-fourth of the acid content of the rosin. Stirring was discontinued and the mixture allowed to cool. Seeding facilitates crystallization of the sodium complex salt ($C_{19}H_{29}COONa.3C_{20}H_{30}O_2$). The entire solution sets into a white, solid, sponge-like mass composed of small, needle-like crystals which may be pressed or centrifuged to remove the mother liquor. Without washing, the salt contained less than $^1/_2$ of 1% of resene. A single alcoholic wash gives a pure sodium complex salt ($C_{19}H_{29}COONa.3C_{20}H_{30}O_2$), melting at 177°. Regeneration of abietic acid with subsequent precipitation does not raise the melting point.

Twenty grams of the complex sodium salt ($C_{19}H_{29}COONa.3C_{20}H_{30}O_2$) gave the following titration and gravimetric values.

Anal. Calcd. for 2.540 *N* alkali: 19.2 cc. Found: 19.1. Calcd.: Na, 0.3739 g. Found: 0.3734, 0.3729.

The calculated amount of mineral or acetic acid was added to the complex sodium salt in order to free the abietic acid. It melted when dry at 166°. Recrystallization does not raise the melting point.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.47; H, 9.93. Found: C, 78.98; H, 10.33.

Sodium abietate was prepared by treating the pure complex sodium salt with sufficient alkali and slowly drying with constant stirring in an atmosphere of carbon dioxide. The small lumps were finely pulverized and dried in a vacuum oven at 100° for four hours. The acid formed by treating the dried sodium abietate with acetic acid has the properties of pure abietic acid. This method was employed for preparing sodium abietate in all subsequent experiments where it is used.

Ethyl Abietate ($C_{19}H_{29}COOC_2H_5$).—To one mole (324 g.) of dry sodium abietate, one mole (154 g.) of diethyl sulfate was gradually added and the reaction mixture slowly stirred on a steam-bath for two hours. It was cooled and extracted with benzene. Upon removal of the solvent, a viscous oil remained which is nearly odorless and possesses a light yellow color not removed by repeated distillation. The yield is 85% of the theoretical. Saponification number found: 170.1; calcd.: 169.6. The properties of the following esters are found in Table I.

Propyl Abietate ($C_{19}H_{29}COOC_3H_7$).—One mole of sodium abietate dissolved in 600 cc. of water was refluxed with one mole of *n*-propyl-*p*-toluenesulfonate with constant stirring for two hours. The reaction mixture was allowed to cool. The ester layer was washed with water and distilled. An 80% yield of light yellow, odorless oil was obtained. Saponification number found: 163.0; calcd.: 162.7.

***Iso*propyl Abietate** ($C_{19}H_{29}COOC_3H_7$).—One mole of abietic acid was neutralized with 40 g. of sodium hydroxide in 600 cc. of water and heated until all the abietic acid was dissolved. Upon cooling, the soap set to a gel which was treated by the *p*-toluenesulfonate method as described above.

The following esters were also prepared by the *p*-toluenesulfonate method as described above.

n-Butyl abietate ($C_{19}H_{29}COOC_4H_9$); yield, 95%; saponification number found: 155.9; calcd.: 156.4.

*iso*Butyl abietate ($C_{19}H_{29}COOC_4H_9$); yield, 80%.

iso-Amyl abietate ($C_{19}H_{29}COOC_5H_{11}$); yield, 72%.

Allyl abietate ($C_{19}H_{29}COOC_3H_5$); yield, 45%.

Menthyl abietate ($C_{19}H_{29}COOC_{10}H_{19}$); yield, 65%.

Phenyl Abietate ($C_{19}H_{29}COOC_6H_5$).—One mole (116 g.) of carefully dried and powdered sodium phenolate was thoroughly mixed with one mole (324 g.) of well-dried and powdered sodium abietate. The mixture was placed in a glass tube in a well-ventilated hood and phosgene allowed to pass through the powder. No heat was applied but the heat of reaction was quite noticeable. A characteristic change to a resinous, viscous mass was noted and in one-half hour the reaction was complete. The reaction products were well washed with water and dilute alkali. The remaining semi-solid ester distilled at 330–333° at 4 mm., giving a dark-colored gum which did not become lighter in color by redistilling. The experiment was repeated in a bomb tube with liquid phosgene at room temperature and a yield of 87% was obtained. The specific gravity of the ester was 1.056 (15°/4°) and refractive index 1.5354. Upon saponification with 10% alkali and subsequent acidification, abietic acid crystals and phenol were again obtained.

The following esters were prepared by the phosgene method as described for phenyl abietate.

Hexalin abietate ($C_{19}H_{29}COOC_6H_{11}$); yield, 73%; saponification number found; 144.6; calcd.: 145.8.

m-Tolyl abietate ($C_{19}H_{29}COOC_7H_7$); yield, 78%.

α-Naphthyl abietate ($C_{19}H_{29}COOC_{10}H_7$); yield, 78%.

Terpineol abietate ($C_{19}H_{29}COOC_{10}H_{17}$).

Bornyl abietate ($C_{19}H_{29}COOC_{10}H_{17}$); yield, 75%.

Benzyl Abietate ($C_{19}H_{29}COOC_7H_7$).—One-fourth mole of abietic acid was dissolved in carbon tetrachloride with one-fourth mole of benzyl chloride. Twenty-five cc. of 40% sodium hydroxide was slowly added and then 25 cc. of water. The mixture was refluxed for three hours at which time the odor of benzyl chloride had disappeared. The ester was washed and the solvent removed by distillation. A yield of 85% was secured. Saponification number found: 141.7; calcd.: 142.8.

Cholesteryl Abietate ($C_{19}H_{29}COOC_{26}H_{43}$).—One-tenth mole of cholesterol was melted with one-tenth mole of abietic acid in the presence of zinc as a catalyst. After heating for two hours at 200°, a resin was obtained. The resin was dissolved in benzene and washed. The solvent was distilled off, leaving a resin which could not be distilled without decomposition. A yield of 94% was secured. Saponification number found: 83.6; calcd. 85.3. This ester was also obtained from cholesteryl chloride and sodium abietate. The cholesteryl chloride was made by treating cholesterol with sulfuryl chloride.

Cetyl Abietate ($C_{19}H_{29}COOC_{16}H_{33}$).—This ester was prepared by heating at 150° for six hours equal molecular quantities of cetyl iodide and sodium abietate. The reaction product was dissolved in benzene and washed. The recovered resin gives no test for halogen.

To determine the applicability of the esters of abietic acid as plasticizers, a number of films were prepared on a copper plate having a surface of mercury amalgam. A standard lacquer composition was prepared in which tricresol phosphate and dibutyl phthalate were used as the plasticizers. By substituting esters of abietic acid for the standard plasticizers, comparisons of the resulting films were made. A typical composition is as follows:

Substance	Per cent.	Substance	Per cent.
Nitrocellulose in ansol	10	Butyl alcohol	20
Ester gum	5	Diethyl carbonate	8
Esters of abietic acid	5	Toluene	32
Ansol	20		

The solubility of the cellulose nitrate in the different esters, the flexibility and adhesion of the film and its strength and elasticity were especially noted. The results obtained indicate that abietic acid esters possess properties allowing their use wherever a neutral or softening effect is desired.

TABLE I

CONSTANTS OF ESTERS

Esters of abietic acid	B. p., °C.	Press., min.	M. p., °C.	Sp. gr. 15°/4°	Refractive index
Methyl	225–226	16	.....	1.050	1.5344
Ethyl	204–207	4	.....	1.032	1.5265
n-Propyl	237–240	4	.....	1.015	1.5229
*iso*Propyl	214–217	4	.....	1.010	1.5200
n-Butyl	247–250	3	.....	1.014	1.5192

Table I (*Concluded*)

Esters of abietic acid	B. p., °C.	Press., mm.	M. p., °C.	Sp. gr. 15°/4°	Refractive index
*iso*Butyl	222–225	4	.....	1.008	1.5171
iso-Amyl	254–257	4	.....	1.001	1.5165
Allyl	282–285	5	.....	1.024	1.5242
Phenyl	330–333	4	.....	1.056	1.5354
Hexalin	299–302	4	.....	1.061	1.535
m-Tolyl	310–313	5	.....	1.039	....
α-Naphthyl	290 (decomp.)	2	.....	1.116	....
Terpineol	310 (decomp.)	2	.....	1.082	....
Benzyl	294–297	4	.....	1.036	1.551
Cholesteryl	.....	..	122–125	...	....
Menthyl	.....	..	77–83 (softens)	...	....
Bornyl	.....	..	75–80 (softens)	...	....
Cetyl	.....	..	42	...	....
Sodium complex abietate	.....	..	177	...	....
Abietic acid	.....	..	166	...	....

Summary

1. A method which is based on the formation of an acid salt of rosin has been employed for purifying rosin to obtain abietic acid in good yield. Some advantages of this method are indicated.

2. A number of new esters of abietic acid have been prepared and their properties determined (see Table I). Certain of these esters have commercial applications wherever a plasticizing or softening effect is desired.

3. A new method has been developed with phosgene for securing esters of phenols and esters with alcohols of the terpene family. It is believed to be a general reaction for such materials.

4. The value of esters of *p*-toluenesulfonic acid as esterifying reagents for preparing esters of abietic acid is shown.

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