

ration of fully methylated carbohydrates or derivatives which contain primary hydroxyl groups.

2. Detailed description of the procedure is given for the exhaustive methylation of sucrose.

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## The Acetone Derivatives of the Mercaptals of Some Monosaccharides. IV.<sup>1</sup> The 4,5-Monoacetone Derivative of the Dibenzylmercaptal and of the Dimethylacetal of *d*-Galactose

BY EUGENE PACSU, S. M. TRISTER<sup>2</sup> AND JOHN W. GREEN

Fifteen years ago it was shown by Pacsu<sup>1</sup> that new isomers of partially methylated hexoses could be obtained by a series of reactions in which the sugar mercaptals should first be converted into their di- and monoacetone derivatives. Subsequent methylation of the free hydroxyl group or groups would yield compounds which on deacetylation and removal of the mercaptan residues would give rise to the respective mono- and trimethyl sugars. The exact positions of the methyl groups once determined, the structure of the intermediate acetone derivatives would be known. On the other hand, the knowledge of the positions of the acetone residues would determine the structure of the methylated sugars. At that time it appeared that the elucidation of the structure of the methylated sugars rather than that of the intermediate acetone derivatives was more feasible since methods for removal of the mercaptan residues without simultaneous hydrolysis of the acetone groups were unknown. Direct determination of the positions of the methyl groups in partially methylated sugars fifteen years ago presented almost insurmountable difficulties mainly due to the lack of suitable experimental methods. It was customary, therefore, to assign the structure of newly discovered partially methylated sugars by taking recourse to the method of elimination and to other indirect procedures. However, conclusions based on such negative evidence are usually valid only as long as the accepted structural formulas of the eliminated compounds remain unchanged. In the special field of partially methylated sugars new interpretation of some old experimental results became necessary after Brigl and Schinle discovered<sup>3</sup> that the true

2-methyl glucose<sup>4</sup> was capable of osazone formation with the loss of the methyl group. This striking discovery cast doubt on the structure of those partially methylated sugars the formulas of which previously had been assigned on the assumption, till then unquestioned, that a 2-methyl aldose could not possibly form an osazone. Among those partially methylated sugars affected by this discovery were the assumed 4-methyl sugars and all their mercaptal and acetylated mercaptal derivatives previously described.<sup>1</sup> As was pointed out by Pacsu,<sup>5</sup> the assignment of position 4 to the methyl group in the new monomethyl glucose was left as the only possibility at the time when the compound was discovered, because a 2-methyl glucose with entirely different properties had been described already both by Pictet<sup>6</sup> and by Irvine.<sup>7</sup> Since Levene and co-workers<sup>8</sup> noticed that this supposed 4-methyl glucose was identical with the true 2-methyl glucose of Brigl, it followed that all the previous conclusions based on an unquestioned existence of the 2-methyl glucose of Pictet and of Irvine became necessarily invalid. In the light of these facts, therefore, a reinvestigation of the entire problem was begun and in the present paper the results concerning the structure of one of the monoacetone galactose mercaptals are presented.

In a preliminary communication<sup>9</sup> it was reported that the formerly described<sup>1c</sup> crystalline "2,3-monoacetone galactose dibenzylmercaptal" with m. p. 102–103° and  $[\alpha]_{D}^{25}$  8.8° in acetylene tetrachloride solution, in spite of its apparent uniformity, is not a chemical individual. By repeated fractional recrystallization from acetone

(1) (a) Part I, Pacsu, *Ber.*, **57**, 849 (1924); (b) Part II, Pacsu and von Kary, *ibid.*, **62**, 2811 (1929); (c) Part III, Pacsu and Löb, *ibid.*, **62**, 3104 (1929); cf. (d) Pacsu, *ibid.*, **58**, 1455 (1925).

(2) Research Assistant on Special Funds from the Rockefeller Foundation.

(3) Brigl and Schinle, *Ber.*, **62**, 1716 (1929).

(4) Brigl and Schinle, *ibid.*, **63**, 2884 (1930).

(5) Pacsu, *ibid.*, **66**, 51 (1932).

(6) Pictet and Castan, *Helv. Chim. Acta*, **3**, 645 (1920).

(7) Irvine, *J. Chem. Soc.*, **125**, 1 (1924).

(8) Levene, Meyer and Raymond, *J. Biol. Chem.*, **91**, 497 (1931); cf. *Science*, **73**, 291 (1931).

(9) Pacsu, *THIS JOURNAL*, **58**, 2076 (1936).

and from ethyl alcohol the substance was separated into two monoacetone mercaptals, one with m. p. 112.5° and  $[\alpha]^{20D}$  17.4° in chloroform solution, and the other with m. p. 103° and  $[\alpha]^{20D}$  31.0° in chloroform solution. Since the latter compound was more easily available in pure form, it was chosen as the first object of our investigation. On removal of the benzyl mercaptan residues in methyl alcoholic solution according to the method of Pacsu and Green,<sup>10</sup> the substance gave rise to a monoacetone galactosedimethylacetal with m. p. 125–126° and  $[\alpha]^{20D}$  37.4° in water solution. Although formation of dimethylacetals by application of this method to *l*-rhamnose and fructosedietiylmercaptal have been reported previously,<sup>11</sup> actually this was the first acetal obtained in this Laboratory, but its structure was unknown when the preliminary communication<sup>9</sup> was published. On the basis of the following experimental results it is now established definitely that the acetone residue is attached to carbon atoms 4 and 5, and, therefore, the starting material represents the 4,5-monoacetone galactose-dibenzylmercaptal. Positive reaction of the latter compound with triphenylmethyl chloride in pyridine solution yielding a trityl derivative<sup>12</sup> was the first indication that a free hydroxyl group may be present in position 6. Acetylation of the 4,5-monoacetone dimethylacetal gave readily a triacetate, the 2,3,6-triacetyl 4,5-monoacetone galactose dimethylacetal with m. p. 55° and  $[\alpha]^{20D}$  17.8° in chloroform solution. In the methylation experiments five consecutive methylations of the 4,5-monoacetone dimethylacetal with silver oxide and methyl iodide failed to raise the methoxyl content (43.1%) to the theoretical value (50.3%). This indicated the presence of a primary hydroxyl group resistant to methylation. Finally by application of the modified Freudenberg procedure<sup>13</sup> to this incompletely methylated product, it was possible to obtain the fully methylated compound in one operation. The substance, representing the 2,3,6-trimethyl-4,5-monoacetone galactosedimethylacetal, was then hydrolyzed and

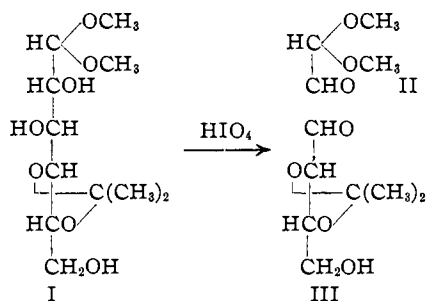
(10) Pacsu and Green, *THIS JOURNAL*, **58**, 1823 (1936), *et seq.*  
 (11) Green and Pacsu, *ibid.*, **60**, 2288 (1938); Pacsu, *ibid.*, **60**, 2277 (1938); **61**, 1671 (1939).

(12) In the preliminary communication<sup>9</sup> it was stated that neither isomer reacted with triphenylmethyl chloride. Subsequently it was found that the triphenylmethyl chloride employed was of a very poor quality since it contained mostly triphenylcarbinol. Reactions carried out with a pure, crystalline preparation gave a positive result for the higher rotating compound but the tests were negative with the low rotating isomer.

(13) Pacsu and Trister, *THIS JOURNAL*, **61**, 2442 (1939).

the 2,3,6-trimethylgalactose obtained was oxidized with bromine yielding crystalline 2,3,6-trimethyl- $\gamma$ -galactonolactone with m. p. 97–98° and initial specific rotation of  $-32.9^\circ$  in water solution, which value changed after ten days to the constant value of  $-21.3^\circ$ .

Application of the periodic acid oxidation method of Jackson and Hudson<sup>14</sup> to the 4,5-monoacetone galactosedimethylacetal (I) showed that one mole equivalent of periodic acid was used up for oxidation.



A survey of the possible structures of monoacetone galactosedimethylacetal indicated that only the 4,6- and 4,5-monoacetone derivatives would require one mole equivalent of periodic acid. If the acetal had its acetone residue at carbon atoms 4 and 6, then the methylated lactone isolated from it would be a 2,3,5-trimethyl derivative, whereas the 4,5-monoacetone derivative would yield a 2,3,6-trimethyl lactone. On oxidation by periodic acid only the latter lactone should require one mole equivalent of periodic acid, whereas the 2,3,5-trimethyl lactone should not use any. Our experiments showed that the lactone in question required one equivalent of periodic acid for oxidation, therefore it could only be the 2,3,6-trimethyl lactone. In order to isolate and identify the scission products, glyoxal dimethyl acetal (II) and 2,3-monoacetone *D*-threose (III), expected from a 4,5-monoacetone galactosedimethylacetal on oxidation by periodic acid, the sugar acetal was treated with this reagent. The mixture of the scission products formed was separated by distillation of the aqueous solution. Glyoxal was found to be present in the distillate and was isolated as the *bis*-phenylhydrazone. The other component of the mixture, 2,3-monoacetone *D*-threose (III), was hydrolyzed by acetic acid to *D*-threose which was identified by its osazone. The *D*-threose was then oxidized with bromine to *D*-threonic acid which was characterized by its

(14) Jackson and Hudson, *ibid.*, **59**, 994 (1937).

brucine salt. Subsequent oxidation of *d*-threonic acid with nitric acid gave rise to *l*-tartaric acid which was isolated as the acid potassium salt. From these experimental results it follows that in the original starting material the acetone residue was attached to carbon atoms 4 and 5.

The investigation is being continued.

### Experimental

**Preparation of 4,5-Monoacetone Galactosedibenzylmercaptan and its 5,6(?)-Isomer.**—Monoacetone galactosedibenzylmercaptan was prepared according to the directions of Pacsu and Löb,<sup>10</sup> and after two crystallizations from chloroform and petroleum ether the fine needles obtained had m. p. 102–104° and  $[\alpha]^{20D}$  8.1° in acetylene tetrachloride solution, which values were in good agreement with those given by the authors for "2,3-monoacetone galactosedibenzylmercaptan." However, a third crystallization, this time from acetone and petroleum ether, gave two fractions with different rotations, which fact indicated that the preparation of Pacsu and Löb was a mixture. Subsequently it was found also that the composition of the preparation varied considerably with minor changes in the conditions of the experiment. In order to secure reproducible results the acetylation was carried out for four hours at about 25° with copper sulfate monohydrate as dehydrating agent in equal weight of the mercaptan which was suspended in ten times its weight of acetone. Under such conditions the acetone solution at the end of the reaction contained only a little diacetone derivative and unchanged mercaptan. The monoacetone derivative was isolated according to the procedure of Pacsu and Löb and then it was submitted to fractional crystallization by addition of small quantities of petroleum ether to the acetone solution. Several fractions with different rotations were obtained. The fractions which had the highest rotations were united and recrystallized from ethyl alcohol. Finally a product was obtained in the form of long needles showing m. p. 102.5–103° and  $[\alpha]^{20D}$  31.0° in chloroform solution, which values did not change on further recrystallizations. Our investigation centered around the structure of this substance, which was proved to be the 4,5-monoacetone galactosedibenzylmercaptan. The fractions with the lower rotations were purified by recrystallizations from acetone and petroleum ether and finally from acetone alone. This substance crystallized in a jelly-like aggregate of very fine needles. The preparation finally obtained had m. p. 112.5° and  $[\alpha]^{20D}$  17.4° in chloroform solution, which values did not change on further recrystallization. This substance probably represents the 5,6-monoacetone galactosedibenzylmercaptan and its structure is being investigated. The two isomers formed in about equal quantities and the yields were quite satisfactory. When tested with pure<sup>12</sup> triphenylmethyl chloride in pyridine solution, the 4,5-monoacetone derivative gave a trityl derivative which, on account of its amorphous nature, was not investigated further. The other isomer gave negative results and the unchanged material was recovered. The two isomers were analyzed for acetone according to the procedure of Elsner.<sup>15</sup>

(15) Elsner, *Ber.*, **61**, 2364 (1928).

In order to take out the mercaptan residues, 0.3 g. of mercuric chloride was added to the 0.15-g. samples in these acetone determinations.

*Anal.* 4,5-Monoacetone galactosedibenzylmercaptan, calcd. for  $C_{16}H_{30}O_6S_2$ : C, 61.3; H, 6.72; acetone, 12.9. Found: C, 61.45; H, 7.1; acetone, 12.75. 5,6(?)-Monoacetone galactosedibenzylmercaptan: Found: C, 61.2, 61.1; H, 6.64, 6.8; acetone, 12.4, 13.0, 12.8.

**Conversion of 4,5-Monoacetone Galactosedibenzylmercaptan into 4,5-Monoacetone Galactosedimethylacetal.**—The removal of the mercaptan residues was carried out at room temperature by the method of Pacsu and Green.<sup>10</sup> A solution of 33 g. of mercuric chloride (2 moles) in 75 cc. of absolute methyl alcohol was added in thirty minutes to a mixture of 27 g. of 4,5-monoacetone galactosedibenzylmercaptan, 27 g. of yellow mercuric oxide and a little drierite in 120 cc. of absolute methyl alcohol. After four hours of continuous stirring the mixture was filtered, the filtrate treated with 5 cc. of pyridine and kept at 0° for two hours. The pyridine mercuric chloride was filtered and the solution evaporated to a sirup *in vacuo* at 40°. The residue was dissolved in a little ice-cold water, the solution filtered and neutralized to phenolphthalein with a few drops of sodium hydroxide solution, then evaporated *in vacuo* at 45°. The residue was evaporated successively under reduced pressure from ethyl alcohol solutions and crystallized first from benzene, then from ethyl acetate. The pure substance represented the 4,5-monoacetone galactosedimethylacetal and had m. p. 125–126° and  $[\alpha]^{20D}$  37.4° in water solution; yield, about 70%. It was soluble in cold water and methyl alcohol, in hot acetone, ethyl acetate and dioxane.

*Anal.* Calcd. for  $C_{11}H_{22}O_7$ : C, 49.62; H, 8.27;  $OCH_3$ , 23.30. Found: C, 49.70; H, 8.22;  $OCH_3$ , 23.30.

On acetylation with acetic anhydride and pyridine, 2,3,6-triacetyl 4,5-monoacetone galactosedimethylacetal was obtained in the form of prismatic needles from petroleum ether, or from a mixture of chloroform and petroleum ether at 0°. The substance is very soluble in most of the organic solvents. It had m. p. 55° and  $[\alpha]^{20D}$  17.8° in chloroform solution (*c*, 2.057). In an acetyl estimation 0.2668 g. of the substance required 20.2 cc. of 0.1 *N* sodium hydroxide solution. The value calculated for the hydrolysis of three acetyl groups is 20.4 cc.

*Anal.* Calcd. for  $C_{17}H_{28}O_{10}$ :  $OCH_3$ , 15.8. Found:  $OCH_3$ , 15.4.

**Preparation of 2,3,6-Trimethyl  $\gamma$ -Galactonolactone from 4,5-Monoacetone Galactosedimethylacetal.**—Ten grams of the acetal was dissolved in 35 cc. of methyl iodide and the solution was treated with 20 g. of silver oxide according to the method of Purdie and Irvine.<sup>16</sup> The methylated material was extracted with chloroform and recovered. After a second methylation with the same amounts of the reagents the isolated sirup had a methoxyl content of 41.2% instead of 50.3% calculated for a fully methylated compound. After a third, fourth ( $OCH_3$ , 42.0%) and fifth ( $OCH_3$ , 43.1%) methylation, it was concluded that probably the primary hydroxyl group of the substance was resistant to methylation with these reagents. Therefore, the sirup was treated with sodium and methyl iodide

(16) Purdie and Irvine, *J. Chem. Soc.*, **63**, 1021 (1903).

according to the modified Freudenberg procedure.<sup>13</sup> A pale yellow liquid with 50.1% methoxyl content was obtained. Seven grams of this 2,3,6-trimethyl galactose-dimethylacetal was then dissolved in 50 cc. of 0.05 *N* hydrobromic acid and the solution was heated on a water-bath at 60–70° until constant rotation was observed (three and one-half hours). The solution, which contained 2,3,6-trimethyl galactose, was treated with 20 g. of bromine and kept at 35–40° for sixty-five hours. The non-reducing solution was then worked up in the usual manner (*i. e.*, bromine removed by aeration, acid neutralized with silver carbonate, silver salt decomposed with hydrogen sulfide). The resulting clear solution was concentrated *in vacuo* at 45–50°. A colorless, crystalline compound, the 2,3,6-trimethyl- $\gamma$ -galactonolactone, separated out; yield, 2.5 g. The substance was recrystallized twice from aqueous methyl alcohol. The fine needles had m. p. 97–98° and an initial specific rotation of  $-32.9^\circ$  in water solution (*c*, 1.686), which value after ten days changed to the constant rotation of  $-21.3^\circ$ .

*Anal.* Calcd. for  $C_9H_{16}O_6$ :  $OCH_3$ , 42.3. Found:  $OCH_3$ , 41.9.

For the oxidation experiment 10 cc. of a 0.1 molar solution of the lactone was treated first with one equivalent of standard sodium hydroxide solution, and then with 20 cc. of a 0.1 molar periodic acid solution which had been neutralized previously. After thirty minutes 5 cc. of the reaction mixture was titrated for the excess of periodate with standard arsenite solution and it was found that 2.27 cc. of periodic acid was used up for the oxidation of the lactone (calcd. for one mole of periodic acid: 2.30 cc.). Five-cc. samples were again titrated after one hour (found: 2.27 cc.), two and one-half hours (found: 2.27 cc.) and twenty-four hours (found: 2.37 cc.). These results indicated that one mole of periodic acid was required for the scission of the lactone, which fact was considered as evidence that the analyzed product was the 2,3,6-trimethyl derivative.

**Oxidation of 4,5-Monoacetone Galactosedimethylacetal with Periodic Acid to Glyoxal and 2,3-Monoacetone *d*-Threose.**—It was found in a preliminary experiment that from an excess of a 0.1 molar periodic acid solution only one mole equivalent was used for the oxidation of the monoacetone derivative provided that the acid was previously neutralized with sodium hydroxide. In another experiment, in which the periodic acid was not neutralized, it was found that after one hour one mole equivalent was used up, but if the reaction mixture was allowed to stand for a longer period of time, then further oxidation occurred. This undoubtedly was due to the reaction of the oxidant with adjacent hydroxyl groups liberated by hydrolysis from the acid-sensitive primary oxidation products.

For the isolation of the scission products 3 g. of the 4,5-monoacetone galactosedimethylacetal was dissolved in 1355 cc. of water and to the solution 45 cc. of a 0.2631 molar periodic acid was added (5% excess). After twenty minutes it was found by titration of a sample with arsenite solution that one mole of periodic acid was used up. The solution was then neutralized with barium hydroxide solution to phenolphthalein. Immediately a white, flocculent precipitate separated out. The mixture was

kept at 0° for two hours, filtered and the precipitated iodates washed with ice water. To the combined filtrate and washings 3 g. of barium carbonate was added and the mixture was allowed to stand overnight at room temperature. The filtered solution was distilled *in vacuo* at 40–50°. On treatment with phenylhydrazine dissolved in five parts of glacial acetic acid, the distillate gave a yellow precipitate. The residual sirup was dissolved in water and concentrated *in vacuo*, this process being repeated until the distillate gave no more reaction with phenylhydrazine (thirty hours of distillation). The combined precipitates were recrystallized from 85% alcohol; yield, 1.9 g. of pale yellow needles; m. p. 168–169°. The substance represented the *bis*-phenylhydrazone of glyoxal first obtained by Fischer,<sup>17</sup> who gave m. p. 169–170°. The presence of the glyoxal in the distillate probably was due to the hydrolysis of the dimethyl semiacetal during the protracted contact of the latter with water.

The residual sirup, 2,3-monoacetone *d*-threose, was dissolved in absolute ethyl alcohol, the solution filtered with activated carbon and the filtrate evaporated *in vacuo* to a sirup (1.74 g.) which reduced Fehling's solution and had an initial specific rotation of 18.7° in water solution (*c*, 1.065) that changed after two days to 12.5°. The presence of the isopropylidene group was shown by an acetone estimation according to the method of Bell and Harrison.<sup>18</sup>

**Conversion of 2,3-Monoacetone *d*-Threose into Potassium Acid *l*-Tartrate.**—A solution of 1.7 g. of 2,3-monoacetone *d*-threose in 20 cc. of 10% acetic acid was heated on a water-bath until constant rotation was obtained (one hour). The solution had  $[\alpha]^{20}_D -10.5^\circ$  which was in good agreement with the values ( $-10.7$  to  $-12.0^\circ$ ) given by Hockett<sup>19</sup> for the rotation of *d*-threose. The acetic acid was removed by distillation of the solution *in vacuo*. A 70-mg. sample of the sirupy product gave a crystalline osazone with m. p. 159–160° (Hockett<sup>19</sup> reported m. p. 164°). The *d*-threose was then oxidized in 25 cc. of aqueous solution with 4 g. of bromine and the *d*-threonic acid formed was isolated in the usual manner. A clear sirup (0.95 g.) was obtained which had  $[\alpha]^{20}_D -26.1^\circ$  in water solution (*c*, 1.645).

Anderson<sup>20</sup> gave rotations varying from  $-20$  to  $-30^\circ$ . From the threonic acid the brucine salt was obtained in a procedure similar to that of Ruff.<sup>21</sup> The salt crystallized from 85% ethyl alcohol in the form of fine needles which melted at 199° and had  $[\alpha]^{20}_D -37.2^\circ$  in water solution (*c*, 1.340). Hockett<sup>19</sup> reported m. p. 197–198° and  $[\alpha]^{20}_D -36.8^\circ$ .

*Anal.* Calcd. for  $C_7H_{14}O_6N_4$ :  $OCH_3$ , 11.69. Found:  $OCH_3$ , 11.60.

The *d*-threonic acid (0.7 g.) was oxidized with 3.5 cc. of nitric acid (*d*, 1.2) to *l*-tartaric acid which was converted into the acid potassium salt as described by Reichstein.<sup>22</sup> The crystalline product had  $[\alpha]^{20}_D -28.1^\circ$  in

(17) Fischer, *Ber.*, **17**, 575 (1884).

(18) Bell and Harrison, *J. Chem. Soc.*, 350 (1939).

(19) Hockett, *This Journal*, **57**, 2260, 2265 (1935).

(20) Anderson, *Am. Chem. J.*, **42**, 423 (1909).

(21) Ruff, *Ber.*, **32**, 3672 (1899).

(22) Reichstein, *Helv. Chim. Acta*, **19**, 1016 (1936).

a 2% potassium hydroxide solution (*c*, 1.425). Hockett<sup>19</sup> recorded  $[\alpha]^{24D} -29.7$  in a 2% sodium hydroxide solution and Reichstein<sup>22</sup> gave  $[\alpha]^{22D} -32.8^\circ$  in a 2% potassium solution.

### Summary

1. The "2,3-monoacetone galactosedibenzylmercaptal" of Pacsu and Löb was found to be a mixture of two isomeric monoacetone derivatives.

2. The chemical structure of the higher rotating isomer was investigated and it was proved that the isopropylidene group was attached on carbon atoms 4 and 5.

3. This conclusion was drawn from the results of a series of transformations in which the substance was first converted into the 4,5-monoac-

etone galactosedimethylacetal. On methylation the latter gave rise to the 2,3,6-trimethyl derivative which on hydrolysis and subsequent oxidation yielded crystalline 2,3,6-trimethyl  $\gamma$ -galactonolactone.

4. Oxidation by periodic acid of the monoacetone galactosedimethylacetal gave glyoxal and 2,3-acetone *d*-threose, which scission products could form only if the starting material had the isopropylidene group at carbon atoms 4 and 5.

5. The glyoxal was isolated as *bis*-phenylhydrazone, the 2,3-acetone threose was converted into *d*-threonic acid from which the acid potassium salt of *l*-tartaric acid was prepared.

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[CONTRIBUTION NO. 168 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

## Acidic Constituents of a California Straight-run Gasoline Distillate

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The acidic constituents of petroleum from various regions have been a source of rather extensive investigation. The isolation and identification of numerous individuals of the acyclic series have been reported. Among these are: formic and oxalic acids from Grosny distillates by Schidkoff<sup>2</sup>; palmitic, stearic, myristic, and arachidic acids from Ishikari distillates by Tanaka and Kuwata<sup>3</sup>; isoamylacetic and diethylpropionic acids from Baku petroleum by Chichibabin<sup>4</sup>; isovaleric, *n*-heptylic, *n*-octylic, and *n*-nonylic acids and ethyl mercaptan from a West Texas pressure distillate by Williams and Richter<sup>5</sup>; *n*-butyric and *n*-valeric acids and dimethylmaleic anhydride from a Texas distillate by Schutze<sup>6</sup>; and isocaproic acid from Rumanian petroleum by Nenitzescu and co-workers.<sup>7</sup>

As to the phenolic constituents, phenol, the three cresols, and several of the xylenols have been isolated.<sup>5,7,8</sup>

(1) This paper represents part of a dissertation submitted to the Graduate School of The University of Texas in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Schidkoff, *J. Soc. Chem. Ind.*, **18**, 360 (1899).

(3) Tanaka and Kuwata, *J. Faculty Eng. Tokyo Imp. Univ.*, **17**, 293 (1928).

(4) Chichibabin, *et al.*, *Chimie et industrie*, Special No., 306 (March, 1932).

(5) Williams and Richter, *THIS JOURNAL*, **57**, 1686 (1935).

(6) H. G. Schutze, Ph.D. Dissertation, The University of Texas, June, 1938, to be published elsewhere.

(7) Nenitzescu, Isăcescu and Volrap, *Ber.*, **71B**, 2056 (1938).

(8) (a) Tanaka and Kobayashi, *J. Faculty Eng. Tokyo Imp. Univ.*, **17**, 127 (1927); (b) Holzmann and von Pilat, *Brennstoff-Chem.*, **11**, 409 (1930).

The isolation of numerous naphthenic acids, varying in complexity from cyclopentanecarboxylic acid to pentacosan-naphthenic acid, has been reported. Later investigation has proved that the majority of these acids were mixtures. Von Braun and co-workers<sup>9</sup> are given credit for the isolation of the first homogeneous naphthenic acid. These investigators isolated 3,3,4-trimethylcyclopentanone from the degradation products from mixtures of decanaphthenic acids from various sources. This ketone was then reconverted to 3,3,4-trimethylcyclopentylacetic acid.

Very recently Nenitzescu and co-workers<sup>7</sup> have reported the isolation, through selective amide formation, and identification of cyclopentanecarboxylic, cyclopentylacetic, and 3-methylcyclopentylacetic acids from Rumanian petroleum.

The material investigated in the present study was a complex mixture of crude petroleum acids from the sodium carbonate wash of Signal Hill straight-run gasoline.<sup>10</sup> The objectives of the investigation were: (1) to study and to improve methods of separation of acid mixtures, (2) to attempt to develop new methods of separation, (3) to attempt the isolation and identification of all of the aliphatic acids from formic through the pentanoic acids, and (4) to study the fractions in

(9) Von Braun, Mannes and Reuter, *Ber.*, **66B**, 1499 (1933).

(10) These crude acids were kindly donated by the MacMillan Petroleum Corporation of Long Beach, California.