readily from a simple molecular still[3] connected to a pair of mercury pumps and heated by a bath at 120–125°. The colorless, non-viscous, water-soluble distillate (D_1) weighed 1.8 g.

Material possessing the same properties was obtained by treatment with an equivalent of aqueous (6 *N*) sodium hydroxide, removal of water by vacuum distillation, filtration to remove sodium chloride, and distillation from the molecular still. The liquid will be called D_2.

From Chloroacetone.—Five grams (0.055 mole) of chloroacetone and 0.16 mole of formaldehyde (as formalin) were mixed and maintained at 20° while 0.055 mole of 6 *N* sodium hydroxide solution was added little by little with stirring in the course of a day. The mixture was then heated to 60° for ten hours to consume the base. The water was removed by evaporation under reduced pressure up to 90° and sodium chloride was precipitated in quantitative yield. The sirupy material (6.5 g.) was not distillable in an ordinary Claisen flask up to 175° (bath) and 5 mm., but it came over readily from a molecular still with the conditions specified above. The limpid distillate, to be referred to as D_3, weighed 1.5–2 g. There was a red-brown, non-volatile residue in the still.

Anal. Calcd. for $C_5H_{10}O_4$: active hydrogen atoms, 3. Found (Zerewitinoff): active hydrogen atoms from D_1, 3.13, 3.09; from D_3, 3.06, 2.98.

***p*-Bromobenzoic Ester.**—A mixture of 0.5 g. of acetylglycerol, 4 g. of *p*-bromobenzoyl chloride and 30 ml. of dry pyridine was maintained at 0° for thirty-six hours, and subsequently treated with 40 ml. of 5% sodium carbonate solution for eight more hours at 0°. Fifty grams of water was added, and the mixture was filtered. The acetylglycerol tris-*p*-bromobenzoate was digested in ethanol and recrystallized from butyl ether; yield of white needles, 2 g. (79%). D_1, D_2 and D_3 all behaved identically, giving products melting at 215–216°. Mixed melting point determinations of these products were not lowered.

The same product was formed but in lower yield if a reaction temperature of 100–115° was maintained.

Anal. Calcd. for $C_{26}H_{19}Br_3O_7$: Br, 35.1. Found: Br, 35.9.

Reduction of Acetylglycerol.—Four grams of acetylglycerol was dissolved in 17 ml. of ethanol and 3 g. of water. Two grams of sodium was added in small pieces during two hours. At first, the mixture was cooled with ice; when the reaction became less vigorous, it was allowed to proceed at room temperature. After ninety minutes the reaction was very slow, so 10 ml. more of alcohol was added. The solution became a deep red and a yellow precipitate formed. After the sodium had been added, the mixture was neutralized with a saturated solution of dry hydrogen chloride in alcohol. The solution was filtered from the salt which precipitated, the solvent was removed, and the 5 cc. of dark residue was distilled in the molecular still with a bath temperature of 80–85°. The yield of colorless distillate was 0.91 g. or 23%.

Anal. Calcd. for $C_5H_{12}O_4$: active hydrogen atoms, 4. Found (Zerewitinoff): active hydrogen atoms, 3.84, 4.02.

Summary

Formaldehyde condenses with chloroacetone to yield 2-chloro-2-acetyl-1,3-propanediol and its cyclic formal. α,α-Dichloroacetone, similarly treated, gives rise to 4-hydroxy-3,3-dichloro-2-butanone. Various reactions of these compounds are developed.

EVANSTON, ILLINOIS
TERRE HAUTE, INDIANA
RECEIVED AUGUST 4, 1947

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[3] Hickman and Sanford, *J. Phys. Chem.*, **34**, 643 (1930).

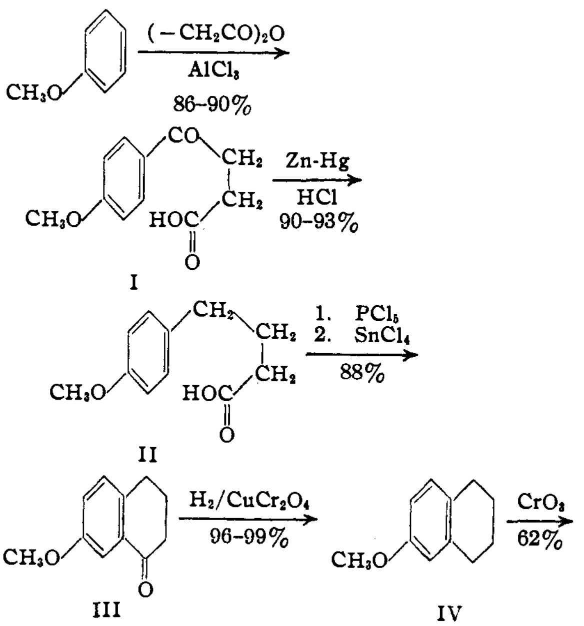
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UPJOHN COMPANY]

6-Methoxy-1-tetralone

BY DONALD G. THOMAS AND ALAN H. NATHAN

Of the various methods[1-6] described for the synthesis of 6-methoxy-1-tetralone (V), the one most generally used is that based on the chromic acid oxidation[5] of 6-methoxytetralin (IV), which usually has been obtained from tetralin by sulfonation, alkali fusion and methylation.[7,8] The over-all yield of 6-methoxy-1-tetralone by this method is about 30–35%.

An alternate route to 6-methoxy-1-tetralone is outlined below, and by this procedure we have obtained 6-methoxy-1-tetralone in over-all yields of 40–45%.



The reaction between anisole and succinic an-

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[1] Thompson, *J. Chem. Soc.*, 2310 (1932).

[2] Robinson and co-workers, *ibid.*, 1285, 1288 (1935); 192, 747 (1936); 1581 (1937).

[3] Chuang and Huang, *Ber.*, **69**, 1505 (1936).

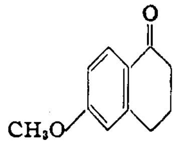
[4] Martin, THIS JOURNAL, **58**, 1438 (1936).

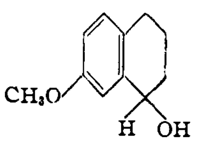
[5] Burnop, Elliott and Linstead, *J. Chem. Soc.*, 727 (1940).

[6] Bachmann and Thomas, THIS JOURNAL, **64**, 94 (1942).

[7] Schroeter, *Ann.*, **426**, 83 (1922).

[8] Since this manuscript was submitted for publication, details of a superior method for the preparation of 6-methoxytetralin by catalytic hydrogenation of β-naphthyl methyl ether have been published by Stork, THIS JOURNAL, **69**, 576 (1947).


V


VI

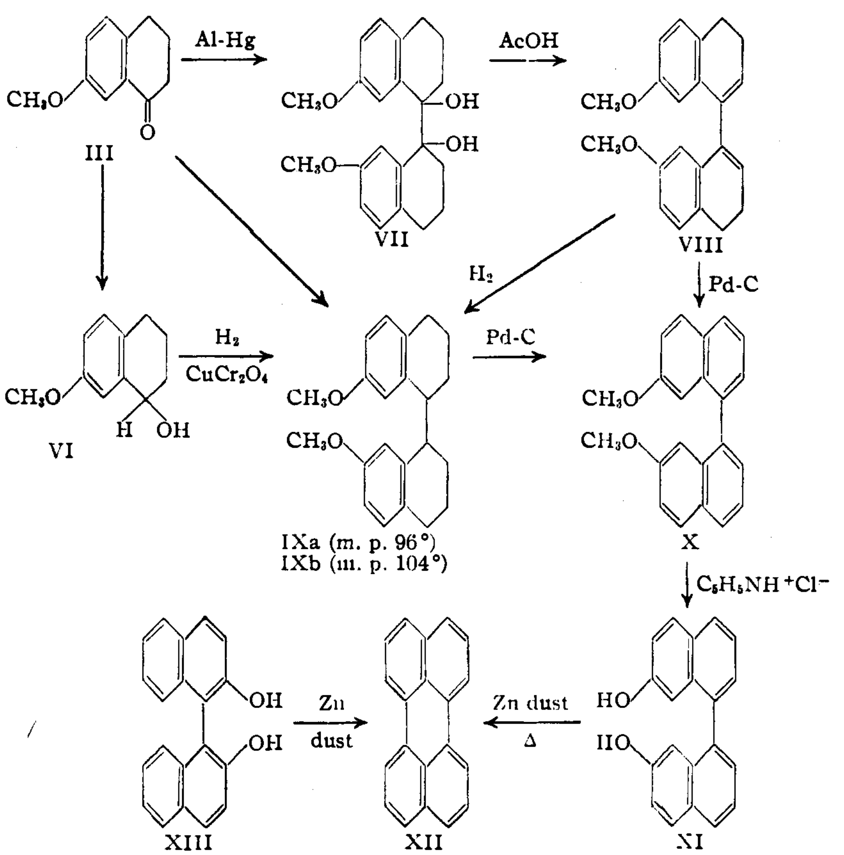
hydride was carried out essentially as described,[9] with minor modifications that shortened the time required. Clemmensen reduction of the resultant β-(*p*-anisoyl)-propionic acid (I) was conducted as described.[10] Cyclization of the reduced acid (II) by treatment of the acid chloride with stannic chloride gave 7-methoxy-1-tetralone (III) in excellent yields. Hydrogenation of 7-methoxy-1-tetralone in the absence of solvent with a barium-free copper chromite catalyst up to 200° and under an initial pressure of 200 atmospheres gave practically quantitative yields of 6-methoxytetralin (IV). The success of the hydrogenation was dependent upon the purification of the ketone and the extent of the purification required was related to the amount of phosphorus pentachloride used in making the acid chloride of II. When the ratio of phosphorus pentachloride to acid was 1.1:1, the yield of purified 7-methoxy-1-tetralone was 83%, and it was essential to purify the ketone by distillation, refluxing with Raney nickel, and recrystallization before hydrogenation. Omission of any of these three steps resulted in only 55–70% yields of 6-methoxytetralin which was then accompanied by variable amounts of 7-methoxy-1-tetralol (VI) and occasionally by a crystalline bimolecular reduction product (see below). When the ratio of phosphorus pentachloride to acid was exactly 1:1, the yield of purified ketone was 88% and the treatment with Raney nickel could be omitted although in this case the yield of IV on hydrogenation was lowered to 92–94%.

The hydrogenation of either 7-methoxy-1-tetralone or 7-methoxy-1-tetralol in absolute alcohol with palladium–charcoal at room temperature and three atmospheres gave IV in 92–95% yield; the ketone did not have to be so rigorously purified. Clemmensen reduction of III gave IV in a maximum yield of only 77%.

Chromic acid oxidation of 6-methoxytetralin gave a 62% yield of distilled and recrystallized 6-methoxy-1-tetralone.

Hydrogenation of 7-methoxy-1-tetralol with copper chromite under the same conditions employed for 7-methoxy-1-tetralone gave a 58–62% yield of 6-methoxytetralin and, in addition, a 23–27% yield of a mixture which, by repeated fractional crystallization, was separated into two forms of 7,7′-dimethoxy-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-binaphthyl (IXa and b), which we conclude are the *cis* and *trans* forms. No attempt was made to determine the configurations of these two forms. The structure of IX was verified by the reactions outlined below.

7-Methoxy-1-tetralone was reduced with aluminum amalgam to the pinacol (VII), which was dehydrated to the diene (VIII).[11] Reduction of the diene with sodium and butyl alcohol gave a mixture from which both IXa and IXb were isolated; only IXb was isolated from the hydrogenation of the diene with Raney nickel. Dehydrogenation of VIII, IXa and IXb gave in each case 7,7′-dimethoxy-1,1′-binaphthyl (X).



The fact that these bimolecular reduction products were joined in the 1,1′-position was proved,

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[9] Fieser and Hershberg, THIS JOURNAL, 58, 2314 (1936).

[10] Martin, "Organic Reactions," Vol. I, John Wiley and Sons, New York, N. Y., 1942, p. 167.

[11] This diene was also obtained on distillation of the high-boiling residues from the Clemmensen reduction of 7-methoxy-1-tetralone.

not only by their formation via the pinacol reduction of 7-methoxy-1-tetralone,[12] but also by the formation from the binaphthol (XI) of perylene (XII), which has been previously prepared by a similar reaction from 2,2′-dihydroxy-1,1′-binaphthyl (XIII).[13]

Experimental

β-(*p*-Anisoyl)-propionic Acid (I).—A solution of 560 g. (4.2 moles) of aluminum chloride in 1 liter of 1-nitropropane[14] was added gradually to a mechanically stirred mixture of 216 g. (2 moles) of anisole and 210 g. (2.1 moles) of succinic anhydride in 500 cc. of 1-nitropropane while the temperature was kept at 0–5°. The mixture was kept at 3–8° for approximately twenty-four hours, allowed to reach 15° in about an hour and hydrolyzed with ice and hydrochloric acid. Isolation of the acid as described[9] gave 358–376 g. (86–90%) of almost colorless to cream-colored acid; m. p. (not recrystallized) 144.5–146.5°.

γ-(*p*-Anisyl)-butyric Acid (II).—Clemmensen reduction[10] of the above keto acid in amounts from 350–900 g. gave yields from 90–93.4%; b. p. 152–156° at 0.6 mm.; m. p. (not recrystallized) 59–61° with softening at 56°.

7-Methoxy-1-tetralone (III).—To a mechanically stirred solution of 194 g. (1 mole) of the reduced acid (II) in 1 liter of dry thiophene-free benzene was added 208.3 g. (1 mole) of phosphorus pentachloride while the temperature was kept at 5–10°. The resulting colorless solution was warmed to 50° for a few minutes and then chilled to 0 to −5°. To it was added rapidly (about forty seconds) a chilled solution of 175 cc. of anhydrous stannic chloride in 175 cc. of dry thiophene-free benzene. A blood-red color developed which quickly turned to a dark brown-green and in ten to fifteen minutes the reaction mixture set to a green semi-solid. Hydrolysis and isolation as described for a similar cyclization[15] followed by distillation from 115–120° at 0.6–0.8 mm. (160–165° at 11 mm.) gave 161.4 g. (91.7%) of colorless crystalline ketone. For hydrogenation with copper chromite the product was refluxed for an hour with about 5 g. of Raney nickel in absolute ethanol and then recrystallized from petroleum ether (60–75°) from which it separated as large colorless prisms; m. p. 61–62.5°; yield, 154.9 g. (88%).

6-Methoxytetralin (IV).—7-Methoxy-1-tetralone (70.4 g., 0.4 mole) was hydrogenated in the presence of 7.0 g. of barium-free copper chromite[16] at 200° without solvent and under an initial pressure (at room temperature) of 3000 pounds. Hydrogenation began at 125° and was complete after an hour at 200°.[17] The product was obtained as a colorless liquid; b. p. 121–128° at 11 mm.; yield, 62.2–64.2 g. (96–99%). Hydrogenation of ketone in whose purification the Raney nickel treatment was omitted gave 92–94% yields.

6-Methoxy-1-tetralone (V).—The oxidation of 113.4 g. (0.7 mole) of 6-methoxytetralin with chromic acid was carried out essentially as described[8] except that the tetralin was dissolved in a solvent consisting of 80% of acetic acid and 20% of propionic acid; this mixture prevented solidification when the solution was chilled. After oxidation, the solvent was removed, but instead of distilling the dark viscous residue with super-heated steam it was warmed with 5% sulfuric acid and the ketone was extracted with ether[18] which was then washed with water, 5% sodium hydroxide solution, water and dried. Distillation at 129–133° at 0.7 mm. (a fore-run of unchanged 6-methoxytetralin was collected) and recrystallization from petroleum ether (60–75°) gave V as large colorless prisms; m. p. 77–78.5°; yield, 76.4 g. (62%).

7-Methoxy-1-tetralol (VI).—Hydrogenation of 7-methoxy-1-tetralone in whose preparation 1.1 moles of phosphorus pentachloride was used and which was not subjected to the full purification procedure gave 55–72% yields of 6-methoxytetralin, 10–30% yields of 7-methoxy-1-tetralol and occasionally a bimolecular reduction product (IX) (see below); when IX was obtained little or no tetralol was isolated. 7-Methoxy-1-tetralol is a colorless viscous liquid; b. p. 118–120° at 0.3 mm. (164–166° at 10 mm.); n^{23}D 1.5553.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.05; H, 7.97.

The *p*-nitrobenzoate crystallized from ethanol as pale yellow prisms; m. p. 73.5–74°.

Anal. Calcd. for $C_{18}H_{17}NO_5$: C, 66.04; H, 5.24; N, 4.28. Found: C, 65.95; H, 5.25; N, 4.29.

7,7′-Dimethoxy-1,1′-dihydroxy-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-binaphthyl (VII).—Eight and eight-tenths grams of 7-methoxy-1-tetralone was reduced with amalgamated aluminum foil in alcohol–benzene according to the procedure described by Newman[12] for 7-methyl-1-tetralone. The pinacol was isolated as a mixture of crystals and an oil which could not be obtained crystalline; both fractions could be converted to the diene (VIII). The crystals, after recrystallization from isopropanol, amounted to 3.9 g. (44%), m. p. 182–184°. After one further recrystallization from benzene–cyclohexane they melted at 183–184.5° and were analytically pure.

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.56; H, 7.40. Found: C, 74.67, 74.77; H, 7.39, 7.37.

7,7′-Dimethoxy-3,3′,4,4′-tetrahydro-1,1′-binaphthyl (VIII).—Dehydration of the pinacol (VII) was accomplished by refluxing for two hours in about seven times its weight of glacial acetic acid. The diene crystallized from solution on cooling. Both the crystalline pinacol and the uncrystallizable oil gave the same diene, which was obtained as colorless octahedra from methanol, m. p. 147.8–148.2°.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 82.99; H, 6.97. Found: C, 83.18; H, 7.15.

The pinacol was also converted to the diene by repeated recrystallization from alcohol. A mixed melting point with a product isolated from the Clemmensen reduction of 7-methoxy-1-tetralone was not depressed.

7,7′-Dimethoxy-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-binaphthyl (IXa and IXb).—Hydrogenation of 71.2 g. (0.4 mole) of 7-methoxy-1-tetralol (VI) under the same conditions employed for the hydrogenation of III gave 40.4 g. (62%) of 6-methoxytetralin and 17.5 g. (27%) of a very viscous yellow oil, b. p. 255–270° at 11 mm., which crystallized rather poorly when triturated in methanol. After a tedious series of fractional crystallizations from methanol two compounds were isolated. One (IXa) formed colorless rhomboidal plates, m. p. 95–96°; the other (IXb) formed colorless hexagonal prisms, m. p. 103–104.5°. Attempts to interconvert these two isomers failed.

Anal. Calcd. for $C_{22}H_{26}O_2$: C, 81.96; H, 8.13. Found: IXa, C, 82.00; H, 8.39. IXb, C, 81.98; H, 8.46.

To a solution of 1.75 g. of the diene (VIII) in 30 cc. of butanol at 60° was added 1.0 g. of sodium; after the reaction had subsided somewhat the mixture was heated until solution was complete. The cooled solution was washed with water until neutral, dried and evaporated. Fractional crystallization of the residue yielded both IXa and IXb.

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(12) *Cf.* Newman, THIS JOURNAL, **62**, 1683 (1940). The reduction of 7-methyl-1-tetralone under identical conditions led to the synthesis of coronene.

(13) Marschalk, *Bull. soc. chim.*, [4] **43**, 1388 (1928).

(14) The 1-nitropropane was purified by treatment with aluminum chloride at room temperature followed by hydrolysis with ice, steam distillation, drying and distillation.

(15) Johnson, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 136.

(16) Lazier and Arnold, "Organic Syntheses," Coll. Vol. II, p. 142.

(17) *Cf.* Mowry, Renoll and Huber, THIS JOURNAL, **68**, 1105 (1946), for the reduction of aryl methyl ketones with copper chromite.

(18) *Cf.* Schwenk and Papa, *ibid.*, **67**, 1432, ref. 13 (1945) for the use of butyl ether in the isolation.

A sample of the diene (VIII) in absolute alcohol was subjected to hydrogenation over Raney nickel at 50° and 160 atmospheres. The product after one recrystallization from methanol was pure IXb, m. p. 104–105°.

7,7′-Dimethoxy-1,1′-binaphthyl (X).—A mixture of the diene (VIII) with about 2.5% of its weight of palladized charcoal,[19] when heated at 290–300° for fifteen minutes, gave a practically quantitative yield of X which, after recrystallization from ethanol, formed colorless rectangular plates, m. p. 110.5–111.5°.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.08; H, 5.77. Found: C, 83.73; H, 5.64.

Similar treatment of the bitetralyl (IXa and IXb) gave in each case the same compound, identified by mixed m. p.

7,7′-Dihydroxy-1,1′-binaphthyl (XI).—The methyl ether (X) was smoothly demethylated in practically quantitative yield by the method of Prey.[20] A mixture of X with three times its weight of pyridine hydrochloride was heated at 200° for six hours, then poured into water. For analysis, the compound was converted to its diacetate by standard methods, because the free phenol was difficult to purify. The diacetate formed white crystals from ethanol, m. p. 173.5–174.5°. After three recrystallizations the compound gave the following analytical values.

Anal. Calcd. for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 77.38; H, 4.66.

Perylene (XII).—A mixture of the binaphthol (XI) with five times its weight of zinc dust was heated in a distilling flask with a free flame. A yellow oil distilled out of the mixture and solidified in the cooler parts of the apparatus. This was removed and recrystallized from benzene; it formed yellow leaflets with a bronze luster, melting at 267–268°. This was identified as perylene by comparison with an authentic specimen prepared by heating 2,2′-dihydroxy-1,1′-binaphthyl (XIII)[21] with zinc, zinc chloride and water.[13] A mixture of the two samples melted at 267–268°. The picrate formed dark violet needles from benzene, m. p. 220° (reported[22] m. p. 221°). The sample of perylene obtained from XI gave the following analytical results.

Anal. Calcd. for $C_{20}H_{12}$: C, 95.21; H, 4.80. Found: C, 94.90; H, 4.65.

Summary

1. A procedure for the preparation of 6-methoxy-1-tetralone in 40–45% yields from anisole is described.

2. A by-product from the catalytic hydrogenation of 7-methoxy-1-tetralone or 7-methoxy-1-tetralol has been shown to be 7,7′-dimethoxy-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-binaphthyl.

KALAMAZOO, MICHIGAN RECEIVED[23] AUGUST 27, 1947

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[19] Linstead and Thomas, *J. Chem. Soc.*, 1130 (1940).

[20] Prey, *Ber.*, **74B**, 1219 (1941).

[21] Julius, *Chem. Ind.*, **10**, 98 (1887).

[22] Brass and Tengler, *Ber.*, **64B**, 1650 (1931).

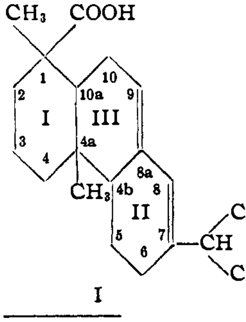
[23] Original manuscript received November 29, 1946.

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

Resin Acids. I. An Improved Method of Isolation of Resin Acids; The Isolation of a New Abietic-Type[1] Acid, Neoabietic Acid

BY GEORGE C. HARRIS AND THOMAS F. SANDERSON

This is the first in a series of papers presenting recent developments made in these laboratories on the isolation and proof of structure of pure resin acids. This paper deals with improved methods of isolation of abietic acid (I)[2] and levopimaric acid (II)[3,4] the most familiar abietic-type acids; the isolation of neoabietic acid (III),[5] a new primary acid of this type, is also described.



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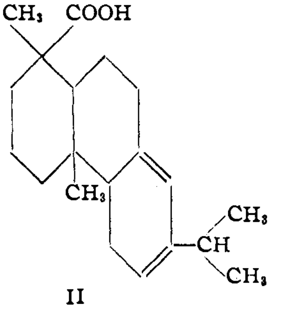

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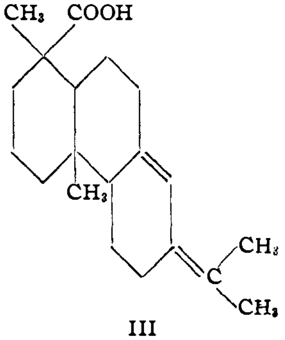

III

Abietic Acid

The difficulty in separating abietic acid from isomeromorphic resin acids has made its isolation from rosin a difficult problem. However, Palkin and Harris[6] were able to obtain a pure abietic acid according to the following procedure: (1) isomerizing rosin by boiling in glacial acetic acid to increase the abietic acid content, (2) concen-

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[1] We wish to designate by this term that type of resin acid that yields retene, 1-methyl-7-isopropylphenanthrene, upon complete dehydrogenation and has an isopropyl or isopropylidene group at C-7.

[2] L. Ruzicka, L. Sternbach and O. Jeger, *Helv. Chim. Acta*, **24**, 504 (1941).

[3] This word has purposely been written as one word since the compound is not stereoisomeric with dextropimaric acid as the prefixes *levo-* and *dextro-* would imply.

[4] L. Ruzicka and S. Kaufman, *Helv. Chim. Acta*, **23**, 1346 (1940); according to Ruzicka and Kaufman the double bonds may be at the positions indicated in Formula II or at positions 5–6 and 7–8, the former being preferred.

[5] G. C. Harris and T. F. Sanderson, Resin Acids. II., THIS JOURNAL, **69**, 339 (1947).

[6] S. Palkin and T. H. Harris, *ibid.*, **56**, 1335 (1934).