carbon of the acetal followed by the attachment of the remainder of the addendum to the carbon carrying the ethoxyl groups. This primary reaction may be followed by one or more subsequent reactions.

In the cases of acetoacetic ester and malonic ester the reaction takes a different course. These compounds do not add as H and O—C(R)=CHCOR, as does dibenzoylmethane, but rather as H and $CH(COR)_2$ and the addition is strongly catalyzed by small amounts of sodium ethoxide. The function of the catalyst in this reaction is discussed.

MADISON, WISCONSIN RECEIVED MARCH 15, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

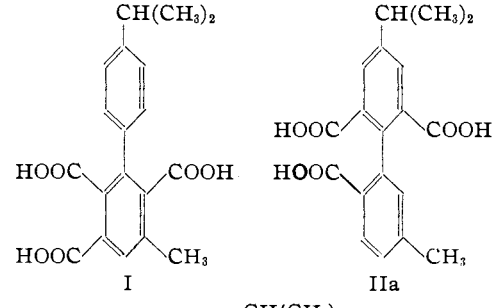
Acetylretene and 6-Retenol

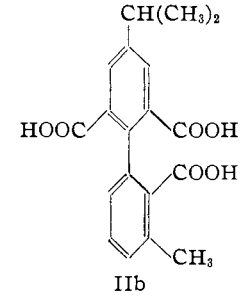
BY WILLIAM P. CAMPBELL AND DAVID TODD

Acetylretene was first prepared by Bogert and Hasselstrom[1] and was shown[2] to have the acetyl group in the same position as the hydroxyl group of the β-retenol of Komppa and Wahlforss[3] by conversion into that substance. Evidence based on the coupling reaction, reduction potential data, and the Dimroth test, indicating that the β-retenol is either the 3- or the 6-derivative had been presented by Fieser and Young[4] and their view that the substituent probably is in the 6-position has been accepted in subsequent literature even though conclusive evidence was lacking. More recently there appeared a paper by Nyman[5] on acetylretene presenting evidence resulting mainly from oxidation experiments which he interprets as indicating that the acetyl group (and, therefore, the hydroxyl group of the β-retenol) occupies the 4- instead of the 6-position.

In the present research the possibility that these groups occupy the 6-position is definitely eliminated[6] by the preparation of 6-retenol (VII) of proven structure, which is different from the β-retenol. A careful study and reinterpretation of the results of Nyman[5] and of Fieser and Young[4] led us to the conclusion that the acetyl and hydroxyl groups must be in the 3-position in these compounds, and this view has been proven to be correct.

All of the arguments by which Nyman eliminated the various possible positions for the acetyl group in acetylretene seem valid with the exception of those regarding the 3-position. The point in question involves a distinction between I which would result from 3-acetylretene and IIa or b



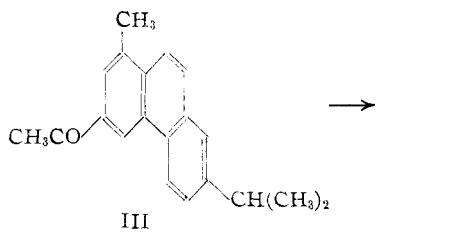


which would result from the 4-isomer. The evidence presented in favor of II was that the substance melts at a high temperature (277°) without apparent loss of water, and fails to form an anhydride on heating with acetyl chloride, although heating with acetic anhydride does produce the anhydride. There is ample contradictory evidence in the literature which can lead only to the conclusion that it is not possible to decide between these compounds on the basis of such evidence. For example, trimellitic acid, which is analogous to I, melts at 238° without apparent loss of water

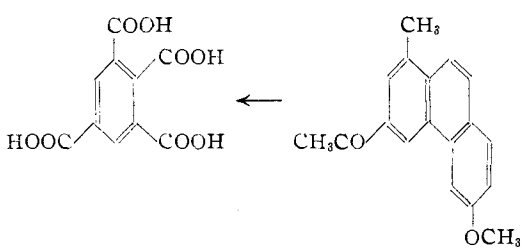
(1) Bogert and Hasselstrom, THIS JOURNAL, **53**, 3462 (1931).
(2) Adelson and Bogert, *ibid.*, **58**, 653 (1936).
(3) Komppa and Wahlforss, *ibid.*, **52**, 5009 (1930).
(4) Fieser and Young, *ibid.*, **53**, 4120 (1931).
(5) Nyman, *Ann. Acad. Sci. Fennicae*, **A48**, No. 6 (1937); *Chem. Abst.*, **33**, 8192 (1939).
(6) In a publication which reached us after this paper was written, Ruzicka and St. Kaufmann (*Helv. Chim. Acta*, **23**, 288 (1940)) arrived at this same conclusion by a comparison of the melting points of 6-ethylretene (prepared by way of 6-acetyldehydroabietic ester) and two of its derivatives with those reported by Bogert and Hasselstrom[1] for their ethylretene obtained from acetylretene. In the present paper, a direct comparison of the corresponding retenols by mixed melting point has been made.

and is only partially converted into the anhydride by three-hour boiling with acetyl chloride or acetic anhydride.[7] On the other hand retene diphenic acid, similar to IIa and b, forms an anhydride[8,9] with acetyl chloride at room temperature. Thus the work of Nyman indicates only that the acetyl group is in the 3- *or* 4-position.

The reduction potentials of retenequinone and the quinones from 2- and β-retenol as determined and interpreted by Fieser and Young[4] provide evidence that the hydroxyl group of β-retenol is either 3 or 6.[10] With the 6-position now eliminated the compounds of the β-series would on this evidence be the 3-derivatives. Proof of this structure was accomplished by the isolation of mellophanic (1, 2, 3, 5) acid (IV) as an oxidation product of acetylretene (III). That Nyman[5] was



III



IV V

unable to isolate this degradation product may be because he used a different method of oxidation.

On the basis of this structure for acetylretene, the cyclopenteno- and benzo-retenes prepared by Adelson and Bogert[11] must be written as the 2,3- or 3,4- instead of the 5,6-derivatives. By analogy with similar work on phenanthrene, the 3,4-position is most probable.

That the retene molecule directs the entering groups to the 3-position in the Friedel and Crafts reaction and to the 2-[4] and 3-positions in sulfonation is interesting in view of the similar behavior of phenanthrene.[12] In addition, dihydroretene undergoes sulfonation in the 2- and 3-positions.[13] Thus it appears that there is some orienting influence inherent in the ring system which overcomes any directive effect of the alkyl groups. On this basis one would expect the acetyl derivative of dihydroretene, which Nyman[14] showed not to be the 3-isomer, to be the 2-derivative.[15]

In the course of this work we had occasion to carry out a Friedel and Crafts condensation of acetyl chloride with 1-methyl-6-methoxyphenanthrene, and in this case also we obtained the 3-acetyl derivative, V. The structure was proved by oxidation to IV, and the compound was characterized by oxidation to the corresponding 3-carboxy derivative. This orientation is in contrast to the results of Burger and Mosettig[16] with derivatives of 6-(or 3-)phenanthrol. The 6-methoxyphenanthrene was converted into the 10-acetyl derivative under conditions similar to those used above. The acetyl group, however, entered the 3-position when the reaction was carried out on 6-acetoxyphenanthrene.

The 6-retenol (VII) was obtained in good yield (68%) by selenium dehydrogenation of methyl 6-hydroxydehydroabietate[17] (VI, R=H), and it has been characterized by the preparation of several derivatives.

The 6-retenol corresponds in its melting point and the melting point of seven of its derivatives with a retenol obtained by Brandt and Neubauer[18] from ferruginol and considered by them to be the 8-isomer. These authors placed the hydroxyl group in the 8-position because of the non-identity of their compound with the β-retenol (3-retenol) previously regarded as the 6-compound, and because the corresponding hydroxyquinone gave a positive Dimroth test. The same retenol has been obtained from hinokiol.[18,19] Table I gives a comparison of the melting points of 6-retenol and its derivatives with those of the retenol obtained from ferruginol and hinokiol. Although a direct comparison by mixed melting point determination

(7) R. P. Linstead, unpublished results.

(8) Adelson, Hasselstrom and Bogert, THIS JOURNAL, **58**, 871 (1936).

(9) Fogelberg, *Chem. Zentr.*, **98**, II, 2299 (1927).

(10) The 6-position was preferred by these authors because it is ortho to the isopropyl group whereas the 3-position, meta to the methyl group, was considered less likely.

(11) Adelson and Bogert, THIS JOURNAL, **59**, 399, 1776 (1937).

(12) Fieser, *ibid.*, **51**, 2460 (1929); Mosettig and van de Kamp *ibid.*, **52**, 3704 (1930).

(13) Komppa and Fogelberg, *ibid.*, **54**, 2900 (1932).

(14) Nyman, *Ann. Acad. Sci. Fennicae*, **A41**, No. 5 (1934); *Chem. Abst.*, **30**, 2958 (1936).

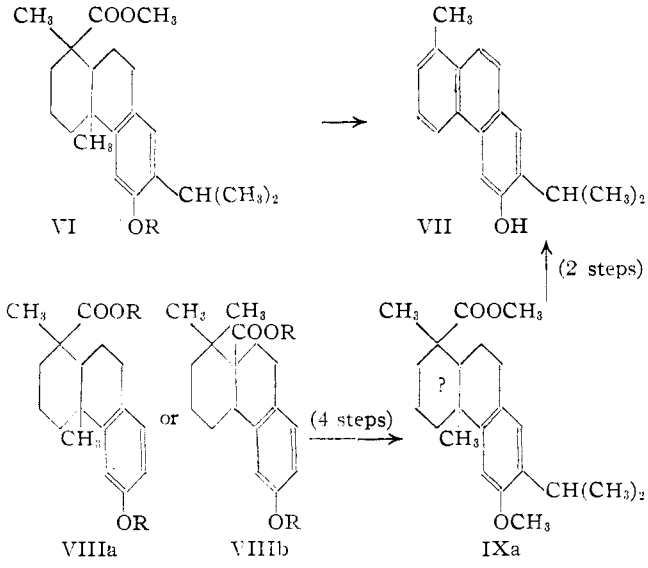
(15) Ruzicka and St. Kaufmann[6] have suggested the 6-position for this group.

(16) Burger and Mosettig, THIS JOURNAL, **56**, 1745 (1934); Mosettig and Burger, *ibid.*, **55**, 2981 (1933).

(17) Fieser and Campbell, *ibid.*, **61**, 2528 (1939).

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

(19) (a) Keimatsu and Ishiguro, *J. Pharm. Soc. Japan (Ger.)*, **55**, 45 (1935); (b) Fukui and Chikamori, *ibid.*, **59**, 86 (1939).



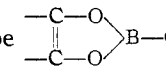
has not been made, the close correspondence of the melting points of all of the derivatives adequately establishes the identity of the substances.

TABLE I

MELTING POINTS

Compound	6-Retenol	Retenol from ferruginol and hinokiol
Retenol	179–180	179–180[19b]
Picrate	177.5–178	176–177[18,19a]
Acetate	91–92	90–91,[18] 94[19]
Methyl ether	78.5–79	80[19b]
Acetoxyquinone	186–189	188–189[18]
Hydroxyquinone	303–304 d.	285 d.,[18] 307[19]
Hydroxyquinoxaline	225–226	223[19a]
Acetoxyquinoxaline	195–196.5	194[19]

The hydroxyl group of 6-retenol is rather highly hindered since the substance is only slightly soluble in aqueous alkali and apparently methylates with difficulty.[18,19] After treatment with diazomethane in ether at 0° for three hours, the retenol was recovered quantitatively unchanged. In one experiment, no ether was obtained on treating the chloromagnesium salt with dimethyl sulfate in ether solution.

A positive Dimroth test, as reported by Brandt and Neubauer for the quinone corresponding to their retenol, was also obtained with the quinone from 6-retenol. This test consists of a comparison of the color of a solution of the hydroxyquinone in acetic anhydride with that of a similar solution containing added boro-acetic anhydride. If the hydroxyl group is ortho to the quinone carbonyl as in 1-hydroxyphenanthrenequinone the highly colored complex, X, is formed; otherwise simple acetylation takes place. As far as is known, the only example of an anomalous test is that reported by Fieser,[20] who found that morpholquinone (XI) gave a positive test. Two possible explanations were offered for this observation. The first postulated a reaction of the boro-acetic anhydride with the tautomeric form, XII, producing the complex, XIII. The second explanation involved the formation of a boron complex of the type  , with the two adjacent hydroxyl groups.

A comparison, made in the present work, of the colors produced when a series of hydroxyphenanthrenequinones were subjected to this test has given results (Table II) which favor the first of the two explanations and permit a slight extension of the idea. The colors were divided roughly into three groups, faint, medium, and intense, which are widely different and easily discernible, although the difference between those listed as "faint" and those

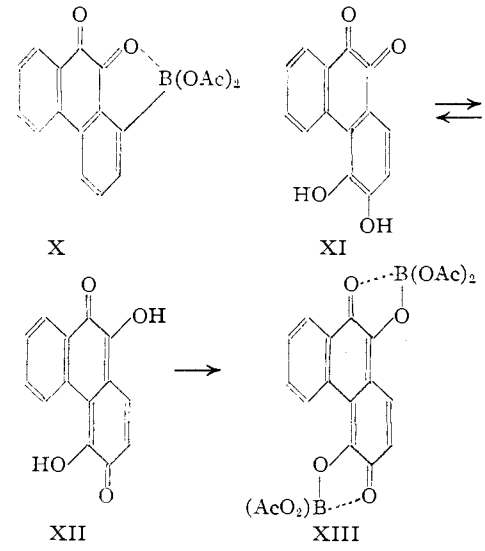


TABLE II

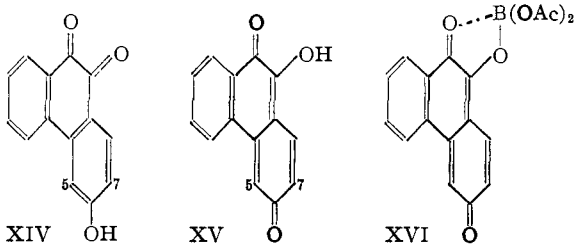
DIMROTH TEST ON HYDROXYQUINONES

Quinone from	Color
2,6-Dihydroxyphenanthrene[a]	None
3-Retenol[a]	None
3-Phenanthrol[a]	Faint
1-Methyl-6-phenanthrol	Faint
6-Retenol	Medium
Morphol[a]	Intense
1-Phenanthrol[a]	Intense

[a] Samples of these compounds were supplied by Professor L. F. Fieser.

(20) Fieser, THIS JOURNAL, 51, 2471 (1929).

giving no color is not considered significant. If the development of color by the 3- and 6-hydroxyquinones is the result of the reaction of boro-acetic anhydride with the tautomeric form, the variation in the color produced can be qualitatively explained. An alkyl group substituted in the 5- or 7-position of XIV would exert only a negligible



effect on the potential of the 9,10-quinone. The same substitution would, however, cause considerable lowering of the potential[21] of the tautomeric amphi-quinonoid form XV. The net effect would be an increase in the quantity of XV available for conversion into the colored complex, XVI, as a result of the increased stability of this form. Thus the quinone from 6-retenol (1-methyl-7-isopropyl-XIV), as would be expected, gives a deeper color than that from 1-methyl-6-phenanthrol. A hydroxyl group in the 5- or 7-position would produce an even greater lowering of the potential (roughly twice[21]) than an alkyl group, and the intense color obtained with morpholquinone (5-hydroxy-XIV) is in line with this view.

The results indicate that neither two ortho hydroxyl groups nor a hydroxyl group ortho to the quinone carbonyl is necessary for the production of color with boro-acetic anhydride, and that the reaction very probably takes place with the tautomeric amphi-quinonoid structure.

During the earlier stages of this research our first attempts to prepare 6-retenol by dehydrogenation of methyl-6-hydroxydehydroabietate met with little success. We sought, therefore, for a more productive source of the retenol and investigated the possibility of preparing the compound from podocarpic acid. In a recent investigation, Sherwood and Short[22] found that the resin acid could be dehydrogenated in good yield to 1-methyl-6-hydroxyphenanthrene, identified by synthesis. The formation of this phenanthrol on dehydrogenation locates all of the carbon atoms in the molecule except the methyl and the carboxyl groups which are eliminated in the reaction. Sherwood and Short considered formulas VIIIa and VIIIb (R=H) for podocarpic acid, favoring VIIIb because the carboxyl group is considerably more hindered than in the abietic acid series where the structure is similar to VIIIa.

Our plan for preparing 6-retenol from this substance involved the introduction of an isopropyl group into the 7-position and subsequent dehydrogenation. This was accomplished without difficulty by introducing an acetyl group into the 7-position by a Friedel and Crafts reaction. The reaction of the 7-acetyl compound with methylmagnesium chloride followed by dehydration and catalytic hydrogenation produced methyl O-methyl-7-isopropylpodocarpate (IXa). Dehydrogenation followed by cleavage of the methoxy group with hydrobromic acid yielded the same retenol (VII) as was obtained from 6-hydroxydehydroabietic ester. This latter reaction, in addition to confirming the location of the hydroxyl group, proved that the acetyl group entered the podocarpate molecule in the 7-position.

In connection with a suggestion advanced by Fieser and Campbell[17] concerning the structure of podocarpic acid, we were interested in comparing methyl O-methyl-7-isopropylpodocarpate (IXa) with methyl 6-methoxydehydroabietate (VI, $R=CH_3$). If podocarpic acid has the structure VIIIa, the two substances should be identical, providing the configuration in both molecules is the same. The melting points of the two compounds, however, are widely different and the mixed melting point showed considerable depression. The two substances, therefore, are either position- or stereo-isomers,

The methylation of methyl 6-hydroxydehydroabietate presented some difficulty. The hydroxyl group is highly hindered by the *o*-isopropyl group, since methylation of podocarpic acid proceeds with great ease. The phenol-ester is practically insoluble in aqueous alkali. In one experiment a small amount of the methyl ether was obtained by the action of dimethyl sulfate in alcoholic alkali but this could not be repeated. Attempts to prepare the ether by reaction with silver oxide and methyl iodide, with diazomethane (alone or with aluminum tertiary butylate), or by treating the sodium or potassium salt with dimethyl sulfate were all unsuccessful. The compound was unaltered by heating with potassium carbonate and dimethyl

(21) Fieser in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, pp. 812–815.

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

sulfate in boiling xylene, although this method was used successfully[18] for the methylation of ferruginol. The ether was obtained in good yield, however, by the action of dimethyl sulfate on the chloromagnesium salt, prepared by treating the phenol with methylmagnesium chloride.

The authors wish to thank Professor L. F. Fieser for suggesting some of this work and for his helpful advice in connection with the interpretation of the results of the Dimroth test.

Experimental Part[23]

3-Acetylretene (III).—In this preparation nitrobenzene, instead of carbon disulfide,[1,2] was used for the solvent. To a solution of 25 g. of retene and 15 cc. of acetyl chloride in 100 cc. of nitrobenzene at −5° was added 29 g. of aluminum chloride. When about half of this material had been added, a deep red, finely divided complex separated accompanied by a slight rise in temperature. After stirring for five hours at −5° and standing at 5° for forty hours, the reaction mixture was poured into ice and 70 cc. of concentrated hydrochloric acid. The black residue remaining after steam distillation was treated with Norit in ether and crystallized from this solvent yielding 13.5 g. (45%) of pure acetylretene, m. p. 99.5–100° (cor.). From the mother liquor, 4.5 g. of product melting at 85–89° and 9.8 g. of a picrate melting at 127–132° were obtained. These materials are being investigated.

Oxidation of 3-Acetylretene to Mellophanic Acid.—A mixture of 0.5 g. of 3-acetylretene, 1 cc. of concentrated nitric acid and 2 cc. of water was heated for thirty-three hours in a sealed tube at 190–200°. Twice, during this time, the tube was opened and 1 cc. of concentrated nitric acid was added. The yellow sirup obtained by evaporation of the solution solidified on stirring with fuming nitric acid. The solid was removed by filtration and washed well on the filter with fuming nitric acid. This product was esterified with diazomethane and the ester was crystallized from methanol, m. p. 108–109°. Recrystallization from methanol raised the melting point to 108.5–109.5° (cor.). The melting point of a mixture of this material with an authentic sample of the tetramethyl ester of mellophanic acid (m. p. 110.5–111°) was 109–110.5° (cor.).

1-Methyl-6-phenanthrol.—This substance (m. p. 160–161°) was prepared by dehydrogenation of podocarpic acid (see below) by the method of Sherwood and Short.[22] It was also obtained from its methyl ether by boiling for four hours with hydrobromic-acetic acid.

1-Methyl-3-acetyl-6-methoxyphenanthrene (V).—This reaction was carried out in the same manner as the preparation of 3-acetylretene, above, using 0.95 g. of 1-methyl-6-methoxyphenanthrene,[22] 0.45 cc. (50% excess) of acetyl chloride, and 1.14 g. of aluminum chloride in 25 cc. of nitrobenzene. The time of reaction was sixty-five hours. The product was washed in ether solution with alkali and after drying the solvent was removed. The residue could not be induced to crystallize and was treated with 0.87 g. of picric acid in ethanol. The orange *picrate* which separated melted at 146–148.5° after two crystallizations from ethanol. Decomposition of the picrate by warming with aqueous sodium carbonate and crystallization of the resulting material from ethanol gave 0.25 g. (21%) of light feather-like crystals melting at 126.5–127°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.79; H, 6.10. Found: C, 81.90; H, 6.07.

For characterization the acetyl derivative (0.34 g.) was treated in dioxane–sodium hydroxide solution with iodine–potassium iodide solution until the iodine color persisted for two minutes at 60°. The **1-methyl-3-carboxy-6-methoxyphenanthrene** was obtained in a pure, crystalline condition after two precipitations from aqueous alkaline solution by hydrochloric acid, m. p. 233–235°. Recrystallization from aqueous ethanol did not change the melting point.

Anal. Calcd. for $C_{17}H_{14}O_3$; neut. equiv., 266. Found: neut. equiv., 266.

For proof of the structure, 0.07 g. of the acid was heated with 1 cc. of concentrated nitric acid and 2 cc. of water at 100° for one hour and at 180–200° for thirteen hours. The product obtained on evaporation of this solution to dryness was esterified in ether with excess diazomethane. The mellophanic tetramethyl ester, crystallized from aqueous ethanol, melted at 107–108° (cor.). Mixed with an authentic sample (m. p. 108.5–109.5°) it melted at 107–109° (cor.).

6-Retenol (VII).—A mixture of 2 g. of methyl 6-hydroxydehydroabietate and 2.1 g. of selenium powder was heated at 280–285° for twenty-four hours and then at 335° for four hours. The mixture was stirred continuously by passing a slow stream of nitrogen through it. The product was extracted with ether, washed with 5% sodium hydroxide, and dried. On concentrating the nearly colorless solution and adding hexane, 0.71 g. of 6-retenol, m. p. 177–178°, separated as thin, colorless flakes. A second crop of 0.27 g., m. p. 173–175°, separated from the concentrated mother liquor. Recrystallization from ether–hexane raised the melting point to 179–180°; yield 68%. In another run under the same conditions but without the nitrogen stirring, the yield was 43%. This product, mixed with the β(3)-retenol (m. p. 158–161°) melted below 138°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.37; H, 7.25. Found: C, 86.58; H, 7.18.

6-Methoxyretene.—Dehydrogenation of 1.75 g. of methyl O-methyl-7-isopropylpodocarpate was carried out as described above using 1.85 g. of selenium. The ether solution, after clarification with Darco, was evaporated and the residue was taken up in methanol. One crop of crystalline material (m. p. 72–74°) was obtained from this solution. Recrystallization from methanol yielded 0.30 g. (22%) of 6-methoxyretene, m. p. 75–77°. By repeated crystallization from methanol the melting point was raised to 78.5–79°.

The non-crystalline residue from the first methanol mother liquor was refluxed for seven hours with 20 cc. of glacial acetic acid and 5 cc. of 48% hydrobromic acid. The product was washed and dried in ether and, after clarification with Darco, was purified by crystallization from ether–hexane. In this way 0.38 g. (30%) of 6-retenol, m. p. 172–175°, was obtained. Recrystallization from ether–

(23) The melting points are uncorrected unless otherwise specified.

hexane gave a product, m. p. 179–180°, which did not depress the melting point of the 6-retenol prepared from methyl 6-hydroxydehydroabietate.

Derivatives of 6-Retenol.—With the exception of the methyl ether, the derivatives of 6-retenol listed in Table I were prepared by methods previously described.[18,19] For the oxidation of 6-acetoxyretene to the quinone the conditions used by Fieser[20] for oxidation of diacetoxyphenanthrenes were found to be most suitable.

Podocarpic Acid (VIII, R = H).—This substance was prepared from "rimu" resin from *Dacrydium cupressinum*.[24] Two crystallizations of the crude resin from aqueous alcohol according to Sherwood and Short[22] gave acid melting at 193–200° in 85% yield. Methylation with methyl sulfate[22] of the material remaining in the mother liquors yielded an additional quantity of product as the more easily purified methyl O-methyl ester, bringing the total yield from the resin to more than 90%.

Methyl O-Methyl-7-acetylpodocarpate.—To a solution of 18 g. of methyl O-methylpodocarpate[22] and 9 cc. of acetyl chloride in 200 cc. of nitrobenzene at 0°, 16.2 g. of aluminum chloride was added over a half-hour period. After stirring at 0° for four hours the clear solution was let stand at 5° for one hundred hours, then at room temperature for five hours. The nitrobenzene was removed by steam distillation, after hydrolysis with ice and hydrochloric acid, and the residue was separated by filtration. The product was decolorized with Darco in hot ethanol solution and on cooling 16.3 g. (80%) of the acetyl derivative melting at 109–117° was obtained. A sample, after several crystalizations from ethanol melted constantly at 119–119.5°. $[\alpha]^{25}D$ + 142° (1.8% in ethanol.)

Anal. Calcd. for $C_{21}H_{28}O_4$: C, 73.23; H, 8.19. Found: C, 73.08; H, 8.26.

The **oxime** (m. p. 190–193° from ethanol) was prepared by treating the acetyl compound (0.1 g.) with a filtered solution of hydroxylamine hydrochloride (0.1 g.) and excess sodium bicarbonate in ethanol. Hydrolysis with dilute hydrochloric acid yielded the original ketone.

Methyl O-Methyl-7-(α-hydroxylisopropyl)-podocarpate.—A solution of 5 g. of the 7-acetyl derivative (m. p. 109–117°) in dry ether was added slowly to excess methylmagnesium chloride in ether and, after refluxing for one-half hour, hydrolysis was brought about by the addition of saturated ammonium chloride solution. The ether layer was washed, dried and evaporated and the residue was crystallized from hexane, yielding 4.6 g. of thick prisms melting at 146–150°. An additional 0.5 g. of product (m. p. 143–147°) was obtained from the mother liquor bringing the yield to 97%. Recrystallized from hexane, the product melted at 148–150°, $[\alpha]^{25}D$ + 119° (2.4% in ethanol).

Anal. Calcd. for $C_{22}H_{32}O_4$: C, 73.28; H, 8.96. Found: C, 73.15; H, 8.78.

(24) Samples of this resin for this and other investigations were very kindly supplied by Dr. John R. Hosking of Kent, England, and by Dr. H. J. Hardon, Buitenzorg, Java, to whom we are greatly indebted. We are also indebted to Dr. C. L. Mantell of the American Gum Importers Association, and to Dr. Jakobs, Buitenzorg, Java, for their courtesy in locating sources of material.—L. F. FIESER.

Methyl O-Methyl-7-isopropenylpodocarpate.—Dehydration of the hydroxyisopropyl derivative was accomplished by boiling 2 g. of the compound in 20 cc. of acetic acid for a few minutes. The residue remaining after evaporation of the solvent was washed and dried in ether and crystallized from hexane; yield, 1.5 g., m. p. 120–121°. A sample, recrystallized from hexane, melted at 120.5–121.5°, $[\alpha]^{25}D$ + 136° (2.1% in ethanol).

Anal. Calcd. for $C_{22}H_{30}O_3$: C, 77.16; H, 8.82. Found: C, 76.97; H, 8.85.

Methyl O-Methyl-7-isopropylpodocarpate (IXa).—Hydrogenation of 0.5 g. of the 7-isopropenyl derivative in 95% ethanol with 15 mg. of Adams catalyst proceeded to completion in thirteen minutes. After removal of the catalyst, water was added to the concentrated solution to incipient turbidity, and crystallization took place on cooling. The product (0.49 g.) melted at 109–109.5° and the melting point was not changed on further crystallization; $[\alpha]^{25}D$ + 124° (1.2% in ethanol).

Anal. Calcd. for $C_{22}H_{32}O_3$: C, 76.68; H, 9.38. Found: C, 76.78; H, 9.28.

Methyl 6-Methoxydehydroabietate (VI, R = CH_3).—Methyl 6-hydroxydehydroabietate (0.5 g.) was refluxed for one hour in dry ether with 2.3 cc. of 0.69 *N* methylmagnesium chloride solution. A solution of 10 cc. of freshly distilled dimethyl sulfate in dry ether was added slowly and refluxing was continued for eighteen hours. After decomposing the excess dimethyl sulfate with alkali, the ether solution was evaporated and the product was crystallized from aqueous ethanol. On recrystallization from the same solvent, there was obtained 0.32 g. (61%) of broad flakes melting at 65.5–66.5°, $[\alpha]^{25}D$ + 87° (1.6% in ethanol).

Anal. Calcd. for $C_{22}H_{32}O_3$: OCH_3, 18.01. Found: OCH_3, 17.82.

Summary

1. Acetylretene and β-retenol are shown to be the 3- instead of the 6-derivatives.

2. The preparation of 6-retenol is described and this substance is shown to be identical with the retenol, reported to be the 8-isomer, obtained from ferruginol and hinokiol.

3. The preparation and proof of structure of 1-methyl-3-acetyl-6-methoxyphenanthrene, and the corresponding 3-carboxy derivative are reported.

4. It is shown that suitably substituted 3-hydroxyphenanthrenequinones give a positive Dimroth test and a satisfactory explanation for this anomalous action is offered.

5. The 7-isopropyl derivative of podocarpic acid is not identical with 6-hydroxydehydroabietic acid.

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