n. d. 1.300, was converted to its amide, m. p. 102-104°, mixed m. p. 101-103°; and to its *p*-toluidide. m. p. 74°. mixed m. p. 73-74°.

n-**Heptanoic Acid.**—Early in the separation procedures the presence of large amounts of *n*-heptanoic acid had been indicated by the boiling point of the acid, and particularly that of the methyl ester, since methyl esters in mixture appear to boil close to their true boiling points, and this acid and its methyl ester were used as convenient dividing points between the lower and the higher series of acids and esters. Williams and Richter[10] had previously isolated this acid (*n*-octanoic, and *n*-nonanoic) from Texas pressure distillate. The amide was prepared in our work by treating the methyl ester with an equal volume of concentrated ammonium hydroxide and leaving the mixture for a week in a stoppered flask before filtering off the amide formed. After five recrystallizations the melting point was 94.5-95.0° and a mixed melting point with an authentic sample was 95.0°; *o*-phenylenediamine derivative, m. p. 136° mixed m. p. 136°.

n-**Octanoic Acid.**—One liter of acids obtained from ester fractions 580-590, Fig. 1, was dissolved in 8 liters of petroleum ether (b. p. 65-80°) and stirred vigorously for two hours with 350 cc. of 10% sodium hydroxide solution. The layers were separated and an attempt made to remove another fraction of acids in the same way, but emulsification prevented further use of this method at this stage without extensive further dilution of the petroleum ether as well as the aqueous solution; so the remaining acids were neutralized in one step, dried, and fractionated, b. p. 236-238°, n^{20}D 1.4327, d^{20}_4 0.9185, n. d. 1.317. The n. d.

value indicated that the acid was practically all aliphatic in nature and the large volume of this series available and physical properties indicated *n*-octanoic acid. The amide melted at 105-106° and there was no depression in a mixed melting point with the amide of authentic *n*-octanoic acid.

n-**Nonanoic Acid.**—Ester fraction 710, Fig. 1, b. p. 213°, n^{20}D 1.4257, yielded an amide melting at 99°. Mixed with the amide of known *n*-nonanoic acid the melting point was unchanged. This with the large volume available and physical properties showed the presence of this acid, b. p. 254-256.5°, n^{20}D 1.4379.

Summary

By careful and extensive fractionation of certain California petroleum acids and their esters a series of 720 fractions of esters was obtained. Curves of ester fraction number plotted against boiling point and against index of refraction are presented as Fig. 1.

By studying various series of ester fractions with low index of refraction and with essentially constant boiling point the following aliphatic acids were isolated and identified: 2- and 3-methylpentanoic and *n*-hexanoic acids; 2-, 3-, 4-, and 5-methylhexanoic and *n*-heptanoic acids, and *n*-octanoic and *n*-nonanoic acids.

No evidence for the presence of 2,2-dimethylpropanoic or 2-methylbutanoic acid could be found.

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

[CONTRIBUTION NO. 316 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

Petroleum Acids. VI. Naphthenic Acids from California Petroleum

BY W. O. NEY,[1] W. W. CROUCH,[1] C. E. RANNEFELD[2] AND H. L. LOCHTE

All except the last of the series of naphthenic acids reported in this paper were isolated from the series of 720 fractions of methyl esters of petroleum acids shown in Fig. 1 of the preceding paper of this series[3] (hereafter referred to as Fig. 1).

Preliminary experiments had shown that procedures used at the refinery and supplemented here had removed phenolic compounds from these acids. This made it possible to decide which of the 720 fractions of esters were derived from naphthenic acids by noting the index of refraction of the fraction. The first 180 fractions consisted almost entirely of esters of aliphatic acids,

but "peaks" in the refractive index curve showed an accumulation of naphthenic acids at fractions 210-220, 370-380, 460-470, 510-520, 530-540, 560-565, 650-660 and 680-690 with possibly minor concentrations at various other series of fractions. The curve did not indicate, however, whether any particular "peak" was due to a single naphthenic acid or to several; and the boiling point curve showed that, in all cases, fractions consisted of mixtures of esters of both aliphatic and naphthenic acids. The isolation and identification of aliphatic acids from this mixture was relatively simple in those cases in which a single main acid of this type was present since partial neutralization in practically all cases removed naphthenic acids to a sufficient extent to permit preparation of solid derivatives of the aliphatic

acid. While there were large losses at each step and while the yield of pure acid was usually low, identification could often be accomplished. In the case of the naphthenic acids partial neutralization removed them first—mixed, however, with a considerable amount of aliphatic acids—and recourse had to be taken to efficient but tedious counter-current extraction or neutralization and other schemes useful in difficult separations.

Cyclopentanecarboxylic acid was isolated from ester fractions 200–220, Fig. 1. Much more than the "peak" (totalling 70 cc. of material) was present originally but portions of this region were used in preliminary separation experiments and were not recombined for the final fractionation and study. Its structure was confirmed by comparison with the synthetic acid. Nenitzescu,[4] working on acids from Ploesti petroleum, reported the isolation of this acid.

2-Methylcyclopentanecarboxylic acid was isolated from the acids derived from ester fractions 377–384, Fig. 1, through counter-current fractional neutralization and recrystallization of solid derivatives. Its structure was confirmed by comparison with the synthetic acid synthesized from cyclohexane through 2-methylcyclopentyl methyl ketone and oxidation of this compound by the haloform reaction. Aschan[5] and Markownikoff,[6] working on different supplies of European petroleum acids, isolated but did not definitely identify a seven-carbon naphthenic acid boiling at 215–217° having a methyl ester boiling at 164–167°. Since the California ester boiled at 165–167° and the acid boiled at 220° this would appear to be the same acid were it not for the fact that both Aschan and Markownikoff reported that their amide melted at 123.5° (Markownikoff 121–123.5°) while the amide of the California acid melted at 147–148°.

The next "peak" at ester fractions 460–470, Fig. 1, appeared to be part of a large naphthenic acid region extending to fraction 490; but, so far, only one naphthenic acid has been isolated from it, in spite of the use of a more efficient batch type of counter-current extraction column, Fig. 2. The drop in index of refraction after fraction 464 may be due to accumulation of the methyl ester of the plentiful normal heptanoic acid in the last 20 fractions of the series. Hydrazoic acid degradation of the acids obtained from the first ten

(4) Nenitzescu, Isacescu and Volrap, *Ber.*, **71B**, 2056 (1938).
(5) Aschan, *ibid.*, **23**, 870 (1890).
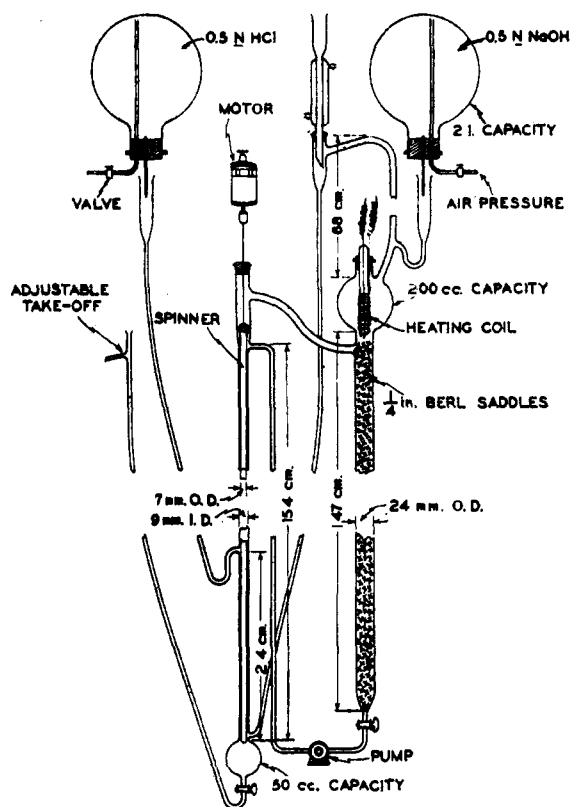(6) Markownikoff, *Ann.*, **307**, 367 (1899).

Fig. 2.

fractions yielded a mixture of amines that gave no clues as to the identity of the acid or acids. The amide of the acid melted at 147–148°, and this was depressed when mixed with the amide of synthetic 2-methylcyclopentanecarboxylic acid. The amide of synthetic cyclopentaneacetic acid melted at 148–149°, and the amide of California acid melted at 146–148° when mixed with the amide of synthetic cyclopentaneacetic acid. In view of this behavior and the fact that Nenitzescu[4] reported the isolation of cyclopentaneacetic acid from petroleum it was at first thought that our acid was cyclopentaneacetic acid, but a mixed melting point of the corresponding *p*-toluidides was depressed 30°, thus definitely eliminating this acid. This eliminated all probable structures except 3-methylcyclopentanecarboxylic acid, which was synthesized and found to be identical with the petroleum acid.

Ester fractions 510–520, Fig. 1, were found to represent a complex mixture of at least two naphthenic and at least one aliphatic acid, all in large concentration. The steps involved are described in some detail since this separation is certainly the most difficult yet accomplished in naphthenic acid separations and involved the use of nearly all

types of methods applicable to the separation of mixtures containing large concentrations of at least three similar compounds.

The ester mixture was saponified and the resulting acid fractionally neutralized by 7% sodium hydroxide. Each of the six fractions was studied and results indicated the presence of a mixture of two or more C_7 naphthenic acids and one or more C_8 aliphatic acids. Fractional neutralization in the spinner column removed the naphthenic acids first and left most of the aliphatic acids in the column. Fractional silver salt formation of the extract did not effect an appreciable separation of the two naphthenic acids; but solid derivatives could now be obtained and these and various physical properties indicated that both cyclohexanecarboxylic and cyclopentaneacetic acids were present. This conclusion was arrived at because: (1) The n. d. values[7] indicated that the acids were now essentially naphthenic in nature. (2) The neutralization equivalents now agreed well with those expected of C_7 acids. (3) Carbon and hydrogen analyses confirmed the presence of only C_7 naphthenic acids. (4) Nitrogen analyses on mixed amides and mixed p-toluidides now obtainable in solid form agreed with those calculated for C_7 naphthenic acids. (5) The boiling points of the acids excluded all C_7 naphthenic acids except the two mentioned.

As no solid derivative at this stage could be purified to constant melting point, further fractionation was required. Since secondary alcohols are esterified more slowly than primary alcohols and since secondary acids are esterified more slowly than primary acids, fractional esterification of this mixture of primary and secondary acids with a secondary alcohol like isopropyl alcohol might have been expected to result in extensive separation of the acids. Experiments using both a rate and an equilibrium procedure led to very little separation, however.

Repeated batch spinner column extraction—starting the second extraction with only the first fraction obtained in the first extraction and adding additional fractions in order as second extraction fractions were removed—produced a considerable accumulation of different acids in earlier and in later fractions but even these yielded derivatives that could not be purified.

In the hope that the various series of fractions

could now be separated by fractionation of the corresponding acids, the first series of acids was fractionated at 10 mm. through an 8 mm. by 150 cm. spinning band column.[8] Three of the first fractions and the last two now solidified on cooling in an ice–salt mixture. The amide of the first fractions melted correctly for that of cyclopentaneacetic acid, and a mixed melting point showed no depression; and the amide of the last fraction showed the same behavior when mixed with synthetic cyclohexanecarboxylic acid; but in both cases neither the p-toluidide nor the p-phenylphenacyl ester was obtained in pure form.

An attempt to extend separation of the fractions obtained from the spinning band column—by steam distilling a mixture of the sodium salts of a series of similar fractions until no more acid was distilled, then adding aliquots of dilute hydrochloric acid and continuing the steam distillation—proved less effective than the spinning band column.

Fractionation at 60 mm. pressure through the spinning band column of the acid chlorides obtained from the steam distillation fractions also failed to lead to appreciable additional separation.

Von Braun[9] reported that separation of the amines obtained on degradation of naphthenic acids was much more easily accomplished than separation of the acids or the esters. Recrystallization of the picrates of the amines obtained from California acids did not prove promising, but, again following von Braun's lead, recrystallization of the acid oxalates of the amines obtained on degradation of these acids yielded pure oxalates that proved identical with the oxalates obtained from synthetic cyclopentaneacetic and cyclopentanecarboxylic acids. It was later found that cyclohexanecarboxylic acid is also present in fraction 535 and fairly easily isolated here. This appears to be the first time that cyclohexanecarboxylic acid has been isolated from petroleum acids even though a number of investigators have attempted to find it. Our difficulties may explain why earlier workers failed in their attempts.

Simple fractional neutralization of the acids obtained from ester fractions 550–570, Fig. 1, yielded, as first fractions, sufficiently pure naphthenic acid to permit purification of the amide by recrystallization. Since there was no clue as to the identity of the acid concerned, the acid was

(7) Schutze, Shive and Lochte, Ind. Eng. Chem., Anal. Ed., 12, 262 (1940).

(8) Lesesne and Lochte, ibid., 10, 450 (1938).

(9) Von Braun, Ann., 490, 100 (1931).

degraded by the hydrazoic acid method, the resulting amine treated with nitrous acid, and the mixture of alcohol and olefin oxidized with alkaline permanganate to yield 3-methyladipic acid as the only acid isolated. This acid could have been obtained from 3- or 4-methylcyclohexanol or from one of their dehydration products. These, according to the theory of Whitmore,[10] could have been derived from 3- or 4-methylcyclohexanecarboxylic acid without rearrangement or from 2- or 3-methylcyclopentaneacetic acid with rearrangement. A comparison of physical properties of the acids and amides concerned eliminated all but 3-methylcyclopentaneacetic acid and the unknown stereoisomers of 3-methylcyclohexanecarboxylic and of 2-methylcyclopentaneacetic acids. Since the unknown stereoisomers were apparently not obtained as by-products in syntheses of the known acids they probably represent the less stable isomers. The petroleum acids presumably would represent the more stable forms and these were not isolated. Nenitzescu[4] isolated a petroleum amide with the same melting point as that of this California amide. He synthesized 3-methylcyclopentaneacetic acid and reported properties for the acid and derivatives that agreed well with corresponding compounds from the California acid so that there appeared to be no doubt that Nenitzescu's synthetic acid was identical with ours; so the rather tedious synthesis of this acid was not repeated in this work.

The naphthenic acids present as esters in fractions 640–670, Fig. 1, appeared to represent a complex mixture of naphthenic and aliphatic acids from which 2,3-dimethylcyclopentaneacetic acid was fairly easily isolated. The other acids presented great difficulties due to a strong tendency to emulsification in any of the extraction processes so that very dilute solutions would have had to have been employed, thus making still more tedious any attempt to separate the acids concerned. Fractions 645–655 were refractionated in vacuum through the Stedman column. This process appeared to lead to little additional separation, but the amide obtained from the third fraction was readily purified and found, by analysis, to be derived from a C_9 naphthenic acid. Since very little is known of the many possible isomeric C_9 naphthenic acids, an α-hydrogen determination according to von Braun[11] was made. It indicated

that the carboxyl was not attached to a ring carbon. A sample of methyl ester was then degraded by the method of Skraup and Schwamberger,[12] in which the ester is treated with phenylmagnesium bromide, the product hydrolyzed to the carbinol, which is dehydrated, and the resulting olefin oxidized to the acid. The acid obtained in this case proved to be 2,3-dimethylcyclopentanecarboxylic acid on comparison with the synthetic acid. To complete the proof of structure 2,3-dimethylcyclopentanecarboxylic acid was converted to the acetic acid which was identical with the C_9 naphthenic acid isolated.

Tertiary and Sterically Hindered Acids

Hancock[13] isolated dimethylmaleic anhydride and dl-camphonanic acid (1,2,2-trimethylcyclopentanecarboxylic acid) from acids which could not be esterified by a twenty-four-hour treatment with boiling methanolic hydrogen chloride. Horeczy,[14] continuing the study of hindered acids, isolated trans-2,2,6-trimethylcyclohexanecarboxylic acid and, from lower boiling material, additional amounts of camphonanic acid. A considerable amount of liquid acids was obtained as filtrates when these two solid acids were removed. Further study has resulted in the isolation of larger amounts of the two solid acids and 61 g. of a new solid acid that proved to be identical with cis-2,2,6-trimethylcyclohexanecarboxylic acid obtained by Shive[14] in the course of the synthesis of the trans-isomer. This is the first case in which both stereoisomers of naphthenic acids have been isolated from petroleum. Much difficulty was expected from geometric isomers in this work, but—either because one of the forms is present in very small concentration and is lost in the separation processes or because the less stable form does not ordinarily occur in petroleum acids—this is the first case encountered so far.

Work on naphthenic acids with eight and more carbon atoms is continuing, particularly in a study of the acidic material obtained in the second (sodium hydroxide) tower of the Macmillan Petroleum Refinery at Long Beach, California.

Experimental

Cyclopentanecarboxylic Acid.—Fractions 215–216 of the "peak" at fractions 200–220, Fig. 1, were combined, b. p. 157°, $n^{30}D$ 1.4215. Hydrolysis yielded the acid, b. p. 210°, $n^{20}D$ 1.4438, d^{20}_4 0.9965, n. d. 1.4397. The acid was con-

(10) Whitmore, THIS JOURNAL, **54**, 3274 (1932).

(11) (a) von Braun, Jostes and Munch, Ann., **453**, 113 (1927).

(b) von Braun ibid., **490**, 108 (1931).

(12) Skraup and Schwamberger, ibid., **462**, 141 (1928).

(13) Hancock and Lochte, THIS JOURNAL, **61**, 2448 (1939).

(14) Shive, Horeczy, Wash and Lochte, ibid., **64**, 385 (1942).

verted to the chloride and this to the amide, m. p. 176–177°; and to the *p*-toluidide, m. p. 134–135°.

Anal. of *p*-toluidide. Calcd. for C₁₃H₁₇ON: N, 6.89. Found: N, 6.81, 6.79.

The analysis, physical properties, and n. d. values indicated that this was cyclopentanecarboxylic acid isolated from Roumanian petroleum by Nenitzescu[4] and this acid was synthesized from cyclopentanone through hydrogenation to the alcohol, conversion to the bromide, and preparation of the acid from this by the Grignard reaction. The purified acid, b. p. 215–216°, *n*²⁰D 1.4520, *d*²⁰₄ 1.0545, n. d. 1.530, was converted to the amide, m. p. 177–178°, mixed m. p. 176–177°; and to the *p*-toluidide, m. p. 135°, mixed m. p. 134–135°.[15]

2-Methylcyclopentanecarboxylic Acid.—Fractions 377–384, Fig. 1, were combined and saponified to yield the acids, b. p. 220°, *n*²⁰D 1.4330, *d*²⁰₄ 0.9606, n. d. 1.375. The low n. d. value indicated a considerable concentration of aliphatic acids so the material was dissolved in 5 volumes of petroleum ether and extracted in a counter-current spinner column[16] with 0.5 *N* sodium hydroxide as neutralizing agent. Only the first two of six fractions had n. d. values above 1.390. Extraction fraction 1 had a neutralization equivalent of 129 (calcd. neut. eq. for a C₇ naphthenic acid, 128). Its amide, after repeated recrystallizations from water and from a petroleum ether–benzene mixture melted at 147–148°, its *p*-phenylphenacyl ester at 73.5–74.5°; its *p*-toluidide could not be purified to a constant melting point.

2-Methylcyclopentanecarboxylic acid was synthesized by the method of Nenitzescu and Ionescu[17] from 2-methylcyclopentyl methyl ketone. This ketone was carefully fractionated through a 6-ft. spinning band column[8] to yield a product, b. p. 170°, *n*²⁰D 1.4425. The methyl ketone was oxidized by sodium hypobromite to the acid, b. p. 220°, *n*²⁰D 1.4521, *d*²⁰₄ 1.0184, n. d. 1.475. The acid was converted to its amide, m. p. 149–150°, mixed m. p. 147–149°; to its *p*-toluidide, m. p. 96–97°; and to its *p*-phenylphenacyl ester, m. p. 74–75°, mixed m. p. 73.5–75°.

3-Methylcyclopentanecarboxylic Acid.—Fractions 458–472 out of the naphthenic series 455–490, Fig. 1, were combined and hydrolyzed to yield 35 g. of acids, b. p. 220–224°, *n*²⁰D 1.4395, *d*²⁰₄ 0.9709, n. d. 1.398. Since preliminary tests showed that derivatives could not be purified readily at this stage they were treated in the new batch counter-current spinner column, Fig. 2, using petroleum ether (b. p. 60–75°) as circulating solvent. The new column differs from ones described previously from this Laboratory in the fact that the mixture to be fractionated is now placed in a separate packed column from which the strongest (or most soluble) acids, as sodium salts, are continuously transferred to the top of the spinner column by means of a variable stroke reciprocating pump. This innovation assures thorough contact of the sodium hydroxide with the acid mixture and permits preliminary fractionation of the material in the packed column. The material was cut into six main fractions of 3.4–4.7 cc. and

three final fractions of 1.3–0.3 cc. The first three fractions were naphthenic while later fractions contained more and more *n*-heptanoic and overlapping C₈ aliphatic acids. Fraction 2 was converted to its amide, m. p. 147–148°; its *p*-toluidide, m. p. 106–107°; and its *p*-phenylphenacyl ester, m. p. 72.5–73.5°.

Anal. of amide. Calcd. for C₇H₁₃ON: C, 66.10; H, 10.30. Found: C, 66.11; H, 10.32. *Anal.* of *p*-toluidide. Calcd. for C₁₄H₁₉ON: N, 6.45. Found: N, 6.26.

The amide of synthetic cyclopentaneacetic acid melted at 148–149° and mixed with this petroleum acid amide melted at 146–148°, but the mixture of the *p*-toluidides showed a melting point depression of 30°, so this acid was eliminated and 3-methylcyclopentanecarboxylic acid synthesized. 4-Methylcyclohexanol was oxidized to 3-methyladipic acid with nitric acid. The cyclization of 3-methyladipic acid was accomplished by the method of Nenitzescu and Ionescu[18] by heating with finely divided copper oxide under a 12-in. fractionating column until no more product distilled over. The 3-methylcyclopentanone was hydrogenated at 100° with Raney nickel as catalyst at 2200 lb./sq. in. The resulting alcohol was converted to the acid over the bromide and the Grignard reaction. The acid, b. p. 222°, *n*²⁰D 1.4500, *d*²⁰₄ 1.0106, n. d. 1.468, was converted to its amide, m. p. 147–148°, mixed m. p. 147–148°; its *p*-toluidide, m. p. 106–107°, mixed m. p. 106–107°; and to its *p*-phenylphenacyl ester, m. p. 73–74°, mixed m. p. 73–74°.

Cyclopentaneacetic and Cyclohexanecarboxylic Acids.—Ester fractions 514–20, Fig. 1, were saponified by adding the esters slowly to a mixture of 440 g. of sodium hydroxide, 880 cc. of water, and 275 cc. of methanol and heating on a steam cone under a reflux condenser for fifteen hours. This procedure avoided violent reaction and loss of material that tended to occur at a critical stage in the saponification when the ester mixture was added in one batch at the start. Since the resulting acids failed to yield solid derivatives, they were treated with six portions of 7% sodium hydroxide solution. The six neutralization fractions obtained boiled at 232 to 233° and had neutralization equivalents ranging from 136.3 to 139.9 (calcd. for C₇ naphthenic acid, 128). The n. d. values were all within the lower range of naphthenic acid products so that the material appeared to be probably a mixture of C₇ naphthenic and C₈ aliphatic acids. To separate the naphthenic from aliphatic acids the fractions were now fractionally neutralized in the new batch spinner column at 1:1 reflux using 0.5 *N* solutions of sodium hydroxide and of sulfuric acid as neutralizing and liberating agents. This operation was repeated adding the acid fractions in order in which they were obtained, as sodium salt fractions were removed. These operations concentrated the aliphatic acids very largely in the final fractions and residue and appeared to separate the naphthenic acids into two series differing in index of refraction. While solid derivatives could be obtained, these could not be recrystallized to constant melting point. Fractional silver salt formation[19] failed to separate the naphthenic acids which boiled now at 230–231°.

(15) Mixed melting point determinations were routinely carried out between derivatives of petroleum acids as well as between these and the corresponding synthetic compounds wherever the melting points of purified compounds were as little as 10–12° apart.

(16) Schutze, Quebedeaux and Lochte, *Ind. Eng. Chem., Anal. Ed.,* 10, 675 (1938).

(17) Nenitzescu and Ionescu, *Ann.,* 491, 207 (1931).

(18) Nenitzescu and Ionescu, *Bull. soc. chim. Romania,* 14, 65–68 (1932), through *C. A.,* 27, 1329 (1933).

(19) Schutze, Quebedeaux and Lochte, *Ind. Eng. Chem., Anal. Ed.,* 10, 676 (1938).

Fractional esterification with isopropyl alcohol and hydrogen chloride might lead to the ester of the primary acid (cyclopentaneacetic) rather than to that of the secondary acid (cyclohexanecarboxylic) so a number of attempts were made to separate them by this method. In one series the mixture of acids was treated with an excess of isopropyl alcohol and hydrogen chloride for various lengths of time; in another series various fractions of the calculated amount of alcohol and acid were added to the acid mixture and refluxed for twenty-four hours. In no case was there any appreciable difference between the index of refraction of unchanged acid and of acid obtained from the ester formed.

The first series of extraction fractions from the batch column were next combined and fractionated as acids through an 8 mm. $\times$ 150 cm. spinning band column in the hope that the partially purified acids could now be fractionated by distillation. Three of the first fractions and the last two of 17 fractions now solidified on cooling in an ice–salt freezing mixture. The amide of one of the first fractions showed no depression in a mixed melting point determination with the amide of synthetic cyclopentane-acetic acid, m. p. 149–150°, while the amide, m. p. 184–185°, of the last fraction showed no depression in a similar test with synthetic cyclohexanecarboxylic acid, but neither first nor last fractions yielded *p*-toluidides or *p*-phenylphenacyl esters whose melting points could be raised to the melting points of the corresponding synthetic acid derivatives.

Steam distillation of the sodium salts of a mixture of first fractions until no more acid came over, addition of an aliquot of dilute hydrochloric acid and renewed steam distillation, and repetition of these steps until all acids had been liberated and steam distilled was much less efficient than the spinning band fractionation.

The steam distillation fractions were now combined and converted to acid chlorides and these fractionated through the spinning band column, but again the separation was not so good as in the first fractionation as acids. The acid chlorides were combined, hydrolyzed to acids, and degraded by the hydrazoic acid method of K. F. Schmidt as modified by Oesterlin.[20] The resulting amines were fractionated and picrates of the first two and the last two fractions were prepared, but both picrates melted lower than picrates of amines obtained from the two synthetic acids. Therefore, following von Braun's[9] procedure, the oxalates of the amines obtained from the synthetic acids as well as of those obtained from the petroleum acids were prepared.

Cyclopentaneacetic acid was prepared by the malonic ester synthesis,[21] b. p. 231° (740 mm.), n^{20}D 1.4524. The amine, b. p. 137–138° (743 mm.), n^{20}D 1.4560, obtained on degradation of cyclopentaneacetic acid by the method used on the petroleum acids, was converted to the picrate, m. p. 168.5–169.5°; and to the oxalate, m. p. 171.5–172.5°. The melting point of the synthetic oxalate was not lowered when mixed with the oxalate of the amine obtained from petroleum acid. A nitrogen determination on the oxalate of the petroleum product showed 6.98% while $C_8H_{15}O_4N \cdot 1/2H_2O$ requires 7.07.

Synthetic cyclohexanecarboxylic acid, b. p. 234°, n^{20}D

1.4588, was degraded to the amine as above, and this converted to the picrate, m. p. 159–160°; and to the oxalate, m. p. 245° with decomposition. The mixture of this oxalate and that resulting from the amine obtained from petroleum acid showed the same behavior. A nitrogen determination on the oxalate showed 9.72%, while that required for the dibasic oxalate, $C_{14}H_{28}O_4N_2$, is 9.72%.

From the physical properties of the acids and esters and from the melting point behavior of their amides and of the oxalates of these amines there can be no doubt that both cyclohexanecarboxylic and cyclopentaneacetic acids were present in these fractions.

3-Methylcyclopentaneacetic Acid.—To determine the nature of the "peak" at ester fractions 550–570, Fig. 1, 1200 cc. of esters, b. p. 189–192°, n^{20}D 1.426–1.430, was saponified, the resulting acids dissolved in 6 l. of petroleum ether, and fractionally neutralized by stirring with 300-cc. aliquots of 10% sodium hydroxide. As usual, the volume of acids obtained from various treatments varied and naphthenic acids were concentrated in the earlier fractions.

Neutralization fractions 1–3 yielded naphthenic acids, b. p. 239°, n^{20}D 1.4487, d^{20}_4 0.9760, n. d. 1.405, neut. equiv. 144. The usual procedure and recrystallization from dilute ethanol, and then from benzene–petroleum ether yielded the amide, m. p. 141–142°.

Anal. Calcd. for $C_8H_{15}ON$: N, 9.92. Found: N, 9.99.

Nenitzescu[4] prepared 3-methylcyclopentaneacetic acid and reported b. p. 236–238°, d. 0.9818, n^{20}D 1.4504. His amide melted at 142° and the acid chloride boiled at 192–194°.

Fifteen grams of acids from extraction fractions 1–3 was dissolved in 100 cc. of chloroform and added to 45 cc. of concentrated sulfuric acid.[20] To the mixture was added slowly 12 g. of sodium azide, external cooling being used to keep the temperature from rising above 40°. The reaction was allowed to continue for six hours below 40°, then for half an hour under reflux. The chloroform was then distilled off, the sulfuric acid diluted and the solution made alkaline with concentrated sodium hydroxide. An amine layer separated and was removed by steam distillation. It was then dissolved in dilute sulfuric acid and 9 g. of sodium nitrite added. Dilute sulfuric acid was added as needed to continue gas evolution. After twelve hours the layer of alcohol–olefin mixture was removed and the aqueous layer extracted with ether. The ether was removed from the combined alcohol–olefin mixture and this was added to a solution of 1.8 g. of sodium hydroxide and 17 g. of potassium permanganate in 50 cc. of water. The temperature was kept below 10° while the mixture was stirred for two hours, until the permanganate was decolorized. The manganese dioxide was filtered off and unchanged alcohol extracted with ether. The alkaline solution was concentrated to 25 cc., acidified with concentrated hydrochloric acid, and extracted repeatedly with ether. The residue obtained on evaporating off the ether yielded 0.5 g. of acid, m. p. 92–94°. Mixed with an authentic sample of 3-methyladipic acid the melting point was 93–94°. The low yield was partly due to the fact that only half of the calculated amount of permanganate was used in the oxidation, but Vogel[22] in the oxidation of pure 4-

(20) Oesterlin, *Angew. Chem.*, **45**, 536 (1932).
(21) Verwey, *Ber.*, **29**, 1996 (1896).
(22) Vogel, *J. Chem. Soc.*, 911 (1931).

methylcyclohexanol with nitric acid obtained a yield of only 35%.

2,3-Dimethylcyclopentaneacetic Acid.—Ester fractions 645–655, Fig. 1, were combined to yield 1100 cc. of esters, b. p. 201–202°, n^{20}D 1.4342–1.4350, and the mixture fractionated through the 6-ft. Stedman column. The acid obtained from the third fraction had an index of refraction n^{20}D 1.4483, and a neutralization equivalent of 155.5, indicating a C_9 naphthenic acid. Six grams of this acid yielded an amide which after repeated recrystallization melted at 159°.

Anal. Calcd. for $C_9H_{17}ON$: N, 9.02. Found: N, 9.07.

The first 30% of the volume of Stedman column fractions was saponified and the resulting acids fractionally neutralized with 10% sodium hydroxide to yield 10 fractions. Five grams of the first neutralization fraction obtained was used to determine the number of α-hydrogen atoms present by the chlorine number method of von Braun[11] whose directions were followed in detail. The imide chloride obtained boiled at 140° at 5 mm. It was hydrolyzed to the chloroamide, which distilled at 150–154° at 5 mm.

Anal. Calcd. for $C_{11}H_{20}ONCl$: Cl, 16.28; for $C_{11}H_{19}ONCl_2$: Cl, 28.12. Found: Cl, 26.50.

Since this test showed that the acid did not have the carboxyl attached to a ring carbon atom, degradation by the method of Skraup and Schwamberger[12] was next carried out, following their directions, on the second neutralization fraction. Esterification yielded 20 g. of methyl ester which yielded finally 29 g. of olefin, b. p. 188–193° at 5 mm. The viscous yellow liquid readily absorbed bromine in carbon tetrachloride solution. Chromic acid oxidation first in acetic acid and then in sulfuric acid solution according to the directions of Skraup and Schwamberger yielded 7 g. of acid, b. p. 125° at 12 mm.; n^{20}D 1.4492. The acid was converted to the amide which melted at 168.5–169.5° after repeated recrystallization from dilute methanol and from benzene–petroleum ether.

Anal. Calcd. for $C_8H_{15}ON$: N, 9.92. Found: N, 10.06.

The only C_8 naphthenic amide melting as high as 169° is that of 2,3-dimethylcyclopentanecarboxylic acid, m. p. 170°. This acid was synthesized by the method of Nenitzescu[23] starting with 500 cc. of methylcyclohexane, 400 g. of anhydrous aluminum chloride and 200 g. of acetyl chloride. The methyl ketone obtained was carefully fractionated yielding a main fraction of 86 g. boiling at 103–109° at 54 mm. Oxidation at 0° by 125 cc. of bromine in 4780 cc. of water and 286 g. of sodium hydroxide yielded 48 g. of acid, b. p. 128–131° at 12 mm., n^{22}D 1.4520, d^{20}_4 0.9952, n. d. 1.445. The amide required several recrystallizations to obtain a pure product so the acid obviously was not pure—the synthesis is known to yield small quantities of isomeric C_8 acids. The pure amide melted at 169° and the melting point was not depressed by mixing with the amide obtained from the petroleum acid. The synthetic amide was analyzed and found to contain 9.99% nitrogen (calcd. 9.92).

As an additional proof of the structure of the acid 2,3-

dimethylcyclopentanecarboxylic acid was next converted to the corresponding acetic acid by the following steps.

The natural acid obtained as explained in a preceding paragraph was converted to the methyl ester, b. p. 97–100° at 44 mm., n^{20}D 1.4350, yield 37 g. The ester was reduced to the alcohol by sodium and absolute alcohol according to the procedure of Crouch and Lochte.[24] The yield of alcohol was 21 g. of which 16 g., b. p. 107–110° at 44 mm., was converted to the bromide, b. p. 107–110° at 63 mm., yield 12 g. This was changed to the Grignard reagent and from it to the acid, b. p. 138° at 5 mm., yield 5 g. The amide, obtained in the usual manner over the acid chloride, was analyzed. It melted at 159° and showed no depression in melting point on mixing with the amide of the natural acid.

Anal. Calcd. for $C_9H_{17}O_2N$: N, 9.02. Found: N, 9.13.

cis-2,2,6-Trimethylcyclohexanecarboxylic Acid.—Shive, Horeczy, Wash and Lochte[14] obtained 2030 cc. of acids which were not esterified by two treatments with dry methanol containing hydrogen chloride. A third esterification treatment followed by distillation yielded an additional 400 cc. of esters and left 1600 cc. of unchanged acids which were changed to the sodium salts. Fractional liberation by carbon dioxide and finally by dilute hydrochloric acid, filtering off solid acids as they formed on treatment with carbon dioxide and with hydrochloric acid, yielded 940 g. of solid and 700 cc. of liquid acids. Recrystallization of the solid acids yielded 280 g. of *dl*-camphonanic acid, 500 g. of solid acids melting 70–80° and 100 cc. of liquid acids. Further recrystallization of the impure solid acids yielded 400 g. of *trans*-2,2,6-trimethylcyclohexanecarboxylic acid and another 100 cc. of liquid acids. All liquid acids obtained (900 cc.) were combined and fractionated at 5 mm. pressure through a 6-ft. column packed with 0.25 inch Berl saddles and operated at a reflux of 10:1 or greater. Solid camphonanic acid separated from the first and *trans*-2,2,6-trimethylcyclohexanecarboxylic acid from the last fractions and, in addition, some crystalline material was obtained from some of the middle fractions. Refractionation followed by chilling in an ice–salt mixture yielded additional amounts of the new solid acid. After three such fractionations a total of 154 g. of camphonanic acid, 242 g. of the *trans*-form, and 61 g. of the new solid acid melting at 66–70° had accumulated. The remaining liquid acids were stored.

The acid melting at 66–70° was recrystallized from dilute acetic acid and finally from dilute alcohol to yield colorless rhombic crystals, m. p. 74–75°. A mixed melting point with synthetic *cis*-isomer of 2,2,6-trimethylcyclohexanecarboxylic acid prepared previously showed no depression, but a similar test with the *trans*-form was depressed to 45–55°.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66; neut. equiv., 170.24. Found: C, 70.48; H, 10.79; neut. equiv., 170.5.

The acid chloride was prepared by treatment with thionyl chloride and converted to the amide: cubical crystals, m. p. 191°. A mixed melting point with the amide of synthetic *trans*-acid showed no depression, thus

(23) Nenitzescu, Cioranescu and Cantuniari, *Ber.*, **70**, 280 (1937).

(24) Crouch and Lochte, This Journal, **63**, 1331 (1941).

confirming the previous finding that the cis is converted to trans-form on treatment with thionyl chloride.

Anal. Calcd. for $C_{10}H_{19}ON$: N, 8.28. Found: N, 8.36.

The anilide prepared in a similar manner melted at 192° and showed no depression in melting point when mixed with anilide prepared from cis-synthetic acid.

Anal. Calcd. for $C_{16}H_{23}ON$: N, 5.71. Found: N, 5.87.

Summary

Through the use of a number of fractionation procedures in a continuation of the study of acids from California petroleum, the following naphthenic acids have been isolated and identified for the first time from petroleum: 2-methylcyclopentanecarboxylic, 3-methylcyclopentanecarboxylic, 2,3-dimethylcyclopentaneacetic, cyclohexanecarboxylic, and cis-2,2,6-trimethylcyclohexanecarboxylic acids.

The following acids previously reported by Nenitzescu from European petroleum were isolated also from California acids: cyclopentanecarboxylic, cyclopentaneacetic and 3-methylcyclopentaneacetic acids.

New Methods for the Resolution of Enantiomorphs.   II.   Liquid–Liquid Extraction[1]

By E. Shapiro[2] and Roy F. Newton

In the first paper of this series Bailey and Hass[3] showed that resolution of enantiomorphs could be brought about by their conversion to volatile diastereoisomers followed by rectification and reconversion to the original compounds. This report deals with resolution by means of distribution between two liquids.

The use of liquid–liquid extraction to separate diastereoisomers depends upon the fact that these compounds have different distribution ratios between two incompletely miscible solvents. The concentrations of one of the diastereoisomers, A, in the solvents S and S′ may be expressed as C_A and C'_A, respectively, and those of the other, B, as C_B and C'_B. The relative ease with which the diastereoisomers may be separated is then determined by the quantity $C'_A C_B / C_A C'_B$, which is the ratio of the two distribution ratios C'_A/C_A and C'_B/C_B. If this quantity is unity, no separation is possible, and the greater its deviation from unity, the more easily can separation be made.

Fractional distribution of two solutes between two solvents may be carried out either by a multiple contact method, for which separatory funnels were used, or by a countercurrent contact method, using a column. Both methods were successfully applied in this investigation.

(1) Based on a doctoral thesis, Purdue University. Presented before the Division of Physical and Inorganic Chemistry at the Buffalo meeting of the American Chemical Society, September, 1942.

(2) Eli Lilly Research Fellow, 1941–1942.

(3) Bailey and Hass, This Journal, 63, 1969 (1941).

Experimental

Method and Apparatus.—The scheme used for fractional distribution by the multiple contact method was that described by Hunter and Nash.[4] The solutions in each case were shaken vigorously in separatory funnels for one-hour periods to ensure the attainment of equilibrium.

Separations by the countercurrent contact method were made in an extraction apparatus represented schematically in Fig. 1. Brucine d-mandelate and brucine l-mandelate were the compounds chosen for trial. The column was designed for operation in a manner entirely analogous to that of a rectification apparatus. Solute in water and in chloroform correspond, respectively, to the vapor and liquid phases. Removal of water from the solute and its replacement by chloroform corresponds to condensation, and removal of chloroform and its replacement by water corresponds to evaporation. The water solution after leaving the top of the column is raised by a water vapor lift D, to a boiler E, provided with an overflow tube H. The solution is concentrated in the boiler and the concentrated solution flows through the overflow tube back to the column. On its way to the column it passes through a section of 10-mm. Pyrex tubing, M, packed with glass helices. At the same time chloroform, which has distilled from the chloroform boiler, C, passes over the helices so that some transfer of brucine mandelate from the aqueous phase to the chloroform occurs. Similarly in the packed section G, concentrated chloroform solution from C is put into contact with distilled water from E. The column A was packed with a nickel screen spiral as described by Lecky and Ewell.[5] The diameter of the column was 28 mm., the packed height was 95 cm., and there was one turn of 60-mesh screen per cm.

Analyses of samples taken from the water boiler showed a large excess of mandelic acid over brucine. Evidently,

(4) Hunter and Nash, Ind. Eng. Chem., 27, 836 (1935).

(5) Lecky and Ewell, Ind. Eng. Chem., Anal. Ed., 12, 544 (1940).