Optical Crystallographic Properties.—(a) L-Iditol Hexaacetate.—*In ordinary light*, the material consists of hexagonal plates which break up into angular fragments. The crystal system appears to be hexagonal. Refractive indices (determined by the immersion method in organic oily liquids): $n_\omega = 1.505$, $n_\epsilon = 1.463$, both ± 0.002. *In parallel polarized light (crossed nicols)*: the birefringence is strong. *In convergent polarized light (crossed nicols)*: uniaxial interference figures are frequently shown. The sign is negative.

(b) **D-Iditol Hexaacetate.**—The D-iditol hexaacetate obtained from 3,4-anhydro-D-talosan$<1,5>\beta<1,6>$ exhibited optical properties which were identical with those of L-iditol hexaacetate.

(c) **Racemic Iditol Hexaacetate.**—*In ordinary light*, this substance consists of glassy hexagonal plates which break up into angular fragments. Refractive indices (determined by the immersion method in organic oily liquids): $n_\alpha = 1.458$; $n_\beta = 1.507$; $n_\gamma = 1.515$, all ± 0.002. All the indices are readily found. *In parallel polarized light (crossed nicols)*: the birefringence is extreme, some fragments extinguishing sharply, others remaining bright with crossed nicols. *In convergent polarized light (crossed nicols)*: partial biaxial interference figures are seen on many fragments, one optic axis being perpendicular to many of them. The sign is negative.

(d) **D-Mannitol Hexaacetate.**—*In ordinary light*, this substance consists of rather massive colorless prisms, which break up into angular fragments. The crystal system is probably monoclinic. Refractive indices (determined by the immersion method in organic oily liquids): $n_\alpha = 1.452$, $n_\beta = 1.520$, $n_\gamma = 1.526$, all ± 0.002. All of the indices are readily found. *In parallel polarized light (crossed nicols)*: the birefringence is extreme. Fragments extinguishing sharply and others remaining bright with crossed nicols are both commonly found. *In convergent polarized light (crossed nicols)*: biaxial interference figures are frequently visible, being seen on practically all of the fragments, showing sections perpendicular to the acute bisectrix and also to an optic axis. The axial angle $2E$ is moderate in size and the sign is negative.

Racemic Iditol Hexaacetate.—A solution of a mixture of 0.055 g. of D-iditol hexaacetate and 0.055 g. of L-iditol hexaacetate in 3 cc. of boiling alcohol deposited 0.1 g. (91%) of racemic iditol hexaacetate upon cooling. The compound was recrystallized from 3 parts of boiling alcohol in the form of plates which melted at 165–166° (cor.) and showed no optical activity in chloroform solution (c, 0.8; l, 4).

Anal. Calcd. for $C_{18}H_{26}O_{12}$: C, 49.77; H, 6.03. Found: C, 49.99; H, 6.05.

Summary

The alkaline detosylation of 4-tosyl-D-mannosan $<1,5>\beta<1,6>$ has been shown to proceed with Walden inversion and *cis* ethylene oxide ring formation to yield an anhydro derivative which is presumably 3,4-anhydro-D-talosan$<1,5>\beta<1,6>$. The anhydro compound, upon treatment with an acid acetylating mixture, yields a mixture of D-mannose and D-idose pentaacetates. The hexoses present have been identified by conversion of the acetates to characteristic hexitol hexaacetates. The reactions outlined are in agreement with other reactions in the carbohydrate series involving Walden inversions with ethylene oxide ring formation and rupture, as studied especially by Robertson and his colleagues, and the present results justify the conclusion that the structure and the configuration of the anhydro compound are those of 3,4-anhydro-D-talosan-$<1,5>\beta<1,6>$.

D- and L-iditol hexaacetates form a crystalline racemate which melts much higher than the components and differs from them in crystallographic optical properties.

The Structure and Configuration of Resin Acids. Podocarpic Acid and Ferruginol

BY WILLIAM P. CAMPBELL[1] AND DAVID TODD

Podocarpic acid was first isolated in 1873 by Oudemans.[2] It was only recently, however, that Sherwood and Short[3] studied the compound and suggested formula II as the most probable structure. The most revealing bit of evidence was the formation of 6-hydroxy-1-methylphenanthrene (III) in good yield by dehydrogenation, thus accounting for all of the carbon atoms except one in a methyl group and one in the carboxyl. On the basis of this evidence the two carbon skeletons shown in formulas I and II were considered. Although formula I is similar to the resin acids, formula II was favored because the carboxyl group of podocarpic acid is much more highly hindered than that of the other resin acids.
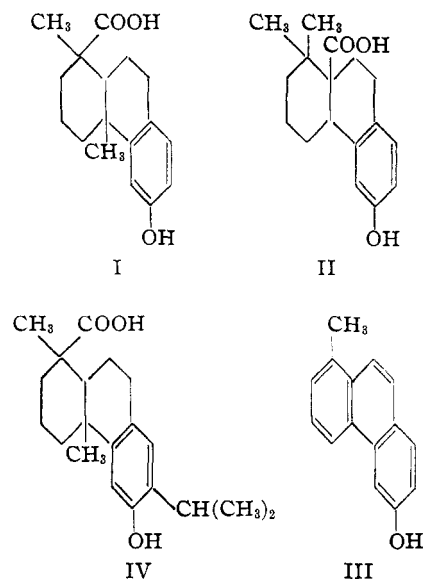
Shortly after the appearance of this work it was pointed out by Fieser and Campbell[4] that, if

(1) Present address: Hercules Experiment Station, Hercules Powder Company, Wilmington, Delaware.

(2) Oudemans, *Ber.*, **6**, 1122 (1873); *Ann.*, **170**, 214 (1873); *J. prakt. Chem.*, **9**, 385 (1874).

(3) Sherwood and Short, *J. Chem. Soc.*, 1006 (1938).

(4) Fieser and Campbell, THIS JOURNAL, **61**, 2528 (1939).

I　　　　　　　　　　II

IV　　　　　　　　　　III

formula I were correct, the 7-isopropyl derivative of podocarpic acid might be identical with 6-hydroxydehydroabietic acid (IV). In a recent publication[5] we have made this comparison and found that the substances are not identical. It was noted that this did not necessarily eliminate formula I since 7-isopropylpodocarpic acid and 6-hydroxydehydroabietic acid may differ in configuration rather than in structure. However, if the two substances differ only in configuration, it is necessary to find a reason for the great difference in the hindrance of the carboxyl groups of the isomers. A study of molecular models showed very clearly that two structures differing only in the configuration at C_1 possessed carboxyl groups with widely different degrees of hindrance. This observation strengthened the possibility that the isomeric podocarpic and dehydroabietic acid derivatives (IV) differ only in the configuration of the carboxyl and methyl groups at C_1.

We set out to test this possibility by eliminating the asymmetry at this point by converting the carboxyl groups of both compounds to methyl groups. The method which we chose is outlined with partial formulas below.
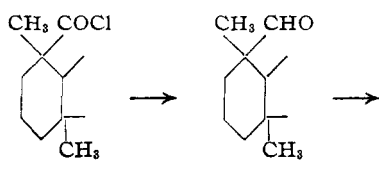

(5) Campbell and Todd, THIS JOURNAL, **62**, 1287 (1940).
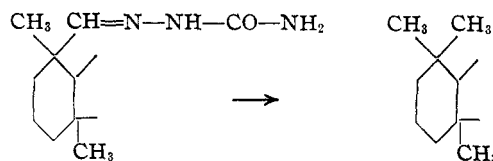
Because we anticipated some difficulty in carrying out these reactions with such highly hindered carboxyl groups, the method was tried first on the more easily available dehydroabietic acid and on podocarpic acid. The Rosenmund reductions of the acid chlorides proceeded smoothly without the use of catalyst poison[6] and yields varying from 38 to 88% were obtained. Surprisingly enough, these highly hindered aldehydes, on treatment with semicarbazide acetate in alcohol–pyridine solution at room temperature, gave the semicarbazones in nearly the theoretical yields. The final reduction by the Wolff-Kishner method was carried out in 70% yield in the case of dehydroabietic acid but with the other substances the reaction was less satisfactory.

The products of this series of reactions on 6-hydroxydehydroabietic acid and 7-isopropylpodocarpic acid would be isomeric with ferruginol, which was isolated recently by Brandt and Neubauer.[7] We have previously shown[5] that the dehydrogenation product obtained by them is the 6- instead of the 8-retenol. Assuming, as they suggest, that the carbon skeleton is similar to that of the resin acids, the structure of ferruginol would be V. If this formula is correct we expected that

V
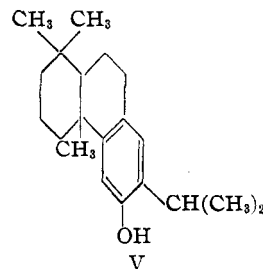
one or both of the corresponding derivatives of podocarpic and dehydroabietic acids would be identical with ferruginol. It was found that all three of these compounds, 6-hydroxydehydroabietane, 7-isopropylpodocarpane, and ferruginol are identical and the structure V is established for these substances by reference to the proven structure of dehydroabietic acid. The identity of these substances was proved by a comparison of the solid acetates as shown in Table I. Although

(6) Ruzicka and Wirz, Helv. Chim. Acta, **22**, 949 (1939).

(7) Brandt and Neubauer, J. Chem. Soc., 1031 (1939).

Acetate of	M. p., °C.	Mixed m. p., °C.	$[\alpha]_{Hg}^{20b}$	$n^{61}D$
6-Hydroxyde- hydroabietane	80–80.5	⎫	+66.3	1.5186
7-Isopropylpodo- carpane	80.5–81.5	⎬ 80–81.5	+67.1	1.5189
Ferruginol[a]	81–82	⎭	+60.3	1.5186

[a] The data for ferruginol were reported by Brandt and Neubauer.[7]

[b] Rotations were determined in 4% ethanol solution. That for ferruginol is in a 10% solution at 16°, using the D line.

we had no ferruginol with which to make a direct comparison, the close correspondence of the data leaves little doubt as to the identity of this substance.

By this evidence the carbon skeleton of podocarpic acid is proved to be that shown in formula I. However, since the carboxyl group was converted to a methyl group in these reactions, there remain two possible structures, I and VI, for the acid.
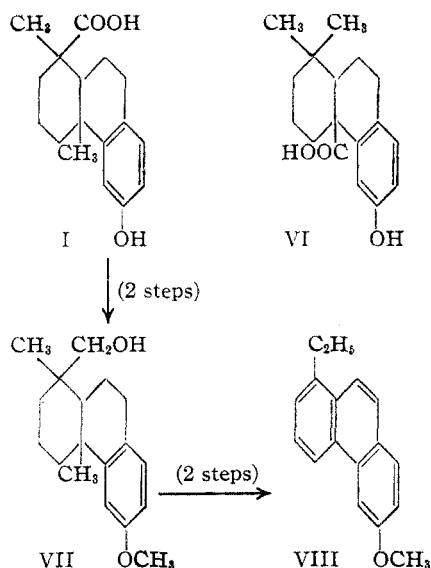
Structure VI was eliminated because podocarpic acid was converted into 1-ethyl-6-methoxyphenanthrene VIII by way of the Wagner–Meerwein rearrangement of the carbinol VII followed by dehydrogenation of the product. These transformations could not lead to VIII when applied to a substance having structure VI. Since, by a similar method, abietinol was converted into 7-isopropyl-1-ethylphenanthrene,[8] the isolation of the

(8) Ruzicka and Meyer, *Helv. Chim. Acta*, **5**, 581 (1922); Ruzicka, de Graaf and Müller, *ibid.*, **15**, 1300 (1932).

methoxy-1-ethylphenanthrene provides positive proof that the structure of podocarpic acid is correctly represented by I. The identity of the 6-methoxy-1-ethylphenanthrene was established by comparison with a sample synthesized by a method which leaves no doubt as to its structure. The comparison of the melting points of the derivatives of both samples of this substance is shown in Table II.

TABLE II

MELTING POINTS OF DERIVATIVES OF 6-METHOXY-1-ETHYLPHENANTHRENE

Derivative	Synthetic comp.	Natural comp.	Mixture
Picrate	127–128	126–126.5	126–128
Styphnate	141	139–140.5	139–140
Trinitrobenzene	140–140.5	137–137.5	137–140

The methoxyethylphenanthrene was synthesized by the method outlined in part below.
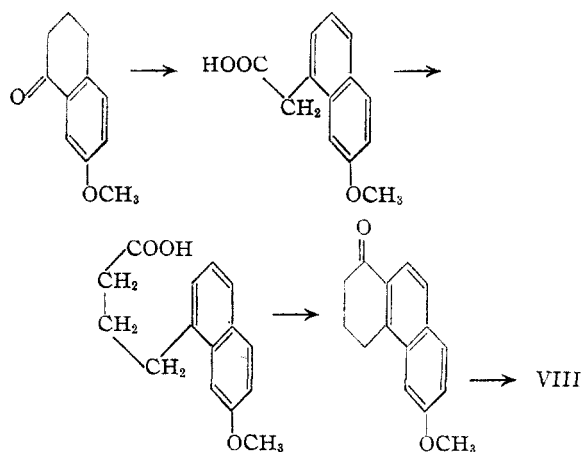
A study of molecular models of these substances indicated that 7-isopropylpodocarpic acid and 6-hydroxydehydroabietic acid differ only in the configuration of the methyl and carboxyl groups at C_1. This has now been proved to be correct. Further consideration of these models has provided evidence which, combined with our present knowledge of the resin acids, permits certain deductions to be made in regard to the stereochemistry of these compounds. To simplify the discussion, the abbreviated formulas shown below will be used to represent the resin acid (either podocarpic or dehydroabietic acid) molecule. There are only four geometric isomers of this molecule. Since podocarpic and dehydroabietic acids differ only in the C_1 configuration, these acids must be represented by IX and X with the ring configuration *cis* or by XI and XII with the rings *trans*.

IX   X   XI   XII

XIII (dl)   XIV (meso)   XIII (dl)   XV (meso)
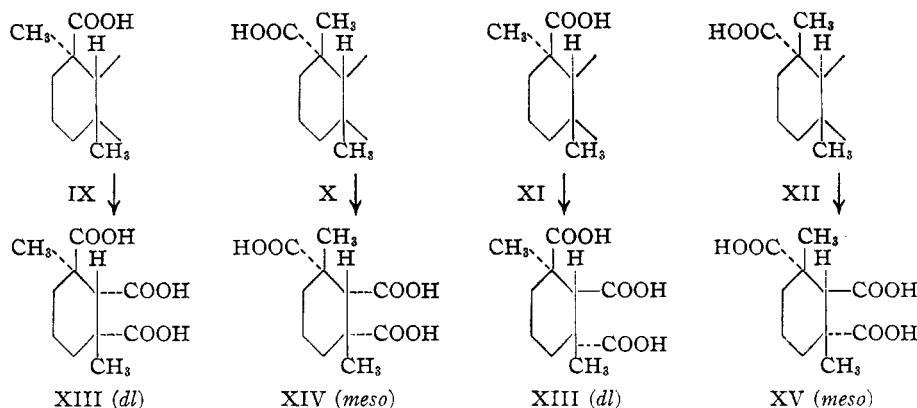
Abietic acid, which has the same configuration as dehydroabietic acid,[9] has been oxidized to an eleven-carbon acid represented by formulas XIII to XV.[10] This acid is optically inactive and was recognized as a *meso* form. This conclusion is supported by the observation that racemization of an optically active acid would not occur under the conditions of the oxidation since the 1- and 3-carboxyl groups are tertiary. In addition Ruzicka and Bernold[11] have obtained a similar derivative, which is optically active, by the oxidation of agathic acid. Since the C-11 acid obtained in the abietic acid series is a *meso* form, it follows that if the ring configuration is *cis*, dehydroabietic (or abietic) acid is X and podocarpic acid is IX; if the ring configuration is *trans*, dehydroabietic acid is XII and podocarpic acid is XI.

The carboxyl group of podocarpic acid is very much more hindered than that of dehydroabietic acid,[12] and it is this fact which provides the evidence which favors the *trans* ring configuration for these substances. Molecular models of the formulas, IX to XII, also show great differences in the hindrance of the carboxyl group. The models in which the ring configuration is *cis* show that the carboxyl group in formula X is considerably more hindered than in IX[13] since, in X, this group is crowded into the sharp angle of the rings. This requires that dehydroabietic acid (X) be more highly hindered than podocarpic acid (IX), and is contrary to the observed behavior of these

substances. In the models of the *trans* compounds, the carboxyl group of XI is much more hindered than that of XII due to the interference of the C_{12} angular methyl group. This is in agreement with the observation that podocarpic acid is more hindered than dehydroabietic acid. Thus, on the assumption that the molecular models give a reasonably accurate picture of the molecule, the *cis* configuration for the rings is eliminated. Podocarpic acid, therefore, has the configuration shown in formula XI and dehydroabietic and abietic acids as well as levopimaric acid have the configuration of XII.

One observation which may be considered as favoring the *cis* ring configuration in these substances should be noted. Of the few sesquiterpenes that have been studied, all have been shown, on the basis of physical properties, to possess the *cis* configuration.[14] It may also be pointed out that in formula X the carboxyl group is close to C_{13}. On the assumption that the formula suggested by Fleck and Palkin[15] for hydroxytetrahydroabietic acid (XVI) is correct, the ease with which this substance lactonizes is most easily explained by this configuration. The position of

XVI
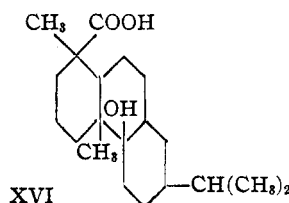
the hydroxyl group of this acid, however, has not been proved.

Our deduction of the ring configuration of these substances on this basis certainly cannot be considered conclusive. It is significant, however, that both the observed difference in the ease of hydrolysis of dehydroabietic and podocarpic esters, and the difference in the hindrance of the carboxyl group in the two *cis* and the two *trans* models, are very great.

(9) Abietic acid has been converted into dehydroabietic acid under mild conditions; Fieser and Campbell, THIS JOURNAL, **60**, 159 (1938).

(10) Ruzicka and Sternbach, *Helv. Chim. Acta*, **21**, 565 (1938).

(11) Ruzicka and Bernold, *ibid.*, **24**, 931 (1941).

(12) This observation originally reported by Sherwood and Short,[8] has been verified in our work.

(13) This observation is not in agreement with the statement of Ruzicka and Bernold,[11] who reported that in both the *cis* and *trans* formulas the carboxyl group is more hindered when it is *cis* to the C_{12} angular methyl group.

(14) Ruzicka, Koolhaas and Wind, *Helv. Chim. Acta*, **14**, 1151, 1171 (1931). See also, Linstead, *et al.*, *J. C hem. Soc.*, 472 (1936; 1140 (1937).

(15) Fleck and Palkin, THIS JOURNAL, **61**, 3197 (1939).

With the evidence now available, it can be said with certainty that podocarpic and agathic acids[11] possess the same configuration at C_1 and C_{12}, although nothing can be said of the position of the C_{11} hydrogen atom in the latter molecule.

Experimental Part

O-Methylpodocarpinal.—The acid chloride of O-methyl-podocarpic acid was prepared by adding 1.45 cc. of thionyl chloride and two drops of pyridine to a solution of 3.0 g. of the acid in 25 cc. of dry ether at ice-bath temperature. After standing at room temperature for five hours, the solution was washed with 1% sodium hydroxide and then with water and dried over sodium sulfate. After removal of the solvent in vacuum it was found necessary to keep the residue in vacuum (water pump) at 100° for at least twenty-four hours to remove the last traces of solvent and reagent, and avoid poisoning the catalyst in the next reaction.

The Rosenmund reduction of the acid chloride from 15 g. of the acid was run in 75 cc. of boiling xylene and with 3.0 g. of 10% palladium–barium sulfate catalyst. The solution was stirred vigorously during the reduction. None of the quinoline–sulfur poison was used. As determined by titration of the hydrogen chloride evolved the reaction was two-thirds complete after thirty minutes and the evolution of hydrogen chloride ceased after fifty minutes when 91% of the theoretical amount had been evolved. The mixture was cooled in a stream of nitrogen, filtered, and steam distilled to remove the solvent. The product, which crystallized as the xylene was removed, was separated and crystallized from 150 cc. of hot ethanol; yield 11.25 g. (80% from the acid); m. p. 131–135°. Recrystallization from ethanol gave the pure aldehyde melting at 133–135°.

Anal. Calcd. for $C_{18}H_{24}O_2$: C, 79.35; H, 8.88. Found: C, 79.60; H, 9.06.

O-Methylpodocarpinal Semicarbazone.—To a solution of 0.5 g. of the aldehyde in 5 cc. of ethanol and 5 cc. of pyridine was added the semicarbazide acetate prepared from 0.5 g. of semicarbazide hydrochloride and 0.5 g. of potassium acetate. After standing for two days at room temperature, the solution was concentrated on the steam-bath and the product was precipitated by the addition of water. Recrystallization from methanol gave the pure semicarbazone m. p. 205° (decomp.) in 92% yield.

Anal. Calcd. for $C_{19}H_{27}O_2N_3$: N, 12.75. Found: N, 12.97.

6-Hydroxypodocarpane.—Ten grams of sodium was dissolved in 75 cc. of absolute ethanol and this solution was heated under nitrogen in an autoclave with 11.2 g. of the semicarbazone at 200° for eight hours. After removal of the solvent the residue was extracted with ether. The ether solution was washed, dried and evaporated. Distillation at 2 mm. gave 4.25 g. of product which solidified in the receiver. Crystallization from hexane gave pure material melting at 140.5–141.5°. That cleavage of the methoxyl group occurred during this reaction was shown by analysis for methoxyl. The theory for 6-methoxypodocarpane is 12.0% whereas 0.6% methoxyl was found. We are unable to account for the low carbon values reported below.

Anal. Calcd. for $C_{17}H_{24}O$: C, 83.53; H, 9.90. Found: C, 82.72, 82.76, 83.03; H, 9.82, 9.78, 10.10.

Dehydroabietane.—The conversion of 3.0 g. of dehydro-abietic acid to the acid chloride and the Rosenmund reduction of this product were run as described above. Since the aldehyde could not be crystallized the crude material was treated with semicarbazide acetate in methanol. **Dehydroabietinal semicarbazone** was obtained in 38% over-all yield (1.3 g.) and melted at 217–219° with decomposition.

The reduction of the semicarbazone (1.0 g.) was carried out in a sealed tube with 1.5 g. of sodium ethylate in 15 cc. of absolute ethanol by heating at 200° for nine hours. The crude product was sublimed at 1.5 mm. The sublimate weighed 0.55 g. (70%) and melted at 41–44°.

Anal. Calcd. for $C_{20}H_{30}$: C, 88.85; H, 11.17. Found: C, 88.65; H, 11.29.

O-Methyl-7-isopropylpodocarpic Acid.—A solution of 2.6 g. of the methyl ester[5] in 50 cc. of diethylene glycol containing 7 g. of potassium hydroxide and a few cc. of water was heated with stirring at 160–170° for four hours.[16] After cooling and diluting with water the product was precipitated by adding acid. The acidic material was extracted into 1% sodium hydroxide from an ether solution and reprecipitated. Crystallization from ethanol gave 2.05 g. (82%) of the acid; m. p. 182–184°. One recrystallization from ethanol gave pure material as small colorless needles melting at 183.5–184°, $[\alpha]^{28}_{Hg} +150°$ (2.0% in ethanol).[17]

Anal. Calcd. for $C_{21}H_{30}O_3$: C, 76.35; H, 9.15. Found: C, 76.33; H, 9.07.

Hydrolysis was only partially complete when the ester was heated in a sealed tube with ethanol and potassium hydroxide at 160° for six hours.

O-Methyl-7-isopropylpodocarpyl Chloride.—This acid chloride was prepared as previously described from 7.4 g. of the acid and 1.9 cc. of thionyl chloride. On cooling the reaction mixture in ice, 6.45 g. (83%) of solid acid chloride was obtained in two crops. One recrystallization from dry ether gave pure product, melting at 179–180.5°.

Anal. Calcd. for $C_{21}H_{29}O_2Cl$: C, 72.30; H, 8.38. Found: C, 72.68; H, 8.59.

O-Methyl-7-isopropylpodocarpinal.—The Rosenmund reduction was run as before with 6.45 g. of the acid chloride (kept in vacuum for twenty-four hours) and 2.0 g. of catalyst. In six hours 86% of the theoretical quantity of hydrogen chloride was evolved. After the steam distillation, crystallization from ethanol gave 5.03 g. (88%) of the aldehyde melting at 133–137°. One recrystallization from ethanol gave pure material, m. p. 136–136.5.

Anal. Calcd. for $C_{21}H_{30}O_2$: C, 80.20; H, 9.61. Found: C, 79.98; H, 9.53.

(16) Redeman and Lucas, *Ind. Eng. Chem., Anal. Ed.*, **9**, 521 (1937).

(17) In our first paper[5] we reported several rotations referred to the sodium D line. Actually, a mercury vapor lamp was used, so all the values reported both in this and our previous communication were found with the mercury line (5461 Å.).

The **semicarbazone** was prepared as described above from 5.03 g. of the aldehyde. After standing for twenty-four hours, the solution was concentrated and 5.62 g. of crude semicarbazone m. p. 113–160° was obtained. Recrystallization from ethanol gave material of m. p. 113–120° (4.8 g.) which was still impure (Calcd.: N, 11.30. Found: N, 10.19) but which was satisfactory for the next reaction.

6-Hydroxy-7-isopropylpodocarpane (Ferruginol).—The reduction of the semicarbazone (4.8 g.) was carried out as before with excess sodium ethylate at 180–200° for ten hours. The product was a mixture of the 6-hydroxy and 6-methoxy compounds. (Calcd.: OCH_3, 10.3. Found: OCH_3, 5.3; 5.6.) The index of refraction of a sublimed drop of the viscous oil was n^{61}D 1.5272.

The product was refluxed with 10 cc. of constant-boiling hydrobromic acid and 25 cc. of acetic acid for four hours, n^{61}D 1.5290. This treatment was repeated twice more when the index of refraction became constant. After the second treatment n^{61}D 1.5399 and after the third, n^{61}D 1.5400. The specific rotation of this sample, $[\alpha]^{25}$Hg +59°. A sample of this material, purified by crystallization as the solid acetate (see below) and regenerated by alkaline hydrolysis gave the following constants, n^{61}D 1.5414, $[\alpha]^{27}$Hg +37.8° (5.5% in ethanol). Brandt and Neubauer[7] have reported n^{61}D 1.5346 and $[\alpha]^{16}$D +40.6 (14% in ethanol) for ferruginol prepared by distillation and not purified through a solid derivative.

Anal. Calcd. for $C_{20}H_{30}O$: C, 83.87; H, 10.54. Found: C, 83.72; H, 10.53.

6-Acetoxy-7-isopropylpodocarpane (Ferruginyl Acetate).—The crude hydroxyisopropylpodocarpane ($[\alpha]^{25}$Hg +59°) was acetylated by refluxing for two hours with 20 cc. of acetic anhydride and 2 g. of fused sodium acetate. The reaction mixture was poured into excess cold alkali, extracted with ether and the ether solution was evaporated. The residue was sublimed and seeded with a crystal of 6-acetoxydehydroabietane (see below). The crystallized acetate was recrystallized from methanol and then petroleum ether; m. p. 80.5–81.5°; $[\alpha]^{30}$Hg +67.1° (4% in ethanol); n^{61}D 1.5189. Brandt and Neubauer[7] have reported for ferruginyl acetate: m. p. 81–82°; $[\alpha]^{16}$D +60.3° (10% in ethanol); n^{61}D 1.5186.

Anal. Calcd. for $C_{22}H_{32}O_2$: C, 80.40; H, 9.83. Found: C, 80.20; H, 9.57.

6-Methoxydehydroabietic Acid.—The corresponding methyl ester (9.33 g.)[5] was hydrolyzed by refluxing for three hours with 10 g. of sodium hydroxide in 90 cc. of n-butanol and 4 cc. of water. After steam distillation, the residue was dissolved in ether and the acid was extracted into 1% sodium hydroxide. Acidification precipitated the acid and crystallization from ethanol gave 8.45 g. (94%) of pure product; m. p. 202.5–203.5°.

Anal. Calcd. for $C_{21}H_{30}O_3$: neut. equiv., 330. Found: neut. equiv., 327.

6-Methoxydehydroabietinal.—The corresponding acid (8.45 g.) was converted into the acid chloride as before and the oily product was heated in vacuum at 100° for forty-eight hours. The Rosenmund reduction with 2 g. of catalyst required fifty minutes and 81% of the calculated amount of hydrogen chloride was evolved. Crystalliza-

tion from ether–hexane gave 4.5 g. (56%) of feathery crystals melting at 135–137°. Recrystallization gave pure aldehyde as small rectangular plates; m. p. 137–138°; $[\alpha]^{28}$Hg +90.3° (1.0% in ethanol).

Anal. Calcd. for $C_{21}H_{30}O_2$: C, 80.20; H, 9.61. Found: C, 79.98; H, 9.20.

The **semicarbazone** prepared as before from 4.5 g. of the aldehyde melted at 236–237°. The yield was 4.8 g.

6-Acetoxydehydroabietane (Ferruginyl Acetate).—The reduction of the semicarbazone (4.5 g.) was run as described above at 165° for ten hours and 210° for two hours. The brown oily product was refluxed for eight hours with 8 cc. of hydrobromic acid and 30 cc. of acetic acid. The sublimed product of this reaction gave n^{61}D 1.5375. Another treatment with hydrobromic–acetic acids gave n^{61}D 1.5402; $[\alpha]^{27}$Hg +62.8° (4.8% in ethanol).

Acetylation of this crude ferruginol as before gave an oil which, after much difficulty, was induced to crystallize. Recrystallization from methanol and then from petroleum ether gave the pure acetate; m. p. 80–81°. The index of refraction was determined on the supercooled liquid, n^{61}D 1.5186, $[\alpha]^{30}$Hg +66.3° (4.0% in ethanol). The constants for ferruginyl acetate are: m. p. 81–82°; n^{61}D 1.5186; $[\alpha]^{61}$D +60.3° (10% in ethanol). The 6-acetoxy-dehydroabietane did not depress the melting point of 6-acetoxy-7-isopropylpodocarpane.

O-Methylpodocarpinol.—O-Methylpodocarpinal (10.75 g.) in 40 cc. of ethanol was reduced in six hours with 2 g. of copper chromite and hydrogen at 1200 pounds pressure at 200°. After removal of the catalyst and solvent, the product was crystallized from ether–hexane, yielding 9.4 g. (87%); m. p. 89–90°. One recrystallization gave the pure carbinol; m. p. 90–91.5°, as small needles.

Anal. Calcd. for $C_{18}H_{26}O_2$: C, 78.78; H, 9.55; OCH_3, 12.5. Found: C, 77.59, 77.68; H, 9.30, 9.31; OCH_3, 11.3.

1-Ethyl-6-methoxyphenanthrene from O-Methylpodocarpinol. (a) Dehydration and Rearrangement.—A mixture of 3.6 g. of the podocarpinol and 7 g. of freshly fused potassium acid sulfate was heated with stirring at 230–240° for twenty minutes. The product was washed in ether, dried and, after evaporation of the solvent, distilled at 1 mm. The distillate (2.7 g.) was a light green-yellow oil which darkened on standing. **(b) Hydrogenation of the Rearrangement Product.**—This was carried out on 0.51 g. of the above product in 40 cc. of acetic acid using 30 mg. of Adams catalyst. The theoretical amount of hydrogen for one double bond was absorbed in one hour when the reaction stopped. (In another run on 4.9 g. of material 35% excess hydrogen was absorbed.) The product, obtained in the usual manner, was an oil. **(c) Selenium Dehydrogenation.**—The hydrogenated material from 2.7 g. of the rearrangement product was heated with nitrogen stirring with 4 g. of selenium at 280° for eighteen hours and at 310–330° for six hours. The product was taken up in ether, washed with alkali, and dried. Evaporation gave 2.6 g. of oil which was distilled at 2 mm. The product was precipitated from alcohol solution as the picrate and regenerated by treatment with sodium carbonate. Distillation gave 0.45 g. of 1-ethyl-6-methoxyphenanthrene.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.38; H, 6.85. Found: C, 86.30; H, 6.81.

The **picrate** crystallized from ethanol as a light orange powder and melted at 126–126.5°.

Anal. Calcd. for $C_{17}H_{18}O.C_6H_3O_7N_3$: mol. wt., 236. Found: mol. wt. (by titration),[18] 245, 239.

The **styphnate**, crystallized from methanol, melted at 139–140.5°.

The **trinitrobenzene derivative** melted at 137–137.5° after crystallization from methanol.

The Synthesis of 1-Ethyl-6-methoxyphenanthrene

7-Methoxy-1-tetralone.—This substance was prepared by cyclization of 57.7 g. of γ-(p-anisyl)-butyric acid[19] with 150 g. of anhydrous hydrogen fluoride at room temperature for thirty-six hours. The product was poured into water, extracted into ether, and washed with alkali. The ketone crystallized from ether–hexane in large prisms, 32 g.; m. p. 62–63°.[20] By acidification of the alkaline solution 19.8 g. of the starting material was recovered. The yield of ketone, based on the acid consumed, was 93%.

7-Methoxy-dihydronaphthyl-1-acetic Acid.—The Reformatsky reaction was run according to procedure of Bachmann, *et al.*,[21] using 15.4 g. of the above tetralone, 30 g. of zinc and 10.4 cc. of methyl bromoacetate in 100 cc. each of ether and benzene. After refluxing for two hours, 150 cc. of methanol was added to dissolve the yellow precipitate. The crude product, obtained in the usual manner, was refluxed for ten minutes with 25 cc. of 88% formic acid. The formic acid was evaporated and the crude ester was hydrolyzed by heating for three hours with aqueous alcoholic sodium hydroxide. The neutral material was removed by extraction of the alkaline solution with ether, and the acidic product precipitated by the addition of hydrochloric acid as an oil which solidified on standing. Crystallization from ethanol gave 9.5 g. (50%) of fine needles melting at 141–142°. Recrystallization raised the melting point to 142–143°.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.53; H, 6.46. Found: C, 71.39; H, 6.33.

7-Methoxynaphthyl-1-acetic Acid.—A solution of 14.25 g. of the methyl ester of the corresponding dihydro derivative (prepared with excess diazomethane) and 16 g. of chloranil in 50 cc. of xylene was refluxed for nineteen hours. The hydroquinone which separated on cooling in ice was removed by filtration and the filtrate was distilled with steam. The residue was washed in ether solution and hydrolyzed by refluxing with alcoholic sodium hydroxide. After dilution with water, the aqueous alkaline solution was washed with ether and acidified. The precipitated acid was collected and crystallized from methanol; yield 10.2 g. (77%) of light brown crystals melting at 152–154.5°. Recrystallization from ether–hexane raised the melting point to 155–155.5°.

(18) Campbell, Soffer and Steadman, THIS JOURNAL, **64**, 425 (1942).

(19) Fieser and Hershberg, *ibid.*, **58**, 2314 (1936); Martin, *ibid.*, **58**, 1438 (1936).

(20) Haworth and Sheldrick, *J. Chem. Soc.*, 1950 (1934), have reported a melting point of 66–67° for this substance, prepared in a different way. Extensive purification of our sample by crystallization and distillation failed to raise the melting point above the value given here.

(21) Bachmann, Cole and Wilds, THIS JOURNAL, **62**, 832 (1940).

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.20; H, 5.60. Found: C, 72.10; H, 5.50.

The dehydrogenation was also carried out with palladium–charcoal[22] on the ester and the acid. The yields in these reactions varied from 30 to 50%.

β-(7-Methoxynaphthyl-1)-propionic Acid.—A suspension of 2.6 g. of the naphthylacetic acid in dry ether was treated with 1.0 cc. of thionyl chloride and a drop of pyridine for two hours. The filtered solution was evaporated and kept in vacuum for one-half hour. Benzene was added and evaporated in vacuum leaving a crystalline residue.

To a solution of diazomethane in dry ether prepared from 7 cc. of nitrosomethylurethan[23] was added, dropwise, a solution of the above acid chloride in dry ether. The solution was cooled in an ice-bath and vigorously stirred. After standing overnight, the solution was evaporated in vacuum. The residual crystalline diazoketone in dioxane solution was dropped slowly into a stirred solution of 5 g. of sodium thiosulfate in 400 cc. of water at 65–70°. During this time silver oxide, freshly prepared from 5 g. of silver nitrate, was added in small portions. After being stirred for one hour, the solution was made alkaline with sodium hydroxide, and stirring at 65–70° was continued for one-half hour. The alkaline solution was extracted with ether after filtration and the acid which precipitated on acidification was taken up in ether, and crystallized from ether–hexane. The crude product weighed 0.9 g. (30%). Repeated crystallization from ether–hexane and from methanol gave a product melting at 162.5–164°.

Anal. Calcd. for $C_{14}H_{14}O_3$: neut. equiv., 230. Found: neut. equiv., 225.

γ-(7-Methoxynaphthyl-1)-butyric Acid.—In a manner similar to that employed in the above experiment, 1.04 g. of the naphthylpropionic acid was converted to the corresponding butyric acid. The yield was 0.42 g. (40%) of product melting at 101.5–105°. No attempt was made to purify this material further since it was found to be suitable for the next reaction. Plimmer, Short and Hill[24] prepared this substance by a different method and reported a melting point of 105–106°.

6-Methoxy-1-oxo-1,2,3,4-tetrahydrophenanthrene.—The above butyric acid (0.42 g.) was cyclized by treating with 100 g. of anhydrous hydrogen fluoride overnight. The product was taken up in ether, washed with alkali, and crystallized from hexane; yield, 0.12 g. of stout yellow needles; m. p. 99–102°. Plimmer, Short and Hill[24] obtained this product as a non-crystalline glass by another method.

Due to the lack of material the **2,4-dinitrophenylhydrazone** was prepared from the residue from the hexane mother liquor with 0.2 g. of the hydrazine in alcohol and hydrochloric acid. On successive recrystallization from benzene the product melted constantly at 284° with decomposition.[25]

1-Ethyl-6-methoxyphenanthrene.—A solution of 0.12 g. of the ketone in dry ether was added slowly to an ice-cold

(22) Bachmann and Wilds, *ibid.*, **60**, 624 (1938).

(23) Meerwein and Burneleit, *Ber.*, **61**, 1845 (1928).

(24) Plimmer, Short and Hill, *J. Chem. Soc.*, 694 (1938).

(25) Plimmer, Short and Hill[24] reported a melting point of 261–262° for this product.

solution of an excess of ethylmagnesium bromide in ether. After standing at room temperature for some time, the product was hydrolyzed with saturated ammonium chloride solution. The ether layer was separated, dried and evaporated. The residue was heated with 0.2 g. of 10% palladium–charcoal under nitrogen at 270° for one-half hour and at 320° for ten minutes. The product was treated with 0.12 g. of picric acid in ethanol. On concentrating and cooling, the picrate was obtained as orange needles; m. p. 124–125.5°. Recrystallization from ethanol gave a product of m. p. 127–128°. When mixed with the picrate of the phenanthrene derivative from podocarpinol (m. p. 126–126.5°), the substance melted at 126–128°.

The **styphnate,** was prepared from the compound recovered from the picrate by treatment with sodium bicarbonate. Treatment with 70 mg. of styphnic acid in ethanol gave light orange crystals melting at 141°. When mixed with the styphnate of the natural derivative (m. p. 139–140.5°) the substance melted at 139–140°.

The **trinitrobenzene derivative** prepared in a similar manner was obtained as fluffy needles from methanol; m. p. 139–140°. Recrystallization from methanol raised the melting point to 140–140.5°. Mixed with the trinitrobenzene derivative of the natural product (m. p. 137–137.5°), the substance melted at 137–140°.

Summary

The structures of podocarpic acid and ferruginol are proved by the conversion of both podocarpic and dehydroabietic acids into ferruginol.

The 6-hydroxy derivative of dehydroabietic acid differs from the 7-isopropyl derivative of podocarpic acid only in the configuration of the methyl and carboxyl groups at C_1.

The stereochemistry of these substances is discussed.

Reactions Between sym-Diphenyltriazene and Mercury(II) Salts

BY CECIL M. KNOWLES AND GEORGE W. WATT

In a recent publication, Mandal[1] described products obtained by the interaction of solutions of mercury(II) salts and alcoholic solutions of sym-diphenyltriazene (diazoaminobenzene). The properties described suggested that these products might be identical with the mercury salt previously prepared by the reaction between mercury and sym-diphenyltriazene.[2] Although the compounds prepared by Mandal were formulated as having the composition represented by the formula $(C_6H_5N=N-NHC_6H_5)_4HgX_2$, where $X = Cl$, Br, NO_3, or $C_2H_3O_2$, the present study shows that either a salt of the base is formed or molecular compounds which contain one equivalent of the mercury salt combined with two of the base, and not four as claimed by Mandal.

Experimental

Reaction with Mercury(II) Chloride.—To a saturated solution of pure sym-diphenyltriazene (10.0 g.), m. p. 98°, in ethanol was added with stirring a saturated ethanolic solution of 6.9 g. of mercury(II) chloride. Dilution with water followed by cooling resulted in the precipitation of a tan-colored solid which was separated by filtration, treated with "Norite," and recrystallized from 50% ethanol. The purified product consisted of a tan-colored crystalline solid, m. p. 161–165° dec. (cor.); yield, 13.7 g. or 81%. *Anal.* Calcd. for $C_{24}H_{22}Cl_2N_6Hg$: C, 43.40; H, 3.32; N,

12.62. Found: C, 43.15; H, 3.16; N, 12.78. Qualitative tests for mercury and chlorine were positive.

Reaction with Mercury(II) Bromide.—By a similar reaction involving 2.19 g. of sym-diphenyltriazene and 2.00 g. of mercury(II) bromide there was obtained 3.0 g. (71% yield) of the corresponding tan-colored mercury(II) bromide addition compound, m. p. 132–134° dec. (cor.). The color of this product is slightly more intense than that of the corresponding mercury(II) chloride compound. *Anal.* Calcd. for $C_{24}H_{22}Br_2N_6Hg$: N, 11.15. Found: N, 11.30. Qualitative tests for mercury and bromine were positive.

Reaction with Mercury(II) Acetate.—By the reaction between 10.0 g. of sym-diphenyltriazene and 4.6 g. of mercury(II) acetate in ethanol there was obtained immediately (*i. e.*, without dilution, etc.) 8.5 g. (99% yield) of the lemon yellow mercury salt of the triazene. The product was purified by recrystallization from benzene and from pyridine. With rapid heating the pure salt melted at 232° dec. (cor.) which corresponds to the melting point recorded by Ciusa and Pestalozza.[3] Upon slow heating, melting occurred at 227° dec. (cor.) which agrees with the melting point reported by Watt and Fernelius.[2] *Anal.* Calcd. for $C_{24}H_{20}N_6Hg$: N, 14.18; Hg, 33.84. Found: N, 14.03; Hg, 33.70.

Reaction with Mercury(II) Nitrate.—To an ethanolic solution of 5.0 g. of sym-diphenyltriazene was added an ethanolic solution and suspension of 4.25 g. of mercury (II) nitrate.[4] If (1) the resulting yellow precipitate was filtered immediately, or (2) the reaction mixture was immediately made alkaline by addition of aqueous ammonia,

(1) Mandal, *Science and Culture,* **6,** 59–60 (1940).

(2) Watt and Fernelius, *Z. anorg. allgem. Chem.,* **221,** 187 (1935).

(3) Ciusa and Pestalozza, *Gazz. chim. ital.,* **41,** 1, 394 (1911).

(4) Identical results are obtained when finely divided *solid* mercury(II) nitrate is added to ethanolic solutions of the triazene.