of 2 hr. Dilution of the reaction mixture with water followed by filtration produced 1.9 g. of crude material which was recrystallized once from pyridine and three times from acetic anhydride to yield 0.4 g. (18%) of red-brown needles melting 330–333° dec. A mixture melting point with material from run I showed no depression.

2,8-Dibromo-3,7-dinitrodibenzo-*p*-dioxin.—To a stirred solution of 50 ml. of concentrated nitric acid and 30 ml. of concentrated sulfuric acid was added slowly 1.5 g. (0.0044 mole) of 2,8-dibromodibenzo-*p*-dioxin at room temperature. Stirring was continued for 20 min. at room temperature, the mixture warmed to 60° and then allowed to cool. Dilution of the reaction mixture, then filtration, produced 1.5 g. of crude material. Four recrystallizations from glacial acetic acid yielded 0.5 g. (26%) of yellow needles, m.p. 276–278°.

Anal. Calcd. for $C_{12}H_4O_6N_2Br_2$: N, 6.48. Found: N, 6.51, 6.38.

2,3-Dibromo-7,8-dinitrodibenzo-*p*-dioxin.—A solution of 0.5 g. of dibromo compound and 10 ml. of glacial acetic acid was cooled to ice-bath temperature. Then 5 ml. of concentrated nitric acid was added. The temperature was slowly raised to reflux and held there for 0.5 hr. Dilution of the reaction mixture and then three recrystallizations of the crude material from benzene–petroleum ether (b.p. 60–70°) resulted in the isolation of 0.3 g. of yellow plates melting at 267–270°.

Anal. Calcd. for $C_{12}H_4O_6N_2Br_2$: N, 6.48. Found: N, 6.35, 6.40.

2-Amino-X-bromodibenzo-*p*-dioxin.—A solution of 2 g. (0.01 mole) of 2-aminodibenzo-*p*-dioxin, 3.6 g. (0.02 mole) of bromine and 100 ml. of carbon tetrachloride was stirred for 2.5 hr. at room temperature. The now green solution was washed with aqueous sodium bisulfite and then dilute potassium hydroxide. Evaporation of the carbon tetrachloride layer and then two recrystallizations of the residue from ethanol–water resulted in the isolation of 0.8 g. (28%) of fine, pink needles, m.p. 152–154°. The infrared spectrum has a sharp band at 13.3 μ, indicating that both groups are in one ring. However, there is no simple way of determining the position of the bromine atom.

Anal. Calcd. for $C_{12}H_8O_2NBr$: Br, 28.77. Found: Br, 29.33, 29.37.

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[CONTRIBUTION FROM THE NAVAL STORES STATION, U. S. DEPARTMENT OF AGRICULTURE[1]]

A Preparation and Some of the Properties of *trans*-6,14-Dihydrolevopimaric Acid-6,14-*endo*-α,β-succinic Acid

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Rosin and the abietic-type acids of rosin were found to undergo a normal Diels–Alder type condensation with fumaric acid to yield tricarboxylic acids. A practical procedure is presented for separating the major reaction product, one of the isomers of *trans*-6,14-dihydrolevopimaric-acid-6,14-*endo*-α,β-succinic acid, as a crystalline hemihydrate. By means of partition chromatography a non-crystalline tricarboxylic acid was obtained as a minor product from the residual resin. Infrared spectra and neutralization equivalents indicate the crystalline and non-crystalline acids to be geometric isomers. The crystalline isomer was converted to maleopimaric acid when heated at 280°. Isodextropimaric acid, one of the pimaric-type acids of rosin, did not react with fumaric acid under conditions commonly employed.

The patent literature contains many references to the reaction of rosin with fumaric acid. The modified rosin has commercial value in the formulation of materials such as coating compositions and printing inks. Information is not available on the chemical composition of the modification. It was therefore of interest to examine the products resulting from the treatment of the individual resin acids and rosin with fumaric acid and to characterize the major products of this reaction.

Levopimaric acid which is present in gum oleoresin condenses at room temperature with maleic anhydride to form the Diels–Alder addition compound,[2] maleopimaric acid. During distillation of oleoresin, the levopimaric acid present isomerizes to other resin acids, the end products of the thermal isomerization being abietic, neoabietic and palustric acid.[3] All of these acids react with maleic anhydride under vigorous reaction conditions to form maleopimaric acid.[4] To account for a normal Diels–Alder reaction of the abietic-type acids it has been assumed that levopimaric acid is in equilibrium with abietic acid under conditions[5] required for the reaction. Maleopimaric acid in alkali and under high temperature and pressure has been reported to isomerize[6] to fumaropimaric acid[7] (I), the expected product if the less reactive dienophile, fumaric acid, forms the normal Diels–Alder reaction product with levopimaric acid. However, the products obtained from direct combination of fumaric acid and rosin have not been investigated.

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[1] One of the laboratories of the Southern Utilization Research & Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

[2] (a) R. G. R. Bacon and L. Ruzicka, *Chemistry & Industry*, 546 (1936); (b) H. Wienhaus and W. Sandermann, *Ber.*, **69**, 2202 (1936).

[3] (a) V. M. Loeblich, D. E. Baldwin, R. T. O'Connor and R. V. Lawrence, THIS JOURNAL, **77**, 6311 (1955); (b) J. Köhler, *J. prakt. Chem.*, **85**, 534 (1912); (c) L. Ruzicka, F. Balas and F. Vilim, *Helv. Chim. Acta*, **7**, 458 (1924).

[4] (a) V. M. Loeblich, D. E. Baldwin and R. V. Lawrence, THIS JOURNAL, **77**, 2823 (1955); (b) B. Arbuzov, *J. Gen. Chem., U.S.S.R.*, **2**, 806 (1932) (*C. A.*, **27**, 2688 (1933)).

[5] L. F. Fieser and W. P. Campbell, THIS JOURNAL, **60**, 159 (1938).

[6] G. C. Harris (to Hercules Powder Co.), U. S. Patent 2,517,563, August 8, 1950.

[7] Fumaropimaric acid is the trivial name for *trans*-6,14-dihydrolevopimaric-acid-6,14-*endo*-α,β-succinic acid. The conventional name used here is analogous to that previously used in naming anthracene adducts. See W. E. Bachmann and L. B. Scott, THIS JOURNAL, **70**, 1458 (1948). The prefix *trans* refers to the configuration about the central C–C bond of the succinic acid grouping. The crystalline fumaropimaric acid isomer, isolated here as the major product of the reaction discussed, will be referred to simply as fumaropimaric acid. When the non-crystalline isomer of fumaropimaric acid is discussed it will be so designated.

Characterization of rosin–fumaric acid adducts in this Laboratory[8] has shown that maximum yields of tricarboxylic acid with minimum anhydride formation are obtained at reaction temperatures of about 200° for 2 to 3 hours. Examination of these products led to the observation that a crystalline hydrate of fumaropimaric acid was obtained when an aromatic hydrocarbon or chloroform solution of fumaric-modified rosin was contacted with water. Depending on the drying conditions it could be obtained as fumaropimaric acid hemihydrate (II) or the anhydrous acid. Using the optimum conditions as found for rosin,[8] small scale runs were made with abietic, neoabietic, palustric, levopimaric and isodextropimaric acid. The abietic-type acids (that is, all of the above acids except isodextropimaric acid) reacted to give a single crystalline fumaropimaric acid in 50–60% yield. The triacid chloride (V) of the abietic adduct was prepared and the acid regenerated. All of the adducts including the one regenerated from the triacid chloride were identical, indicating that only one geometric isomer had been isolated in crystalline form. No reaction was observed between fumaric acid and the pimaric type acid; isodextropimaric acid was recovered unchanged. This is of interest since the acidic portion of rosin is composed of approximately 12% pimaric-type acids.[9] Dextropimaric acid has been reported to form ill-defined polymeric condensation products[10] with maleic anhydride.

To determine the ease of reaction of levopimaric acid, an alcoholic solution was refluxed with an excess of fumaric acid. A low yield was obtained, which was expected, because of the tendency of levopimaric acid to isomerize under the reaction conditions used. Baldwin, *et al.*,[11] have reported the complete acid isomerization of levopimaric acid to the other abietic-type acids after 2 hours reflux in 95% alcohol using 0.1 *N* hydrochloric acid as catalyst.

Crystalline fumaropimaric acid was obtained in 72% yield from the reaction of abietic acid with an excess of fumaric acid under the conditions[8] used for rosin. The non-crystalline portion of this reaction product was separated by partition chromatography and found to contain 9% maleopimaric acid and 16% of a non-crystalline fumaropimaric acid based on the weight of abietic acid used. A second fumaropimaric acid was not unexpected since there are four possible isomeric forms of the addition product.

It was found[8] previously that higher concentrations of maleopimaric acid were formed in fumaric modifications prepared at higher temperatures. Fumaric modifications have been obtained which contain negligible amounts of maleopimaric acid and unreacted dienophile. However, further heating of these products resulted in modified rosins containing appreciable maleopimaric acid. A sample of pure fumaropimaric acid was converted to maleopimaric acid in 62% yield by heating it at its melting point under nitrogen. It therefore seems likely that the major portion of any maleopimaric acid present in fumaric modified rosin is formed by isomerization after adduct formation. The formation of maleopimaric acid from fumaropimaric acid indicates that the dienophile in each case has added to the same side of the ring.

The unreacted resin acids of a rosin–fumaric acid reaction product prepared with an excess of fumaric acid were concentrated and then isolated by the partition chromatographic technique of Ramsey and Patterson[12] as modified by Loeblich, *et al.*[13] The acids from the columns were eluted in two peaks. Peak effluent volumes, compared to those determined by Loeblich,[13] indicated that the acids eluted were isodextropimaric acid and dehydroabietic acid. Examination of the infrared spectrum of the acids of the first peak showed that 65–70% of the acid was isodextropimaric acid. The ultraviolet spectrum of the acids of the second peak showed that 75–80% of the material present was dehydroabietic acid. The total amount of unreacted resin acids was 17.4% based on the weight of the original rosin. There was no ultraviolet absorption characteristic of the abietic-type acids in the unreacted materials isolated.

Fumaropimaric acid formed a triacid chloride in 87% yield when refluxed with an excess of thionyl chloride. The triacid chloride was subsequently converted to the triamide which was isolated as a hemihydrate. Catalytic hydrogenation in acetic acid allowed the crystalline fumaropimaric acid to absorb 1 molal equivalent of hydrogen to yield the completely saturated compound, dihydrofumaropimaric acid (IV).

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Experimental[14]

***trans*-6,14-Dihydrolevopimaric-acid-6,14-*endo*-α,β-succinic Acid (Fumaropimaric Acid) (I). A. From Abietic Acid.**—Abietic acid ($[\alpha]^{25}\text{D}$ −92°, 202.0 g., 0.67 mole) prepared according to the procedure of Palkin[15] was heated under nitrogen to 200° prior to the addition of 124.0 g. (1.07 moles, 60% excess) of fumaric acid. Heating of the reaction mixture was continued at 200° for 2.5 hr. with stirring under nitrogen. A weight loss of 4.11 g. during the reaction was found to be due mostly to decarboxylation as indicated by carbon dioxide trapped from the exhaust gas as barium carbonate. A portion of the product, 307.1 g., was dissolved in 1 l. of benzene–alcohol (85:15). The solution was washed 3 times with water (500 ml. portions) to remove the alcohol and cause the formation of a crystalline hydrate of I. The crystalline hydrate was recovered by filtration and dried in vacuum at 110° for 5 hr. to yield 195.7 g. (72%) of fumaropimaric acid hemihydrate (II), neut. equiv. 145.0, $[\alpha]^{25}\text{D}$ +29.5°. A 10.00-g. sample of II was recrystallized twice from 150 ml. of chloroform–methanol (85:15). The solutions were washed with water, filtered and allowed to stand overnight for crystallization. This procedure yielded

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(8) N. J. Halbrook and R. V. Lawrence, *Ind. Eng. Chem.*, in press.

(9) (a) G. C. Harris and T. F. Sanderson, This Journal, **70**, 2079 (1948); (b) E. E. Fleck and S. Palkin, *ibid.*, **62**, 2044 (1940).

(10) L. Ruzicka, P. J. Ankersmit and B. Frank, *Helv. Chim. Acta*, **15**, 1289 (1932).

(11) D. E. Baldwin, V. M. Loeblich and R. V. Lawrence, This Journal, **78**, 2015 (1956).

(12) L. L. Ramsey and W. I. Patterson, *J. Assoc. Offic. Agr. Chemists*, **31**, 441 (1948).

(13) V. M. Loeblich, D. E. Baldwin and R. V. Lawrence, This Journal, **77**, 2823 (1955).

(14) All reported melting points are uncorrected. Optical rotations were determined on 2.0–2.5% solutions in 95% ethanol.

(15) S. Palkin and T. H. Harris, This Journal, **56**, 1935 (1934).

a crystalline hydrate of I which when dried as above yielded 7.25 g. of II, $[\alpha]^{25}\mathrm{D}$ +42.5°, neut. equiv. 142.5. Drying of II at 152° in vacuum for 6 hr. yielded I, m.p. 280–282° (sintered at 190° and recrystallized before final melting), $[\alpha]^{25}\mathrm{D}$ +42.7°.

Anal. Calcd. for $C_{24}H_{34}O_6$: C, 68.87; H, 8.19; neut. equiv., 139.5. Found: C, 68.85; H, 8.29; neut. equiv., 140.0.

The benzene filtrate from the first crystallization of I hydrate was evaporated to yield 73.2 g. of resin, neut. equiv. 179.0. The resin was subjected to partition chromatography on a column similar to that described by Marvel.[16] The eluting solvent was prepared by washing 200 ml. of toluene with 20 ml. of water–methanol (70:30). The column was packed with 20 g. of silicic acid which had been previously mixed with 15.5 ml. of the aqueous phase which was separated from the toluene wash. Samples (150 mg.) were introduced to the column and developed with the toluene solvent. The first peak, eluted at 40 ml., contained 33% of the acids placed on the column, and was impure maleopimaric acid. A second peak, eluted at 140 ml., contained 57% of the acids placed on the column. A composite sample of the second peak was prepared by passing several samples through the column. On evaporation of the toluene from the acids of the second peak and drying the residue in vacuum at 110° for 5 hr., a non-crystalline fumaropimaric acid was obtained, m.p. 225° dec., $[\alpha]^{25}\mathrm{D}$ +12.8°, neut. equiv. 144.0. There was no appreciable difference between the infrared spectra of this non-crystalline fumaropimaric acid and I. The non-crystalline solid was not further examined.

B. From Abietic-type Acids, Levopimaric, Palustric, Neoabietic and Abietic Acid. Small Scale Runs.—Each of the acids 2.00 g. (0.07 mole) was mixed with 0.90 g. (0.08 mole) of fumaric acid and heated in an oil-bath for 2.5 hr. at 200°. During the course of the reaction, the samples were blanketed with nitrogen and stirred occasionally. The reaction mixtures were crystallized and dried as in procedure A to yield 50–60% of I. Each acid gave a fumaropimaric acid which showed no depression in m.p. when mixed with I of procedure A.

C. From Levopimaric Acid, Low Temperature Reaction.—A solution of 3.02 g. (0.01 mole) of levopimaric acid and 1.86 g. (0.16 mole) of fumaric acid in 20 ml. of ethyl alcohol was heated at reflux for 8 hr. Ultraviolet spectral data were used to follow the disappearance of levopimaric acid. Complete reaction was indicated at the end of 8 hr. The acids of the reaction mixture were recovered by addition of water to the alcoholic solution. Crystallization from benzene followed by recrystallization from chloroform and drying as above gave 1.64 g. (39%) of I, m.p. 280–282°. Admixture with I of procedure A gave no depression in melting point.

D. From Rosin.—An adduct was prepared as described in procedure A using 300.0 g. of rosin (containing approximately 180 g. (0.53 mole) of abietic-type acids) and 96.0 g. (0.83 mole) of fumaric acid. A 50.0-g. sample of this modified rosin containing the adduct was subjected to the recovery and drying procedures for I as described in procedure A above. A yield of 14.8 g. (38.8% based on rosin) of I, m.p. 280–282°, was obtained. Admixture with I prepared from abietic acid showed no m.p. depression. Infrared spectra of I from abietic acid and rosin were identical.

The unreacted resin acids of a 26.00-g. sample of the modified rosin product were concentrated by dissolving the reaction product in a minimum of 3 *N* sodium hydroxide, diluting the solution to 1 l., and adjusting the *p*H to 6.2 with dilute hydrochloric acid. The resin acids which precipitated were collected by filtration. The neutralization and recovery procedure was repeated. Finally, the precipitated acids were dissolved in ether. The ether solution was washed free of acid and dried over sodium sulfate prior to evaporation of the ether to yield 3.65 g. of resin. The partition chromatographic technique of Ramsey and Patterson[12] as modified by Loeblich[13] was used to isolate the acids from the resin. A 1.62-g. sample of the resin concentrate was eluted in two fractions from the column at peak effluent volumes of 300 and 580 ml. The acids were separated from the eluting solvent as cyclohexylamine salts. Yields of resin acids eluted from the column, as calculated from their cyclohexylamine salts, were: first peak 0.89 g. (55.0%), second peak 0.29 g. (17.9%). The salts were dissolved in ether and the acid freed by addition of 3 *N* hydrochloric acid. The ether solution was washed with water and dried over sodium sulfate. Evaporation of the ether yielded the free acids. Ultraviolet spectra of the isolated acids showed that only traces of the abietic-type acids were present. Isodextropimaric acid was estimated from the infrared absorption data to be 65–70% of the acids of the first peak. The ultraviolet absorption spectrum of the acids of the second peak indicated them to be 75–80% dehydroabietic acid.

Attempted Reaction of Isodextropimaric Acid with Fumaric Acid.—A mixture of 2.00 g. (0.07 mole) of isodextropimaric acid and 0.08 mole of fumaric acid were subjected to reaction conditions as described in procedure B. The product was dissolved in benzene–alcohol (85:15) and after washing with water did not crystallize, indicating that compound I was not present. The benzene was evaporated and the residue dissolved in acetone–water (90:10). On standing in an open dish, this solution precipitated crystalline isodextropimaric acid, yield 95% (1.91 g.). Recrystallization from acetone–water gave the analytical sample, $[\alpha]^{25}\mathrm{D}$ 0°, m.p. 163.5°. Admixture with an authentic sample of isodextropimaric acid showed no m.p. depression.

Conversion of Fumaropimaric Acid to Maleopimaric Acid (III).—A 5.0-g. sample of I was heated 40 minutes at 200° under nitrogen. The resulting product was dissolved in benzene–acetone (90:10), washed with water, and allowed to stand overnight. No crystals of I formed. The benzene was removed and the sample dissolved in 10 ml. of ether, from which 2.30 g. of III was precipitated on standing at 5° overnight. The ether liquor was evaporated to dryness and the residue dissolved in carbon tetrachloride. The carbon tetrachloride adduct of III was recovered by filtration and dried at 150° for 6 hr. in vacuum to yield an additional 0.7 g. of III (total yield 60%). The two portions were combined and recrystallized from ether to yield the analytical sample, $[\alpha]^{25}\mathrm{D}$ −26.8°, m.p. 225–227°. The melting point was not depressed when the acid was mixed with an authentic sample of maleopimaric acid.

Dihydrofumaropimaric Acid (IV).—A solution of 0.600 g. of I in 15 ml. of glacial acetic acid was hydrogenated at atmospheric pressure and room temperature over 0.60 g. of 5% palladium-on-carbon catalyst. After 27 hours 1 mole-equivalent of hydrogen had been absorbed. Reaction conditions were continued for an additional 24 hours without further absorption of hydrogen. The palladium was removed by filtration and the hydrogenated product precipitated by addition of water. Two recrystallizations from acetone–water (75:25) afforded IV which was dried under vacuum for 6 hr. at 152°. The yield was 0.51 g. 85%) of IV, m.p. 261–262°, $[\alpha]^{25}\mathrm{D}$ +7.80°.

Anal. Calcd. for $C_{24}H_{36}O_6$: C, 68.54; H, 8.63. Found: C, 68.53; H, 8.43.

Fumaropimaric Acid Chloride (V) and Amide VI.—A solution of 8.3 g. of I in 30 ml. of thionyl chloride was heated at reflux for 16 hr. Excess thionyl chloride was removed by distillation. The crude product was dissolved in ether–benzene (90:10) and crystallized at −20° to yield 7.4 g. (87%) of the triacid chloride V. The analytical sample of V, m.p. 129–130°, was prepared by recrystallizing the crude product from ether–benzene (90:10) and drying the crystals in vacuum at 110° for 3 hr. The triacid chloride was refluxed with 0.6 *N* alcoholic potassium hydroxide and acidified. The precipitate was crystallized from benzene–methanol and dried to yield I, identical to the starting material.

Anal. Calcd. for $C_{24}H_{30}O_3Cl_3$: C, 60.83; H, 6.59; Cl, 22.44. Found: C, 60.91; H, 6.60; Cl, 22.34.

The triamide of I was prepared by passing a stream of dry ammonia through a solution of 2.5 g. of V in 100 ml. of dry acetone and allowing the solution to stand at 5° for 3 days. A precipitate of ammonium chloride was removed by filtration and water was added to induce crystallization of the amide. The yield was 2.0 g. (80%). Two recrystallizations from acetone–water and then drying in vacuum at 150° for 6 hours gave the analytical sample, the hemihydrate of VI, m.p. 303–304°.

Anal. Calcd. for $C_{24}H_{37}N_3O_3\cdot0.5H_2O$: C, 67.89; H, 9.02; N, 9.89. Found: C, 67.88; H, 8.95; N, 9.84.

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[16] C. S. Marvel and R. D. Rands, Jr., THIS JOURNAL, **72**, 2642 (1950).