2. Refinements in previous experimental procedure have been introduced.

3. A study of the ease of dehydration of mono-acylethylenediamines has been made.

4. The cyclic and acyclic bases prepared in this study have been fully characterized as picrates, hydrochlorides, chloroplatinates and phenyl ureas.

Lactonization of Dihydro-*l*-abietic and Dihydro-*l*-pimaric Acids

BY ELMER E. FLECK AND S. PALKIN

As is well known in the pine resin acid series, isolation of the individual isomers, because of pronounced isomorphism, is attended with considerable difficulty. Similar difficulties are encountered in isolating the individual isomers from dihydro mixtures obtained on hydrogenating *l*-abietic or *l*-pimaric acid. Thus there are reported in the literature dihydroabietic acids ranging from $[\alpha]D$ −23 to +108°, and melting points of 141 to 218°, and dihydro-*l*-pimaric acids from $[\alpha]D$ +24 to +35°, and melting points of 135 to 144°.

Ruzicka and co-workers[1] first showed that dihydroabietic acid, $[\alpha]D$ −12°, m. p. 167–168°, may be converted with strong mineral acids into a completely saturated lactone, $C_{20}H_{32}O_2$. It has now been found possible to prepare this same lactone from the high-rotating dihydro-*l*-abietic acid, $[\alpha]D$ +108°,[2] and from dihydro-*l*-pimaric acid, $[\alpha]^{20}D$ +35°. This raises the question as to the identity of the dihydro acid shown to exist in pine oleoresin and in rosin,[3] since the dihydro acid was isolated as the lactone and therefore may be any one or a mixture of the three dihydro compounds shown to give this lactone.

Up to the present time there has been little evidence as to the point of lactonization in lactonized dihydroabietic acid. The C-10 position has been suggested[4] and seemed possible on the basis that the positions of the double bonds in *l*-abietic acid I are such that, on hydrogenation to the dihydro compound, lactonization could occur on the residual double bond in ring B, with the postulation of a shift to the 9,10-position, thus forming a five-membered lactone. There are, however, other possibilities for this lactone that appear more plausible.

(1) Ruzicka and Meyer, *Helv. Chim. Acta*, **5**, 333 (1922); Ruzicka, Waldmann, Meier and Hösli, *ibid.*, **16**, 178 (1933).
(2) Fleck and Palkin, THIS JOURNAL, **60**, 2621 (1938).
(3) Fleck and Palkin, *ibid.*, **61**, 1230 (1939).
(4) Hasselstrom and McPherson, *ibid.*, **60**, 2340 (1938).
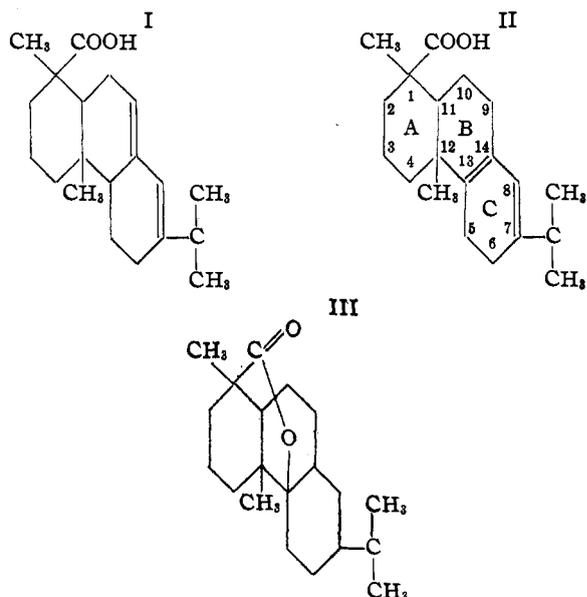
l-Pimaric acid II[5] is now represented as containing a system of conjugated double bonds confined to ring C. *l*-Abietic acid I[5] is represented as having a conjugated system of double bonds distributed in rings B and C. An inspection of the structure of *l*-pimaric acid and *l*-abietic acid indicates the $\Delta^{13,14}$ for dihydro-*l*-pimaric acid, and $\Delta^{9,14}$ for dihydro-*l*-abietic acid, assuming hydrogenation to take place at the $\Delta^{7,8}$ position in both cases, that is, under the simplest possible conditions. A 1:4 addition to the conjugated system of either *l*-pimaric or *l*-abietic acid would produce a $\Delta^{14,8}$ dihydro derivative.

On saturation of one of the double bonds of either acid, formation of a series of isomeric dihydro-*l*-pimaric and dihydro-*l*-abietic acids which have the residual double bond in any one of the positions, 14,13, 14,9, 14,8 and 7,8 would seem quite possible.

It may be shown how the three possible positions of the double bond in dihydro derivatives

(5) Fieser and Campbell, *ibid.*, **60**, 159 (1938).

(14,13, 14,9, 14,8) might conceivably give rise to the same lactone at C-14, but this would necessitate an assumption of a 7-membered lactone. A more probable view would be lactonization at C-13, with formation of a six-membered lactone, such as shown in formula III. This is possible by assuming a shift of the double bond from the 9,14 or 8,14 to the bridge-head position, 13,14, a reasonable assumption, when these acids are under the influence of strong mineral acids. Lactonization on C-10, as previously suggested,[4] would, on the other hand, necessitate a much greater shift of double bonds, and hence becomes less probable.

An effort was made to obtain additional information on the point of lactonization by the preparation of typical derivatives and by oxidation experiments with tetrahydrohydroxyabietic acid obtained by hydrolysis of the lactone. Of the three possible points of lactonization two, C-9 and C-10, should yield secondary hydroxyl groups when the lactone is opened. Either of these should yield a ketone on oxidation. The third possibility, C-13, would give rise to a tertiary hydroxyl group and should be stable against oxidation. Actually, the oxidation experiments led to no ketone and, while such evidence would tend to support the assumption of a tertiary hydroxyl and consequently the C-13 position for lactonization, the weakness of such negative evidence is recognized. Moreover, the strong tendency of tetrahydrohydroxyabietic acid and even its methyl ester to lactonize further complicated the oxidation experiments and the attempts to prepare derivatives.

The tetrahydrohydroxyabietic acid was prepared by an improved procedure involving fusion of lactonized dihydroabietic acid III with potassium hydroxide and subsequent acidification of the reaction mass. This acid was methylated with diazomethane to obtain a crystalline tetrahydrohydroxyabietic methyl ester, m. p. 50–51°, $[\alpha]^{20}D + 21°$. The methyl ester could be distilled unchanged and showed the usual stability against alkaline hydrolysis. In warm acetic acid, however, the methyl ester was rapidly converted into the lactone. All attempts to acetylate the methyl ester with acetic anhydride and sodium acetate, acetyl chloride and acetic anhydride gave only the lactone. No benzoate was obtained by the pyridine and benzoyl chloride method. Attempts to oxidize the methyl ester with chromic

anhydride in acetic acid at room temperature and above yielded only the lactonized dihydroabietic acid. The hydroxy methyl ester was completely stable against potassium permanganate in acetone solution. Similarly alkaline potassium permanganate at room temperature for twenty hours did not materially affect tetrahydrohydroxyabietic acid.

Experimental Part

Lactonization of Dihydro-*l*-pimaric Acid.—One gram of dihydro-*l*-pimaric acid, m. p. 144–146°, $[\alpha]^{20}D +35°$,[6] was added to 10 cc. of concentrated sulfuric acid cooled to −5 to −10°. Stirring and cooling was continued for forty-five minutes. The light yellow-colored solution was poured on ice and the resulting mixture was extracted with ether. The ether solution was washed with water, then 0.25 N sodium hydroxide and finally with water until neutral to phenolphthalein. When the ether was distilled and the residue dried in vacuum at 80°, 1 g. of crystalline material was obtained that melted at 127–129°. The product when recrystallized from alcohol melted at 131–132°, $[\alpha]^{20}D$ −4°. Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.88; H, 10.60. Found: C, 78.91; H, 10.87. No depression of melting point was observed when this compound was mixed with lactonized dihydroabietic acid.[3]

Tetrahydrohydroxyabietic Acid from Lactonized Dihydroabietic Acid.—A solution of 0.3 g. of the lactone from dihydro-*l*-pimaric acid, in 10 cc. of 10% *n*-butyl alcoholic potassium hydroxide, was hydrolyzed as previously outlined.[2] The resulting acid melted at 164–165° with effervescence. When the melt was cooled and allowed to crystallize, it remelted at 130–131°. Anal. Calcd. for acid, $C_{20}H_{34}O_3$: C, 74.47; H, 10.63. Found: C, 74.48; H, 10.79. There was no lowering of the melting point when the acid was mixed with tetrahydrohydroxyabietic acid.

Lactonization of High-Rotating Dihydroabietic Acid Isomer.—Two cc. of concentrated sulfuric acid was cooled to −5 to −10° and 50 mg. of dihydroabietic acid, $[\alpha]D +108°$,[2] was added. Stirring and cooling were continued for forty-five minutes. The reaction mass was poured on ice and worked up as described for dihydro-*l*-pimaric acid. Twenty-five mg. of neutral residue was obtained. Stout prisms were obtained from methyl alcohol that melted at 130–131°. No lowering of melting point was observed when mixed with authentic lactonized dihydroabietic acid. Owing to the small amount of material available and the difficulty involved in preparing more of the dihydroisomer, no further characterization of the product was feasible.

Tetrahydrohydroxyabietic Methyl Ester.—Six grams of lactonized dihydroabietic acid was hydrolyzed with *n*-butyl alcoholic 10% potassium hydroxide.[2] The resulting tetrahydrohydroxyabietic acid was esterified with diazomethane in the usual manner. The methyl ester was crystallized as needles from methyl alcohol by slow addition of water. When dried in vacuum at room temperature the methyl ester melted at 50–51°, $[\alpha]^{20}D +21°$.[6] Anal. Calcd. for $C_{21}H_{36}O_3$: C, 74.94; H, 10.79; OCH_3, 9.22. Found: C,

(6) The specific rotations recorded in this publication were all taken on 2% absolute alcoholic solutions.

74.92; H, 10.94; OCH$_3$, 9.20. The Zerewitinoff test showed 5.38% OH; calcd. for C$_{21}$H$_{36}$O$_3$, 5.06.

Saponification with 0.1 N sodium hydroxide in alcoholic solution for four hours at reflux temperature: Calcd.: 4.34 cc. of 0.1 N sodium hydroxide; found, 0.23 cc.

One gram of the methyl ester distilled at 175–180° at 2 mm. Found: C, 75.06; H, 10.92; OCH$_3$, 9.16.

Fusion of Lactonized Dihydroabietic Acid with Potassium Hydroxide.—Four grams of 88% potassium hydroxide was melted and heated to 200° in a nickel crucible. To this one gram of lactonized dihydroabietic acid was added. The mixture was stirred and the heating was continued for fifteen minutes. As the reaction proceeded the insoluble potassium salt separated as a white powder that floated on the surface of the caustic. The fusion mass was cooled and dissolved in 200 cc. of water and shaken with ether to remove any unchanged lactone. The alkaline solution was made acid to litmus with 10% acetic acid. The tetrahydrohydroxyabietic acid that separated as pearly plates was filtered and washed with water. When dried in vacuum the acid melted at 164–165° with effervescence and showed no depression with tetrahydro-

hydroxyabietic acid prepared by the *n*-butyl alcoholic hydrolysis. When the melted acid was allowed to cool and crystallize, it remelted at 130–131°.

Summary

Dihydro-*l*-pimaric acid and dihydro-*l*-abietic acid, [α]D +108°, have been lactonized to form lactones identical with lactonized dihydroabietic acid.

Formulations for these dihydro compounds have been advanced to show how they may all yield the same lactone.

Oxidation and acylation experiments have been shown to indicate the C-13 position as a more probable point of lactonization than C-10.

A rapid method for hydrolysis of lactonized dihydroabietic acid by caustic fusion has been developed.

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The Stereochemistry of Complex Inorganic Compounds. V. The Reaction of Carbonates with Dichloro-dipropylenediamine Cobaltic Chloride. A New Method of Determining Relative Configurations

BY JOHN C. BAILAR, JR., AND J. P. McREYNOLDS[1]

The reaction of dichloro-diethylenediamine cobaltic chloride with potassium and silver carbonates yielded the first example of the Walden inversion in the field of optically active inorganic complex compounds.[2] Bailar, Jonelis and Huffman[3] found that either enantiomorph of the re-

$$L[Co\ en_2Cl_2]Cl \xrightarrow{\begin{array}{c} K_2CO_3 \\ \\ Ag_2CO_3 \end{array}} \begin{array}{l} D[Co\ en_2CO_3]Cl \\ \\ D\ or\ L[Co\ en_2CO_3]_2CO_3 \end{array}$$
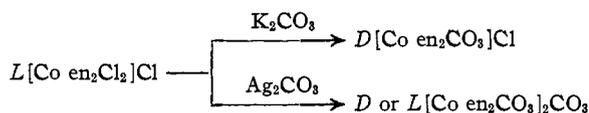
sulting carbonato compound could be produced by the action of silver carbonate, depending upon the conditions under which the reaction took place.

Mathieu[4] checked the Walden inversion reaction of Bailar and Auten[2] and from circular dichroism measurements came to the conclusion that the carbonato diethylenediamine cobaltic salt resulting from the use of potassium carbonate was the non-inverted form.

It was thought that the use of rotatory dis-

persion curves for closely related compounds might lead to valuable information in respect to this reaction. Lowry, Pickard and Kenyon[5] found that the rotatory dispersion curves for a series of secondary alcohols showed similarities as to dispersion ratios. The rotatory dispersion curves for a large number of diethylenediamine cobaltic complexes are given by Mathieu.[6] A comparison of these curves with those of analogous members of the di-levo-propylenediamine (*l*-pn) cobaltic series was undertaken as a method of attacking the Walden inversion problem.

Evidence has been presented to show that cobaltic complexes containing optically active diamines do not exist in all of the possible stereochemical forms, but only in certain preferred configurations. Hürlimann,[7] working with dinitro-dipropylenediamine cobaltic compounds, could isolate only half of the calculated number of *cis* forms. Jaeger,[8] using active cyclopentylenediamine, observed the same result. He assigned

(1) Taken from a portion of the doctorate thesis of J. P. McReynolds, 1938. Presented at the Baltimore meeting of the American Chemical Society, April, 1939.

(2) Bailar and Auten, THIS JOURNAL, **56**, 774 (1934).

(3) Bailar, Jonelis and Huffman, THIS JOURNAL, **58**, 2224 (1936).

(4) Mathieu, *Bull. soc. chim.*, [5] **3**, 497 (1936).

(5) Lowry, Pickard and Kenyon, *J. Chem. Soc.*, **105**, 94–102 (1914).

(6) Mathieu, *Bull. soc. chim.*, [5] **3**, 463–475 (1936).

(7) Hürlimann, Dissertation, Zurich, 1918.

(8) Jaeger, *Rec. trav. chim.*, **38**, 170 (1919).