[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE]

Synthetic Studies on Resin Acids. IV[1]

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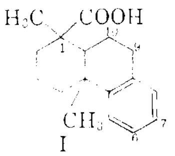
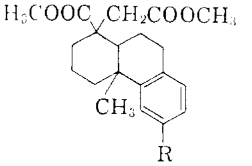
A synthesis of two enantiomers of desoxypodocarpic acid and of *dl*-podocarpic acid is described along with a discussion of the stereochemistry of these acids. A synthesis of desisopropyldehydroabietic acid is given.

In connection with the assignment of definite stereochemistry to a synthetic acid (I) melting at 146–147°,[1c] it became of importance to study the stereochemical behavior of other racemates melting at 232–233°,[2] 205–207°,[3] and 186–187.°[3]

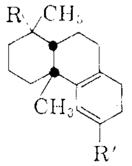


I

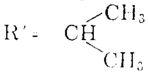
In the beginning it was attractive to settle this point through the synthesis of dehydroabietic acid *via* the introduction of isopropyl group at the C-7 position of the acid I. Moreover it appeared quite plausible that introduction of the acetyl group in the octahydrophenanthrene nucleus would take place preferentially at C-7, as this is sterically less hindered than C-6. The Friedel–Crafts reaction was first studied with the more accessible material II,[1c] and it was definitely established that the acetyl group entered at the 6-position through the isolation of 1-methyl-6-ethylphenanthrene. The behavior of the ester IV was also found to be similar and ultimately led to the synthesis of an isomer (VI) of dehydroabietic acid, which is both structurally and stereochemically different. Exhaustive attempts through chromatography over silica gel of the residue from the mother liquor failed to indicate the presence of any other isomer. These results are also in keeping with observations recently recorded by Wenkert and Jackson.[4] Next an attempt was made to develop new methods of synthesis for the other possible racemates of I and to study their interconversion with a view to correlating the stereochemical aspects of these acids.

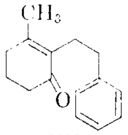


II. R = H
III. R = $-COCH_3$

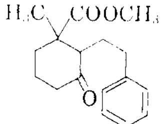


IV. R = $COOCH_3$
R' = H
V. R = $COOCH_3$
R' = $COCH_3$
VI. R = COOH

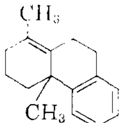

$R' = CH\begin{smallmatrix}\nearrow CH_3\\ \searrow CH_3\end{smallmatrix}$



VII



VIII



IX

2-(β-Phenethyl)-3-methyl-Δ^2-cyclohexenone (VII)[5] afforded 2-(β-phenethyl)-3-methyl-3-carbomethoxycyclohexanone (VIII) in a good yield through the conjugate addition of hydrocyanic acid[6] followed by alkaline hydrolysis and esterification. The compound VIII was allowed to react with methylmagnesium iodide and the crude carbinol on subsequent dehydration with oxalic acid in boiling toluene[7] yielded a slightly yellowish liquid. This was found to be a complex mixture as indicated by the presence in the infrared of a γ-lactonic band (5.67s μ) and an ester band (5.77s μ). The above mixture on cyclization with polyphosphoric acid[8] afforded a crystalline acidic product and a neutral liquid material. The acidic product on crystallization from ethyl acetate–methanol afforded an acid (I) with m.p. 232–233° (methyl ester, m.p. 131–132°). Prof. Haworth was kind enough to compare the mixed melting points of the acid and the methyl ester with his samples and found no depression. From the mother liquor, another acid (I) was isolated, m.p. 206–207° (methyl ester m.p. 85–86°). This acid most probably corresponded to the isomer described by Parham, *et al.*,[3] but an authentic sample was not available for direct comparison. These two acids showed a tendency to form a eutectic melting at 190–192°, and both afforded 1-methylphenanthrene on dehydrogenation. The relative proportion of the acidic and neutral materials during ring closure with polyphosphoric acid varies considerably with slight variation of the experimental conditions. The neutral material on hydrolysis with butanolic potassium hydroxide[9] afforded a further quantity of acid, m.p. 206–207°, besides some other low melting products, which on extensive chromatographic purification did not yield any of the isomers melting at 146–147° or 174–175° (*vide infra*). The unhydrolyzed material yielded a small amount of the methyl ester, m.p. 131–132°, along with a product which is practically free from

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[1] (a) A part of this investigation has been taken from the thesis submitted by U. R. Ghatak for the degree of Doctor of Philosophy (Science) of the University of Calcutta, January, 1957. (b) A preliminary report of another part of this work has appeared; U. R. Ghatak, *Tetrahedron Letters*, 19 (1959); (c) Part III, N. N. Saha, B. K. Ganguly and P. C. Dutta, THIS JOURNAL, **81**, 3670 (1959).

[2] R. D. Haworth and R. L. Barker, *J. Chem. Soc.*, 1299 (1939).

[3] W. E. Parham, E. L. Wheeler and R. M. Dodson, THIS JOURNAL, **77**, 1166 (1955).

[4] E. Wenkert and B. G. Jackson, *ibid.*, **80**, 217 (1958).

[5] (a) G. Stork and A. Burgstahler, *ibid.*, **73**, 3544 (1951); (b) N. N. Saha, P. N. Bagchi and P. C. Dutta, *ibid.*, **77**, 3408 (1955).

[6] (a) J. O. Jilek and M. Protiva, *Collection Czech. Chem. Commun.*, **23**, 692 (1958); (b) J. A. Hogg, THIS JOURNAL, **70**, 161 (1948).

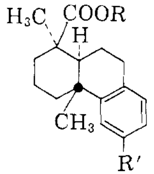
[7] T. Weil and D. Ginsberg, *J. Chem. Soc.*, 1291 (1957).

[8] F. E. King, T. J. King and J. G. Topliss, *Chemistry & Industry*, 113 (1956).

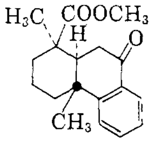
[9] W. P. Campbell and D. Todd, THIS JOURNAL, **64**, 928 (1942).

carbomethoxyl group as revealed from the infrared spectra and elemental analysis, and has been tentatively assigned the structure IX. This observation runs parallel to that recently reported by Barltrop, *et al.*[10] The stereochemistry of the acid, m.p. 232–233°, appeared to belong to podocarpic acid on the basis of the results recently recorded by King, *et al.*,[8] and has been fully substantiated through the synthesis of *dl*-podocarpic acid from the ester (m.p. 131–132°), through the introduction of hydroxyl group in the 6-position.[4] The methyl ester was allowed to react with acetyl chloride and the ketonic product X on oxidation with perbenzoic acid in chloroform[11] yielded methyl *dl*-podocarpate acetate (XI). This on alkaline hydrolysis afforded methyl podocarpate (XII) and finally *dl*-podocarpic acid (XIII) and the identity of the latter has been established by direct mixed melting point determination (through the courtesy of Dr. T. J. King) with an authentic sample.

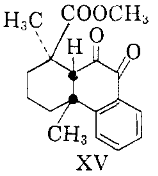
The methyl ester (m.p. 131–132°), on oxidation with chromic acid in acetic acid solution[12] afforded methyl 9 - keto - desoxy - *dl* - podocarpate (XIV), thereby establishing the *trans* junction of the A/B rings. The keto-ester exists in two polymorphic forms, both of which however afford the same 2,4-dinitrophenylhydrazone. On oxidation under identical conditions the methyl ester (m.p. 85–86°) yielded the diketo-ester XV, a bright yellow crystalline solid. The diketo ester was converted to the corresponding enol-acetate and the crude gummy product on catalytic hydrogenation gave the methyl ester, m.p. 131–132°, alone or mixed with the sample described before. The formation of the mono- and diketo esters on oxidation[12] and the subsequent transformation through the enol-acetate conclusively proved that the epimeric centers at C-1 are identical in both the acids and these differ only at ring junctions, *i.e.*, the acid with m.p. 232–233° (XVI) being *trans*-locked desoxypodocarpic acid and the acid with m.p. 206–207° (XVII) is *cis*-locked *cis*-desoxypodocarpic acid.



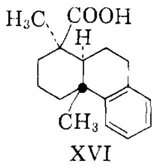
X, $R = CH_3$; $R' = COCH_3$
XI, $R = CH_3$; $R' = OCOCH_3$
XII, $R = CH_3$; $R' = OH$
XIII, $R = H$; $R' = OH$



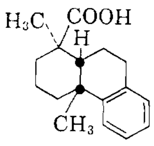
XIV



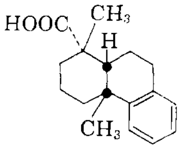
XV



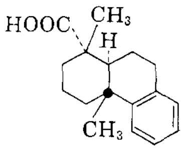
XVI



XVII



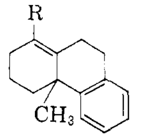
XVIII



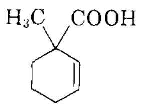
XIX

The mechanism of the ring closure yielding only the podocarpic acid system[2,3,10,13] with A/B-*cis*- and *trans*-juncture deserves some comments.[14] The acid I with m.p. 146–147° has now been proved to be *cis*-desisopropyldehydroabietic acid (XVIII).[1c] The remaining isomer desisopropyldehydroabietic acid (XIX) remains to be described and it is unlikely that the acid[3] melting at 186–187°, which is again derived along with the acid, m.p. 205–207° from 10-keto-acid,[3] can be assigned this stereochemistry because of the improbability of epimerization at C_1 through Wolff–Kishner reduction. The possibility of this acid being an eutectic of the acids melting at 232–233° and 205–207° cannot be altogether ruled out.

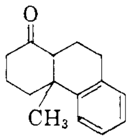
As reported previously, attempts to develop a synthesis of the podocarpic acid system[1c,15] through the conjugate addition of methylmagnesium iodide to the α,β-unsaturated cyano-ester having failed, the alkylation of α,β-unsaturated acids[16] and ketones[17] appeared attractive. With this end in view, attempt was made to synthesize the unsaturated acid XX, because preliminary studies with cyclohexenecarboxylic acid showed that methylation proceeded in an almost quantitative yield to afford the acid XXI. The tricyclic ketone[5] XXII was converted to the cyanohydrin which on dehydration and on drastic alkaline hydrolysis afforded a crystalline acid in a moderate yield, which analyzed well for the expected formula. Attempts at methylation failed completely. This failure was originally ascribed to the insolubility of the potassium salt in liquid ammonia. So the acid was converted to a methyl ketone through dialkylcadmium. Curiously enough, it did not exhibit any absorption in the ultraviolet



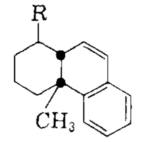
XX, $R = COOH$
XXVI, $R = COCH_3$



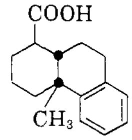
XXI



XXII



XXIII, $R = COOH$
XXV, $R = COCH_3$



XXIV

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[10] J. A. Barltrop and A. C. Day, *J. Chem. Soc.*, 671 (1959).

[11] S. L. Friess, THIS JOURNAL, **71**, 14 (1949).

[12] E. Wenkert and B. G. Jackson, *ibid.*, **80**, 211 (1958).

[13] B. K. Bhattacharyya, *J. Indian Chem. Soc.*, **22**, 165 (1945).

[14] Non-formation of isomeric compounds with equatorial carbmethoxyl may be due to the presence of sp_2-hybridized carbonyl of carbmethoxyl, the latter being sterically favored to occupy an axial position as compared to sp_3-methyl. The repulsion between the two polar methyl groups is also avoided thereby lowering the activation energy of the transition complex.

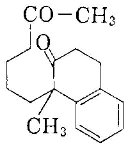
[15] U. R. Ghatak, N. N. Saha and P. C. Dutta, THIS JOURNAL, **79**, 4487 (1957).

[16] A. J. Birch, *J. Chem. Soc.*, 1551 (1950).

[17] R. B. Woodward, A. A. Patchett, D. H. R. Barton, D. A. J. Ives and R. B. Kelly, *ibid.*, 1131 (1957).

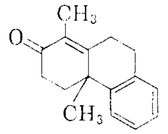
(240–250 mμ) and it afforded a bright yellow 2,4-dinitrophenylhydrazone. The acid should now be represented by the structure XXIII as it readily took one equivalent of hydrogen on catalytic hydrogenation to afford XXIV and absorbed in the ultraviolet at 264 mμ.[18] Evidently the ketone is represented by structure XXV. The saturated acid must have *cis*-locking of the A/B rings[18,19] and in support of this statement the saturated acid was converted to the *t*-amyl ester and methylated in presence of potassium amide in liquid ammonia.[20] The acid so obtained was found to be identical with the acid XVII, thereby establishing the stereospecificity of the alkylation process.

Attempts were made to prepare the α,β-unsaturated ketone XXVI through the ring closure of the diketone XXVII, but this route did not lead to any promising result.

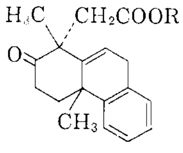


XXVII

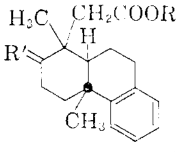
For the synthesis of the remaining isomer, *i.e.*, desisopropyldehydroabietic acid (XIX) it was attempted to generate the *trans* junction from the acid melting at 146–147°, through the diketo-ester.[1c] A small amount of a product, melting at 142–143°, was isolated. This could not be characterized because of the extremely small amount obtained.



XXVIII



XXIX, R = C_2H_5
XXX, R = H



XXXI, R = H; R′ = O
XXXII, R = CH_3; R = O
XXXIII, R = CH_3; R = H_2

Having failed to achieve the desired objective the synthesis of desisopropyldehydroabietic acid has been carried out by following the method employed successfully for the synthesis of dehydroabietic acid.[21] Tetralone[22] was condensed with β-chloroethyl ethyl ketone to afford the crystalline tricyclic ketone XXVIII. This readily condensed with ethyl bromoacetate to form XXIX, from which a crystalline unsaturated acid (XXX) was obtained on alkaline hydrolysis. The unsaturated acid underwent catalytic hydrogenation to afford the solid saturated acid XXXI (methyl ester m.p. 95°) in almost quantitative yield. The reduction has proceeded in a stereospecific way for obvious steric reasons.[12,21] The carbonyl group was removed through the preparation of the thioketal followed by treatment with Raney nickel and the desulfurized ester XXXIII was subjected to a Barbier–Wieland degradation to afford in a very poor yield the desired acid XIX as the only crystallizable product. The melting point approaches very closely that of the optically active desisopropyldehydroabietic acid (m.p. 172–173°).[23] This completes the four racemates of the acid I and all of them are now fully described. The order of the melting points shows some regularity:

	trans	*cis*
Desoxypodocarpic acid	232–233°	206–207°
Desisopropyldehydroabietic acid	174–175°	146–147°

Acknowledgments.—We are indebted to Prof. P. C. Dutta for his kind interest and valuable suggestions. Grateful thanks are due to Mrs. Chhabi Dutta of the Microanalytical Laboratory, University College of Science and Technology, Calcutta 9, and to Mr. Akhil Bandhu Dutta of this Laboratory for analyses.

Experimental[24]

Methyl 1,2,3,4,4a,9,10,10a-Octahydro-1-carbomethoxy-4a-methyl-6-acetyl-1-phenanthreneacetate (III).—To an ice-cold and well-stirred solution of the ester II (6.6 g., 0.02 mole) in nitrobenzene (30 ml.) containing anhydrous aluminum chloride (6.4 g., 0.048 mole), freshly distilled acetyl chloride (2.4 ml.) was added dropwise and it was kept at 0° for one hour and at room temperature (25–30°) for another 20 hours. On removal of nitrobenzene the gummy residue was re-esterified (diazomethane) and converted to the semicarbazone. The regenerated ketonic product (2.3 g., 31%), on crystallization twice from methanol furnished rhombic white crystals, m.p. 137–138°, $\lambda_{\max}^{\text{alc}}$ 259 mμ (log ε 4.16).

Anal. Calcd. for $C_{22}H_{28}O_5$: C, 70.94; H, 7.58. Found: C, 71.07; H, 7.53.

The 2,4-dinitrophenylhydrazone crystallized from ethyl acetate in orange fluffy crystals, m.p. 227–228°.

Anal. Calcd. for $C_{28}H_{32}O_8N_4$: C, 60.86; H, 5.84. Found: C, 61.03; H, 6.01.

1-Methyl-6-ethylphenanthrene.—The keto-ester (III, 1.2 g.) was reduced (Huang-Minlon modification) and the thick semi-solid acidic residue (1 g.) was mixed with powdered selenium (1.5 g.) and heated at 325–340° for 12 hours. The neutral fraction was dissolved in petroleum ether (40–60°) and purified by passing through a column of alumina (10 g.). A colorless oil (0.3 g., 42%) so obtained failed to solidify but easily yielded a deep-yellow **2,4,6-trinitrobenzene complex**, m.p. 129–130°. On recrystallization from ethanol it yielded bright-yellow needles, m.p. 141–142°, alone or mixed with an authentic sample.

Anal. Calcd. for $C_{23}H_{19}O_6N_3$: C, 63.7; H, 4.4. Found: C, 63.4; H, 4.6.

Methyl 1,2,3,4,4a,9,10,10a-Octahydro-1,4a-dimethyl-6-acetyl-1-phenanthrenecarboxylate (V).—The methyl ester IV (2.18 g., 0.008 mole) was condensed with acetyl chloride (1 ml.) in nitrobenzene (15 ml.) in the presence of anhydrous aluminum chloride (2.6 g., 0.0195 mole) as before. The ketonic fraction (1.6 g., 64%) was isolated through its semicarbazone and purified through evaporative distillation at 165–175° (0.3 mm.). It easily formed an orange **2,4-dinitrophenylhydrazone**, which on crystallization from ethyl acetate yielded fluffy orange crystals, m.p. 226°.

Anal. Calcd. for $C_{26}H_{30}O_6N_4$: C, 63.14; H, 6.11. Found: C, 62.88; H, 6.09.

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[18] E. Wenkert and T. E. Stevens, THIS JOURNAL, **78**, 2318 (1956).

[19] E. M. Fry, *J. Org. Chem.*, **22**, 1710 (1957).

[20] C. R. Hauser and W. J. Chambers, THIS JOURNAL, **78**, 3837 (1956).

[21] G. Stork and J. W. Schulenberg, *ibid.*, **78**, 250 (1956).

[22] F. H. Howell and D. A. H. Taylor, *J. Chem. Soc.*, 1248 (1958).

[23] E. Wenkert and J. W. Chamberlin, THIS JOURNAL, **81**, 688 (1959).

[24] All boiling points and melting points are uncorrected.

1,2,3,4,4a,9,10,10a-Octahydro-1,4a-dimethyl-6-isopropyl-1-phenanthrenecarboxylic Acid (VI).—To a well-stirred solution of the above keto-ester (1.5 g., 0.0048 mole) in ether (10 ml.) at −5°, an ethereal solution of methylmagnesium iodide (magnesium, 0.24 g., 0.01 g. atom), methyl iodide (1 ml.) and dry ether (7 ml.), was added dropwise under nitrogen. After 15 minutes the mixture was decomposed (ammonium chloride). The residual gummy mass (1.4 g.), was refluxed with W-6 Raney nickel catalyst (50 g. of the alloy) in ethanol (150 ml.) for 12 hours.[25] The catalyst was filtered off and alcohol evaporated to afford a colorless product (1.1 g.). It was refluxed for 5 hours with 1-butanolic potassium hydroxide solution (25 ml.) containing potassium hydroxide (2.5 g.). 1-Butanol was removed by passing steam through the acidified solution, and the oily product was extracted with ether. The aqueous alkaline (5% potassium hydroxide) extract on acidification, afforded a finely suspended solid, which furnished on sublimation at 165–175° (0.1 mm.), a glassy mass, and solidified on trituration with aqueous ethanol. On recrystallization from the same solvent it gave silky-white flakes (50 mg.), m.p. 155–156°.

Anal. Calcd. for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 80.31; H, 9.0.

A portion of the Grignard product (0.1 g.), without further purification, was heated with selenium (0.2 g.) at 325–340° for 12 hours. The hydrocarbon was obtained as a colorless oil (40 mg.) on distillation over metallic sodium at 160–170° (1 mm.). It yielded an orange picrate, which on recrystallization from ethanol gave shining orange needles, m.p. 142–143°, alone or mixed with an authentic sample of the picrate of 1-methyl-6-isopropylphenanthrene (lit.[26] m.p. 143°).

Anal. Calcd. for $C_{24}H_{21}O_7N_3$: C, 62.20; H, 4.57. Found: C, 62.50; H, 4.21.

2-(β-Phenethyl)-3-methyl-3-carbomethoxycyclohexanone (VIII).—To a solution of 2-(β-phenethyl)-3-methyl-Δ^2-cyclohexenone (VII, 62 g., 0.29 mole) in ethanol (500 ml.), was added a solution of potassium cyanide (62 g., 0.954 mole) in water (300 ml.). The solution was slowly refluxed for 10 hours, whereupon the color gradually turned light brown. On cooling, a solution of potassium hydroxide (80 g., 1.43 moles) in water (900 ml.) was added and refluxing continued for another 55 hours. The reaction mixture afforded an acidic product and a neutral material. The neutral fraction yielded a solid (3.5 g.) on trituration with aqueous ethanol. It crystallized from ethanol in shining colorless prisms, m.p. 184–185°.

Anal. Found: C, 71.03, 71.12; H, 7.60, 7.57; N, 5.28.

The dried gummy acid (68 g.) was refluxed with methanol (200 ml.) and concentrated sulfuric acid (20 ml.) for 30 hours. The neutral fraction yielded a colorless sweet-smelling liquid (49 g.), b.p. 178–180° (0.6 mm.), and the recovered acid was re-esterified. Total yield was 54.1 g. (68%).

Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.15; H, 8.06.

The 2,4-dinitrophenylhydrazone was obtained as bright yellow needles from ethanol–ethyl acetate, m.p. 163°.

Anal. Calcd. for $C_{23}H_{26}O_6N_4$: N, 12.33. Found: N, 12.50.

Desoxypodocarpic Acid (XVI) and its Enantiomer XVII.—To a well-stirred ice-cold solution of the above ester (49 g.), in ether (120 ml.), methylmagnesium iodide (magnesium, 5.4 g.) was added dropwise during one hour and left as such for another 1.5 hours. The product was dissolved in toluene (150 ml.) and refluxed for 3 hours with oxalic acid (20 g.), whereby the water formed in the reaction was continuously removed. It afforded a colorless oil (38.5 g.), b.p. 145–157° (0.4 mm.). It rapidly decolorized bromine in carbon tetrachloride.

Anal. Calcd. for $C_{18}H_{26}O_3$ (alcohol): C, 74.44; H, 9.03; $C_{18}H_{24}O_2$ (unsaturated ester): C, 79.37; H, 8.88; $C_{17}H_{22}O_2$ (lactone): C, 79.03; H, 8.58. Found: C, 76.19; H, 8.55.

A well-stirred mixture of polyphosphoric acid (phosphorus pentoxide, 96 g., and orthophosphoric acid, 82 ml., 89 w./w.) and the above lactone-ester mixture (38.3 g.) was heated in a water-bath (80–90°) for 1.25 hours. The light orange reaction mixture was decomposed (ice). The ethereal extract was washed with 5% sodium hydroxide solution (140 × 3 ml.) and with water (100 ml.). The basic aqueous extracts yielded a crystalline acid, which was freed from the adhering oil by washing with petroleum ether (b.p. 40–60°). A white crystalline solid (13.2 g.) was obtained, m.p. 209–211° (softening at 190°), which on fractional crystallization from ethyl acetate–ethanol yielded XVI as colorless prisms (6.2 g.), m.p. alone or mixed, 232–233°.

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.66; H, 8.64.

The methyl ester (diazomethane) was crystallized from methanol as colorless cubes, m.p. 131–132° alone or mixed with an authentic sample.

Anal. Calcd. for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.39; H, 8.95.

The acid (XVI, 100 mg.) was heated with 10% palladium-on-charcoal (100 mg.) for 4 hours at 320–330°, and the hydrocarbon (30 mg.) had m.p. 122–123°, alone or mixed with an authentic sample of 1-methylphenanthrene.

The melting point of an acid (6.6 g.), obtained from the mother liquor remained constant at 190–192°, even after repeated crystallization. Fractional crystallization of the ester (diazomethane) from methanol yielded two products with m.p. 130–131° (1.8 g.), identical with the ester described earlier and another product, m.p. 78–80° (4.4 g.). The latter one was hydrolyzed by refluxing for 6 hours with a solution of 1-butanolic potassium hydroxide solution (80 ml., 10%). On extraction of the alkaline aqueous solution with chloroform, it yielded a crystalline solid (1.64 g.), m.p. 125–127°. On crystallization twice from methanol it afforded the known ester, m.p. 131–132°. The acidic product was recovered and extracted with chloroform yielding a crystalline solid (XVII, 1.95 g.); on crystallization from methanol it melted at 206–207°.

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.85; H, 8.63.

The methyl ester (diazomethane) crystallized from methanol in shining colorless prisms, m.p. 85–86°.

Anal. Calcd. for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.02; H, 8.90.

The above acid (XVII, 50 mg.) was dehydrogenated with 10% palladium-on-charcoal (50 mg.) and afforded 1-methylphenanthrene. The neutral residue obtained from ring closure yielded a light yellow liquid (16.1 g.), b.p. 135–160° (0.2 mm.). This (16.1 g.) was refluxed for 10 hours with 1-butanolic potassium hydroxide solution (300 ml., 10%). The neutral yellowish liquid (5 g.), b.p. 130–140° (0.4 mm.), on standing in the cold, yielded the ester (*ca.* 200 mg.), m.p. 130–131°. The alkaline extract afforded a crystalline acidic product (5.5 g.), m.p. 153–155°, and on laborious fractional crystallization it yielded colorless flakes (2.4 g.), m.p. and mixed m.p. 206–207°. The mother liquor again yielded a crystalline solid (1.3 g.), m.p. 152–155°, and its methyl ester (diazomethane) was chromatographed over neutral alumina. Elution with petroleum ether (b.p. 40–60°)-benzene mixture yielded the known ester, m.p. 85–86°. The neutral fraction left after separation of the methyl ester, m.p. 130–131°, was rehydrolyzed under drastic condition by heating for 5 hours with a solution of potassium hydroxide (1 g.) in diethylene glycol (15 ml.) under nitrogen and yielded IX (3.1 g.), b.p. 128–130° (0.4 mm.).

Anal. Calcd. for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 90.84; H, 9.58.

The basic solution yielded the acid XVI (*ca.* 100 mg.) m.p. 232–233°.

Methyl 9-Ketodesoxypodocarpate (XIV).—The methyl ester (3.2 g., m.p. 131–132°) in acetic acid (40 ml.) was oxidized with a solution of chromic acid (4 g.) in water (8 ml.) and acetic acid (30 ml.). The neutral ketonic product was isolated through its semicarbazone (2.4 g.) and was finally crystallized from methanol (charcoal) as shining colorless needles (1.7 g., 50%), m.p. 124–125°, $\lambda_{\max}^{\text{alc}}$ 249 mμ (log ε 4.07).

Anal. Calcd. for $C_{18}H_{22}O_3$: C, 75.49; H, 7.74. Found: C, 75.44; H, 7.97.

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(25) D. Y. Curtin and S. Schmukler, THIS JOURNAL, **77**, 1105 (1955).

(26) S. N. Slater, *J. Chem. Soc.*, 68 (1941).

On slow crystallization from methanol the keto-ester formed shining colorless prisms, m.p. 146–147°.

Anal. Calcd. for $C_{18}H_{22}O_3$: C, 75.49; H, 7.74. Found: C, 75.07; H, 7.90.

The 2,4-dinitrophenylhydrazone crystallized from ethyl acetate in orange flocculent crystals, m.p. 219–220°.

Anal. Calcd. for $C_{24}H_{26}O_6N_4$: N, 12.01. Found: N, 12.26.

Methyl 9,10-Diketo-*cis*-desoxypodocarpate (XV).—The methyl ester (3.1 g., m.p. 84–85°) in acetic acid (30 ml.) was oxidized with a solution of chromic anhydride (3.9 g.) in water (8 ml.) and acetic acid (32 ml.). The yellow neutral residue was dissolved in a minimum quantity of benzene and diluted with petroleum ether (b.p. 40–60°), whereupon shining yellow crystals (920 mg., 27%), m.p. 124° (softening at 118°), separated out. On crystallization from benzene–petroleum ether, it yielded shining yellow cubes, m.p. 129–130°, λ^{alc}_{max} 288 mμ (log ε 3.87).

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 72.30; H, 6.82.

Methyl *dl*-Desoxypodocarpate.—A mixture of the above diketo-ester (400 mg.), freshly fused sodium acetate (200 mg.) and acetic anhydride (20 ml.) was gently refluxed for 1.5 hours.[12] A mixture of the crude enol-acetate (420 mg., λ^{alc}_{max} 259 mμ, log ε 4.04), 10% palladium-on-carbon (200 mg.), 60% perchloric acid (0.3 ml.) and acetic acid (12 ml.) was hydrogenated. The neutral yellowish gummy residue was triturated with methanol, whereupon a white solid, m.p. 108–110°, separated out. On recrystallization from methanol it yielded colorless cubes (154 mg., 42%), m.p. alone or mixed 131–132°.

Anal. Calcd. for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.16; H, 8.68.

Methyl 6-Acetyl-*dl*-desoxypodocarpate (X).—To an ice-cold stirred solution of the methyl ester (1.7 g., 0.0063 mole, m.p. 131–132°) in nitrobenzene (12 ml.) containing anhydrous aluminum chloride (2 g., 0.015 mole), was added freshly distilled acetyl chloride (0.85 ml.) and left as such for 1 hour and at room temperature (28–32°) for another 17 hours. The ketonic material, purified through its semicarbazone, was evaporatively distilled, b.p. 140–150° (0.15 mm.). The colorless distillate on two crystallizations from aqueous methanol yielded silky white needles (700 mg., 35%), m.p. 133–134°, λ^{alc}_{max} 259 mμ (log ε 4.17).

Anal. Calcd. for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34. Found: C, 76.41; H, 8.55.

The 2,4-dinitrophenylhydrazone crystallized from ethyl acetate in orange flocculent crystals, m.p. 234–235°.

Anal. Calcd. for $C_{26}H_{30}O_6N_4$: C, 63.14; H, 6.11. Found: C, 63.16; H, 6.31.

Methyl *dl*-Podocarpateacetate (XI).—To a solution of the keto-ester X (450 mg.) in chloroform (2 ml.), a chloroform solution of perbenzoic acid (6.8 ml. containing 0.257 g. of perbenzoic acid) was added and the whole covered with a black paper was left at 10° for 2 days and finally at room temperature (28–32°) for 3 days. The neutral residue on recrystallization from petroleum ether–ethyl acetate yielded colorless rhombic prisms (375 mg., 79%), m.p. 125–126°.

Anal. Calcd. for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.35; H, 8.01.

Methyl *dl*-Podocarpate (XII).—A mixture of methyl podocarpateacetate (300 mg.) and potassium hydroxide (450 mg.) in water (25 ml.) and ethanol (40 ml.) was refluxed for 4 hours. Yellowish crystals (250 mg., 94%), m.p. 185–190°, separated out on acidification. After recrystallization from aqueous methanol it yielded fluffy colorless needles, m.p. 193°.

Anal. Calcd. for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 75.02; H, 8.50.

***dl*-Podocarpic Acid (XIII).**—A mixture of methyl podocarpateacetate (XI, 120 mg.), potassium hydroxide (400 mg.) and diethylene glycol (5 ml.) was heated under nitrogen at 160–180° (bath temperature) for 5 hours. The aqueous alkaline layer on acidification yielded a brown-colored solid, which was sublimed at 180–190° (0.1 mm.), whereupon a white crystalline sublimate (75 mg., 70%), m.p. 264–266°, was obtained. Crystallization from ethyl acetate–petroleum ether gave white crystals, m.p. 266–268°, alone or mixed with an authentic sample.

1-Methyl-Δ²-cyclohexenylcarboxylic Acid (XXI).—To a well-stirred solution of potassium amide (potassium 8 g.) in liquid ammonia (*ca.* 500 ml.), cyclohexenylcarboxylic acid (6.3 g.) was added in a lot, when the color of the solution turned deep orange-green. The solution was left for 5 minutes, after which methyl iodide (*ca.* 50 g.) was added in dropwise, whereupon the color disappeared. The acid was recovered and the above process was repeated twice for complete methylation to afford a colorless liquid (4 g., 57%), b.p. 105–107° (3 mm.).

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.31; H, 8.40.

1-Methylcyclohexylcarboxylic Acid.—The above acid (XXI, 2.1 g.) was hydrogenated over platinum oxide (0.1 g.) in ethanol (10 ml.). A colorless product (2 g., 94%), b.p. 105° (4 mm.), was obtained.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.75; H, 9.66.

The amide crystallized from petroleum ether (b.p. 40–60°) in needles, m.p. 66–67° (lit.[15] 68–69°) alone or mixed with an authentic sample.

(With D. K. Datta and S. C. Ray). 1,2,3,4,4a,10a-Hexahydro-4a-methyl-1-phenanthrene-carboxylic Acid (XXIII).—4a-Methyl-1-keto-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (XXII, 45 g.) was treated at −10° with hydrocyanic acid from potassium cyanide (150 g.) and dilute sulfuric acid (300 ml., 1:1). The dried crude cyanohydrin was dissolved in pyridine (45 ml.), treated with thionyl chloride (32 ml.) at 0°, and allowed to stand at the same temperature for an hour. It was finally heated on the steam-bath for 2 hours and the unsaturated nitrile was distilled; b.p. 165–170° (0.8 mm.), yield 24 g. (51%). A pure sample could not be prepared for analysis due to its contamination with dissolved sulfur. To a solution of sodium hydroxide (4.5 g.) in diethylene glycol (60 ml.) and water (1 ml.) maintained at 80°, the above nitrile (15 g.) was added under nitrogen, and heated at 200–210° for 4 hours. The gummy acidic residue afforded on evaporative distillation at 170–180° (0.6 mm.) (bath temperature) a hard glassy mass (5.3 g., 32%). It crystallized from aqueous ethanol as stout prisms (2 g.), m.p. 172–173°, λ^{alc}_{max} 265 mμ (log ε 4.0).

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.30; H, 7.51.

1,2,3,4,4a,10a-Hexahydro-4a-methyl-1-acetylphenanthrene (XXV).—Acid chloride prepared from the acid (XXIII, 1 g.), and dissolved in benzene (2 ml.), was added to a hot, vigorously stirred solution of cadmium alkyl (anhydrous cadmium chloride (3.6 g.) and methylmagnesium iodide (magnesium 190 mg.)). The reaction mixture was refluxed for 1.5 hours, cooled and decomposed. A thick yellow liquid (200 mg., 20.2%) was isolated, which afforded a yellow 2,4-dinitrophenylhydrazone almost quantitatively. On crystallization from ethanol–ethyl acetate (1:1), the **2,4-dinitrophenylhydrazone** separated in bright-yellow micro-needles, m.p. 186–187°.

Anal. Calcd. for $C_{23}H_{24}O_4N_4$: C, 65.70; H, 5.75; N, 13.33. Found: C, 66.09; H, 5.87; N, 13.20.

1,2,3,4,4a,9,10,10a-Octahydro-4a-methyl-1-phenanthrene carboxylic Acid (XXIV).—A solution of the unsaturated acid (XXIII, 1.8 g.) in dry ethanol (20 ml.) was hydrogenated over 10% palladium-on-charcoal (0.2 g.). The product solidified, which on crystallization from aqueous ethanol yielded colorless, shining prisms (1.7 g., 93%), m.p. 203–204°.

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.71; H, 8.22.

1,2,3,4,4a,9,10,10a-Octahydro-1,4a-dimethyl-1-phenanthrenecarboxylic Acid (XVII).—To a cooled suspension of potassium *t*-amylate (containing 2 g. of the metal) in ether (25 ml.), the acid chloride (1.7 g.) in ether (15 ml.) was added dropwise with shaking. The resulting mixture was allowed to stand at room temperature for an hour, followed by refluxing for 1 hour more. After decomposing the reaction mixture with ice-cold water, the ester was finally dried at 100° in vacuum. To a solution of potassium (1 g.) in liquid ammonia (100 ml.) the above *t*-amyl ester (1.6 g.) in ether (20 ml.) was added in one lot with constant stirring, whereupon the color changed through green to chocolate-red. After an hour, methyl iodide (5 ml.) in ether (5 ml.) was slowly added, whereupon the color was discharged. Ammonia was then evaporated off slowly with occasional addition of moist ether and the residue decomposed (ammonium chloride). The brown gummy product (1.5 g.) was remethylated as before. The crude gummy ester (*ca.* 1.3 g.) was dissolved in dioxane (10 ml.) containing concentrated hydrochloric acid (15 ml.) and refluxed for 2 hours. The acidic product was dissolved in methanol (charcoal) from which crystals (510 mg., 29%) gradually separated, and were recrystallized from ethanol as shining white cubes, m.p. 207–208°, alone or on admixture with XVII; the mixed melting point with the acid XXIV (m.p. 203–204°) was 190–195°.

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.03; H, 8.80.

1-Methyl-1-γ-acetopropyl-2-tetralone(XXVII).—To a solution of potassium *t*-butoxide (potassium, 2.8 g., 0.072 atom) in dry toluene (80 ml.), 1-methyltetralin-2-one (12.8 g., 0.08 mole) in toluene (20 ml.) was added under *nitrogen*. The solution was heated on a small flame for half an hour and a white solid gradually crystallized out. Trimethylene dibromide (44 g., 0.218 mole) was added in the cold and it was allowed to stand overnight and finally refluxed for 3 hours. The product (11.6 g.) distilled at 153–154° (0.8 mm.). In the presence of sodium (1.03 g., 0.045 atom) in dry ethanol (20 ml.), this was condensed with ethyl acetoacetate (9.3 g., 0.071 mole) in the presence of dry sodium iodide (1.5 g.) by refluxing for 12 hours. The condensation product was again refluxed under nitrogen with potassium hydroxide (16 g.) in methanol (160 ml.) for 6 hours. A colorless heavy oil (4.5 g., yield 49% based on the bromo-compound) was obtained at 160–180° (0.5 mm.).

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.21; H, 8.60.

1-Acetyl-2,3,4,4a,9,10-hexahydro-4a-methylphenanthrene (XXVI).—A mixture of the diketone XXVII (1.8 g.), acetic acid (50 ml.) and concentrated hydrochloric acid (5 ml.) was refluxed under nitrogen for 5 hours, whereupon a greenish solution was obtained. A thick yellowish liquid (1.3 g.) distilled at 155–160° (0.4 mm.), λ_{max}^{alc} 248 mμ (log ϵ 3.6).

The semicarbazone, on repeated crystallization from ethanol, formed white crystals, melting at 222°, λ_{max}^{alc} 260 mμ (log ϵ 3.9).

Anal. Calcd. for $C_{18}H_{23}ON_3$: C, 72.69; H, 7.80; N, 14.13. Found: C, 72.56; H, 7.81; N, 14.12.

4,4a,9,10-Tetrahydro-1,4a-dimethyl-2(3H)-phenanthrone (XXVIII).—To a solution of sodium (8.8 g., 0.384 g. atom) in magnesium-dried methanol (150 ml.) 1-methyltetralin-2-one (30.5 g., 0.192 mole) in methanol (25 ml.) was added with external cooling under nitrogen. On stirring and refluxing for 30 minutes, the mixture was cooled thoroughly in ice and a solution of β-chloroethyl ethyl ketone (25 g., 0.192 mole) in methanol (20 ml.) was added during 50 minutes. Stirring was then continued for another 2 hours in the cold, followed by refluxing for an hour. The reaction mixture was decomposed with glacial acetic acid (30 ml.) and ice. An orange-yellow solid precipitated, which crystallized from petroleum ether (40–60°) (28 g., 65%) as shining white needles, m.p. 88–88.5°, λ_{max}^{alc} 248 mμ (log ϵ 4.2).

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.92; H, 8.02.

The 2,4-dinitrophenylhydrazone gave glistening red crystals from ethyl acetate, m.p. 238°.

Anal. Calcd. for $C_{22}H_{22}O_4N_4$: C, 65.01; H, 5.46. Found: C, 65.20; H, 5.45.

Ethyl 1,2,3,4,4a,9-Hexahydro-1,4a-dimethyl-2-keto-1-phenanthreneacetate (XXIX).—To a solution of potassium *t*-amylate (containing 7.8 g., 0.2 g. atom of the metal) in benzene (200 ml.) under nitrogen, a solution of the tricyclic ketone (XXVIII, 15 g., 0.066 mole) in benzene (70 ml.) was added with shaking. It was heated at 60–70° for 45 minutes, whereupon the solution developed a red color and was cooled in ice. Ethyl bromoacetate (36 g., 0.215 mole) was added dropwise; the mixture was allowed to stand for 30 minutes, followed by refluxing for an hour (nitrogen). The product had b.p. 175–185° (0.2 mm.), yield 15.5 g. (72%), a thick yellow liquid. It was redistilled and a central cut, b.p. 165–170° (0.1 mm.), was analyzed.

Anal. Calcd. for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.86; H, 7.65.

1,2,3,4,4a,9-Hexahydro-1,4a-dimethyl-2-keto-1-phenanthreneacetic Acid (XXX).—The unsaturated keto-ester XXIX (12 g.) was boiled for 4 hours with potassium hydroxide (15 g.) in methanol (220 ml.). The acidic product which was obtained as a flocculent white mass which in the cold turned gradually to an extremely sticky solid and was finally crystallized from methanol; white fibrous needles, m.p. 148–149° (5.1 g., 46%).

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.0; H, 7.05.

1,2,3,4,4a,9,10,10a-Octahydro-1,4a-dimethyl-2-keto-1-phenanthreneacetic Acid (XXXI).—(a) A solution of the unsaturated keto-acid XXX (5 g.) in glacial acetic acid (20 ml.) was shaken under hydrogen over platinum oxide (0.1 g.). The saturated acid on crystallization from methanol melted at 137–138°, yield 4.2 g. (83%).

Anal. Calcd. for $C_{18}H_{22}O_3$: C, 75.49; H, 7.74. Found: C, 75.91; H, 7.28.

(b) A solution of the unsaturated keto-ester XXIX (15 g.) in acetic acid (40 ml.) was hydrogenated over platinum oxide (0.5 g.). The light-yellow viscous product (*ca.* 15 g.) so obtained was refluxed with potassium hydroxide (18 g.) in methanol (300 ml.) for 4 hours. The crude acid was crystallized from methanol to give 7.1 g. (52%) of crystals, m.p. 135–136°. It showed no depression in melting point on admixture with the above sample.

Methyl 1,2,3,4,4a,9,10,10a-Octahydro-1,4a-dimethyl-2-keto-1-phenanthreneacetate (XXXII).—A solution of the keto-acid XXXI (7 g.) was converted to the methyl ester (diazomethane). Crystallization from dilute methanol yielded a white solid, m.p. 94–95°. The residue from the mother liquor was evaporatively distilled at 150–160° (0.1 mm.) (bath temperature) affording the 5.7 g. (77%) of solid ester. Crystallization from methanol afforded white prisms, m.p. 95°.

Anal. Calcd. for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 76.01; H, 7.67.

Methyl 1,2,3,4,4a,9,10,10a-Octahydro-1,4a-dimethyl-1-phenanthreneacetate (XXXIII).—To freshly fused zinc chloride (1.9 g.) and freshly ignited sodium sulfate (1.2 g.) was added with continuous shaking and cooling in ice, the keto-ester XXXII (4.4 g.), followed by ethylene dithiol (7 ml.). After allowing it to stand overnight, the solid reaction mixture was mixed with cold water (*ca.* 100 ml.) and extracted thoroughly with chloroform. The chloroform extract was washed with a cold 10% sodium hydroxide solution followed by water and the thioketal-ester was obtained as a shining white crystalline mass, m.p. 132–135°, yield 6 g. A solution of the thio-ketal ester (5.2 g.) in ethanol (300 ml.) and ethyl acetate (50 ml.) was added to W-6 Raney nickel (from 180 g. of the alloy) and the resulting mixture was refluxed with stirring for 10 hours. The filtrate was evaporated and the residue distilled yielding a colorless viscous oil (2.75 g., 65%), b.p. 160–162° (0.25 mm.).

Anal. Calcd. for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 80.02; H, 9.05.

***dl*-Desisopropyldehydroabietic Acid (XIX).**—To the well-cooled Grignard reagent from magnesium (0.6 g.) and bromobenzene (3.9 g.), the solution of the ester (XXXIII, 2.5 g.) in ether (5 ml.) was added dropwise. After refluxing for 3 hours, it was decomposed. On removal of the lower boiling materials up to a temperature of 160° (7 mm.), a gummy residue (3.2 g.) was left. A stirred solution of this product in purified acetic acid (40 ml.) was oxidized with a solution of chromium trioxide (4 g.) in water (7 ml.) and acetic acid (15 ml.) during a period of 5 hours at 75–80°. After decomposing the excess of chromium trioxide with ethanol, acetic acid was removed by passing through steam. The aqueous residue was extracted repeatedly with ether (sodium chloride). The acidic material was taken out by extracting twice with 5% sodium hydroxide solution and finally with ether on acidification. On removal of the solvent, the gray residue was evaporatively distilled at 150–160° (0.4 mm.) (bath temperature). The distillate was dissolved in aqueous methanol whereupon a solid separated.

On removing most of the adhering oily material on a porous tile, the solid (*ca.* 20 mg.) was repeatedly crystallized from aqueous methanol to give shining white flakes melting at 174–175°.

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.95; H, 8.46.

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[CONTRIBUTION FROM THE NAVAL STORES RESEARCH STATION][1]

Air Oxidation of Resin Acids. II. The Structure of Palustric Acid and its Photosensitized Oxidation[2]

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The final proof of structure of palustric acid has been accomplished with the location of the two double bonds in the 7,8–13,14 positions of the substituted perhydrophenanthrene nucleus. This assignment is based on the following observations: (a) the ultraviolet absorption maximum of 266 mμ, (b) the formation of a maleic anhydride adduct, (c) the rapid formation of a transannular peroxide in a photosensitized oxidation, (d) the stability of the transannular peroxide in excess base, (e) the presence of only one vinyl hydrogen atom in the transannular peroxide, (f) the similarity of specific rotations of palustric and dehydroabietic acids, and (g) the presence of only one vinyl hydrogen atom in palustric acid.

In spite of the considerable amount of research which has been carried out on pine gum and gum rosin, only about eight resin acids have been isolated and fully characterized from these sources[3a,4–6] A recent addition to this group was palustric acid, isolated by Lawrence and co-workers[5] from pine gum and gum rosin by means of chromatographic techniques.

The similarity of the carbon skeleton of this new resin acid to the well characterized *l*-abietic, levopimaric and neoabietic acids was revealed by the acid-catalyzed isomerization of palustric acid to *l*-abietic acid; the acid-catalyzed isomerization of levopimaric acid to palustric acid; the heat-catalyzed isomerization of levopimaric acid to palustric acid; and the formation of a maleic anhydride adduct from palustric acid on heating identical to the adduct obtained from *l*-abietic acid and neoabietic acid under similar conditions and from levopimaric acid at room temperature.[5]

The formation of a maleic anhydride adduct was also taken as indicative of the presence of a conjugated diene system in palustric acid. The ultraviolet absorption maximum of 266 mμ (absolute ethanol) found for palustric acid was recognized as being within the range characteristic of homoannular conjugated dienes.[3b] The final proof of structure involving the location of the two double bonds in the molecule, was not possible on the basis of the available information.[5] The isomerization data were interpreted as possibly favoring a 7,8–13,14 assignment of the two double bonds in palustric acid. Using Fieser's extension[3b] to homoannular dienes of Woodward's rule, the ultraviolet absorption maximum was calculated[5] for each of the six possible positions for the location of two conjugated double bonds in ring B (see structure I). Only the value for the structure corresponding to the 5,6–7,8 arrangement (calcd. λ_{max} 268 mμ) closely approximated the experimentally observed maximum of 266 mμ. The calculated values for the two possible positions of a conjugated homoannular diene system in ring C are 273 mμ (9,10–13,14) and 283 mμ (10,11–9,14). However, the extension of Woodward's rule to homoannular dienes[3b] is based upon a very limited number of examples and in its present form may not be as reliable as the parent rule often is in the area of acyclic and heteroannular conjugated diene systems.

In the present work, palustric acid was dissolved in 95% ethanol containing a suitable sensitizing dye and the solution was simultaneously aerated and irradiated with visible light. A rapid reaction was observed to take place, proceeding at essentially the same rate as the photosensitized oxidation of levopimaric acid under the same conditions.[7] The reaction rate was found to be independent of the concentration of the resin acid for all dyes tested, based on the change in optical rotation and on the decrease in the specific extinction coefficient at 266 mμ. In an experiment in which pure oxygen was used and the amount of oxygen absorbed was measured quantitatively, it was found that exactly one mole of oxygen per mole of palustric acid was taken up in the reaction. The crystalline product was characterized as a transannular peroxide on the basis of (a) the lack of any characteristic absorption in the ultraviolet region of 220–320 mμ; (b) the elemental analyses and neutralization equivalent; (c) the initiation of polymerization of the vinyl monomers styrene, acrylic acid and methyl methacrylate on heating in the presence of the photoperoxide; and (d) the absence of an O–H stretching band in the infrared region of 3 μ in the corresponding cyclohexylamine salt and methyl ester. The photosensitized 1,4-addition of oxygen to yield transannular peroxides is limited to homoannular, conjugated dienes and proceeds *via* addition to the terminal carbon atoms in the conjugated diene system, without prior rearrangement of the

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(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

(2) Presented at the Florida Section, Meeting-In-Miniature of the American Chemical Society, May 8, 1959, St. Petersburg, Florida.

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