version of configuration at C-4 of the 1-*O*-methyl-L-sorbose, I, by way of the 3,4-enediol,[6] II, followed by operation of the Nef-Isbell mechanism on 1-*O*-methyl-L-*erythro*-hexose-2,3-enediol, III. Alternatively, it is conceivable that fragment recombination is involved in the conversion of I to IV.[7]

EXPERIMENTAL

*2,3:4,6-Di-O-isopropylidene-1-O-methyl-*L*-sorbose.* 2,3:4,6-Di-*O*-isopropylidene-L-sorbose[8] (m.p. 77–78°) was methylated by the Haworth procedure according to the general directions of Hibbert and co-workers[9] for the methylation of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside. The product was isolated from the cooled methylation reaction mixture by extraction with ether. The extract was washed with water, dried over sodium sulfate, and concentrated to a crystalline residue. The crude product (90% yield) was recrystallized from ethanol by the addition of water to give pure 2,3:4,6-di-*O*-isopropylidene-1-*O*-methyl-L-sorbose, m.p. 54–55°, $[\alpha]^{22}_{D}$ −11° in acetone, *c* 4.

Anal. Calcd. for $C_{13}H_{22}O_6$: C, 56.9; H, 8.08. Found: C, 57.0; H, 8.12.

*1-O-Methyl-*L*-sorbose.* A solution of 5 g. of the above product in 50 ml. of 50% ethanol, containing 0.175% of hydrogen chloride, was heated at 80° for 12 hr. The cooled solution was de-ionized over Duolite A-4, decolorized, and concentrated at reduced pressure. The resulting pale yellow sirup, obtained in nearly quantitative yield, showed a methoxyl content of 15.8% (calculated for 1-*O*-methyl-L-sorbose, 16% OCH_3).

*Reaction of 1-O-methyl-*L*-sorbose and calcium hydroxide.* A solution of 65 g. of 1-*O*-methyl-L-sorbose in 1200 ml. of oxygen-free water was treated with 55 g. of calcium hydroxide. After 16 days at room temperature, acid production, as determined by successive decationization and titration of aliquots, had practically stopped. The solution was then filtered, saturated with carbon dioxide, again filtered, and passed over Amberlite IR-100 cation exchange resin to remove calcium ions. Decolorization and concentration at reduced pressure then gave 48 g. of a light-colored, acidic sirup.

Samples of the above sirup were subjected to descending chromatography on Whatman no. 1 paper with *n*-butyl alcohol-ethanol-formic acid-water (45:5:1:49 by volume). Spraying the thoroughly dried papers with bromcresol green showed a strong zone at R_f 0.76, whereas spraying with ammoniacal silver nitrate revealed strong zones with R_f values of 0.60, 0.52, 0.43, and 0.28 with weaker zones at 0.66, 0.38, and 0.16. In the same solvent system, the following known compounds showed R_f values as follows: lactic acid, 0.76; "α"-D-glucosaccharinic lactone, 0.52; "α"-D-isosaccharinic lactone, 0.43; "α"-D-galactometasaccharinic lactone, 0.28; 1-*O*-methyl-L-sorbose, 0.27; and L-sorbose 0.12.

*Isolation and identification of "α"-*L*-glucosaccharinic lactone.* A sample of the above acidic sirup was extracted continuously with ether for 1 day to remove the bulk of the lactic acid. The residue (1.33 g.) was chromatographed through a column containing 150 g. of Whatman Standard Grade cellulose powder, using the developing solvent mixture described above. Fractions of 5 ml. each were collected and examined by paper chromatography. Fractions 91–99, which showed the presence only of the two components with respective R_f values of 0.43 and 0.52, were pooled and concentrated to yield 0.242 g. of sirup. Crystals appeared in this sirup after several months, and these were used to inoculate the main, sirupy reaction product. After several days, there was obtained 1.0 g. of crude crystals, m.p. 159–161°, R_f 0.52. Recrystallization from water gave pure "α"-L-glucosaccharinic lactone (2-*C*-methyl-L-*ribo*-pentonic γ-lactone), m.p. 162–163°, $[\alpha]^{22}_{D}$ −93.4° in water, *c* 1. The corresponding constants for "α"-D-glucosaccharinic lactone[10] are m.p. 160–161°, $[\alpha]_D$ +93.5° in water. The infrared spectra of the enantiomorphic lactones were identical.

Anal. Calcd. for $C_6H_{10}O_5$: C, 44.4; H, 6.21; equiv. wt., 162. Found: C, 44.7; H, 6.29; equiv. wt., 161.

Acetonation[7] of "α"-L-glucosaccharinic lactone gave the 2,3-*O*-isopropylidene derivative, m.p. 60–62°, $[\alpha]^{22}_{D}$ +39.5° in chloroform, *c* 2. The corresponding constants for 2,3-*O*-isopropylidene-2-*C*-methyl-D-*ribo*-pentonic γ-lactone[7] are m.p. 62–63° and $[\alpha]^{25}_{D}$ −38.4° in chloroform, *c* 3.4. The enantiomorphic acetonated lactones showed identical infrared spectra.

"α"-L-Glucosaccharinic lactone gave a phenylhydrazide with m.p. 164–165° and $[\alpha]^{22}_{D}$ −50° in water, *c* 1. The reported[11] constants for "α"-D-glucosaccharinic phenylhydrazide are m.p. 167–169° and $[\alpha]_D$ +50.3° in water.

Recrystallization of a mixture of equal parts of α-D- and "α"-L-glucosaccharinic lactones from water gave the race mate, m.p. 155–156°, $[\alpha]^{22}_{D}$ 0° in water.

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(6) Evidence for the participation of the 3,4-enediol in the alkaline isomerization of hexoses is given by J. C. Sowden and R. R. Thompson, *J. Am. Chem. Soc.*, **80**, 1435 (1958).

(7) Evidence for fragment recombination in the formation of "α"-D-glucosaccharinic acid from D-mannose and alkali is given by J. C. Sowden, M. G. Blair, and D. J. Kuenne, *J. Am. Chem. Soc.*, **79**, 6450 (1957).

(8) We are indebted to Dr. J. A. Aeschlimann, Hoffman-La Roche, Inc., Nutley, N. J., for the generous gift of this substance.

(9) T. H. Evans, I. Levi, W. L. Hawkins, and H. Hibbert, *Can. J. Research*, **20**, 175 (1942).

(10) C. Scheibler, *Ber.*, **13**, 2212 (1880).

(11) E. Fischer and F. Passmore, *Ber.*, **22**, 2728 (1889); J. U. Nef, *Ann.*, **376**, 1 (1910).

The Nitrogen Compounds of Petroleum Distillates. XXIX. Identification of 5-Methyl-6,7-dihydro-1,5-pyrindine

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Received February 25, 1960

In a previous article[1] the isolation of two dihydropyrindines from California petroleum and a new method of synthesis for the methyl-6,7-dihydro-1,5-pyrindines were described. One of the dihydropyrindines from petroleum was identified as 2-methyl-6,7-dihydro-1,5-pyrindine, while the other was assumed to be an isomer with the methyl group located in the cyclopentane ring.

We wish to report the identification of this second dihydropyrindine as 5 - methyl - 6,7 - dihydro - 1,5-

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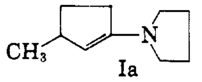
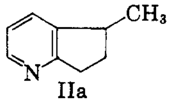
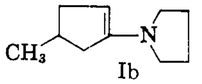
(1) H. L. Lochte and A. G. Pittman, *J. Am. Chem. Soc.*, **82**, 469 (1960).

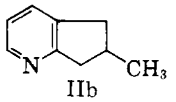
pyrindine (IIa). This is the first report of the occurrence of this compound from any natural source.

The isomeric 5- and 6-methyl-6,7-dihydro-1,5-pyrindines (IIa and IIb) were synthesized by utilizing the method previously reported for the preparation of methyl-6,7-dihydro-1,5-pyrindines.[1] The reaction of pyrrolidine with 3-methylcyclopentanone resulted in the formation of the enamines Ia and Ib, which in turn were converted to the dihydropyrindines IIa and IIb.


Ia

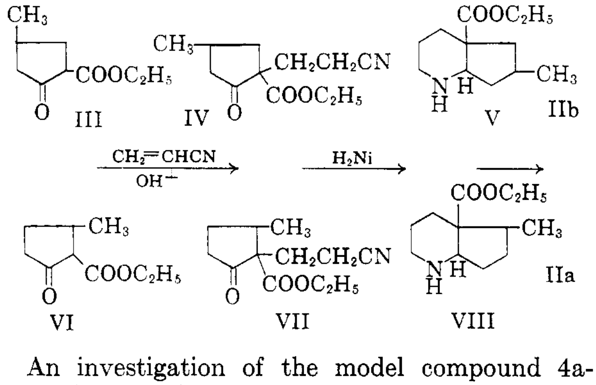

IIa


Ib

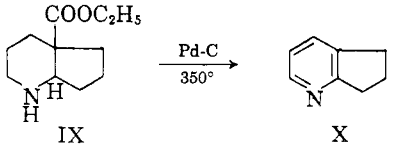

IIb

Separation of the isomers IIa and IIb was accomplished by fractional recrystallization of their picrate derivatives. This operation yielded a picrate melting at 135–136° and another melting at 147–149°. This latter picrate proved identical with the picrate (m.p. 147–149°) of the petroleum base previously isolated.[1]

The position of the methyl group in the two amines obtained *via* the enamine synthesis was established by an alternate synthetic route. Dieckmann has shown[2] that during the base-catalyzed intramolecular cyclization of diethyl β-methyladipate, the product obtained consists mainly of 2-carbethoxy-4-methylcyclopentanone (III), while the isomeric 2-carbethoxy-3-methylcyclopentanone (VI) occurs to a smaller extent. Monocyanoethylation of this product, followed by a reductive ring closure and subsequent dehydrogenation and decarbethoxylation, would then be expected to produce 6-methyl-6,7-dihydro-1,5-pyrindine (IIb) as the major product.



An investigation of the model compound 4a-carbethoxyoctahydro-1,5-pyrindine (IX) to determine the most convenient method of removing the bridge carbethoxy group was initiated. The bridge carbethoxy group could be removed with simultaneous dehydrogenation of the piperidine ring by passing the vapors of the amine slowly over palladium-on-charcoal at 350°. When the mixture of V and VIII, which had been obtained previously, was submitted to this treatment, the product, after conversion to picrate derivatives, was found to consist of an 80:20% mixture of 135–136°:147–149° melting picrates. According to the reasoning outlined above, the picrate which melted at 147–149° corresponds to the derivative of 5-methyl-6,7-dihydro-1,5-pyrindine (IIa), as it is not the major product. Consequently, 5-methyl-6,7-dihydro-1,5-pyrindine is the structure of the petroleum base in question.



EXPERIMENTAL[3,4]

Enamines of 3-methylcyclopentanone (Ia and Ib). The enamine preparation was carried out in the manner previously reported[1] using 80 g. of 3-methylcyclopentanone (0.82 mole) and 125 g. of pyrrolidine (1.8 moles). The 3-methylcyclopentanone was prepared by the oxidation of 4-methylcyclohexanol to β-methyladipic acid by the method of Hartman[5] and cyclization of β-methyladipic acid by distilling with barium hydroxide according to the method of Harries and Wagner.[6]

Monocyanoethylation of Ia *and* Ib. Monocyanoethylation of the crude mixture of Ia and Ib was conducted as before during the monocyanoethylation of cyclopentanonepyrrolidine enamine[1] except that reflux time was continued for 16 hr. After hydrolysis and work-up in the usual manner the product was distilled through a Todd column packed with glass helices yielding 74 g. of colorless liquid (60%), b.p. 97° (0.5 mm.), n_D^{30} 1.4615.

Anal. Calcd. for $C_9H_{13}NO$: C, 71.52; H, 8.61; N, 9.27. Found: C, 71.42; H, 8.68; N, 9.52.

5- and 6-Methyloctahydro-1,5-pyrindine. The ketonitrile mixture obtained in the preceeding preparation was reductively cyclized as before in the preparation of octahydro-1,5-pyrindine.[1] Work-up and distillation gave a colorless liquid, b.p. 88° (29 mm.), n_D^{27} 1.4757.

Anal. Calcd. for $C_9H_{17}N$: neut. equiv. 139.2. Found: neut. equiv. 138.3.

5- and 6-Methyl-6,7-dihydro-1,5-pyrindine (IIa *and* IIb). Dehydrogenation of the mixture of 5- and 6-methyloctahydro-1,5-pyrindine over 30% palladium-on-charcoal in the vapor phase at 310° yielded a colorless liquid, b.p. 207° (753 mm.) n_D^{22} 1.5230.

Anal. Calcd. for $C_9H_{11}N$: neut. equiv. 133.2. Found: neut. equiv. 133.0.

This dehydrogenated product was converted to the picrate derivatives by treatment with a saturated solution of picric acid in 95% ethanol. Fractional recrystallization of

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(2) W. Dieckmann, *Ann.*, **317,** 27 (1901); W. Dieckmann and A. Groeneveld, *Ber.*, **33,** 595 (1900).

(3) All melting points are corrected; all boiling points are uncorrected. Microanalyses were performed at the Huffman Microanalytical Laboratories, Wheatridge, Colo.

(4) Neutralization equivalents were determined by non-aqueous titration by the method of J. S. Fritz, *Anal. Chem.*, **22,** 1028 (1950).

(5) W. W. Hartman, *Org. Syntheses*, **Coll. Vol. I,** 19, Note 1. (1941).

(6) Harries and Wagner, *Ann.*, **410,** 36 (1915); see also Thorpe and Kon, *Org. Syntheses*, **Coll. Vol. I,** 192 (1941).

the solid thus obtained from 95% ethanol gave a picrate, m.p. 135–136°, as the major fraction. This picrate was subsequently shown to be the derivative of 6-methyl-6,7-dihydro-1,5-pyrindine (IIb).

Anal. Calcd. for $C_{15}H_{14}N_4O_7$: C, 49.72; H, 3.86. Found: C, 49.73; H, 3.93.

Two grams of this picrate was converted to the free base (IIb) by treatment with concd. ammonium hydroxide. The free base (IIb) was dried over sodium hydroxide and distilled giving a colorless liquid, b.p. 208° (751 mm.), n_D^{23} 1.5239, d_{20}^{20} 1.0007.

Anal. Calcd. for $C_9H_{11}N$: neut. equiv. 133.2. Found: neut. equiv. 132.1.

A styphnate derivative of the amine (IIb) was made m.p. 156–157°.

Anal. Calcd. for $C_{15}H_{14}N_4O_8$: C, 47.62; H, 3.70. Found: C, 47.79; H, 3.72.

Another picrate, m.p. 147–149°, was obtained in smaller amounts during the fractional recrystallization mentioned above. This picrate was subsequently shown to be the derivative of 5-methyl-6,7-dihydro-1,5-pyrindine (IIa). A mixed melting point with the petroleum base picrate previously isolated,[1] m.p. 147–149°, showed no depression. The infrared spectra of the petroleum base picrate (m.p. 147–149°) and the synthetic base picrate were identical.

Anal. Calcd. for $C_{15}H_{14}N_4O_7$: C, 49.72; H, 3.86; N, 15.46. Found: C, 49.88; H, 4.08; N, 15.40.

Conversion of 100 mg. of this picrate to the free base (IIa) by treatment with ammonium hydroxide yielded a liquid which, after drying and distillation, boiled at 207–208° (746 mm.).

A styphnate derivative of IIa was prepared by adding about 30 mg. of the amine (IIa) to about 1 cc. of a saturated solution of styphnic acid in 95% ethanol. Recrystallization from 95% ethanol yielded small yellow needles, m.p. 172–173.5°.

Anal. Calcd. for $C_{15}H_{14}N_4O_8$: C, 47.6; H, 3.7. Found: C, 47.5; H, 3.8.

6,7-Dihydro-1,5-pyrindine (X) *from 4a-carbethoxyoctahydro-1,5-pyrindine* (IX). One-half gram of the aminoester (IX), prepared according to Albertson,[7] was slowly distilled through 30% palladium-on-charcoal which was held between 350–360°. As before, hydrogen was used as a carrier gas for the vapors. The reaction was complete in 48 hr. The product was converted to a picrate derivative and after two recrystallizations from 95% ethanol gave 0.28 g. (31%) of picrate, m.p. 180–181°. This picrate showed no melting point depression on admixture with an authentic sample of the picrate derivative of X.

Alternate synthesis of 5- and 6-methyl-6,7-dihydro-1,5-pyrindine (IIa *and* IIb). Dieckmann condensation of diethyl β-methyladipate afforded the β-ketoester mixture (III and VI) b.p. 117–119° (16 mm.); (lit.,[2] m.p. 107–108°, 11–12 mm.). This mixture was monocyanoethylated by adding 17 g. of acrylonitrile (0.32 mole) slowly with stirring to 52 g. of the mixture of β-ketoesters (III and VI) (0.30 mole) in 60 g. of 1,4-dioxane containing 4.2 g. of Triton B. The temperature of the reaction mixture was maintained between 30–40° by external cooling during the addition. After 45 min. the addition was complete and the reaction mixture was stirred an additional hour. After adding about 40 cc. of diethyl ether to the reaction mixture it was washed briefly with 5% hydrochloric acid, then once with water. After drying over sodium sulfate, the solvents were removed *in vacuo* and the residue distilled giving 48 g. of colorless material (73%), b.p. 136° (0.5–1 mm.), n_D^{20} 1.4642.

Anal. Calcd. for $C_{12}H_{17}O_3N$: C, 64.57; H, 7.62. Found: C, 64.58; H, 7.73.

The monocyanoethylated product (IV and VII) obtained above was then reductively cyclized as in the preparation of octahydro-1,5-pyrindine.[1] After removal of Raney nickel and ethanol, the product was distilled giving a colorless liquid, b.p. 151° (35 mm.).

Anal. Calcd. for $C_{12}H_{21}NO_2$: neut. equiv. 211.3. Found: neut. equiv. 212.7.

The aminoester mixture (V and VIII) was dehydrogenated and decarbethoxylated in the manner described in the preparation of X. The product obtained by this procedure was chromatographed on a preparative gas chromatographic unit[8] and the amines (IIa and IIb), which occurred as a single peak, were collected. This material was treated with equimolar quantities of picric acid in 95% ethanol. The melting point of the crude picrate mixture which resulted was 121.5–127.5°. This corresponds to an 80:20% mixture of 135–136:147–149° melting picrates according to a previously prepared melting point mixture diagram of the two isomers. After four recrystallizations of a portion of this crude picrate mixture 146 mg. of picrate, m.p. 135–136°, was obtained which did not depress the melting point of the 135–136° melting picrate obtained by the enamine route. The filtrates from the recrystallizations were combined and solvent removed under reduced pressure. After twelve recrystallizations of the crude picrate residue which remained, 24.3 mg. of picrate, m.p. 147–149°, was obtained. This picrate, m.p. 147–149°, showed no melting point depression on admixture with the picrate, m.p. 147–149°, obtained by the enamine route. The filtrates from the last recrystallizations were combined and solvent removed under reduced pressure. The residual crude picrate, after drying, consisted of 106 mg. and melted at 113–117°. According to the melting point mixture diagram of the two isomeric picrates this residue corresponded to a 45:55% mixture of 135–136°:147–149° melting picrates.

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(7) N. F. Albertson, *J. Am. Chem. Soc.*, **72**, 2594 (1950).

(8) See ref. 1 for a description of the gas chromatographic apparatus.

Six and Twelve Carbon Fluorocarbon Derivatives of Sulfur Hexafluoride

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T. E. Taylor, and J. A. Young

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Electrochemical reactions of organic sulfides in anhydrous hydrogen fluoride have received some attention in recent years.[1] This work extends these investigations to include hexyl and phenyl sulfide. As in previous work, the compounds R_fSF_4, $(R_f)_2SF_4$, R_fF and R_f-R_f (where R_f is C_6F_{13} or cyclo C_6F_{11}) were isolated or detected. The yields of isolable product were low for phenyl sulfide. Many of the above products that were liquids at 25° were purified by preparative scale chromatog-

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(1) (a) A. F. Clifford, H. K. El-Shamy, H. J. Emeleus, and R. N. Haszeldine, *J. Chem. Soc.* 2372 (1953). (b) W. A. Severson, T. J. Brice, and R. I. Coon, 128th Meeting ACS, Minneapolis, Minn., Sept. 11–16, 1955. (c) R. Dresdner, *J. Am. Chem. Soc.* **79**, 69 (1957). (d) F. W. Hoffman, T. C. Simmons, R. B. Beck, H. V. Holler, T. Katz, R. J. Koshar, E. R. Larsen, J. E. Mulvaney, F. E. Rogers, B. Singleton, and R. S. Sparks, *J. Am. Chem. Soc.* **79**, 2424 (1957). (e) R. D. Dresdner and J. A. Young, *J. Am. Chem. Soc.* **81**, 574 (1959). (f) J. A. Young and R. D. Dresdner, *J. Org. Chem.* **24**, 1021 (1959). (g) R. N. Haszeldine and F. Nyman, *J. Chem. Soc.* 2684 (1956).