221°. Admixture with 5,6-methylenedioxy-*o*-toluic acid failed to depress the melting point.

The combined acid washings of the ether solution mentioned above were basified with a large excess of 50% sodium hydroxide and the precipitated base extracted with several portions of ether. The residue from the combined extracts was rapidly distilled *in vacuo*. The fraction distilling up to 200° (1 mm.) was collected and redistilled when the bulk boiled at 175–180° (1 mm.) (0.724 g.). This was dissolved in dry ether (10 cc.) containing a few drops of methanol and methyl iodide (1 cc.) was added to the solution. The methiodide which began to separate immediately, crystallized on rubbing, m. p. 225° (1.05 g.). After one recrystallization from methanol–ether, however, the melting point was 208–209°. The crystalline forms of the two products were different. The high-melting form crystallized in small prisms whereas the low-melting form separated as long prismatic needles. A mixture of the high-melting form with the corresponding cryptopine compound melted at 219° but admixture of the latter with the low-melting form did not affect the melting point. Calcd. for $C_{14}H_{22}O_3NI$: C, 44.33; H, 5.80. Found: C, 44.64, 44.82; H, 5.76, 5.70.

Some of the methiodide (m. p. 225°) was dissolved in acetone containing a trace of potassium hydroxide and the solution allowed to stand several days. The yellow crystalline precipitate which had been deposited was recrystallized from boiling methanol. It melted at 253° either alone or in admixture with the corresponding product obtained in the cryptopine degradation.

Summary

The alkaloid cryptocavine has been found to be isomeric with cryptopine. The oxidative degradation of both alkaloids by the classical method of Perkin gave rise to identical products. It is concluded that the —CH_2CO— grouping of cryptopine is probably reversed in cryptocavine, for which a constitutional formula is suggested.

OTTAWA, CANADA RECEIVED JUNE 7, 1940

[CONTRIBUTION FROM THE NAVAL STORES RESEARCH DIVISION, BUREAU OF AGRICULTURAL CHEMISTRY AND ENGINEERING, U. S. DEPARTMENT OF AGRICULTURE]

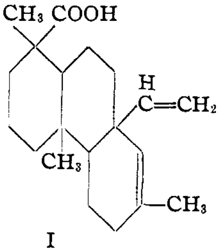
A Hydroxy-lactone from *d*-Pimaric Acid[1]

BY ELMER E. FLECK[2] AND S. PALKIN[3]

It recently has been shown[4] that concentrated sulfuric acid, at −5 to −10°, converted *d*-pimaric acid into a mixture of approximately equal parts of a non-crystalline acid and neutral substance. It has now been found that when the temperature of the sulfuric acid, in this procedure, was held at −20 to −30°, a crystalline hydroxy-lactone was obtained in 25 to 30% yields. This lactone, $C_{20}H_{32}O_3$, melted at 181–182°, $[\alpha]^{20}D$ −4°; it could be distilled unchanged at 1 mm. and it contained one active hydrogen atom. It was not found possible to prepare either the acetate or the benzoate of the indicated hydroxyl group. The tetranitromethane test showed the compound to be completely saturated.

As in the case of lactonized dihydroabietic acid[5] the lactone was only partially saponified by dilute alcoholic sodium hydroxide but was easily opened with *n*-butyl alcoholic potassium hydroxide. The free acid melted at 150–151° and contained water of crystallization. Diazomethane yielded the methyl ester, $C_{21}H_{36}O_4$, of melting point 156–157°.

Ruzicka and Sternbach[6] have recently advanced formula I for *d*-pimaric acid.



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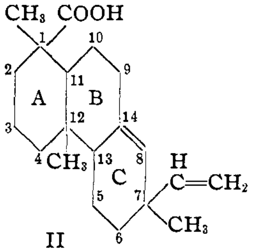

II

On the basis of this formula the point of lactonization of *d*-pimaric acid would have to be on the ethylenic side chain at C-14. This would mean the formation of an 8 or 9 membered lactone.

They also suggested formula II as a possibility wherein the double bond in ring C may be located between any of the 6, 5, 13, 14 and 8 positions. These authors regarded formula II as improbable, however, in view of the fact that only 1,7-dimethylphenanthrene and no 1-methyl-7-ethylphenanthrene could be isolated as dehydrogenation products. However, since the isolation of pure hydrocarbons from dehydrogenation

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(1) Not subject to copyright.

(2) Associate chemist.

(3) Senior chemist.

(4) Fleck and Palkin, THIS JOURNAL, **61**, 1230 (1939).

(5) Fleck and Palkin, *ibid.*, **60**, 2621 (1938).

(6) Ruzicka and Sternbach, *Helv. Chim. Acta*, **23**, 124 (1940).

mixtures is very difficult, and since the per cent. of pure hydrocarbon obtained is very small, the possibility that some 1-methyl-7-ethylphenanthrene may also have been formed, but in amounts too small for isolation, is not excluded and hence formula II cannot finally be eliminated on this basis.

The similar stability of the lactone to that of lactonized dihydroabietic acid would suggest lactonization at C-13. The necessary shift of a double bond to the 13,14 position is, however, blocked by the lack of a hydrogen atom at C-14 in formula I. This shift becomes possible with formula II in which the double bond in ring C is located in the 8,14 position. Under the influence of the acid the double bond would shift to the bridgehead position, 13,14, which is favorable to lactonization of the carboxyl group on the C-13 carbon atom.[7]

A double bond in the 8,14 position in formula II would explain the reaction products of Ruzicka and Sternbach just as well as the 7,8 position advocated in formula I. Thus, the oxide would be formed between the 8,14 position and methylmagnesium iodide would introduce the methyl group at C-8. Dehydrogenation, then, would produce the 1,7,8-trimethylphenanthrene which they have identified.

The ease with which strong acid lactonizes dihydroabietic and dihydro-*l*-pimaric acids and the relative insolubility of the resulting lactone in methyl alcohol provide a useful diagnostic test for the presence of these acids.[7] By this means about 5% of dihydro acid was shown to be present in *d*-pimaric acid which had been purified by way of the sodium salt.[8]

Also, the presence in "purified" *d*-pimaric acid of residual traces of *l*-pimaric acid was shown by the isolation of the *l*-abietic acid "quarter salt" from the acid portion remaining after the lactonization treatment with sulfuric acid.[9] The *l*-pimaric acid originally present was isomerized to *l*-abietic acid by this treatment.[4] However, purification of *d*-pimaric acid, by treatment with maleic anhydride for removal of any traces of *l*-pimaric acid,[10] and further purification by fractional recrystallization of the diethylamine salt led to a final acid with no higher melting point and with but a slight increase in specific rotation. Dextro-pimaric acid so purified still showed the presence of dihydro acid by the lactonization test. No *l*-abietic acid could be detected.

It is therefore doubtful that any *d*-pimaric acid has thus far been obtained from *P. palustris* or *P. caribaea* rosin or resin acids that would not contain some dihydro acid. This probably accounts for the variation in the melting point and specific rotation of *d*-pimaric acid as reported by many workers.[8]

The action of concentrated sulfuric acid on *d*-pimaric acid was found to give a fairly constant 50–50 mixture of acid and neutral material over a relatively wide range of sulfonation conditions. The explanation for this is obscure but the relatively constant proportion of acid and neutral material affords a method for the approximation of the maximum amount of *d*-pimaric acid present in rosin and resin acid mixtures.

As was shown earlier,[4] when such mixtures, freed from all neutral material, are sulfonated a neutral fraction is obtained. From this neutral fraction lactonized dihydroabietic acid was easily isolated due to its insolubility in methyl alcohol. By assuming the remaining neutral material to be due to *d*-pimaric acid it becomes possible to calculate the maximum amount of *d*-pimaric acid present in the original acid mixture. Calculations based on such experiments[4] show the presence of a maximum of 10% *d*-pimaric acid in *P. palustris* oleoresin and rosin and a maximum of 14% in *P. caribaea* oleoresin and rosin. Synthetic mixtures of *d*-pimaric acid and *l*-pimaric acid were analyzed by this method. The results are somewhat high but are accurate within 5 to 10%.

The semi-micro carbon and hydrogen determinations were made by S. A. Hall.

Experimental Part

Hydroxy-lactone $C_{20}H_{32}O_3$ (Obtained by Sulfonation at −20 to −30°).—Ten cc. of concentrated sulfuric acid (1.84), in a short, wide test-tube, was frozen solid in an acetone–dry-ice-bath. To this was added 2 g. of powdered *d*-pimaric acid and cooling was continued for several minutes. The sulfuric acid was then allowed to warm up to the melting point and the *d*-pimaric acid was stirred in. Stirring and intermittent cooling were continued for fifteen minutes with the temperature of the reaction mass maintained between −20 and −30°. A light yellow solution resulted. Crushed ice was stirred into the sulfonation mass until the product separated as a white precipitate. The temperature was kept as low as possible during

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[7] Fleck and Palkin, THIS JOURNAL, **61**, 3197 (1939).

[8] Palkin and Harris, *ibid.*, **55**, 3677 (1933).

[9] The presence of *l*-pimaric acid in *d*-pimaric acid has also been indicated by unpublished results of absorption spectra measurements made by Dr. B. A. Brice.

[10] Bacon and Ruzicka, *Chemistry and Industry*, **55**, 546 (1936); Wienhaus and Sandermann, *Ber.*, **69**, 2202 (1936).

this operation without freezing the mixture. This precipitate was poured into 100 cc. of ice and water and, after standing for fifteen to twenty minutes, was filtered and washed with water. The filter cake was dissolved in ether and washed twice with 15 cc. of water, then 0.25 *N* sodium hydroxide, and finally with water. When the ether was distilled on the steam-bath, 1.0 g. of neutral residue was obtained that crystallized on standing.

Acidification of the alkaline extracts yielded 1.0 g. of non-crystalline acid.

The crystalline neutral residue was boiled with 25 cc. of hexane, and the mixture was cooled and filtered. The undissolved portion, dried in vacuum at room temperature, weighed 0.55 g. and its melting point was 170–173°. The product was recrystallized to constant melting point from 1 part of hot acetone by addition of 3 parts of hexane. The lactone separated as prisms that melted at 181–182°. It was readily soluble in methyl alcohol and in acetone and very insoluble in hexane. A solution in tetranitromethane gave no yellow color: $[\alpha]^{20}\mathrm{D}$ $-4°$ (1% absolute alcohol). *Anal.* Calcd. for $C_{20}H_{32}O_3$: C, 74.94; H, 10.07; mol. wt., 320.45. Found: C, 74.93, 74.96; H, 10.23, 10.19; mol. wt., 321 (Rast). Direct titration of the lactone in alcohol showed no free acidity. Saponification with 0.1 *N* sodium hydroxide in alcoholic solution for four hours at reflux temperature: calcd., 0.477 cc. Found: 0.21 cc. The Zerewitinoff test showed 5.57% OH; calcd. for $C_{20}H_{32}O_3$, 5.31%.

A small amount of the lactone was distilled at 1 mm. from a bath heated between 200–250°. There was no decomposition and the distillate crystallized at once on cooling; melting point, 181–182°. *Anal.* Found: C, 74.86; H, 10.23.

Saponification of the Lactone, $C_{20}H_{32}O_3$.—The lactone, $C_{20}H_{32}O_3$, was saponified with 10% potassium hydroxide.[5] The free acid that separated as needles was filtered and washed with water. This product was dissolved in 200 cc. of ether and the ether solution was shaken several times with water. The ether was then distilled until the volume of the residue was about 15 cc. The crystals that separated were filtered and washed with ether. The product was recrystallized from hot methyl alcohol by the addition of water. The crystals melted at 150–151° when dried in vacuum at room temperature. A solution in tetranitromethane showed no yellow color. *Anal.* Calcd. for $3C_{20}H_{34}O_4{\cdot}2H_2O$: C, 68.54; H, 10.16. Found: C, 68.71, 68.59; H, 10.05, 10.18. When the acid was dried in vacuum at 100°: Calcd. for $C_{20}H_{34}O_4$: C, 70.95; H, 10.13. Found: C, 71.78, 71.58; H, 10.20, 10.18. Direct titration of the hydrate in alcohol showed 16.12 mg. substance required 0.540 cc. of 0.1 *N* sodium hydroxide. Calcd. for one equivalent, 0.462 cc.

Methyl Ester of the Acid, $C_{20}H_{34}O_4$.—The methyl ester of the acid $C_{20}H_{34}O_4$ was prepared in the usual manner by esterification with diazomethane and then recrystallized from hot methyl alcohol by addition of water. The resulting needles melted at 156–157° when dried in vacuum at 100°. *Anal.* Calcd. for $C_{21}H_{36}O_4$: C, 71.53; H, 10.30; OCH_3, 8.80. Found: C, 71.14, 71.62; H, 10.48, 10.30; OCH_3, 8.98.

Presence of Dihydro Acid and *l*-Pimaric Acid in *d*-Pimaric Acid Purified by Way of Sodium Salt (Sulfonation of *d*-Pimaric Acid at −5 to −10°).—Four grams of powdered *d*-pimaric acid[8] (melting point 218–220°) was sulfonated at −5 to −10° for forty-five minutes and then worked up as outlined previously.[4] The sulfuric acid solution acquired a reddish cast. By this procedure 2 g. of neutral and 2 g. of acid material were obtained.

The neutral material yielded 0.2 g. of prisms from alcohol. After several recrystallizations from alcohol the product melted at 130–131° and showed no lowering of melting point when mixed with lactonized dihydroabietic acid. *Anal.* Calcd. for $C_{20}H_{32}O_2$: C, 78.88; H, 10.60. Found: C, 79.14; H, 10.73.

For final identification the free acid was prepared by saponification of the lactone with *n*-butyl alcoholic potassium hydroxide.[5] The resulting acid melted at 163–164° with effervescence and then remelted at 125–127°. The melting point of the acid was not lowered when mixed with tetrahydrohydroxyabietic acid. *Anal.* Calcd. for $C_{20}H_{34}O_3$: C, 74.47; H, 10.63. Found: C, 74.28; H, 10.64.

The acid portion obtained from the original sulfonation was distilled at 1 mm.: fraction I, b. p. 170–185°, 0.55 g., $[\alpha]^{20}\mathrm{D}$ $-32°$ (2% absolute alcohol); fraction II, b. p. 185–200°, 0.5 g., $[\alpha]^{20}\mathrm{D}$ $-32°$ (2% absolute alcohol). One-fourth of fraction II was dissolved in 1 cc. of alcohol and titrated with 5% sodium hydroxide. The remainder of the fraction was added and solution effected by warming on the steam-bath. A small amount of needles, characteristic of the acid sodium salt ($C_{19}H_{29}COONa{\cdot}3C_{20}H_{30}O_2$), separated and was recrystallized from alcohol. The free acid was obtained as triangular crystals characteristic of *l*-abietic acid. The melting point was 160–164° and no lowering was observed when mixed with authentic *l*-abietic acid. Under the conditions of the sulfonation experiment any *l*-pimaric acid present in the original *d*-pimaric acid preparation would be isomerized to *l*-abietic acid.[4]

No crystalline material could be obtained from fraction I by the same procedure.

When *d*-pimaric acid, purified with maleic anhydride, was used in the sulfonation, no *l*-abietic acid or partial salt could be isolated. The lactonized dihydroabietic acid, however, was isolated.

Sulfonation of *d*-Pimaric Acid at 25 to 30°.—One gram of *d*-pimaric acid was sulfonated for fifteen minutes, as outlined above, at 25 to 30°. The sulfuric acid solution was cherry red in color. The resulting product yielded 0.55 g. of neutral material and 0.45 g. of acid material. Neither fraction could be crystallized.

Determination of *d*-Pimaric Acid in Mixtures with *l*-Pimaric Acid.—Mixtures of 25 and 50% *d*-pimaric acid with *l*-pimaric acid were sulfonated at −5 to −10° as outlined above and reaction products were separated into acid and neutral portions and finally dried in vacuum at 100°. In one instance 1.90 g. of a mixture containing 25% *d*-pimaric acid yielded 0.27 g. of neutral and 1.60 g. of acid product. Assuming that the yield of neutral substance represents half of the *d*-pimaric acid, the % *d*-pimaric acid = (2 × 0.27)/1.90 = 28%. Similarly, 0.93 g. of a mixture containing 50% *d*-pimaric acid yielded 0.26 g. neutral and 0.63 g. acid product: the % *d*-pimaric acid = (2 × 0.26)/0.93 = 55%.

Purification of *d*-Pimaric Acid.—A solution of 11 g. of *d*-pimaric acid[8] (melting point 218–220°) and 5 g. of freshly distilled maleic anhydride in 100 cc. of xylene was refluxed for five hours. The solution was allowed to stand at room temperature overnight and the crystals that separated were filtered off and discarded. The filtrate was shaken with water until the aqueous extract reacted neutral to congo red. The xylene was distilled with steam and the crystalline residue was dissolved in 200 cc. of acetone and 3 g. of diethylamine. The resulting diethylamine salt was recrystallized six times from acetone, then the acid was freed by addition of dilute hydrochloric acid and extracted with ether. The washed ether solution was evaporated to dryness and the residue recrystallized from alcohol. When dried in vacuum at room temperature, the *d*-pimaric acid melted at 218–219°; $[\alpha]^{20}_{D}$ +75° (2% absolute alcohol), yield, 3.5 g.

Summary

A hydroxy-lactone, $C_{20}H_{32}O_3$, has been prepared from *d*-pimaric acid by sulfonation at low temperatures.

Modifications of the structural formula of *d*-pimaric acid have been proposed.

A new method for the estimation of the maximum amount of *d*-pimaric acid present in the acid portion of oleoresin and rosin has been advanced.

The presence of dihydro-*l*-pimaric or dihydroabietic acid and *l*-pimaric acid in *d*-pimaric acid preparation has been demonstrated.

WASHINGTON, D. C. RECEIVED MAY 24, 1940

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. XXV. The Effect of Metals on the Addition of Hydrogen Bromide to Allyl Bromide

BY M. S. KHARASCH, W. R. HAEFELE[1] AND FRANK R. MAYO

It has been shown by Kharasch and Mayo[2] that in the absence of air and peroxides, or in the presence of antioxidants, the interaction of allyl bromide and hydrogen bromide results in the formation of the normal addition product, 1,2-dibromopropane, whereas the oxygen- or peroxide-promoted reaction gives rise to the abnormal addition product, 1,3-dibromopropane.[3] It was subsequently reported by Urushibara and Takebayashi that when the reaction takes place in the presence of finely divided and freshly reduced iron, nickel, or cobalt, the major product is also the abnormal 1,3-dibromide[4a,c] even in the absence of oxygen and peroxides.

According to the hypothesis proposed by Kharasch, Engelmann and Mayo,[5] the abnormal addition is a chain reaction in which bromine atoms are chain carriers. At one time, Urushibara and co-workers maintained that the abnormal addition was the result of a physical effect due to the paramagnetism common to oxygen and the effective metals.[4d,6] They have now accepted the chain mechanism for the oxygen-promoted abnormal addition.[4j] Other work from their laboratory has shown that the metals are attacked to varying degrees by hydrogen bromide,[4a,b,c,i] and that catechol and hydroquinone,[4f] but not diphenylamine,[4b,f] inhibit the metal-promoted abnormal addition of hydrogen bromide to allyl bromide, as well as to undecenoic acid[4e,g,h] in toluene solution.

The present work was undertaken to verify the effects of metals on the addition of hydrogen bromide to allyl bromide and to correlate these effects with the bromine atom chain hypothesis for the abnormal addition reaction. This correlation has been accomplished in a study of the action of several metals and their bromides on hydrogen bromide–allyl bromide mixtures and of their effects on the normal and abnormal addition reactions.

Addition in the Presence of Iron.[7]—In a series of experiments in which 1.5–1.6 mole of hydrogen

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[1] This paper is a condensation of a thesis submitted by W. R. Haefele in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The University of Chicago, 1939. The dissertation should be consulted for exact details of the experiments cited in this paper.

[2] Kharasch and Mayo, THIS JOURNAL, **55**, 2468 (1933).

[3] It is possible to obtain either 1,2- or 1,3-dibromopropane exclusively. This correction to previous work, which indicated that only about 90% of either product could be formed, is explained in the experimental part of this paper.

[4] Urushibara and Takebayashi, *Bull. Chem. Soc. Japan*, **11**, (a) 692, (b) 754 (1936); **12**, (c) 51, (d) 173 (1937); **13**, (e) 331, (f) 400, (g) 404, (h) 574 (1938); Urushibara and Sinamura, *ibid.*, (i) **13**, 570 (1938); (j) **14**, 323 (1939).

[5] Kharasch, Engelmann and Mayo, *J. Org. Chem.*, **2**, 288 (1937).

[6] That the paramagnetic properties of oxygen might be responsible for the peroxide effect was considered by Kharasch and Mayo,[2] but the lack of effect of the strongly paramagnetic nitric oxide and nitrogen dioxide led to rejection of the hypothesis.

[7] Except as otherwise noted, all of the experiments described in this paper were carried out with peroxide-free allyl bromide at 20–30°, in the absence of air, solvents, and light. Proportions of reagents are expressed in mole % on the basis of the allyl bromide used. About 50% excess hydrogen bromide was used.