amine salt which was recrystallized several times to obtain the constant rotating salt (same as that from which the acid was isolated), $[\alpha]^{24}_{\mathrm{D}}$ +102°. The resin acid was regenerated in the usual manner with the same rotation, $[\alpha]^{24}_{\mathrm{D}}$ +159°, and the same ultraviolet absorption characteristics, particularly the height of the most intense band, 250 mμ, at $\alpha = 80.0$. The methyl ester, prepared with diazomethane as above, was obtained with the same constant melting point 61.5–62°. Saponification in alcoholic alkali with alkali in a sealed tube at 50° for ninety-six hours with subsequent acidification with carbon dioxide and boric acid resulted in the quantitative isolation of neoabietic acid with unchanged rotation, $[\alpha]^{24}_{\mathrm{D}}$ +159°.

Isolation of Neoabietic Acid from Gum Rosin.—A 200-g. sample of gum rosin was dissolved in 400 g. of acetone and treated, at 50°, with 45 g. of diethylamine in an equal weight of acetone. The complete precipitation of salts was allowed to take place over a long period of time (twenty-four hours) at room temperature. No attempt was made to hasten the crystallization by cooling because the necessary fractionation was not obtained in this manner. The salts were fractionated from acetone to a rotation $[\alpha]^{24}_{\mathrm{D}}$ +70° and converted to the butanolamine salts by dissolving in acetone and adding the necessary amount of butanolamine. The latter were, in turn, crystallized to a rotation $[\alpha]^{24}_{\mathrm{D}}$ +102° and the pure neoabietic acid isolated in 5% yield (10.0 g.) with rotation $[\alpha]^{24}_{\mathrm{D}}$ +159°.

Summary

1. An improved method, based on the amine salt technique, for the isolation of abietic acid from acid-isomerized wood rosin and levopimaric acid from the gum oleoresin of *Pinus palustris* is described.

2. The isolation of a new, abietic-type acid, termed neoabietic acid, from heat-isomerized abietic acid, the gum oleoresin of *Pinus palustris* and gum rosin is described.

3. The ultraviolet absorption spectra, utilizing specific absorption coefficients, α, have been determined for each of the three abietic-type acids.

WILMINGTON, DELAWARE RECEIVED[24] AUGUST 12, 1947

---

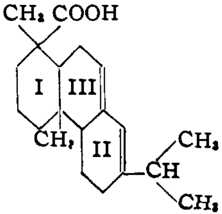
[24] Original manuscript received August 9, 1946.

[CONTRIBUTION FROM THE HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

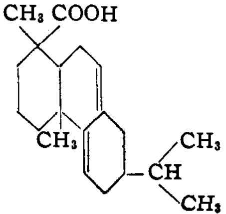
Resin Acids. II. The Structure of Neoabietic Acid

BY GEORGE C. HARRIS AND THOMAS F. SANDERSON

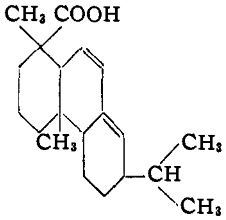
Neoabietic acid[1] has been isolated from the oleoresin and rosin of *Pinus palustris*. It has now been proved that this acid is an abietic-type acid since upon dehydrogenation with palladium–carbon catalyst retene, 1-methyl-7-isopropylphenanthrene, was isolated. The presence of two double bonds was shown by catalytic hydrogenation to the tetrahydro acids and by absorption in the ultraviolet region.[2] The intense band (Fig. 1, Curve 1) at 250 mμ, indicated also that the two double bonds are conjugated between two rings or that one is exocyclic with respect to the other in analogy with the absorption of abietic acid at 241 mμ and in contrast with that of levopimaric acid at 272 mμ. With this information, the structures I–V came into consideration.



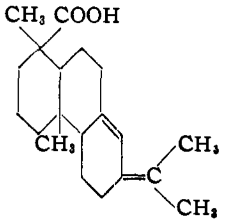
242 mμ
I



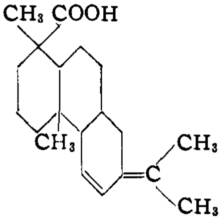
247 mμ
II



237 mμ
III



252 mμ
IV



242 mμ
V

From the work of R. B. Woodward[3] predictions can be made concerning the wave length of the most intense band of absorption of this type of conjugated system. These predictions are based on the degree of substitution of the double-bond carbon atoms; they are given below each formula. Since neoabietic acid demonstrates its most intense band at 250 mμ and since the predicted value for abietic acid, I, was so close to that found, 241 mμ, formula IV was at once suspected as that for neoabietic acid.

If formula IV were that for neoabietic acid, ozonization and decomposition of the ozonide with water would result in the formation of acetone, as one of the products. The experiment was carried out and acetone was isolated as its 2,4-

---

[1] G. C. Harris and T. F. Sanderson, Resin Acids. I, THIS JOURNAL, 70, 334 (1948).

[2] The ultraviolet absorption data were determined by Dr. Evelyn V. Cook of this Laboratory.

[3] R. B. Woodward, THIS JOURNAL, 64, 72 (1942).

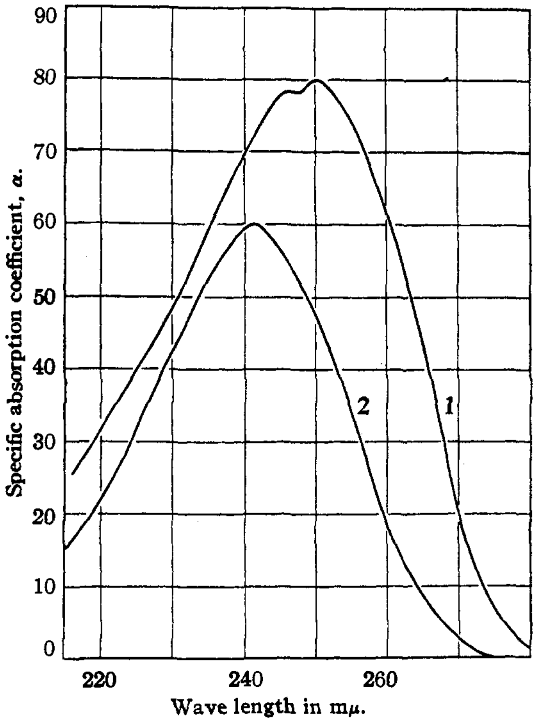
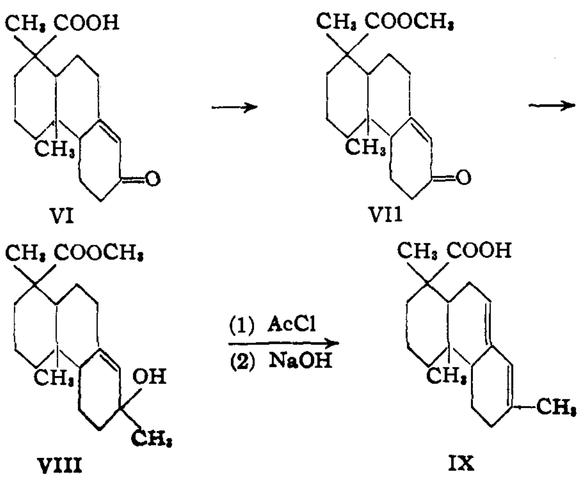


Fig. 1.—Ultraviolet absorption spectra: 1, neoabietic acid; 2, ketone (VI).

dinitrophenylhydrazone which was shown to be that of acetone after a mixed melting point with an authentic sample. After partial ozonolysis, that is, ozonization of only the exocyclic double bond of the isopropylidene group, in addition to acetone an α,β-unsaturated ketone would be obtained. This was found to be the case in the isolation of the ketone, VI, with melting point 187–188°. The functionality of the α,β-unsaturated keto acid was shown in the following manner. The neutral equivalent of the crystalline compound was 276, theory for the unsaturated keto acid 276. Its methyl ester, VII, was prepared with diazomethane and melted at 127–128°. The presence of the keto group was shown after the preparation of its 2,4-dinitrophenylhydrazone, m. p. 221–222°, and the isolation of the crystalline methyl Grignard addition product of the ester, VIII, m. p. 100–102°. The quantitative absorption of 1.0 mole of hydrogen of the latter in absolute ethanol with Adams catalyst indicated the residual unsaturation. Upon removal of the tertiary hydroxyl group of the Grignard product, VIII, with acetyl chloride or dry hydrogen chloride in benzene, hydrolysis of the ester group with alkali in diethylene glycol and redistribution of the double bonds, an abietic acid analog, IX, was obtained with rotation, $[\alpha]^{24}\text{D}$ − 125°, m. p. 187–190°, and specific absorption coefficient, α = 80.0 (Fig. 2).



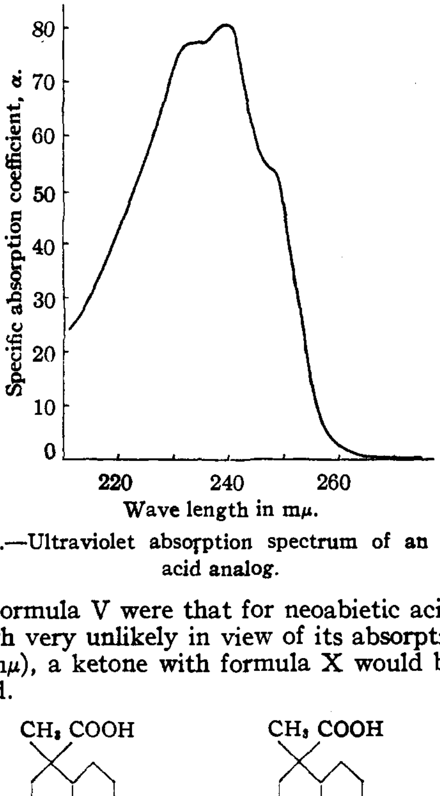
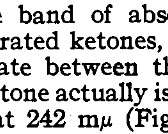
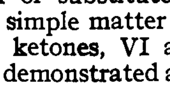


Fig. 2.—Ultraviolet absorption spectrum of an abietic acid analog.

If formula V were that for neoabietic acid (although very unlikely in view of its absorption at 242 mμ), a ketone with formula X would be obtained.



VI



X

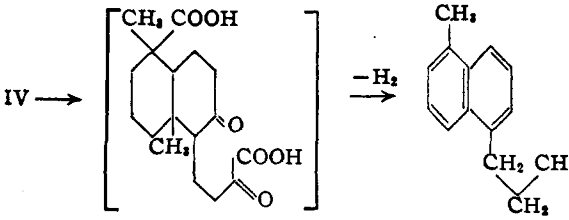
Using Woodward's[4] rules for predicting the most intense band of absorption of substituted α,β-unsaturated ketones, it is a simple matter to differentiate between the two ketones, VI and X. The ketone actually isolated demonstrated a maximum at 242 mμ (Fig. 1, Curve 2), a value that falls well within the limits,[4] 239 ± 5 mμ, set for a system with substitution similar to that of ketone VI and outside of those, 225 ± 5 mμ, set for a system similar to that of ketone X. Therefore

---

[4] R. B. Woodward, This Journal, 63, 1123 (1941).

formula VI is that for the ketone and formula IV that for neoabietic acid.

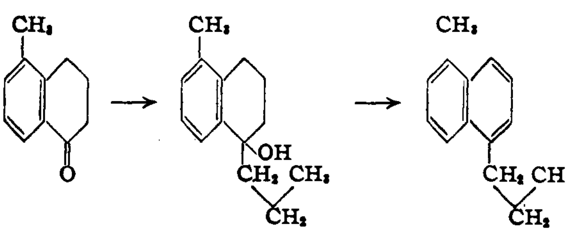
Further evidence for formula IV would be the isolation of a dialkylated naphthalene upon complete ozonization and dehydrogenation of the decomposed ozonide. In the case of the other structures, I through III, V having been eliminated, both rings II and III are split to result in the isolation of a substituted benzene nucleus or complete decomposition. Actually a 1,5-disubstituted naphthalene, XII, was isolated as proved



XI XII

by the similarity of the ultraviolet absorption curves of the trinitrobenzolate of this material with that of the synthetic sample and of an authentic sample of 1,5-dimethylnaphthalene[5] (Fig. 3). The hydrocarbon was isolated from the dehydrogenation mixture as its trinitrobenzolate and analyzed as the derivative and as the pure substance. From the analytical data it was determined to be 1-methyl-5-*n*-propylnaphthalene which could be obtained only from a compound with formula IV.

Hydrocarbon XII was synthesized in the following manner. The *n*-propyl Grignard product, of 5-methyl-1-tetralone,[5] XIII, was prepared and dehydrogenated with a palladium-on-carbon cat-



XIII XIV XII

alyst at 250°. The trinitrobenzolate of the hydrocarbon was prepared and found to melt at 82–84°. A mixed melting of the trinitrobenzolate of the hydrocarbon from the dehydrogenation mixture and this authentic sample showed no depression, m. p. 82–84°. The two derivatives also demonstrated identical X-ray diffraction patterns (Fig. 4).

For the sake of completeness and to eliminate the possibility of obtaining acetone from a structure such as that of abietic acid,[6] I, the same ex-

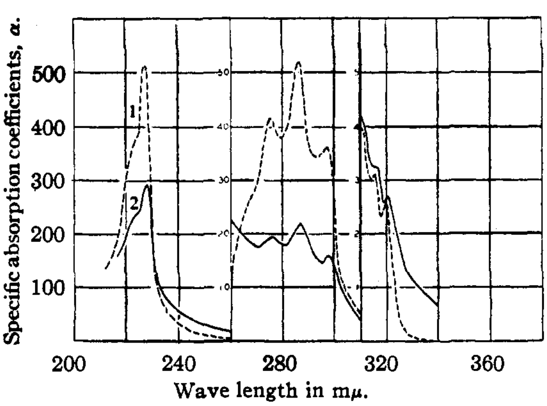


Fig. 3.—Ultraviolet absorption spectra: 1, the hydrocarbon, 1,5-dimethylnaphthalene; 2, the trinitrobenzolates of the isolated and synthetic 1-methyl-5-*n*-propylnaphthalene (identical curves for the two materials).

periments were carried out with abietic acid. The failure to obtain acetone or a di- or tri-alkylated naphthalene upon complete ozonization both lends strength to the structure proof of neoabietic acid and eliminates the possibility of formula V as that of abietic acid in view of its absorption at 241 mμ wave length.

Experimental[7]

Dehydrogenation and Hydrogenation of Neoabietic Acid.—A 2.0-g. sample of neoabietic acid was mixed intimately with 2.0 g. of 5% palladium-on-carbon catalyst and the mixture heated at 300–330° for four hours. Carbon dioxide gas was passed over the reaction mixture to eliminate the reaction gases. After cooling to room temperature, the reaction products were dissolved in ether and separated from the catalyst by filtration. The oil was dissolved in ethanol and treated with a concentrated ethanol solution of trinitrobenzene to obtain 1.9 g. (65% yield) of constant melting derivative, m. p. 143–144°, that was shown to be that of retene when no depression was observed in a mixed melting point with an authentic sample.

Upon quantitative hydrogenation of neoabietic acid, 1.29% of hydrogen (H_2) was absorbed, calcd. for two double bonds 1.32%.

Ozonization of Neoabietic Acid.—The acid, rotation $[\alpha]^{24}_D$ +159°,[8] was ozonized in 1.0-g. batches in 50 cc. of ethyl chloride at −60° to −70° using an oxygen flow of 20–25 liters per hour to obtain an oxygen solution of 5% of ozone. The gas was passed through the solution[9] until a purple coloration developed (*ca.* two hours) which indicated an excess of ozone. At the end of this time, the excess ozone was swept out with oxygen.

Decomposition of the Ozonide: Isolation of Acetone.—The ethyl chloride solution of the ozonide was added dropwise to hot water in an apparatus so designed that the ethyl chloride was evaporated and the acetone–water

---

(5) We wish to thank Dr. E. W. J. Butz of the Bureau of Animal Industry, U. S. Department of Agriculture, for a pure sample of this material; E. W. J. Butz, This Journal, 62, 2557 (1940).

(6) The structure was proved as that of formula I by L. F. Fieser and W. P. Campbell, *ibid.*, 60, 159 (1938), and L. Ruzicka, L. Sternbach and O. Jeger, *Helv. Chim. Acta*, 24, 504 (1941).

(7) All melting points are corrected.

(8) All rotations are of 1% solutions in absolute ethanol.

(9) The subsequent isolation of the hydrocarbon (XII) was indeed difficult until the technique for this type of ozonization was developed. When the solvent in the reaction was not anhydrous, the ozonide was decomposed in the medium and the intermediate ketone (XI) further attacked to form a lactone (A. Baeyer and V. Villiger, *Ber.*, 32, 3625 (1899); 33, 858 (1900). The active agent in Caro's acid is ozone). However, when the solvent was anhydrous, the ozonide remained intact during the ozonolysis to result in the formation of the ketone (XI) upon decomposition of the ozonide and the subsequent isolation of the hydrocarbon in good yield upon dehydrogenation.

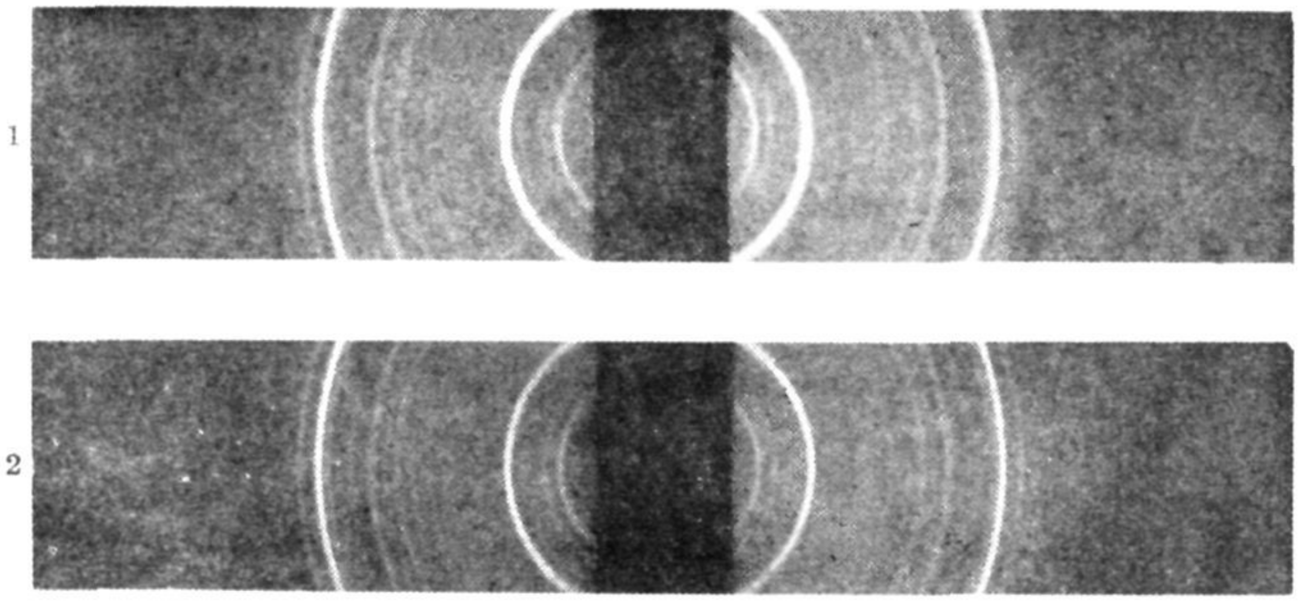


Fig. 4.—X-Ray diffraction patterns of trinitrobenzolates of 1-methyl-5-*n*-propylnaphthalene: 1, isolated; 2, synthesized.

azeotrope refluxed back to the receiver. After two hours of boiling, small portions of distillate were passed periodically for an hour through a saturated alcoholic solution of 2,4-dinitrophenylhydrazine. The alcoholic solution of the reagent (100 cc. of alcohol; 1.0 g. of reagent) was treated with 2 cc. of concentrated hydrochloric acid and boiled until a clear solution was obtained. Upon cooling, in addition to the dark red crystals of reagent, there appeared long, yellow needles which were recrystallized to a constant melting point of 124–126° and were proved to be the 2,4-dinitrophenylhydrazone of acetone when no depression was observed on melting with an authentic sample.

Isolation of 1-Methyl-5-*n*-Propylnaphthalene, XII.—The non-steam-volatile fraction of the decomposed ozonide was dissolved in ether and the bicarbonate-soluble fraction isolated (0.7 g. from 1.0 g. of acid). This was powdered, mixed intimately with 0.7 g. of 5% palladium–carbon catalyst, and dehydrogenated under carbon dioxide gas at 330–350° for four hours. The catalyst was filtered from an ether solution of the dehydrogenation product, the ether evaporated, and the residue dissolved in alcohol and treated with a saturated alcoholic solution of trinitrobenzene. The derivative precipitated and was crystallized to a constant melting point, 82–84°. The molecular weights were determined ebullioscopically, using acetone as solvent.

Anal. Calcd. for $C_{14}H_{16}\cdot C_6H_3N_3O_6$: C, 60.6; H, 4.8; N, 10.6; mol. wt., 199. Found: C, 59.8, 60.3; H, 4.8, 4.6; N, 10.3, 10.0; mol. wt., 201, 203.

The derivative in benzene was passed through a column of alumina to separate the hydrocarbon.

Anal. Calcd. for $C_{14}H_{16}$: C, 91.3; H, 8.7; mol. wt., 184. Found: C, 90.8, 91.0; H, 9.0, 9.2; mol. wt., 185, 188.

Preparation of 1-Methyl-5-*n*-propylnaphthalene, XII.—A 1.0-g. sample of 5-methyl-1-tetralone (XIII), m. p. 49.5–50.5°, was dissolved in dry ether and added to an ether solution of an *n*-propyl Grignard reagent prepared from 0.5 g. of magnesium and 3.3 g. of *n*-propyl iodide. The addition product was decomposed with saturated ammonium chloride and the tertiary alcohol, 1.3 g., isolated in ether. Attempts to crystallize the latter failed.

The oil was mixed intimately with 1.0 g. of 5% palladium-on-carbon catalyst and heated at 250° for two hours. The catalyst was filtered from an ether solution of the dehydrogenation mixture and the trinitrobenzolate of the hydrocarbon prepared in an alcoholic solution of the hydrocarbon using a saturated alcoholic solution of trinitrobenzene and crystallized to a constant melting point, 82–84°. A mixed melting point of the derivative from the dehydrogenation mixture with that of the synthetic sample showed no depression, m. p. 82–84°.

Isolation of Ketone VI.—For the ozonization of only the isopropylidene double bond the experiment was carried out in the same manner as for complete ozonization in respect to solvent, concentration, and temperature, but the time of ozonization was only thirty minutes. The ozonide was decomposed in the same manner and the product isolated in ether. The ketone was crystallized from the mixture from ether, and recrystallized to a constant melting point, 187–188°, and ultraviolet absorption curve with absorption coefficient, $\alpha = 60.2$.

Anal. Calcd. for $C_{17}H_{24}O_3$: C, 74.24; H, 8.72; neut. equiv., 276. Found: C, 74.04, 73.93; H, 8.96, 8.84; neut. equiv., 276.

The methyl ester, VII, was prepared in the usual manner with diazomethane and melted at 127–128°.

Anal. Calcd. for $C_{18}H_{26}O_3$: C, 74.45; H, 9.03. Found: C, 74.49, 74.45; H, 9.27, 9.19.

Derivatives of Ketone VI.—The 2,4-dinitrophenylhydrazone of the pure ketone was prepared in the usual manner in ethanol and recrystallized to a constant melting point, 221–222°.

The Grignard reaction product was prepared in the following manner. The reagent was prepared in a dropping funnel using 1.0 g. of magnesium turnings and 5.7 g. of methyl iodide in 25 cc. of dry ether and added dropwise to an ether solution of 5.8 g. of the ester, VII. A precipitate formed that remained insoluble after one hour of boiling of the mixture. After standing overnight, the reaction product was decomposed with saturated ammonium chloride and the product dissolved in ether. The ether solution was washed well with water, dried and the ether evaporated to obtain, upon recrystallization from ether–hexane, 3.0 g. of material with melting point 100–102°, VIII.

Anal. Calcd. for $C_{19}H_{30}O_3$: C, 74.47; H, 9.87. Found: C, 74.52, 74.43; H, 9.84, 9.87.

Upon quantitative hydrogenation in absolute ethanol with Adams catalyst, the methyl ester of the Grignard addition product absorbed 0.63% of hydrogen, theory for one double bond 0.65%.

Isolation of the Abietic Acid Analog, IX.—A 5.0-g. sample of the Grignard product was dissolved in acetyl chloride at room temperature (same results obtained with dry hydrogen chloride in benzene). After standing for one hour, the reagent was evaporated under vacuum for a period of twenty-four hours. Attempts at crystallizing the ester were not successful; therefore, it was hydrolyzed in the usual manner with alkali (3.0 g.) in diethylene glycol. The acid was readily crystallized from alcohol and water to a constant melting point, 187–190°, $[\alpha]^{24}D$ − 125°, and specific absorption coefficient, $\alpha = 80.0$.

Anal. Calcd. for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.68, 78.69; H, 9.45, 9.50.

Summary

The structure of neoabietic acid has been proved with the aid of Woodward's rules for unsaturated systems, and by the isolation of acetone, a 1,5-dialkylated naphthalene, and a substituted α,β-unsaturated ketone.

WILMINGTON, DELAWARE RECEIVED[10] AUGUST 12, 1947

---

[10] Original manuscript received August. 9, 1946.

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

N,N'N''-Triacylmelamines

BY WILLIAM S. EMERSON AND TRACY M. PATRICK, JR.

Ostrogovich[1] has reported that treatment of melamine with acetic anhydride gives 96% of diacetylmelamine and with benzoic anhydride gives 100% of tribenzoylmelamine. Diacetylmelamine can be further acetylated with a large excess of acetic anhydride to triacetylmelamine.[1] Triacetylmelamine also can be prepared by acetylating melamine with acetic anhydride in the presence of sodium acetate.[2]

We have found that aliphatic anhydrides above acetic give triacylmelamines as the sole products, and have prepared eleven such compounds by this method in 85–99% yields. We have also prepared diacetylmelamine by Ostrogovich's method.

Attempts to hydrolyze tripropionylmelamine to less highly acylated products were unsuccessful. The compound was unaffected by boiling water but was completely hydrolyzed to melamine by hot aqueous sodium hydroxide or sodium carbonate. Hot aqueous hydrochloric acid not only removed the propionyl groups but also hydrolyzed the melamine to what was probably a mixture of ammeline and ammelide.

Our tribenzoylmelamine melted at 201–203° in contrast to the 142–143° reported by Ostrogovich. His product was probably solvated.

Experimental

Preparation of Triacylmelamines.—These compounds were prepared by heating melamine with the appropriate acid anhydride. In the smaller runs a large test-tube (1 in. by 10 in.) with a thermometer as the stirrer, served as the reaction vessel. The larger runs were conducted in three-necked flasks of suitable dimensions. In all cases the temperature was raised by means of an oil-bath to the value indicated in the table and held there for five to thirty minutes. Upon cooling, the reaction mixture was diluted with some solvent such as methanol, ethanol, acetone or ethyl acetate, and filtered. The solid was washed with additional solvent and dried to obtain the crude yield. Further purification was effected by crystallization from glacial acetic acid or from the anhydride used in the preparation of the compound in question. The compounds prepared are summarized in Table I.

TABLE I

N,N',N''-TRIACYLMELAMINES

Acyl	Mol.[b] ratio	Reaction Temp., °C.	Reaction Time, min.	Yield, %	M. p.,[c] °C.	Nitrogen, % Calcd.	Nitrogen, % Found
Acetyl[a]	12	132	15	99[d]	312[e]	40.0	39.6
Propionyl	8.1	158	15	94	282	28.6	28.6[f]
n-Butyryl	12	160	30	98	258	25.0	24.6
n-Valeryl	10	172	30	94	228–229	22.2	22.4[f]
Isovaleryl	12	167	15	85	216–218	22.2	21.8
Caproyl	8.8	175	15	91	220	20.0	19.9
Oenanthyl	10	160	5	90	210	18.2	18.2
Caprylyl	9.3	175	15	94	209	16.7	16.7
Pelargonyl	6.3	185	5	88	194–195	15.4	15.3
Lauryl	6.5	192	15	99	178–179	12.5	12.5
Stearyl	3.5	200	30	93	159–161	9.08	9.66[f]
Oleyl	4.0	197	30	99	138–140	9.14	9.49
Benzoyl	8.3	172	60	84	201–203[g]	19.2	19.2

[a] Diacetylmelamine. [b] Molar ratio of anhydride to melamine. [c] All melting points corrected. [d] Ostrogovich[1] obtained a 96% yield, m. p. 305–306°. [e] Decomposed. [f] Microanalyses by the Oakwold Laboratories, Alexandria, Virginia. [g] Ostrogovich[1] gives m. p. 142–143°.

Hydrolyses of Tripropionylmelamine.—When 5 g. of tripropionylmelamine and 100 cc. of water were boiled under reflux for one hour the tripropionylmelamine was recovered unchanged, m. p. 275–276° (282°).

A 5-g. sample of tripropionylmelamine was boiled one hour with 100 cc. of 5% aqueous sodium hydroxide. Upon cooling, the mixture was neutralized with acetic acid and filtered. The 1.7 g. (81%) of dried solid proved to be melamine, m. p. 350° uncor. (347°).[1]

A similar experiment in which 100 cc. of 5% aqueous sodium carbonate was used yielded 1.7 g. (81%) of melamine, m. p. 353–354° uncor. (347°).[1]

A mixture of 5 g. of tripropionylmelamine and 100 cc. of 5% aqueous hydrochloric acid was boiled under reflux for one hour, cooled and neutralized with aqueous sodium bicarbonate. The solid was separated by filtration, washed with water and dried. It weighed 1.8 g. When heated on a spatula it did not melt but slowly decomposed and sublimed. It was soluble in dilute alkali.

Anal. Found: N, 50.8, 50.7. Calcd. for ammeline: N, 55.1. Calcd. for ammelide: N, 43.8.

Summary

Eleven new triacylmelamines have been prepared in 85–99% yield by treating melamine with the appropriate acid anhydride.

RECEIVED JULY 21, 1947

---

[1] Ostrogovich, *Gazz. chim. ital.*, **65**, 566 (1935).

[2] Cason, THIS JOURNAL, **69**, 495 (1947).