and these workers found that the halogen readily reacted with amines.

Acyl groups were selected for use in this work that ranged from two to eighteen carbons. The dichloroacetyl group was included as a representative as the group is found in chloroamphenicol.[5] Hoover and Day[6] have recently reported the synthesis and use of some 2-acylamino-3-amino-1,4-naphthoquinones in the formation of two substituted 1H-naphthimidazole-4,9-diones.

Although none of the compounds reported in this paper have high amebicidal activity, certain features which correlate this activity with structure are of interest. The lauric acid and stearic acid derivatives, No. 18–26 were inactive in the amebicidal and tubercular tests. Propionic acid and butyric acid derivatives were the most active, and compound No. 9 exhibited the highest activity of any of those tried in the two tests mentioned above. This compound was amebicidal at a dilution of 1:50,000.

EXPERIMENTAL

Acylation of 2-amino-3-chloro-1,4-naphthoquinone. A mixture of 1 mole of 2-amino 3 chloro 1,4-naphthoquinone and 3 moles of the desired acyl halide in 10 parts of dioxane was refluxed for 12 to 15 hr.

A yellow solid separated when the mixture was cooled. This solid was removed and recrystallized from a 50:50 mixture of methanol and dioxane. Most of the acyl derivatives were yellow to tan in color and somewhat light sensitive. The data for these compounds are included in Table I.

2-Acylamino-3-alkyl (or aryl)amino-1,4-naphthoquinones. To a hot solution of 0.01 mole of 2-acylamino-3-chloro-1,4-naphthoquinone in 25 ml. of dioxane was added 0.02 mole of the selected amine. The solution was refluxed for 2 hr., cooled, and filtered. The red product was recrystallized from ethanol. The data for these compounds are given in Table I.

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(6) J. R. E. Hoover and A. R. Day, *J. Am. Chem. Soc.*, **76**, 4148 (1954).

Conversion of 1-*O*-Methyl-L-sorbose to "α"-L-Glucosaccharinic Acid by Alkali

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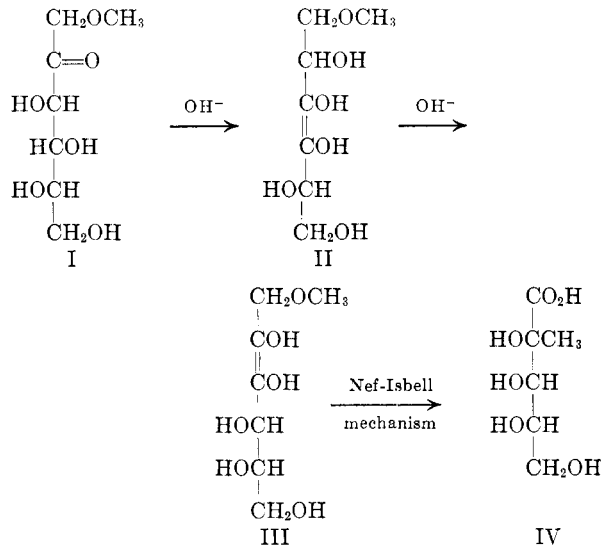
Recent studies by Kenner and his associates have indicated certain general rules, based on the Nef-Isbell mechanism,[1] relating the effects of substitution in a sugar molecule to the course of its conversion to saccharinic acids. For example, treatment of 1-*O*-methyl-D-fructose,[2] 3-*O*-methyl-D-fructose,[3] and 4-*O*-methyl-D-fructose[4] with aqueous calcium hydroxide is reported to lead, respectively, to the preferential formation of the saccharinic, metasaccharinic, and isosaccharinic acid structures.

From the above results, it was to be expected that a new acid of the saccharinic acid class, 2-*C*-methyl-L-*xylo*- or 2-*C*-methyl-L-*lyxo*-pentonic acid, would be the principal product from the treatment of 1-*O*-methyl-L-sorbose with aqueous calcium hydroxide. Accordingly, we have examined the latter reaction in an effort to obtain a reference compound for further studies of alkaline isomerization in the galactose family of sugars. 1-*O*-Methyl-L-sorbose was prepared in amorphous form by methylation of 2,3:4,6-di-*O*-isopropylidene-L-sorbose, followed by hydrolysis of the isopropylidene groups. After reaction of the methylated ketose with aqueous calcium hydroxide, paper chromatography revealed the presence of at least eight components in the product. The mixture was partially separated by column chromatography on powdered cellulose and, although we were unsuccessful in our attempts to isolate and identify either of the two new saccharinic acids indicated above, there was obtained in low yield a crystalline product that proved to be the enantiomorph of the known "α"-D-glucosaccharinic lactone (2-*C*-methyl-D-*ribo*-pentonic γ-lactone[5]).



The unexpected formation of "α"-L-glucosaccharinic acid may be explained by assuming an initial in-

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(2) J. Kenner and G. N. Richards, *J. Chem. Soc.*, 1784 (1954).

(3) J. Kenner and G. N. Richards, *J. Chem. Soc.*, 278 (1954).

(4) J. Kenner and G. N. Richards, *J. Chem. Soc.*, 1810 (1955).

(5) J. C. Sowden and D. R. Strobach, *J. Am. Chem. Soc.*, **82**, 954 (1960).

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°, $[\alpha]_D^{22}$ −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°, $[\alpha]_D^{22}$ −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°, $[\alpha]_D^{22}$ +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 $[\alpha]_D^{25}$ −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 $[\alpha]_D^{22}$ −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 racemate, m.p. 155–156°, $[\alpha]_D^{23}$ 0° in water.

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

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

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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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