To a solution of 0.10 g. of VIII in 15 cc. of glacial acetic acid there was added a solution of 0.5 g. of stannous chloride in 5 cc. of concentrated hydrochloric acid. After refluxing for one hour the solution was diluted with water and the yellow precipitate collected and transferred to a flask containing 0.3 g. of activated zinc dust and 1 gram of sodium hydroxide in 10 cc. of water. The mixture was refluxed for three hours, cooled, filtered and the precipitate digested with hydrochloric acid to remove the excess zinc. Crystallization of the insoluble material from benzene–alcohol yielded 0.05 g. of material, m. p. 160.4–161.4°. A portion dissolved in benzene–alcohol crystallized in colorless plates, m. p. 160.6–161.8°.

Anal.[14] Calcd. for $C_{18}H_{11}Cl$: Cl, 13.50. Found: Cl, 13.75, 13.92.

Summary

The following compounds have been prepared in order to test their biological activity: 6-chloro-10-methyl-1,2-benzanthracene, 6-cyano-10-methyl-1,2-benzanthracene, 6-carboxy-10-methyl-1,2-benzanthracene, and 6-carbomethoxy-10-methyl-1,2-benzanthracene.

(14) Chlorine analysis by Dr. Tsu Sheng Ma using the catalytic combustion method.

COLUMBUS, OHIO RECEIVED NOVEMBER 30, 1938

[CONTRIBUTION FROM THE NAVAL STORES RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

The Composition of So-Called Pyroabietic Acid Prepared without Catalyst

BY E. E. FLECK AND S. PALKIN

In a previous publication[1] a method for the resolution of the so-called "pyroabietic acid" prepared by catalytic means was described. The isolation of dehydro-, dihydro- and tetrahydroabietic acids from this complex established beyond doubt the true nature of this product and confirmed the prior inferences of Fieser and Campbell,[2] based on spectroscopic data and certain nitration derivatives. Since then, these findings have been further confirmed by Ruzicka, Bacon, Sternbach and Waldmann,[3] and by Littmann.[4]

Ruzicka and associates isolated dehydroabietic acid and a dihydroabietic acid (m. p. 193–194°; $[\alpha]^{20}D$ +9°) from pyroabietic acid prepared by heating *l*-abietic acid, without catalyst, for eighty hours at 250°. These authors suggest that other dihydroabietic acids are probably present in the pyroabietic acid mixture.

Littmann, on the other hand, isolated dehydro- and tetrahydroabietic acid from a catalytically treated abietic acid.

In a subsequent paper[5] we have shown that one of the two isomeric dihydro compounds isolated was unique because of its high specific rotation $[\alpha]^{20}D$ +108°. The other dihydro compound was isolated in the form of a lactone in which the acid group lactonized on the double bond, and was identical with that reported by Ruzicka and Meyer,[6] and, more recently, by Hasselstrom, Brennan and McPherson.[7]

In preparing pyroabietic acid by heat alone it has been the practice to heat the rosin or abietic acid at a temperature of about 250° for a period of eighty to one hundred hours. La Lande[8] in his study of the effect of temperature and the length of heating period on *l*-abietic acid, showed that heating for three and one-half hours at 330° formed a product with an acid number of 100, a saponification number of 141, and a specific rotation of $[\alpha]^{20}D$ +47°. La Lande, however, was not concerned with the actual isolation of the pyroabietic acid mixture. Since the yield of this material is as good, if not better, than that obtained by the longer heating period at 250°, this more rapid method of preparing crude pyroabietic acid was used. While the properties of the so-called pyroabietic acid prepared in this manner as reported by Fanica[9] and others agreed well with those of the catalytically prepared pyroabietic acid, it was thought unlikely that the disproportionation reaction involved would be the same in the two cases.

The purpose of this work, therefore, was to prepare pyroabietic acid from pure *l*-abietic acid by heat alone and to determine in what respects this product differs from the pyroabietic mixture obtained when a catalyst, such as palladium–carbon, is used.

(1) Fleck and Palkin, THIS JOURNAL, **60**, 921 (1938).
(2) Fieser and Campbell, *ibid.*, **60**, 159 (1938).
(3) Ruzicka, Bacon, Sternbach and Waldmann, *Helv. Chim. Acta*, **21**, 591 (1938).
(4) Littmann, THIS JOURNAL, **60**, 1419 (1938).
(5) Fleck and Palkin, *ibid.*, **60**, 2621 (1938).
(6) Ruzicka and Meyer, *Helv. Chim. Acta*, **5**, 333 (1922).
(7) Hasselstrom, Brennan and McPherson, THIS JOURNAL, **60**, 1267 (1938).
(8) La Lande, Jr., *Ind. Eng. Chem.*, **26**, 679 (1934), Table 1.
(9) Fanica, *Bull. inst. pin*, 183 (1933).

In the present work *l*-abietic acid $[\alpha]^{20}D$ $-104°$ was heated in a closed system for three and a half hours at 335–340°. The acid fraction was then separated from the neutral material by extraction. Attempts to isolate tetrahydroabietic acid from the resulting pyroabietic acids by the same method used on the catalyst prepared pyroabietic acid gave no homogeneous product. The final product analyzed best for a mixture of dihydroabietic acids.

From the remainder of the acid fraction, dehydroabietic acid, m. p. 172–173°, $[\alpha]^{20}D$ $+62°$, was isolated by sulfonation and hydrolysis of the sulfo-dehydroabietic acid according to the procedure of Fieser and Campbell.[10] The dehydroabietic acid and its methyl ester were identical with those obtained from catalytically prepared pyroabietic acid.

From the neutral portion of the crude sulfonation product, lactonized dihydroabietic acid, m. p. 130–131°, was isolated. This compound and the tetrahydrohydroxyabietic acid derived from it proved to be identical with the lactone and the free acid isolated from catalytically prepared pyroabietic acid.

There was no indication that the dihydroabietic acid, m. p. 174–176°, $[\alpha]^{20}D$ $+108°$, was present in the pyroabietic acid prepared by heat alone. In the catalytic pyroabietic acid numerous fractions of dihydroabietic acids had a higher positive specific rotation than that of pure dehydroabietic acid. On the other hand, none of the dihydroabietic acid mixtures obtained from noncatalytic pyroabietic acid has such high specific rotation. It therefore seems safe to conclude that this particular isomeric dihydroabietic acid probably is not formed without the aid of a catalyst.

Experimental Part

Preparation of Pyroabietic Acid.—Fifty grams of freshly prepared *l*-abietic acid,[11] $[\alpha]^{20}D$ $-104°$ in 2% absolute alcohol, from *Pinus palustris* rosin, was heated in a closed system in an oil-bath held at 340° (inside temperature 335–340°) for three and one-half hours. The product was stirred during the heating period. A total of 2600 cc. of gas (about 0.7 mole) was given off during the course of the experiment. At room temperature the reaction mass remained a light yellow color and was of a thick, sticky consistency. This material was dissolved in ether and the acidic portion was removed by extracting twice with 0.25 *N* sodium hydroxide. The combined alkaline extracts were shaken twice with ether. The aqueous solution was then made acid to congo red by addition of dilute hydrochloric acid and the acids were extracted with ether. The ether solution was washed with water and then evaporated to dryness. The crystalline residue was dried at 80° in vacuum, weight 29.6 g.; $[\alpha]^{20}D$ $+45°$ in 2% absolute alcohol.

The ether solutions from the original extraction yielded 16.5 g. of neutral material that remained a light yellow oil.

Attempt to Isolate Tetrahydroabietic Acid.—A solution of 29 g. of the crude pyroabietic acids in 116 cc. of alcohol was treated with 175 cc. of 0.4 *N* ammonium hydroxide. The crystals that separated on several days of standing at room temperature were removed by filtration. The filtrate was used in the sulfonation experiment. The crystals were subjected to fractional crystallization from alcohol, using the systematic fractional crystallization as previously described in the isolation of tetrahydroabietic acid from catalytically prepared pyroabietic acid.[1] At the end of ten recrystallizations the material was still not homogeneous. The product had a melting point of 172–174°; $[\alpha]^{20}D$ $+13$ in 2% absolute alcohol. *Anal.* Calcd. for $C_{20}H_{34}O_2$: C, 78.36; H, 11.19. Calcd. for $C_{20}H_{32}O_2$: C, 78.88; H, 10.60. Found: C, 79.22, 79.18, 78.52; H, 10.30, 10.62, 10.71.

The tetrahydroabietic acid previously isolated melted at 183–184°; $[\alpha]^{20}D$ $+6°$. It is therefore probable that the material isolated above consists of a mixture of dihydroabietic acid isomers with very little or no tetrahydroabietic acid present.

The filtrate from the original separation of the crystalline ammonium salt was acidified with dilute hydrochloric acid and then extracted with ether. This extract was washed with water and then the ether was distilled. The residue crystallized on standing.

Products of Sulfonation

Twenty grams of this material was added, during the course of ten minutes, to 100 cc. of concentrated sulfuric acid cooled to -5 to $-10°$. Stirring was continued for forty-five minutes during which time complete solution did not take place. The mixture was poured into 400 cc. of ice and water and the white precipitate that separated was filtered, washed with ice water, dissolved in ether and extracted twice with 0.25 *N* sodium hydroxide. The ether solution was used for the isolation of lactonized dihydroabietic acid.

Acid Sodium Salt of Sulfodehydroabietic Acid.—The combined alkaline extracts were acidified to congo red with dilute hydrochloric acid. The precipitate was collected on a filter and then recrystallized three times from glacial acetic acid. The sulfonic acid salt so obtained did not melt or decompose at 270°. Calcd. for $C_{20}H_{27}O_5SNa$: 1.04 cc. of 0.1 *N* NaOH. By direct titration 0.04187 g. required 1.10 cc. of 0.1 *N* NaOH.

Dehydroabietic Acid.—One gram of the acid sodium salt of sulfodehydroabietic acid was hydrolyzed with dilute sulfuric acid according to the method of Fieser and Campbell.[10] When the product was recrystallized from dilute alcohol it separated as triangular crystals that melted at 172–173°; $[\alpha]^{20}D$ $+62°$ in 2% absolute alcohol. *Anal.* Calcd. for $C_{20}H_{28}O_2$: C, 79.94; H, 9.40. Found: C, 80.20, 80.06; H, 9.58, 9.65. When this sample was mixed with

(10) Fieser and Campbell, THIS JOURNAL, **60**, 2631 (1938).
(11) Palkin and Harris, *ibid.*, **56**, 1935 (1934).

an authentic sample of dehydroabietic acid[1] no depression of melting point could be observed.

Dehydroabietic Methyl Ester.—The methyl ester of dehydroabietic acid was prepared in the usual manner by esterification with diazomethane. It separated from methyl alcohol as needles that melted at 62–63°; $[\alpha]^{20}D$ +60° in 2% absolute alcohol. *Anal.* Calcd. $C_{21}H_{30}O_2$: C, 80.20; H, 9.62; OCH_3, 9.88. Found: C, 80.37, 80.11; H, 9.85, 9.78; OCH_3, 10.17. No depression of melting point was observed when this sample was mixed with an authentic sample of dehydroabietic methyl ester.[1]

Lactonized Dihydroabietic Acid.—The ether solution, obtained from the extraction of sulfo-dehydroabietic acid from the crude sulfonation product, was washed with water and then evaporated to dryness. The residue was recrystallized from alcohol. It separated as rectangular plates which melted at 130–131°; $[\alpha]^{20}D$ −4° in 2% absolute alcohol. *Anal.* Calcd. for $C_{20}H_{32}O_2$: C, 78.88; H, 10.60. Found: C, 78.92, 78.87; H, 10.53, 10.75. When mixed with lactonized dihydroabietic acid isolated from catalytically prepared pyroabietic acid,[1] no lowering of the melting point could be observed.

Tetrahydrohydroxyabietic Acid.—A solution of 0.3 g. of the lactone isolated above, in 10 cc. of 10% *n*-butyl alcoholic potassium hydroxide, was refluxed for four hours. The *n*-butyl alcohol was distilled with steam. The residue was diluted with 100 cc. of water and this solution was then extracted three times with ether. The aqueous solution was made acid to litmus by careful addition of 10% acetic acid. The product was extracted with ether, the extract washed with water, and then the ether evaporated to dryness. The residue crystallized from dilute methyl alcohol as thick needles that melted at 164–165° when dried at room temperature; $[\alpha]^{20}D$ +35° in 2% absolute alcohol. *Anal.* Calcd. for $C_{20}H_{34}O_3$: C, 74.47; H, 10.63. Found: C, 74.51, 74.25; H, 10.78, 10.73.

When this compound was mixed with tetrahydrohydroxyabietic acid from catalytically prepared pyroabietic acid[5] no lowering of the melting point could be observed.

Summary

1. Dehydroabietic acid and dihydroabietic acid as the lactone have been isolated from pyroabietic acid prepared without the aid of a catalyst.

2. No tetrahydroabietic acid or dihydroabietic acid, $[\alpha]^{20}D$ +108°, previously found in catalytically prepared pyroabietic acid, could be isolated from pyroabietic acid prepared by heat alone.

3. The one hundred hour heating period, heretofore used for the non-catalytic conversion of *l*-abietic acid into pyroabietic acid, may be shortened to three or four hours by increasing the temperature from the customary 250 to about 330°.

WASHINGTON, D. C. RECEIVED DECEMBER 2, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Alkoxyalkyl Derivatives of Resorcinol

BY CHARLES D. HURD AND GEORGE W. FOWLER[1]

Alkylresorcinols have been studied extensively as germicides, but this work has not been extended to include the effect of an ether linkage in the alkyl chain. Accordingly, the present study was directed toward the synthesis of 4-alkoxyalkylresorcinols and resorcinol alkoxyalkyl monoethers, since it is known[2] that the germicidal behavior of 4-alkylresorcinols and resorcinol alkyl monoethers is comparable.

The reaction: $RO(CH_2)_nX + NaOC_6H_4OH \rightarrow NaX + RO(CH_2)_nOC_6H_4OH$ was investigated for the synthesis of the monoethers. It was successful with alkoxyalkyl bromides, but unsuccessful with β-ethoxyethyl chloride or β-ethoxyethyl sulfite. In view of Swallen and Boord's experience[3] with β-ethoxyethyl chloride and sodium phenoxide, the very slow reaction with sodium resorcinolate was anticipated; but the negligible yield from the sulfite was unexpected, because phenyl β-ethoxyethyl ether was synthesized satisfactorily by this method

$$(C_2H_5OCH_2CH_2O)_2SO + C_6H_5ONa \longrightarrow C_6H_5OCH_2CH_2OC_2H_5 + C_2H_5OCH_2CH_2OSO_2Na$$

The sulfite approach was attractive since the sulfite[4] is an intermediate in the formation of the chloride from the alcohol.

$$2C_2H_5OCH_2CH_2OH + SOCl_2 + 2C_5H_5N \longrightarrow (C_2H_5OCH_2CH_2O)_2SO + 2C_5H_5NHCl$$

$$(C_2H_5OCH_2CH_2O)_2SO + SOCl_2 \longrightarrow 2C_2H_5OCH_2CH_2Cl + 2SO_2$$

Four of the monoethers, *m*-$RO(CH_2)_nOC_6H_4OH$, wherein R = ethyl or *n*-butyl and *n* = 2 or 3, were prepared from the bromides. Smaller quantities of the diethers, $C_6H_4(O—(CH_2)_n—OR)_2$,

(1) Parke, Davis and Company Research Fellow, 1935–1937.

(2) Klarmann, Gatyas and Shternov, THIS JOURNAL, **53**, 3397 (1931).

(3) Swallen and Boord, *ibid.*, **52**, 651 (1930).

(4) Voss and Blanke, *Ann.*, **485**, 258 (1931).