levorotatory, natural isomeride. Their identity, save for the steric arrangement around 5-C, is further supported by their nearly coinciding infra-red spectra.

More recently, the synthesis of both isomerides of (I) from the enantiomeric 2-amino-1-phenylethanols [7] has been accomplished in this laboratory. Upon critical comparison, the synthetic, levorotatory enantiomorph proved identical with the specimen of natural origin.

The synthesis of levorotatory (I) from (−)-2-amino-1-phenylethanol further establishes its absolute configuration, and hence that of the mustard oil derivable from glucobarbarin, because the (−)-amine results from a series of reactions not involving inversions and starting with (−)-mandelic acid [7] whose relationship with (+)-glyceraldehyde has been established by several investigators (*cf.* Ref.[8]). Consequently, the heterocyclic enantiomorph of natural provenance should be depicted as (I), yet with the bonds to the hydrogen atom and phenyl grouping in 5-position projecting above and below the plane of the paper, respectively.

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Infrared Investigation of the Location of the Ethylenic Bonds in the Newly Discovered Palustric Acid

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Recently Loeblich, Baldwin and Lawrence [1,2] isolated a new acid, which they named palustric acid, from the oleoresin of *Pinus palustris* and *Pinus caribaea* by means of partition chromatography. Palustric acid is a primary acid of the abietic type which these authors also isolated as an intermediate product in the acid and heat isomerization of levopimaric acid to abietic acid. This new member of the abietic series is interesting from the standpoint of rosin acid chemistry and may be of value for the elucidation of the conversion of rosin acids into one another.

Palustric acid is reported to contain two conjugated double bonds which according to the location of the maximum in the ultraviolet spectrum appear to be situated between carbon atoms 5—6 and 7—8 (Fig. 1). On the other hand, the close relationship between palustric and *l*-abietic acid shown by the heat isomerization of levoabietic suggests a structure for palustric acid in which the double bonds are located between carbon atoms 7—8 and 13—14 [1,2].

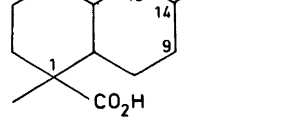

Fig. 1.

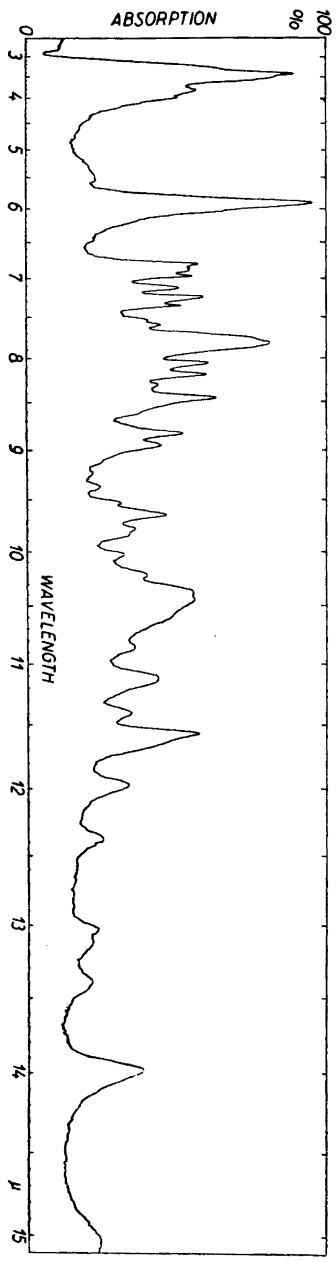

Fig. 2. Infrared absorption spectrum of palustric acid.

The infrared absorption spectrum of the acid could be expected to permit a decision as to the actual locations of the double bonds. Their locations between carbon atoms 5—6 and 7—8 would imply that both would absorb in the infrared range since the bonds would be di- and trisubstituted ethylenic bonds with properties similar to those of the double bonds in *l*-abietic, levopimaric and neoabietic acids, while with the alternative locations between carbon atoms 7—8 and 13—14, only the former double bond would be expected to give rise to infrared absorption bands resembling those of the trisubstituted ethylenic bond in a dihydroabietic acid.

The infrared absorption spectrum of palustric acid is reproduced in Fig. 2. A comparison of this spectrum with the spectra for the other resin acids mentioned above (*l*-abietic acid [3], levopimaric acid [4], dihydroabietic acid [5,3]) * shows that the former spectrum most closely resembles the spectrum of dihydroabietic acid. The following interpretation of bands is presented which confirms that the second alternative, *i. e.* double bonds between carbon atoms 7—8 and 13—14, is the most probable one.

The C=C stretching vibration gives rise to a sharp peak at 6.15—6.17 μ in the spectra of abietic, levopimaric and neoabietic acid, while in the spectra for dihydroabietic and palustric acids there is no peak or possibly only very indistinct shoulder at 6.04 μ. The =C—H out-of-plane vibration gives rise to a sharp absorption band at 12.65 μ in the abietic acid spectrum and at 12.62 μ in the levopimaric acid spectrum. In the spectra of dihydroabietic, neoabietic and palustric acid which, in contrast to the preceding acids, have only one bond of this type (assuming palustric acid to have its double bonds at 7—8 and 13—14), weak bands are seen at 12.48, 12.50 and 12.38 μ, respectively.

Levopimaric and neoabietic acids have in their spectra a band at 14.35 and 14.42 μ, respectively, that is possibly due to the vibration of the ethylenic bond. No bands of this kind are seen in the spectra for dihydroabietic and palustric acids. If the first alternative for the location of the

* The spectrum of neoabietic acid in the solid state differs in several respects from the spectra of the other resin acids, evidently owing to intramolecular transformation and shows a double peak due to the carbonyl group (at 5.93 and 5.80 μ) and a band due to polymer associated OH (at 3.12 μ[4]).

double bonds were correct for palustric acid, one would expect to find bands due to the *cis*-disubstituted double bond between atoms 5 and 6 in its spectrum.

Experimental. The palustric acid employed in the study was kindly sent to the author by E. L. Patton, Head of the Naval Stores Research Section, Naval Stores Section, The United States Department of Agriculture.

The absorption spectrum was recorded with an automatic double-beam spectrophotometer of the type described by Hornig, Hyde and Adcock [6]. The sample was examined using the potassium bromide technique. For further informations, see Ref.[3].

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The Formation of Anhydro Vitamin A_1 in the Study of Vitamin A_1 Isomers

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As described by Edisbury *et al.*[1] and later by Meunier *et al.*[2] and Schantz *et al.*[3] the action of an anhydrous (N/30) ethanolic solution of hydrogen chloride on vitamin A_1 results in the conversion of the vitamin into the hydrocarbon anhydro vitamin A_1. Robeson and Baxter [4] have shown that the two isomers 13-*cis* and all-*trans* vitamin A_1 form the same substance when treated with hydrogen chloride in ethanol, but the rate of reaction (in 0.02 N ethanolic hydrogen chloride) is not the same in the two cases.

During recent years a number of new vitamin A_1 isomers [5-7] have been added to those already known, and when faced with the problem of identifying the individual components — isolated for instance by chromatography — of a mixture of vitamin A_1 isomers, it will be natural, side by side with other identification tests, to utilize the process of anhydro vitamin A_1 formation. The aim of the present work has been to develop a convenient procedure for the formation of anhydro vitamin with a view to the utilisation of this reaction for purposes of identification.

It is possible to follow the course of the reaction by spectrophotometry of the reaction mixture, since the formation of anhydro vitamin A_1 causes an increase in the extinction at wavelengths above approx. 340 mμ. Maximum increase is observed at wavelengths of approx. 350, 368.5 and 390 mμ, *i. e.* very near the three maxima of anhydro vitamin A_1 — 351, 371, 392 mμ[3]. Under the action of the hydrogen chloride solution the process continues, and anhydro vitamin A_1 is converted into *iso*anhydro vitamin A_1 (maxima at approx. 330, 350 and 370 mμ [3,8,9]), causing the maximum at 390 mμ to disappear again. The value of E_{390} measured for the reaction mixture thus does not only comprise the extinction due to the anhydro vitamin A_1, but also the extinction of unconverted vitamin A_1 and *iso*-anhydro vitamin A_1. However, the maximum value of E_{390} will almost exclusively be due to anhydro vitamin A_1.

For the purpose of following the process of anhydro vitamin formation the following two magnitudes may be used: (1) the maximum value of the ratio $E_{390} / E°_{max.}$ and (2) the corresponding time $t_{max.\ anh.}$ In the ratio $E_{390} / E°_{max.}$ is E_{390} the extinction (cell length 1 cm) of the reaction mixture at 390 mμ. $E°_{max.}$ is the extinction (cell length 1 cm) of the reaction mixture being due to vitamin A_1 at zero time, *i. e.* at the moment when the vitamin A_1 solution and the hydrogen chloride solution are mixed. $E°_{max.}$ is not measured directly, but is calculated from the value of $E_{max.}$ already measured for the vitamin A_1 solution. The value of these two magnitudes, $E_{390} / E°_{max.}$ and $t_{max.\ anh.}$ have been determined for all-