respectively. After all of the material had been added to the tube, a slow stream of nitrogen was passed through to sweep out any remaining olefins and water. A total of 17.6 g. (88%) of material was collected. The remainder of the products remained on the alumina as a black deposit. The organic material was taken up in ether and dried over anhydrous copper sulfate. Distillation yielded 15.2 g. (84%) of olefins, b.p. 40–43° (0.2 mm.), n_D^{25} 1.4955.

Dehydration with sulfuric acid. A solution of 5.00 g. (0.027 mole) of 7-hydroxyspiro[5.6]dodecane and 1 drop of concentrated sulfuric acid was heated to 100°, at which point the olefins and water distilled. The distillate was taken up in ether and dried over anhydrous copper sulfate. The ether and then the olefins were distilled to yield 4.13 g. (92%) of product, b.p. 50–60° (0.5 mm.), n_D^{25} 1.4948.

The nitroso chloride[3] was prepared and crystallized as pale blue crystals, but three recrystallizations from large volumes of acetone yielded only white needles, m.p. 141.5–142.5°. A mixed melting point taken with a sample of the nitroso chloride of cyclohexylcyclohexene, prepared by the method of Signaigo and Cramer,[9] was not depressed.

Dehydration with zinc chloride. A mixture of 5.00 g. (0.037 mole) of freshly fused zinc chloride and 5.00 g. (0.027 mole) of 7-hydroxyspiro[5.6]dodecane was heated at 135° for 1 hr. at 130 mm. pressure. The resulting paste was treated with 5 ml. of water and extracted three times with ether. The combined extracts were dried over anhydrous copper sulfate and distilled to yield 4.20 g. (93%) of olefin product, b.p. 78–80° (1 mm.), n_D^{25} 1.4942.

Dehydration with boron trifluoride etherate. A solution of 5.00 g. (0.027 mole) of 7-hydroxyspiro[5.6]dodecane and 10 ml. of boron trifluoride etherate was stirred at room temperature for 4.5 hr. The reaction mixture was treated with 50 ml. of water and the yellow upper layer was separated. The aqueous layer was extracted three times with hexane and the combined material was washed with dilute bicarbonate solution and dried over anhydrous copper sulfate. Distillation yielded 1.20 g. (25.2%) of unchanged spiranol and 3.00 g. (90%, based on spiranol actually dehydrated) of olefins, b.p. 70–80° (1 mm.), n_D^{25} 1.4941.

Analyses. All olefin analyses were made in an Aerograph instrument[14] at 150° using a helium flow rate of 90 ml./min. The column consisted of a 12-foot length of 0.25-inch o.d. copper tubing packed with 30% 1,2,3-tris(β-cyanoethoxy)-propane[15] on 30–60 mesh firebrick. This absorbent, suggested by Anderson,[8] had excellent selectivity for these olefin mixtures.

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[14] Obtained from Wilkens Instrument and Research, Inc., Berkeley, Calif.

[15] H. A. Bruson and T. W. Reiner, *J. Am. Chem. Soc.*, **65**, 27 (1943); H. A. Bruson, U. S. Patent **2,401,607** (*Chem. Abstr.*, **40**, 5450 (1946)).

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

The Thermal Isomerization of Palustric Acid

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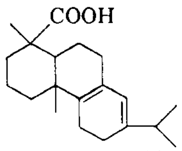
The thermal isomerization of palustric acid was studied at 170 and 200°. Spectrographic and chromatographic examination of the isomerizates showed that abietic and neoabietic acid accounted for all of the detectable products. The formation of abietic acid was favored in this isomerization over the formation of neoabietic acid. The isomerization was found to be a first-order reaction with respect to the palustric acid. Palustric acid was shown to be more stable to heat than levopimaric acid and less stable than neoabietic acid. Methyl palustrate underwent only a slight change on prolonged heating at 200°.

A series of thermal and acid isomerizations was started in this Laboratory on the abietic-type acids in oleoresin and rosin—namely, levopimaric acid,[2,3] neoabietic acid,[4] and palustric acid. Palustric acid, the most recently isolated acid, is one of the major constituents of pine oleoresin and rosin[5]. The structure of this acid was recently established by Schuller, *et al.*[6]:



Palustric acid

This paper describes a study of the thermal isomerization of pure palustric acid at 170 and 200°. Samples of palustric acid were heated in sealed evacuated tubes over a period of twenty-four hours and the progress of the isomerization followed by obtaining the specific rotation, ultraviolet absorption spectrum and chromatographic analysis of each sample. At both temperatures the isomerization product seemed to approach an equilibrium mixture of approximately 13% palustric acid, 80% abietic acid, and 7% neoabietic acid. Palustric acid has a half-life of about four hours at 170°.

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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.

[2] V. M. Loeblich, D. E. Baldwin, R. T. O'Connor, and R. V. Lawrence, *J. Am. Chem. Soc.*, **77**, 6311 (1955).

[3] D. E. Baldwin, V. M. Loeblich, and R. V. Lawrence, *J. Am. Chem. Soc.*, **78**, 2015 (1956).

[4] V. M. Loeblich and R. V. Lawrence, *J. Am. Chem.*, **79**, 1497 (1957).

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

[6] W. H. Schuller, R. N. Moore, and R. V. Lawrence, *J. Am. Chem. Soc.*, **82**, 1734 (1960).

TABLE I

SUMMARY OF DATA ON THE THERMAL ISOMERIZATION OF PALUSTRIC ACID AT 170°

Time, Hr.	$[\alpha]_D$, 2% C_2H_5OH	α at 241 mμ	Palustric, %	Abietic, %	Neoabietic, %	Calcd., $[\alpha]_D$	Calcd., α at 241 mμ
0	+71		99+				
.50	+51	19	86	11	2	+53	21
1	+43	21	78	18	2	+40	25
2	+23	30	[a]				
4	−13	41	48	49	5	−9	47
8	−32	53	31	63	6	−34	57
24	−65	68	13	80	7	−63	67

[a] Sample lost on a poor chromatographic column.

In comparing the isomerization of palustric acid with those of levopimaric acid[2] and neoabietic acid,[4] these observations were made. (1) Palustric acid is more stable to heat than levopimaric acid and less stable to heat than neoabietic acid. After thirty minutes at 200° levopimaric acid was completely isomerized to other acids. Under the same conditions about half of the palustric acid and only 16% of the neoabietic acid was isomerized.

	Time, Hr.	Palustric, %	Abietic, %	Neoabietic, %
Levopimaric acid[2,3]	1/2	34	52	14
Neoabietic acid[4]	1/2	5	11	84
Palustric acid	1/2	54	42	4

(2) The logarithm of the concentration of palustric acid plotted against the time gives a straight line characteristic of first-order reactions. Levopimaric acid also gave a first-order reaction but neoabietic acid does not give a reaction curve characteristic of first- or second-order reactions. This is probably due to a back-reaction in the neoabietic acid isomerization with more neoabietic acid being formed from the original isomerization product, palustric acid. This back-reaction results in a progressive retardation of the reaction rate causing the reaction to fail to exhibit overall first-order kinetics. The same back-reaction effect probably occurs in the palustric acid isomerization from the neoabietic acid formed; however, the isomerization of the neoabietic acid to palustric acid is too slow to have any significant effect on the overall rate.

Thermodynamically heterannular dienes are more stable than homoannular dienes; therefore, palustric acid would be expected to form neoabietic acid more readily than neoabietic acid would form palustric acid.

The rate of isomerization of palustric acid at 200° was found to be approximately eight times as fast as the isomerization at 170°. Chromatographic analysis of the products of the isomerization at 170 and 200° showed that the composition of the eight-hour and the one-hour samples were essentially the same.

Temp.	Time, Hr.	Palustric, %	Abietic, %	Neoabietic, %
170	8	31	63	6
200	1	34	61	6

The isomerization products were shown to consist of abietic acid, neoabietic acid, and palustric acid. The peaks from the chromatographic analysis were checked by ultraviolet absorption analysis and showed only the presence of the three suspected acids. No levopimaric acid was detected in any of the isomerization products. The ultraviolet absorption spectrum and the specific rotation gave no indication that levopimaric acid was present in any of the products.

The rate of isomerization of methyl palustrate was also measured by change in specific rotation and specific extinction coefficient. The ester showed marked stability to heat like methyl neoabietate[4] and methyl levopimarate.[2] It was estimated from the specific rotations that the rate of isomerization of the acid was about 2,000 times as fast as that of the ester.

EXPERIMENTAL

The palustric acid used for the thermal isomerization studies was prepared by the method of Loeblich, Baldwin, and Lawrence.[5] It had an $[\alpha]_D$ +71° (2% in ethanol, m.p. 162–167°), and was shown by chromatographic and ultraviolet absorption analysis to contain more than 99% palustric acid.

One-tenth gram samples of palustric acid were placed in glass tubes and the air replaced with nitrogen by thorough flushing and repeated evacuation. The tubes were sealed off under high vacuum and heated in an oil bath for specified lengths of time.

Analysis of the 170° thermally isomerized palustric acid. The data obtained on each sample included the specific rotation, ultraviolet absorption analysis and chromatographic analysis. The chromatographic procedure and the values used to calculate the specific rotations and specific extinction coefficients are described by Loeblich, Baldwin, O'Connor, and Lawrence.[2] A summary of the data on the thermal isomerization of palustric acid at 170° is given in Table I.

TABLE II

SUMMARY OF DATA ON THE THERMAL ISOMERIZATION OF PALUSTRIC ACID AT 200°

Time (Hr.)	$[\alpha]_D$ 2% C_2H_5OH	α at 241 mμ	Palustric, %	Abietic, %	Neoabietic, %	Calcd. $[\alpha]_D$	Calcd. α at 241 mμ
0	+71		99+				
0.25	+19	27	72	27	2	+26	31
0.50	−3	37	54	42	4	0	42
0.75	−26	45	40	54	6	−21	51
1	−35	51	34	61	6	−31	56
1.5	−48	56	26	67	6	−42	60
2	−53	61	19	72	7	−51	63
4	−63	62	15	77	7	−59	66
8	−68	68	11	80	7	−66	68

The identity of the palustric, abietic and neoabietic acids was confirmed by checking the ultraviolet absorption spectrum of the peaks from a chromatographic analysis.

Thermal isomerization of palustric acid at 200°. The isomerization of palustric acid at 200° was observed by the same method as at 170°. A summary of the data on the thermal isomerization of palustric acid at 200° is given in Table II.

Thermal isomerization of methyl palustrate at 200°. Methyl palustrate was prepared by treating an ether solution of palustric acid with an excess of an ether solution of diazomethane. The solution was extracted with dilute alkali, washed neutral with water and the ether removed by distillation. The ester crystallized from methanol, m.p. 24–27°, $[\alpha]_D$ + 67.0°, α 26.5 at 265–266 mμ. The ester was sealed in an evacuated tube and after heating at 200° for 72 hr. had the following constants; $[\alpha]_D$ + 62.9°, α 22.4 at 265–266 mμ.

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Hydrogenolysis of Ketals

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Hydrogenolysis of ketals in the presence of acid and rhodium or palladium yields ethers and alcohols. Ketals of secondary alcohols react faster than those of primary alcohols. A mechanism is suggested.

The literature contains several references to the hydrogenolysis of aldehyde acetals to ethers and alcohols, usually under conditions of rather high temperature and pressure.[1] Hydrogenolysis of aldehyde and ketone acetals to hydrocarbons has also been reported,[2] but in each of these cases the —$C(OR)_2$— group was a substituent on an aromatic nucleus. By hydrogenation Gorin[3] opened the ring of some cyclic ketals of sugars and obtained ether derivatives of the sugars. Bond scission occurred at the oxygen attached to the secondary carbon atoms of the sugars, indicating that secondary alkoxyl groups are more labile than primary ones in this reaction. Staff[1] stated that ketals could be hydrogenated to ethers and alcohols but gave no experimental data.

We have found that hydrogenation of acidified ketals gives high yields of saturated ethers and alcohols under mild conditions (Reaction 1). The reaction

$$R_2C(OR')_2 + H_2 \xrightarrow{H^+,\ Rh} R_2CHOR' + R'OH \quad (1)$$

has been demonstrated with the dimethyl, dibutyl, diisopropyl, and dicyclohexyl ketals of acetone and with cyclohexanone diisopropyl ketal. With ketals of secondary alcohols the hydrogenation proceeds rapidly to completion at room temperature, and with ketals of primary alcohols appreciable rates are obtained at 50 to 80°. Yields of isolated products, based on conversions calculated from the hydrogen uptake, ranged from 70% to nearly 100%. Recovery of starting materials, absence of by-products, and infrared analyses indicate that actual yields were approximately quantitative.

Tests of several platinum metal catalysts for the hydrogenation of isopropenyl methyl ether showed rhodium the most active. Platinum and ruthenium were almost inactive, and palladium was about half as active as rhodium. As these metals had the same

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