[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Substitution Reactions of Dehydroabietic Acid

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In our paper[2,3] reporting the first preparation of the partially aromatic dehydroabietic acid, obtained from abietic acid by hydroxylation with selenium dioxide and dehydration, we advanced the hypothesis that the so-called pyroabietic acids of the literature are not isomerization products of abietic acid but mixtures of hydro and dehydro acids resulting from the disproportionation of the doubly unsaturated acid. This conception of the pyro acids, based at the time merely on the recognition that the substances contain dehydroabietic acid, as revealed in Pd-treated acid by spectroscopic data and nitration and in heat-treated acid by nitration, was promptly established by Fleck and Palkin,[4] who obtained the first conclusive evidence of disproportionation. From their Pd-treated pyroabietic acid,[5] these investigators succeeded in isolating pure dehydroabietic acid, identical with our material, a tetrahydro acid, and a substance having the composition of a dihydro acid and later identified[6] as an isomeric (known) lactone; in the recent work[6] another dihydro acid was isolated. Littmann[7] also isolated dehydroabietic acid from Pd-treated material and obtained evidence of the presence of a tetrahydride, and Ruzicka and co-workers[8] have reported experiments showing that Pd-treated and heat-treated acids are mixtures. Although heat-treated acids have been characterized less extensively than material prepared by the method of Fleck and Palkin,[5] evidence is available showing that disproportionation also occurs on heating. Hasselstrom and co-workers,[9] in an investigation of the action of sulfuric acid on a heat-treated pyro acid, obtained a crystalline sulfonic acid having the composition of a dehydroabietic acid derivative, and isolated a lactone known to be an isomerization product of a dihydroabietic acid. This is the lactone which Fleck and Palkin[6] subsequently isolated from Pd-treated acid. Ruzicka and co-workers[8] fractionated a heat-treated acid and isolated another dihydro acid and a substance corresponding in properties and spectrum to our dehydroabietic acid.

It is evident that the acid mixtures obtained by heating abietic acid either alone or with a dehydrogenation catalyst constitute a potential and abundant source of dehydroabietic acid. Since the method of preparing the pure acid previously described[2] does not provide a ready means of obtaining the acid in quantity, as required for our projected research,[2] we investigated this possible source. Probably the material richest in dehydroabietic acid is that prepared

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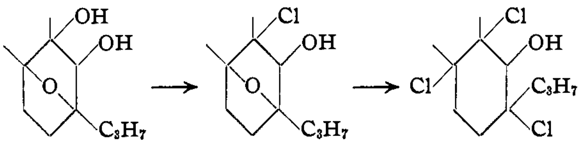
(3) The position regarding the structures suggested in this paper[2] for abietic acid and levopimaric acid is not altered by recent work from other laboratories. The new degradation of levopimaric reported by Wienhaus and Sandermann, *Ber.*, **71**, 1094 (1938), can be explained just as well with our formula (Δ: 7, 8; 14, 13) as with that employed for illustration by these authors (Δ: 5, 6; 7, 8), the reaction of their dihydroxy oxide with hydrogen chloride at 0° being represented as follows



The ready cleavage of the oxide bridge without disturbance of the acetylatable hydroxyl group is indeed better understandable on the assumption that the bridge is linked at each end in a tertiary rather than secondary condition. The degradations of Steele's "abietic acid" and of levopimaric acid by Ruzicka and Sternbach, *Helv. Chim. Acta*, **21**, 565 (1938), and by Ruzicka, Bacon, Lukes and Rose, *ibid.*, **21**, 583 (1938), can be interpreted, as these investigators show, with the formulas suggested. Ruzicka and Sternbach raise an interesting question concerning the validity of the evidence of conjugation in abietic acid furnished by our observation that the compound enters into the diazo coupling reaction but accept the view that conjugation is indicated by the absorption maximum. They point out, however, that some of their degradation products obtained in small amounts from the Steele acid mixture may have arisen from companion substances and not from the conjugated acid responsible for the selective absorption. This does not alter conclusions based upon results obtained with suitably purified (Palkin) abietic acid. Raudnitz, Lederer and Kahn, *Ber.*, **71**, 1273 (1938), have expressed the view that even this acid may not be homogeneous, their evidence being that purified acid and Steele acid were both found to give about 3% of acetone on prolonged treatment with ozone. Since Ruzicka, Meyer and Pfeiffer, *Helv. Chim. Acta*, **8**, 637 (1924), found that Steele acid yields isobutyric acid on ozonization as in the permanganate oxidation, it appears that ozone is capable of breaking the carbon chain as well as adding to the double bonds. The isolation of a small amount of acetone therefore seems of questionable significance. While Schultz, *Bull. inst. pin*, **38**, 25 (1938), regards the isolation of oxalic acid in good yield on oxidation of abietic acid with permanganate as an argument for the Δ: 13, 5; 6, 7-structure, this seems to us less convincing than the evidence against such a formulation, particularly since oxalic acid may arise from various parts of the molecule.

(4) Fleck and Palkin, THIS JOURNAL, **60**, 921 (1938).

(5) Fleck and Palkin, *ibid.*, **59**, 1593 (1937).

(6) Fleck and Palkin, *ibid.*, **60**, 2621 (1938).

(7) Littmann, *ibid.*, **60**, 1419 (1938).

(8) Ruzicka, Bacon, Sternbach and Waldmann, *Helv. Chim. Acta*, **21**, 591 (1938).

(9) (a) Hasselstrom, Brennan and McPherson, THIS JOURNAL, **60**, 1267 (1938); (b) Hasselstrom and McPherson, *ibid.*, **60**, 2340 (1938).

according to Fleck and Palkin[5] by heating pure abietic acid with palladium charcoal at a high temperature (250°), but there are difficulties in the way of effecting a practical recovery of pure acid by fractionation as acid or ester. We investigated the sulfonation of this pyro acid and found that sulfodehydroabietic acid can be obtained easily from this source in 61–63% yield, the non-aromatic hydro compounds and companion substances being left completely in the water-insoluble residue. It was next found that the sulfonic acid group can be removed smoothly by acid hydrolysis at 135° to give, after a single crystallization, dehydroabietic acid of perhaps slightly higher purity than that obtained from hydroxyabietic acid. The entire process is rapid, and the over-all yield of pure material from abietic acid is 42–43%.

Our purified sulfodehydroabietic acid melts with decomposition at about 248°, depending upon the manner of heating, and the analytical data correspond most closely with the formula for a hemihydrate. Hasselstrom and McPherson,[9b] on the other hand, obtained a trihydrate, m. p. 224° (uncorr.) dec., and Fanica,[10] who probably had the same sulfonic acid in hand, reports the m. p. 214° (uncorr.), dec. The free acid does not appear suitable for identification or determination of the empirical formula, but Hasselstrom and McPherson[9b] found that the diesters and the diamide fulfil these purposes, and they showed that the acid indeed belongs to the dehydro series. Our sample of the sharply melting dimethyl ester, prepared with diazomethane, corresponded exactly with theirs and analyses of this derivative and of the *p*-toluidine salt confirmed their conclusion. We can also supply the further evidence that the acid is a derivative, specifically, of the known[2] partially aromatic dehydroabietic acid, for we obtained the same acid, identified as the diester, from the pure dehydro acid as from pyro acid, and converted it into the dehydro acid as described above.

Attempts to convert sulfodehydroabietic acid into the corresponding phenol were unsuccessful. The acid is resistant to the action of alkali until a critical temperature is reached at about 300°, and at this temperature complex changes occur. The fusion was conducted in an autoclave in an atmosphere of nitrogen to avoid oxidation, but the product was found to be a mixture of at least four substances. The top fraction gave a nicely crystalline substance (A) of constant melting point (196.5–197.5°), but analyses indicated the presence of 2.5 atoms of oxygen and the substance yielded two distinctly different anilides. One of these (m. p. 257°) corresponded in composition to the anilide of an acid $C_{19}H_{24}O_3$ or $C_{20}H_{26-28}O_3$. The substance evidently contains one oxygen atom beyond that coming from the carboxyl group and may be the anilide of the desired hydroxydehydroabietic acid, $C_{20}H_{28}O_3$. The analyses of the second anilide agree best with the formula $C_{19}H_{22}O_2$ for the acid; this would be dehydroabietic acid less one molecule each of methane and hydrogen (naphthalene nucleus?). The more soluble fraction from the alkali fusion yielded only crystallizates of varying melting point, and one of these (B, composition: $C_{19}H_{26}O_2$) gave two constantly melting products on reaction of the acid chloride with aniline. One of these corresponds to the anilide of an acid $C_{19}H_{26}O_2$ (compare dehydroabietic acid: $C_{20}H_{28}O_2$). The anilides are resistant to hydrolysis, and the corresponding acids were not isolated. The results show only that the alkali fusion of the sulfonic acid is accompanied by extensive side reactions involving considerable alteration of the original structure. The phenolic hydroxyl group, if produced, is largely lost, and the molecule seems to suffer dehydration, dehydrogenation, or loss of a carbon atom in the alkali melt. Since substance A, which appears to be a molecular aggregate, was found to yield retene in 68% yield on dehydrogenation with palladium catalyst, it is probable that the carbon atom lost is that of the angular methyl group at C_{12}. With the realization that a phenolic derivative is at least not easily obtainable in quantity from this source, a further study of the fusion was not pursued.

Nitration of sulfodehydroabietic acid with mixed acid at a low temperature gave dinitrodehydroabietic acid, identical with that obtained directly from the dehydro acid.[2] A mononitro compound has not been obtainable in either reaction, even under very gentle conditions, and the smooth introduction of two nitro groups must mean that they enter meta positions. Since the only such positions available are 6 and 8, the dinitro compound very probably is the 6,8-derivative, as previously formulated.[2]

Having been unable to establish the point of attack in monosubstitution from a study of the

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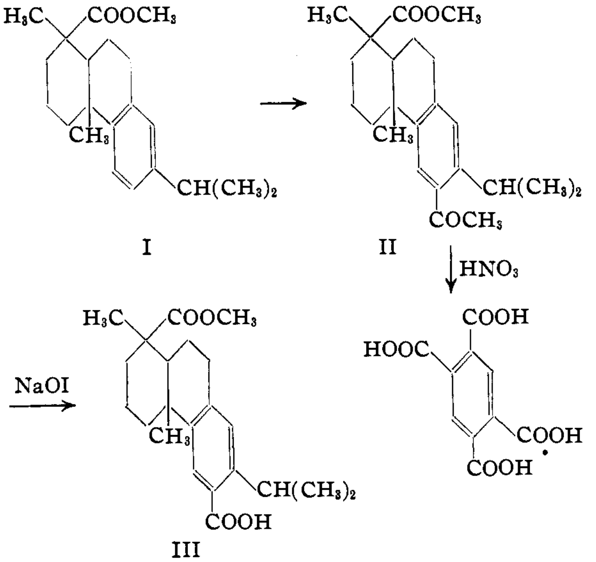
[10] Fanica, *Bull. inst. pin*, **44**, 151 (1933).



sulfonic acid, we investigated the Friedel and Crafts condensation of methyl dehydroabietate with acetyl chloride in nitrobenzene solution. This gave in good yield a beautifully crystalline and sharply melting monoacetyl derivative (II) which was characterized as the oxime and which yielded a crystalline acid on saponification. The structure was established by oxidation with dilute nitric acid, which gave a substance identified as pyromellitic acid. This proves that the acetyl group occupies the 6-position (II). Oxidation with hypoiodite in dioxane–alkali, following the procedure of Fuson and Tullock's[11] haloform test as used by Adelson and Bogert[12] for a similar oxidation of 6-acetylretene, gave methyl 6-carboxydehydroabietate, III. These and other substitution products are being investigated further.

Experimental Part[13]

Sulfodehydroabietic Acid.—One gram of the pyroabietic acid mixture of Fleck and Palkin[5] was sulfonated at $-5°$ by a procedure similar to that of Fanica[10] and described in more detail below. The crystalline material separating from the filtered aqueous solution was crystallized once from glacial acetic acid, giving 0.76 g. (60%) of the sulfonic acid, m. p. 230° dec. After a second crystallization from this solvent the material was taken up in hot water and a small amount of insoluble resin was removed with Norite before crystallization. A further crystallization from glacial acetic acid gave very fine silky needles which when dried at 110° and 15 mm. over phosphorus pentoxide had the m. p. 247–248° dec., the temperature of decomposition varying considerably with the initial temperature of the bath and the rate of heating; $[\alpha]^{25}_{\mathrm{D}}$ $+72.4°$ (2.5% in alcohol[14]).

Anal. Calcd. for $C_{20}H_{28}O_5S \cdot {}^1/_2H_2O$: C, 61.68; H, 7.50; S, 8.22; neut. equiv., 195. Found: C, 61.03; H, 7.65; S, 7.85; neut. equiv., 194.

***p*-Toluidine Salt.**—One-half gram of crude sulfonic acid, m. p. 230° dec., was dissolved in 20 cc. of water and the solution was freed from a trace of resin with Norite and treated with 0.18 g. of *p*-toluidine, brought into solution in 4 cc. of water with the use of the required amount of acetic acid. The mixture was heated to boiling and enough acetic acid was added to dissolve the gelatinous precipitate which initially separated. On cooling there was obtained 0.48 g. of crystalline salt, m. p. 271° dec. Recrystallization from alcohol gave fine silky needles of the same m. p.; $[\alpha]^{25}_{\mathrm{D}}$ $+57°$ (1.3% in alcohol).

Anal. Calcd. for $C_{27}H_{37}O_5SN$: N, 2.87. Found: N, 3.19.

Dimethyl Ester.—On adding excess diazomethane solution to a suspension of 0.5 g. of the pure sulfonic acid in ether the material rapidly dissolved, and after evaporating the filtered solution 0.34 g. of fine needles separated on cooling, m. p. 175–176°, $[\alpha]^{25}_{\mathrm{D}}$ $+76.2°$ (0.5% in alcohol). Further crystallization did not change the melting point.

Anal. Calcd. for $C_{22}H_{32}O_5S$: C, 64.69; H, 7.88. Found: C, 64.79; H, 8.06.

Sulfonation of Pure Dehydroabietic Acid.—A 0.5-g. sample of the dehydro acid prepared from hydroxyabietic acid[2] was sulfonated as before and the product crystallized once from glacial acetic acid. The yield of material, m. p. 230° dec., was 0.48 g. (73%). Esterified with diazomethane, 0.2 g. of this acid gave 0.15 g. of the dimethyl ester, m. p. 175–176°, and this did not depress the m. p. of the above sample.

Nitration of the Sulfonic Acid.—A solution of 0.6 g. of the sulfonic acid in 2.5 cc. of concentrated sulfuric acid was stirred in a salt–ice bath and treated with 0.1 cc. of concentrated nitric acid. After fifteen minutes the solution was poured into 300–400 cc. of water, giving a gelatinous precipitate containing a considerable amount of unchanged sulfonic acid. On bringing this into solution by heating there remained a small amount of water-insoluble precipitate. This was collected, washed well with water, and treated with excess diazomethane in ether. Crystallization of the product from hexane gave shiny, flat plates, m. p. 188–188.5°. A mixed melting point determination established the identity of this substance with methyl dinitrodehydroabietate[2] (m. p. 189–189.5°).

A mononitro derivative could not be obtained on nitration with mixed acids or in acetic acid solution.

Preparation of Pure Dehydroabietic Acid.—Pure abietic acid (47.5 g.) of the quality previously specified[2] was heated with palladium catalyst at 250° according to Fleck and Palkin[5] and the acidic product was extracted from an ethereal solution with 1% sodium hydroxide, precipitated with dilute acid, and crystallized once from aqueous alcohol, giving 38.5–40.5 g. (81–86%) of pyro acid. This acid (38.5–40.5 g.) was powdered and added rather rapidly (about ten minutes) with mechanical stirring to 200 cc. of concentrated sulfuric acid, keeping the tempera-

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[11] Fuson and Tullock, THIS JOURNAL, **56**, 1638 (1934).

[12] Adelson and Bogert, *ibid.*, **58**, 653 (1936).

[13] All melting points are corrected. Analyses by the Arlington Laboratories and Lyon Southworth.

[14] 95% Ethyl alcohol.

ture at −8 to −4°. After forty-five minutes the mixture was poured into 800 cc. of ice and water and the precipitated sulfonic acid was collected and washed with cold water until the wash water became cloudy on mixing with the mother liquor. Crystallization from water at this point was unsatisfactory, for the resin present formed an emulsion which could not be filtered, and the moist product was therefore crystallized from glacial acetic acid (about 200 cc.), giving 27.5 g. of satisfactory acid. The mother liquor was concentrated to a volume of about 50 cc. and poured into 800 cc. of water; some resin was removed by filtering through glass wool, and the sulfonic acid was precipitated by the addition of 200 cc. of concentrated hydrochloric acid and crystallized from glacial acetic acid, giving 3.6 g. of product. The total yield of material, m. p. 230°, dec., was 30.5–31 g. (61–63%).

A suspension of 31 g. of the powdered sulfonic acid in a mixture of 750 cc. of concentrated sulfuric acid and 1000 cc. of water was refluxed for ten hours, the temperature of the liquid being about 135°. The appearance of the suspended solid changes considerably during the heating and the progress of the hydrolysis is followed readily. After cooling, the solid was collected and washed with hot water. A solution of the dried material (19.1 g.) in 200 cc. of alcohol was clarified with a little Norite and water was added at the boiling point to incipient turbidity. On slow cooling there was obtained 17.3 g. (71%) of crystalline dehydroabietic acid, m. p. 173–173.5°,[15] $[\alpha]^{25}\text{D}$ +62° (2.3% in alcohol[16]). The mother liquor and washings were combined and treated with 400 cc. of concentrated hydrochloric acid, and after standing overnight at 5° the crystalline sulfonic acid which separated was collected and dried; weight 5 g. Based on the amount of sulfonic acid consumed, the yield of dehydroabietic acid in the hydrolysis is 84% of the theoretical amount and the overall yield from abietic acid averaged 42–43%.

The melting point is slightly higher and sharper than observed with samples prepared by the earlier method. A further indication of the purity of the acid is that esterification with diazomethane gave an ester which crystallized at once and melted at 61–62.5° without further purification. For the pure ester Fleck and Palkin[4] give the m. p. 62–63°.

Alkali Fusion of the Sulfonic Acid.—In trial fusions carried out in the open at atmospheric pressure there was so much oxidation and decomposition that in subsequent experiments the fusion was run in an autoclave in an atmosphere of nitrogen. The acid was recovered entirely unchanged after heating with 25% potassium hydroxide solution under nitrogen at 280–285°, whether the heating was continued for fifteen minutes or for ten hours; fusion occurred, however, when the temperature was raised to 300°.

After heating 10.5 g. of sulfonic acid with 45 g. of potassium hydroxide and 90 cc. of water under nitrogen in an autoclave at 300° (thermocouple) for one hour, a solid layer separated on top of the aqueous solution on cooling. The solid was dissolved in water, acidified, and the precipitate washed, dried, and taken into ether. After filtering and concentrating, the ether was displaced by hexane, and on cooling 0.85 g. of solid, m. p. 183–187°, separated. The material in the mother liquor was distilled at 3 mm., and crystallization of the distillate from hexane gave a further batch of the above high-melting solid. The combined solid was distilled at 3 mm. and on crystallization from ether–hexane gave 0.75 g. of colorless prisms, m. p. 193–194.5°. The substance is moderately soluble in ether or methanol and slightly soluble in hexane. Repeated crystallization from methanol gave material melting constantly at 196.5–197.5° (Product A).

Anal. Found: C, 78.45, 78.77; H, 8.15, 8.28; neut. equiv., 301; mol. weight (Rast), 291.

An empirical formula calculated from the analytical data would contain 2.5 atoms of oxygen, which indicates that the material is a mixture or a molecular aggregate. The same substance was obtained on fusing the dimethyl ester of the sulfonic acid under similar conditions. The substance is slowly attacked by alkaline or neutral permanganate. Dehydrogenation by heating 0.4 g. of material, m. p. 194–195°, with 0.1 g. of 10% palladium charcoal under nitrogen at 290–300° for three hours gave, after extraction of the product and crystallization from methanol, 0.21 g. (68%) of retene, m. p. 99–99.5°. Treatment with sulfur at 300° also yielded retene.

No constantly melting substance could be isolated from the mother liquors remaining after removal of the high-melting product. The material is very soluble in all organic solvents. One fraction, m. p. 159.5–160.5°, had the neutralization equivalent 310; another, m. p. 167–169° (Product B), from a fusion of the dimethyl ester, gave the values: C, 79.45; H, 9.13. This corresponds to $C_{19}H_{26}O_2$ (Calcd.: C, 79.68; H, 9.15), and the result shows at least that no phenolic hydroxyl group is present.

Anilides from Fusion Product A.—One gram of material (m. p. 194–195°) was warmed on the steam-bath with 0.7 g. of phosphorus pentachloride, then stirred with 2.5 cc. of aniline, and the product washed in ether with water, acid and alkali. On concentrating the dried solution, a 0.32-g. crop of crystals, m. p. 250–255°, was obtained, and the mother liquor material on crystallization from methanol gave 0.38 g. of crystals, m. p. 110°. The higher melting anilide on crystallization from acetone gave diamond shaped leaves melting constantly at 255.5–257°. It is slightly soluble in ether and moderately soluble in acetone or methanol.

		C	H	N
Anal.	Calcd. for $C_{25}H_{29}O_2N$:	79.97	7.78	3.73
	$C_{26}H_{31}O_2N$:	80.17	8.02	3.60
	$C_{26}H_{33}O_2N$:	79.77	8.50	3.58
	Found:	80.29	8.06	3.78

The lower melting anilide, after removal of the less soluble product by partial solution in ether, was crystallized from methanol to the constant m. p. 114--114.5° (fine needles).

Anal. Calcd. for $C_{25}H_{27}ON$: C, 84.00; H, 7.61; N, 3.92. Found: C, 84.10; H, 7.81; N, 4.30.

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[15] Ruzicka and co-workers[5] comment on their observation that a sample of dehydroabietic acid prepared from the purified ester did not show a sharp melting point, as reported in our first description of the compound. We have obtained sharply melting samples by both the previous and present method of preparation on numerous occasions, and Fleck and Palkin's[4] sample of acid from the pure ester melted over a 1°-range.

[16] In stating that we did not specify the solvent used in determining the rotation, Ruzicka and co-workers[5] evidently overlooked Note 45 of our paper.

Anilides from Fusion Product B.—Material melting at 165° gave a mixture of anilides from which the following seemingly homogeneous products were isolated: fine needles from aqueous acetone, m. p. 214–215°; long flat needles from methanol, m. p. 147.5–148°. The second substance was analyzed as follows:

Anal. Calcd. for $C_{25}H_{31}ON$: C, 83.07; H, 8.63; N, 3.87. Found: C, 83.31; H, 8.87; N, 3.89.

Attempts to hydrolyze various samples of anilides were unsuccessful. The trials included treatment with boiling 10% butyl alcoholic potassium hydroxide (unattacked), aqueous alkali and ethylene glycol at 150° (unattacked), and sodium ethylate at 180° (acidic gum).

Methyl 6-Acetyldehydroabietate.—A solution of 9.4 g. of methyl dehydroabietate and 2.3 cc. of acetyl chloride in 50 cc. of nitrobenzene was stirred at 0–5° and treated with 8.25 g. of aluminum chloride. After this had gone into solution the mixture was allowed to stand for thirty-six hours at 5° and then poured onto ice and 20 cc. of concentrated hydrochloric acid and steam distilled. The residue, which solidified on cooling, was taken up in ether and after washing with aqueous bicarbonate the solution was dried over sodium sulfate and treated with Darco 6–60, which removed practically all of the color. After concentration the solution deposited in three crops 6.6 g. of long, heavy transparent prisms, often 2–3 mm. thick. On working the mother liquor as described below there was obtained 0.4 g. more of the prisms (pure); total yield of prisms, 66%. The acetyl compound was purified by crystallization from ether (prisms) and aqueous acetone (flat needles of the same m. p.) and melted sharply at 133.5–134°, $[\alpha]^{25}D$ +56° (0.9% in alcohol).

Anal. Calcd. for $C_{23}H_{32}O_3$: C, 77.47; H, 9.03. Found: C, 77.49, 77.14; H, 8.84, 9.00.

For proof of structure 0.5 g. of the 6-acetyl compound was heated in a sealed tube with 1 cc. of concentrated nitric acid and 2 cc. of water at 190° for thirteen hours, and for twelve hours longer after adding 1 cc. of fresh acid. Evaporation of the clear solution to dryness gave a white solid which was stirred and washed with fuming nitric acid and sublimed at 250° (20 mm.) to yield pyromellitic anhydride, m. p. and mixed m. p. with an authentic sample, 282–285°.

The oxime was prepared by refluxing for one hour a mixture of 0.25 g. of the 6-acetyl compound, 0.5 g. of hydroxylamine hydrochloride, 0.7 g. of potassium acetate, 3 cc. of water, and 10 cc. of alcohol. The product was thrown out with water and crystallized from ether–petroleum ether to give needles, m. p. 151.5–152°; yield, 0.2 g. (77%); $[\alpha]^{25}D$ +83° (1.6% in alcohol). Using pyridine in place of potassium acetate solution the yield was 90%.

Anal. Calcd. for $C_{23}H_{33}O_3N$: N, 3.77. Found: N, 3.94.

From the ethereal mother liquor of the Friedel and Crafts reaction product there was obtained what appears to be a different crystalline modification of the 6-acetyl ester. After removal of the 6.6 g. of prisms, the solution on concentration deposited a crystallizate consisting largely of needles, which when crystallized twice from ether–petroleum ether gave 0.45 g. of fine needles, m. p. 117–119°. The remaining ethereal mother liquor when concentrated and treated with petroleum ether then gave crops consisting chiefly of the higher melting prisms, mixed with some needles, and purification by mechanical separation and crystallization gave 0.4 g. of pure prisms. After two recrystallizations of the more soluble, low melting material (0.45 g.) from ether–hexane, the substance was obtained as fine needles melting sharply at 119.5–120° (0.35 g.); $[\alpha]^{25}D$ +58 (0.7% in alcohol).

Anal. Calcd. for $C_{23}H_{32}O_3$: C, 77.47; H, 9.03. Found: C, 77.48, 77.11; H, 8.57, 9.13.

Mixtures of this substance with the prism form melted at intermediate temperatures. The oxime, prepared as above from 0.1 g. of needles, melted at 150–150.5° and did not depress the m. p. of the other sample. A 0.1-g. sample of needles was oxidized as above but using only one charge of acid (seventeen hours) and the reaction product treated with excess diazomethane. The resulting ester when crystallized twice from methanol melted at 141–142°, with some previous softening, and a mixture of this with authentic pyromellitic acid tetramethyl ester, m. p. 142.5–143.5° (sharp) melted at 141–143°. The structure therefore is that of methyl 6-acetyldehydroabietate, and since the rotation, as tested on small samples, is practically the same for the needles as for the prisms, stereoisomerism is unlikely. Consequently, although an interconversion was not observed, it is believed that the two substances are different modifications of the same chemical individual.

6-Acetyl Dehydroabietic Acid.—One-half gram of the acetyl ester was refluxed for three hours with 15 cc. of alcohol containing 1 g. of potassium hydroxide. A small amount of white solid precipitated on adding water and was removed by filtration (plates from ether–petroleum ether, m. p. 117–117.5°). The alkaline filtrate was acidified and the precipitate dried in ether and crystallized from ether–petroleum ether (20–40°), giving fine, silky needles, m. p. 174.5–175° (0.2 g.); $[\alpha]^{25}D$ +74° (1% in alcohol).

Anal. Calcd. for $C_{22}H_{30}O_3$: C, 77.14; H, 8.82; neut. equiv., 342. Found: C, 76.89; H, 9.05; neut. equiv., 344.

Methyl 6-Carboxydehydroabietate.—Iodine–potassium iodide solution was added to a solution of 2.5 g. of methyl 6-acetyldehydroabietate in 100 cc. of dioxane and 20 cc. of 10% sodium hydroxide solution until the color persisted for two minutes at 60° after a fresh addition. The solution was diluted with 600 cc. of water, filtered from iodoform, treated with a little bisulfite and acidified. The gummy yellow precipitate was extracted from ether into 1% alkali, and the substance then separated on acidification as a white solid. One crystallization from hexane gave 0.4 g. of material, m. p. 165–180°, and on three crystallizations from acetone the compound formed fine, silky needles melting constantly at 190–191.5°; $[\alpha]^{25}D$ +74° (0.9% in alcohol).

Anal. Calcd. for $C_{22}H_{30}O_4$: C, 73.69; H, 8.44; neut. equiv., 358. Found: C, 73.38; H, 8.50; neut. equiv. (40-mg. sample), 344.

Summary

Pure dehydroabietic acid may be obtained readily in quantity by sulfonating the palladium-

treated pyroabietic acid of Fleck and Palkin and hydrolyzing the crystalline sulfonic acid. Fusion of the sulfonic acid with alkali results in extensive alteration of the molecule and under the conditions studied gives a mixture of several products.

Methyl dehydroabietate reacts smoothly with acetyl chloride in nitrobenzene solution in the presence of aluminum chloride and gives a sharply melting product characterized as the 6-acetyl derivative. This was hydrolyzed to the free acid and oxidized with hypohalite to methyl 6-carboxydehydroabietate.

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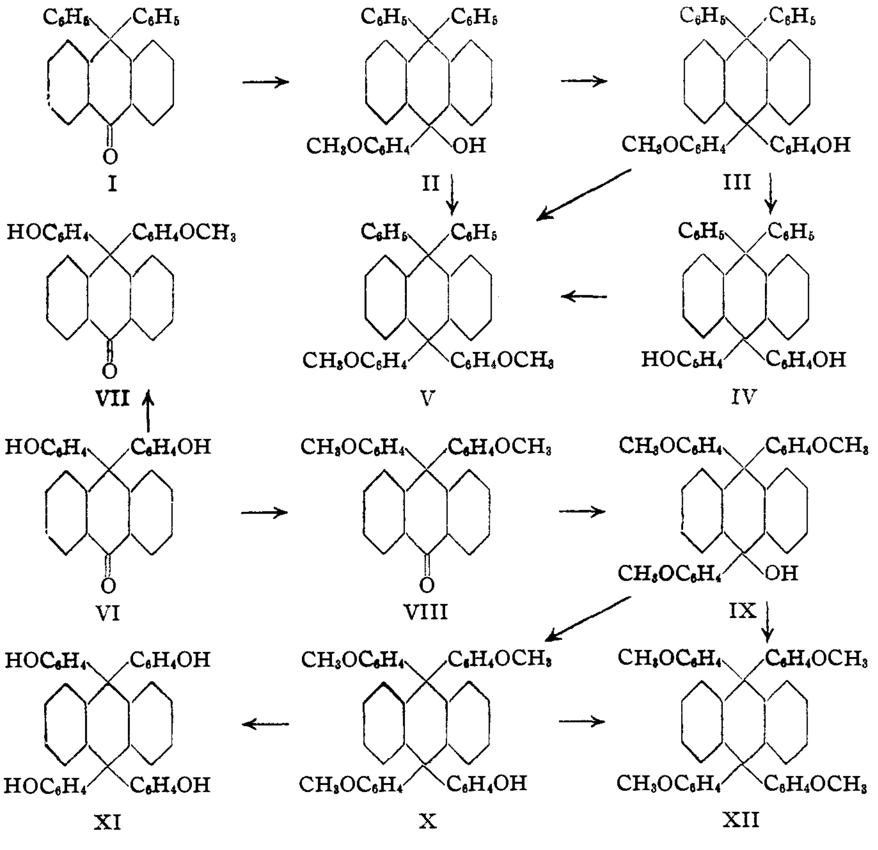
[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

Hydroxy- and Methoxyphenyldihydroanthracenes

BY F. F. BLICKE AND R. A. PATELSKI[1]

Very few substitution products of 9,10-dihydroanthracene are known in which aryl groups occupy *meso* positions and it seems that hydroxyaryl derivatives such as 9,9,10-tri- and 9,9,10,10-tetra-(*p*-hydroxyphenyl)-9,10-dihydroanthracene, compounds in which we were especially interested, have never been prepared.



Since the carbonyl group in a 9,9-diarylanthrone-10 reacts toward an arylmagnesium halide in the characteristic manner, it was possible to convert the carbonyl compound into a tertiary carbinol which represents a 9,9,10-triaryl-10-hydroxy-9,10-dihydroanthracene. The hydroxyl group of the latter proved to be especially reactive toward phenol and anisole in the presence of a small amount of sulfuric acid, hence the hydroxyl group could be replaced by the hydroxyphenyl and anisyl nuclei and in this way a tetraaryl-9,10-dihydroanthracene could be obtained. Demethylation, in the case of the anisyl compounds, yielded the desired hydroxy derivatives.

It has been found that 9,9-diphenylanthrone-10 (I) reacts with *p*-anisylmagnesium iodide to yield 9,9-diphenyl-10-hydroxy-10-(*p*-anisyl)-9,10-dihydroanthracene (II); this product was converted readily into its carbinol methyl ether by methyl alcohol and hydrogen chloride. Compound II condensed with phenol, in the presence of a small amount of sulfuric acid, to yield 9,9-diphenyl-10-(*p*-hydroxyphenyl)-10-(*p*-anisyl)-9,10-dihydroanthracene (III), and with anisole to produce 9,9-diphenyl-10,10-di-(*p*-anisyl)-9,10-dihydroanthracene (V). Compound V was obtained also by methylation of compounds III and IV. By demethylation of the last named

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