methyl groups of each epoxide molecule remained the same and an aldehyde group was generated, it was concluded that during gas chromatography the nine-membered ring of the caryophyllene skeleton undergoes contraction to an eight-membered ring. Figure 1 illustrates the rearrangement of the epoxides to 4,10,10-trimethyl-7-methylenebicyclo[6.2.0]decane-4-carboxaldehyde (II) and 4,7,10,10-tetramethylbicyclo-[6.2.0]decane-4-carboxaldehyde (V), and also shows the conversion of either aldehyde to the saturated hydrocarbon, 2,5,5,9,9-pentamethylbicyclo[6.2.0]decane (VI). Formulas shown in Figure 1 are also in agreement with Warnhoff's recent work.[4]

Rearrangement of the epoxides failed to take place when the support (acid-washed Chromosorb W) was treated with methanolic KOH,[5] and used under the experimental conditions described. In this case unchanged starting materials only were recovered. Evidently the transformation is triggered by active surfaces of the acidic column support.

The reactions observed are of considerable value for the examination of essential oils and related products. They were applied successfully by the authors for detecting the presence of caryophyllene oxide in oil of marihuana for the first time.[6]

Experimental

Gas chromatographic apparatus and procedures were previously described.[7] Infrared spectra were charted with a Perkin-Elmer Model 221 instrument. N.m.r. spectra were recorded in carbon tetrachloride solution, with a Varian A-60 spectrometer.

Caryophyllene Oxide (I).—The terpenoid was obtained by epoxidation (monoperphthalic acid) of pure caryophyllene (1.0 g.) isolated by preparative gas chromatography from oil of copaiba balsam. Recrystallization of crude product from methanol yielded pure substance (620 mg., m.p. 64°).

Rearrangement of Caryophyllene Oxide to 4,10,10-Trimethyl-7-methylenebicyclo[6.2.0]decane-4-carboxaldehyde.—Caryophyllene oxide (500 mg., in a few drops of benzene) was injected repeatedly into a gas chromatographic column packed with Reoplex 400 (10%) deposited on acid-washed Chromosorb W. (column temperature 200°, helium flow 75 ml./min.). Effluents corresponding to the major peak observed were collected in small tubes packed with glass wool and moistened with carbon tetrachloride. The aldehyde obtained (280 mg.) possessed the following characteristics: $n^{25}D$ 1.499, d^{20}_{20} 0.993, retention time 8.4 min.

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.75; H, 10.97. Found: C, 81.4; H, 11.2.

Dihydrocaryophyllene Oxide (IV).—Caryophyllene oxide (I) (101 mg.) was dissolved in 5 ml. of ethanol and hydrogenated in the presence of Adams catalyst (8 mg.) at room temperature and atmospheric pressure (hydrogen uptake 13.6 ml., yield of crude dihydrocaryophyllene oxide 95 mg.).

4,7,10,10-Tetramethylbicyclo[6.2.0]decane-4-carboxaldehyde.

A. From Aldehyde (II).—The conversion was carried out in two steps.

Hydrogenation to Alcohol III. A sample (200 mg.) was hydrogenated in ethanolic solution in the presence of Adams catalyst (25 mg.) (volume of hydrogen absorbed 40 ml.). The product of hydrogenation (192 mg.), recovered after usual processing, displayed strong hydroxyl absorption at 3390 cm.$^{-1}$. Retention time on Reoplex 400 (10%) was 10.9 min. (temperature 200°; helium flow 75 ml./min.).

Oxidation of Alcohol III.—The alcohol (180 mg.) was dissolved in pyridine (2 ml.) and allowed to react overnight with a solution of chromium trioxide (180 mg.) in pyridine (4 ml.). The reaction mixture was diluted with water and extracted with ether. The ether extract was treated with dilute sulfuric acid and, after washing with water, dried over sodium sulfate. The crude aldehyde (130 mg.) obtained following evaporation of solvent was chromatographed over 6.5 g. grade II alumina, using petroleum ether and benzene as eluents. The sample recovered from the benzene fraction and purified by gas chromatography exhibited a retention time of 7.8 min. on Reoplex 400 (10%) (column temperature 200°, helium flow 75 ml./min.).

B. From Dihydrocaryophyllene Oxide.—Small samples (15 μl.) of dihydrocaryophyllene oxide (IV) were passed through the Reoplex column at 200° and the major component was collected for analysis. Gas chromatographic and infrared characteristics of the product obtained were identical with those of the sample prepared in accordance with method A. Hydrogenation of the aldehyde yielded the saturated alcohol III, its identity being established by infrared and gas chromatographic analysis.

2,5,5,9,9-Pentamethylbicyclo[6.2.0]decane (VI).—Boron trifluoride etherate (50 μl.) was added slowly to an ice-cooled mixture containing the saturated aldehyde V (10 mg.) and ethanedithiol (45 μl.). Glacial acetic acid was added drop by drop until a homogeneous solution was obtained. The reaction mixture was kept at room temperature for 1 hr., poured into an aqueous solution of potassium carbonate, and extracted with ether. The ether extract was washed repeatedly with 10% sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated. The residue was refluxed with 2 ml. of a suspension of Raney nickel overnight, the catalyst was filtered off, and the filtrate was diluted with 10 ml. of water and extracted with petroleum ether. The extract was dried over anhydrous sodium sulfate and evaporated. The residue (9 mg.) was analyzed by gas chromatography. Retention time of hydrocarbon relative to caryophyllane was 0.69 (column 10% silicone nitrile XE-60, temperature 130°, helium flow 75 ml./min.).

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The Isolation of Palustric Acid from Gum Rosin

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Palustric acid, one of the major components of rosin, was first isolated by Loeblich, *et al.*,[2] and its structure was established by Schuller, *et al.*[3]

This acid represents about 10% of the acidic portion of pine gum and up to 18% of the acidic portion of gum rosin. It is a homoannular, conjugated-diene resin acid, λ^{alc}_{max} 265–266 mμ (ε 3300), $[\alpha]D$ +71.8°, and m.p. 162–167°.

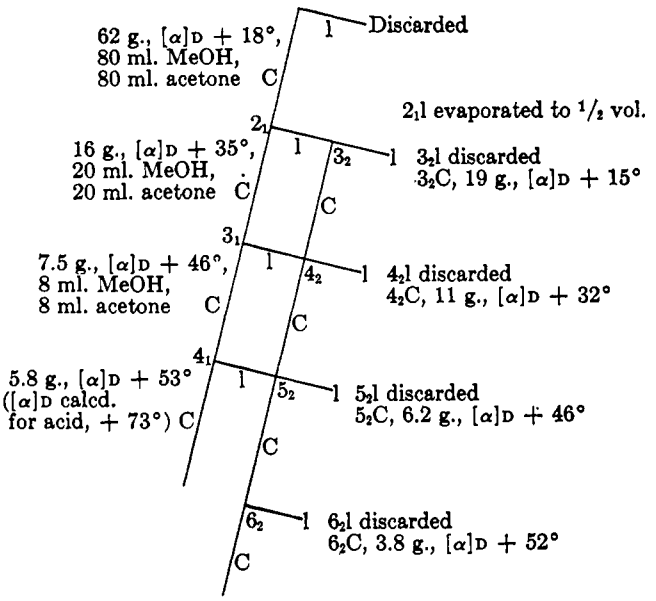
(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) V. M. Loeblich, D. E. Baldwin, and R. V. Lawrence, *J. Am. Chem. Soc.*, **77**, 2823 (1955).

(3) W. H. Schuller, R. N. Moore, and R. V. Lawrence, *ibid.*, **82**, 1743 (1960).

CHART I

Starting material: 200 g. of gum rosin + 600 ml. of acetone + 68 g. of 2,6-dimethylpiperidine



Palustric acid is an intermediate and a product of the thermal and acid isomerization of levopimaric[4,5] and neoabietic[6,7] acids. On thermal isomerization palustric acid yields an equilibrium mixture of abietic, neoabietic, and palustric acids.[8]

The only method available for the isolation of palustric acid has been by partition chromatography.[2] The method described in this paper is based on the precipitation of the 2,6-dimethylpiperidine salt of the resin acids from an acetone solution of pine oleoresin or rosin followed by selective crystallization of the salt from a methanol–acetone (1:1) solution. The yield of pure palustric acid from slash gum rosin was 4%. Gum rosin is preferable as a starting material since, as shown in Table I, abietic acid is coprecipitated along with palustric acid and gum rosin has a more favorable palustric acid to abietic acid ratio than either S.D. wood rosin or tall oil rosin.

TABLE I

COMPOSITION OF METHYL ESTER SAMPLES

	%[a] of each peak off g.l.c.				
Peak[b]	Gum rosin	Crude salt	Salt 2₁C	Salt 3₁C	Salt 4₁C
Me pimarate	6	2.0	..	..	..
Unidentified	2.8	..	..	..	..
Me elliotinoate	3.2	..	..	..	..
Me palustrate	20.4	47.3	76.9	83.7	96.7
Me isopimarate	21.2	5.4	..	..	..
Me abietate	33.6	37.2	22.0	16.3	3.3
Me neoabietate	12.8	8.1	1.4	..	..

[a] Per cent of the material that comes off the column at 225°, 5% Craig Polyester. [b] Each peak except 2 was identified by comparison with an authentic sample of the resin acid methyl ester.

(4) V. M. Loeblich, D. E. Baldwin, R. T. O'Connor, and R. V. Lawrence *J. Am. Chem. Soc.*, **77**, 2823 (1955).

(5) D. E. Baldwin, V. M. Loeblich, and R. V. Lawrence, *ibid.*, **78**, 2015 (1956).

(6) V. M. Loeblich and R. V. Lawrence, *ibid.*, **79**, 1497 (1957).

(7) D. E. Baldwin, V. M. Loeblich, and R. V. Lawrence, *J. Chem. Eng. Data*, **3**, 342 (1958).

(8) N. M. Joye, Jr., and R. V. Lawrence, *J. Org. Chem.*, **26**, 1024 (1961).

The composition of the starting rosin, the crude salt, and the salt at each step in the purification was determined by gas chromatography of the methyl esters. Table I shows the progress of the purification.

Experimental

Isolation of the 2,6-Dimethylpiperidine Salt of Palustric Acid from Gum Rosin.—WW gum rosin (200 g., acid no. 168) was dissolved in 600 ml. of acetone. To the rosin solution was added with stirring 68 g. of 2,6-dimethylpiperidine. The solution was allowed to stand at room temperature overnight and the precipitated salt was removed by filtration. The salt was removed from the filter and washed twice by slurrying with 200-ml. portions of warm acetone. The resulting white, crystalline amine salt was dissolved in an equal weight of hot methanol, filtered, and an equal volume of acetone was added. A modified scheme of triangular recrystallization diagrammed in Chart I was used.

Combination of fractions 4_1C and 6_2C gave 9.6 g. of salt with $[\alpha]^{25}D$ +52° (*c* 1.0, alcohol), λ_{max}^{alc} 265 mμ (ε 8300), and m.p. 156–162° (sealed evacuated tube). This weight of amine salt represents a 4% yield of palustric acid based on the acid number of the rosin.

Conversion of Amine Salt to the Acid.—A 10-g. portion of the amine salt was converted to the free acid by dissolving it in 350 ml. of 95% ethanol and adding, with stirring, 100 ml. of cold 3 *N* H_3PO_4. Ice–water was added to the cold acidified solution until no further cloud appeared. The precipitated acid was washed with water to remove excess mineral acid and recrystallized once from a minimum amount of hot 95% ethanol. Since palustric acid is isomerized to abietic acid by strong acids it should be separated from the acidified solution as rapidly as possible. The specific rotation of the final product was +69°,[9] while α at 265–266 mμ was 28.2, and m.p. 162–167°. Further recrystallizations showed no improvement in purity.

(9) The difference in the specific rotation of the free acid and that calculated for the acid from the salt is assumed to be caused by some resolution of the amine during recrystallization.

New Syntheses of Pyrrolo[2,3-*d*]- and Pyrrolo[3,2-*d*]pyrimidines[1]

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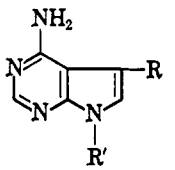
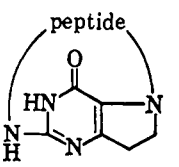
Interest in pyrrolopyrimidines has been greatly heightened as a result of the recent discovery that both the [2,3-*d*]- and [3,2-*d*-] systems occur as heterocyclic bases in a number of antibiotics. Tubercidin (**1a**) and Toyocamycin (**1b**) have been shown to be derivatives of 4-aminopyrrolo[2,3-*d*]pyrimidine,[2] and Viomycin (**2**) has recently been shown to possess a dihydropyrrolo-



1a, R = H; R' = β-D-ribose
b, R = CN; R' = D-ribose



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(2) For a recent discussion and literature references, see E. C. Taylor and R. W. Hendess, *J. Am. Chem. Soc.*, **86**, 951 (1964).