Table II. Included also are the experimental and calculated liquid phase activity coefficients and the Carlson and Colburn modified (*1*) van Laar constants. The *t*-*x*-*y* data are shown on Figures 1 and 2 and the γ-x data on Figures 3 and 4. The activity coefficients were calculated by

$$\gamma = \frac{yP_T}{xP}$$

where y, x = vapor and liquid equilibrium compositions, P = pure component vapor pressure, and P_T = total pressure. The authors assumed that at the pressure of the investigation, the deviation of the vapor phase from ideal behavior was small enough to be neglected. Similarly, the correction for the specific volume of the liquid was neglected for the same reason.

From a larger scale temperature-composition plot using the calculated data from the van Laar constants, $A_{\text{C-DMB}} = 0.188$, $B_{\text{C-DMB}} = 0.265$, $A_{\text{A-DMB}} = 0.722$, $B_{\text{A-DMB}} = 0.620$, the azeotrope compositions and temperatures were: acetone–2,3-dimethylbutane, $x_{\text{acetone}} = 0.47$, $t = 44.7°$ C.; chloroform–2,3-dimethylbutane, $x_{\text{chloroform}} = 0.47$, $t = 55.5°$ C. These compare, respectively, with the values reported in Horsley (*5*): $x_{\text{acetone}} = 0.42$, $t = 46.5°$ C.; $x_{\text{chloroform}} = 0.47$, $t = 55.5°$ C.

The van Laar constants were determined by an iterative method devised to reduce the deviation of all experimental data points from the van Laar-type curve. The values of the constants were adjusted until a minimum deviation from the activity coefficient composition curve was experienced.

The data were checked for consistency by the Redlich-Kister (*8*) method wherein the values of log γ_1/γ_2 were plotted *vs.* the mole fraction of the lighter component, and the areas between the curve above and below the zero log activity coefficient ratio were compared. (The Redlich-Kister method for consistency is based on Scatchard's excess free energy relation and assumes the vapor phase to behave ideally.) The curve represented the best fit of the data determined by a least squares method. The areas differed by 7.9% for the acetone-DMB binary and 10.6% for the chloroform-DMB system.

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Composition of the Branched Paraffin-Cycloparaffin Portion of Petroleum, 140° to 180° C.

BEVERIDGE J. MAIR and ZALMAN RONEN
Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

Thirty-eight hydrocarbons were isolated from the paraffin-cycloparaffin portion of petroleum boiling between 140° and 180° C. These are comprised of 13 branched paraffins, 17 monocycloparaffins, and eight bicycloparaffins. Together with 10 compounds isolated in previous investigations this accounts for 84% of the portion, or 10.2% of the total crude. The compounds were isolated by distillation and gas-liquid chromatography and identified principally by infrared, nuclear magnetic resonance, and mass spectrometry. Several of the compounds isolated—2,6-dimethyloctane, 2-methyl-3-ethylheptane, and 4-isopropylheptane—appear to be derived from the terpenoids and are of interest in connection with the genesis of petroleum.

THIS INVESTIGATION is part of the program of the American Petroleum Institute Research Project 6 on the composition of its reference petroleum (*15*). Specifically, it describes the analysis of the branched paraffin-cycloparaffin portion boiling from 140° to 180° C. The work was undertaken primarily to obtain information concerning the structures of the bicycloparaffin components.

The polycycloparaffins constitute an important class of petroleum hydrocarbons. In the higher molecular weight range, above C_{25}, they are more abundant than any other class, constituting, in many cases, from 30 to 50% of the material. Yet, relatively little is known concerning their molecular structures. The most favorable place to obtain structural information is with the bicycloparaffins in the lower molecular weight range, where it is still possible, because of the limited number of isomers, to separate individual compounds and in some cases establish their identity.

Of course, the branched paraffins and monocycloparaffins are also of interest and where possible they were separated and identified. Three of the branched paraffins isolated appear to be derived from the monoterpenoids.

PROCEDURE

The starting material consisted of all the paraffin-cycloparaffin portion boiling from 140° to 180° C. except for samples of 10 hydrocarbons isolated in previous work. These hydrocarbons and their normal boiling points are as follows: 2,3-dimethylheptane, 140.5°; 1,*trans*-2,*trans*-4-trimethylcyclohexane, 141.22°; 4-methyloctane, 142.48°; 2-methyloctane, 143.26°; 3-methyloctane, 144.18°; 1,*trans*-2,*cis*-3-trimethylcyclohexane, 145.6°; 1-methyl-*cis*-bicyclo-[3.3.0]octane, 146.7°; *n*-nonane, 150.798°; 4-methylnonane, 165.7°; 2-methylnonane, 166.8°; 3-methylnonane, 167.8°; *n*-decane, 174.123° C.

Although 1,*trans*-2,*cis*-3-trimethylcyclohexane and 1-methyl-*cis*-bicyclo[3.3.0]octane were isolated previously, as the above list indicates, a complete identification was made only in this work.

The following steps were used for the isolation and identification of the individual hydrocarbons: distillation of the material in columns of high separating efficiency; separation of selected fractions throughout the entire range of the distillate by preparative scale gas-liquid chromatography to give, where possible, individual hydrocarbons; identification of the individual hydrocarbons from their physical and spectroscopic properties; and determination of the amounts of the individual hydrocarbons by analytical gas-liquid chromatography.

The results of the regular distillation, utilizing high efficiency columns (*16*), are shown in Figure 1.

For the separation by preparative scale gas-liquid chromatography, a Beckman Megachrom was used. Diethylene glycol succinate, silicone nitrile, and *m*-bis[*m*-(*m*-phenoxyphenoxy)phenoxy]benzene were used as partitioning liquids. The techniques used in this laboratory have been described (*9*).

The infrared spectra were obtained on a Perkin-Elmer Model 137 B Infracord spectrometer scanning the range 2.0 to 15.0 microns. Liquid samples were used without dilution in sodium chloride cells which ranged in thickness from 0.025 to 0.1 mm.

The proton resonance spectra were obtained using a Varian A-60 High Resolution NMR spectrometer, operating at a frequency of 60 megacycles and a field strength of 14,093 gauss. A concentration of 5 volume % hydrocarbon in carbon tetrachloride was used. Tetramethylsilane was used as an internal reference standard.

The distillate range from 140° to 180° C. is composed principally of C_9 and C_{10} components. All of the C_9 and several C_{10} cyclohexanes and a few of the 55 C_9 cyclopentanes are available as API standard samples. In these cases, a direct comparison of infrared and nuclear magnetic resonance spectra with those of the reference compound serves to identify the compound from petroleum.

Spectral data are not available for the majority of the C_{10} branched paraffins, and indirect methods are necessary. Although many of the C_{10} branched paraffins have not been synthesized, calculated values are available for their boiling points and refractive indices (*3*). The separation obtained with the highly efficient distillation columns used in this work (*16*) is sufficient to concentrate the bulk of any given hydrocarbon in the distillate fractions which boil within ±1.5° C. of its normal boiling point. Thus it is necessary to consider only those hydrocarbons boiling within ±2° C. of the distillate fraction from which the hydrocarbon was isolated. Since most components were obtained in fairly pure condition, the refractive indices are also of value in the identification process.

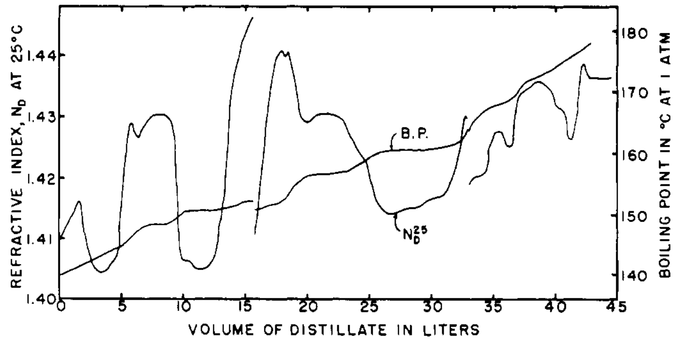


Figure 1. Results of the regular distillation of the branched paraffin-cycloparaffin portion boiling between 140° and 180° C.

Infrared spectroscopy is particularly useful in helping to identify branched paraffins and in establishing the nature of alkyl chains in some cycloparaffins. Molecules containing isopropyl groups or internal *gem*-dimethyl groups show a strong doublet with peaks of almost equal intensity at 7.22 to 7.28 and 7.29 to 7.35 microns. [Exceptions to this rule have been noted for 2,3-dimethylhexane (*1*) and 2,3-dimethyloctane (*4*), which do not show a distinct doublet.] It is possible to distinguish *gem*-dimethyl from isopropyl groups, since isopropyl groups also show a moderately strong band in the 8.5- to 8.6-micron region, whereas internal *gem*-dimethyl groups do not.

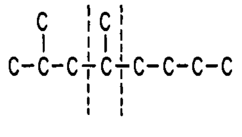
Molecules containing a terminal *tert*-butyl group may be distinguished by a characteristic band of moderate intensity near 8 microns. The authors discovered that a moderately strong band occurs at 8.8 to 8.9 microns in all doubly and most triply branched paraffin hydrocarbons, if the branches are on adjacent carbon atoms—for example, with 2-methyl-3-ethylheptane (*12*); 2,3-dimethyloctane (*4*); 2,3-dimethylpentane; 2,3-dimethylhexane; 3,4-dimethylhexane; 2-methyl-3-ethylpentane; 2,3-dimethylbutane; 2,3,5-trimethylhexane; 2,3,4-trimethylpentane; 2,4-dimethyl-3-ethylpentane; and 2,2,4,5-tetramethylhexane (*1*).

An ethyl terminal in a branched paraffin always produces a band of medium intensity near 13 microns, but the existence of such a band does not necessarily establish the presence of an ethyl terminal in the molecule, since other branched paraffins—for example, 2,2,4,5-tetramethylhexane and 2,3,5-trimethylhexane—also show a band in this region (*1*). A normal propyl terminal or a chain of three methylene groups between branches gives a band of medium intensity at 13.5 to 13.6 microns. This band moves to 13.8 to 13.9 microns for butyl or longer terminals or for an unbroken chain of methylene groups four or more carbon atoms in length. In some instances, these bands may be used to determine the structure of side chains in cycloparaffin molecules. This is by no means as satisfactory as with paraffins, because bands from the cycloparaffin portion of the molecule sometimes occur in the same regions.

The determination of structure of paraffinic chains by NMR is discussed by Bartz and Chamberlain (*5*). For paraffins, the peaks due to methylene and methine hydrogens are usually sufficiently well separated from those due to methyl hydrogens, so that an integration of peak areas can be used to determine the number of methyl groups in the molecule. The use of mass spectrometry for the determination of the empirical formula of a hydrocarbon is well known. Also, the tendency of molecules to split preferentially at positions adjacent to branches frequently gives significant information concerning their structures.

As an illustration of the application of these methods the identification of 2,4-dimethyloctane may be considered. This compound was isolated from fractions boiling near 156° C. The refractive index, n_D at 25° C., was 1.4077 in satisfactory agreement with the reported value, 1.4069 (*3*). The mass spectrometric examination showed that it was a C_{10} paraffin. Integration of the NMR spectrum showed that the molecule contained four methyl groups. The names, normal boiling points, and refractive indices (n_D at 25° C.) of the three branched paraffins which boil sufficiently close to 156° C. to be considered are as follows (*3*): 2,4-dimethyloctane, 155.9°, 1.4069; 2,2-dimethyloctane, 156.9°, 1.4060; 4,4-dimethyloctane, 157.5° C., 1.4122. The infrared spectrum

(Figure 2) shows the presence of an isopropyl terminal (doublet at 7.27 to 7.31 and peak near 8.6 microns). The peak at 13.8 microns attributable to the presence of an unbroken chain containing four or more methylene groups suggests the presence of a terminal butyl group. The compound is not 2,2-dimethyloctane, since the infrared spectrum does not show the peak near 8 microns characteristic of a *tert*-butyl group. Also, the NMR spectrum does not show the intense peak characteristic of three equivalent methyl groups in a *tert*-butyl terminal. 4,4-Dimethyloctane can be eliminated on several counts, including its high refractive index, its infrared spectrum (this shows peaks at 13.6 and 13.8 microns, corresponding to normal propyl and normal butyl terminals) and its NMR spectrum which shows a strong peak due to the *gem*-dimethyl group. Additional evidence that the compound from petroleum is 2,4-dimethyloctane is obtained from the mass spectrum for the C_nH_{2n+1} series. A very intense C_6 peak is accounted for by the splitting of the molecule at either of the positions shown



$$\mathrm{C{-}\overset{\overset{C}{|}}{C}{-}C{-}\overset{\overset{C}{|}}{C}{-}C{-}C{-}C{-}C}$$

Analytical gas-liquid chromatographic experiments were performed on approximately 160 fractions selected to cover the boiling point range at intervals of 0.2° to 0.3°C. Most of the experiments were performed with a column 20 feet in length and 0.25 inch in diameter, using 25% diethylene glycol succinate on 42- to 60-mesh firebrick as the packing material. In some cases, where a higher resolution was required, a capillary column 200 feet long coated with silicone nitrile was used. In most cases, by comparing the analytical chromatograms with those obtained in the preparative scale separations, it was possible to identify the components which the various peaks represented. The amounts of the individual compounds in each fraction were computed assuming that peak areas were proportional to per cent by volume. A plot of the amount of a component with respect to the volume of distillate was used to determine the total amount of that component (Figures 3 to 5).

RESULTS

Branched Paraffins. A plot showing the amounts of the individual branched paraffins as a function of the volume of distillate is given in Figure 3. Initially, all of these hydrocarbons were identified by the indirect methods described in the preceding section. Later, the identities of 3-ethylheptane, 2,6-dimethyloctane, 4-isopropylheptane, and 2-methyl-3-ethylheptane were confirmed by direct comparison of their infrared and NMR spectra with those of the corresponding synthetic compounds.

Monocycloparaffins. A plot showing the amounts of the individual monocycloparaffins as a function of the volume of distillate is given in Figure 4. All of the C_9 cyclohexanes isolated as well as 1,1,3,*cis*-5-tetramethylcyclohexane and *n*-butylcyclopentane were identified by direct comparison of their infrared and NMR spectra with those of synthetic samples. The other monocycloparaffins were identified by indirect methods. For these, the identification is regarded as tentative.

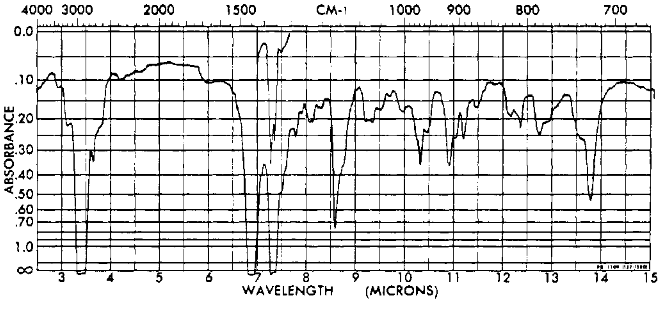


Figure 2. Infrared spectrum of 2,4-dimethyloctane from petroleum

Bicycloparaffins. A plot showing the amounts of the individual bicycloparaffins as a function of the volume of distillate is given in Figure 5.

The five methyl-*cis*-bicyclo[3.3.0]octanes have been synthesized recently by Knotnerus and Schilling (6). They give infrared spectra for the 1-, *exo*-2-, *endo*-2-, and *endo*-3-methyl isomers and for a mixture containing 40% of the *exo*-3- and 60% of the *endo*-3-methyl isomers. They also provided us with samples of the *exo*-2-, *endo*-2-, and *endo*-3-methyl isomers.

1-Methyl-*cis*-bicyclo[3.3.0]octane was tentatively identified from its proton resonance spectra which showed the

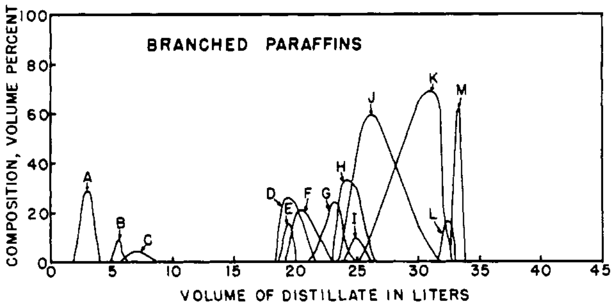


Figure 3. Amounts of the individual branched paraffins as a function of the volume of distillate

A. 3-Ethylheptane
B. 2,4,6-Trimethylheptane
C. 2,2,3,5-Tetramethylhexane
D. 2-Methyl-4-ethylheptane
E. 2,5-Dimethyl-3-ethylhexane
F. 2,4-Dimethyloctane
G. 4,4-Dimethyloctane
H. 2,5-Dimethyloctane
I. 4-Isopropylheptane
J. 2,6-Dimethyloctane
K. 2-Methyl-3-ethylheptane
L. 4,5-Dimethyloctane
M. 3,4-Dimethyloctane

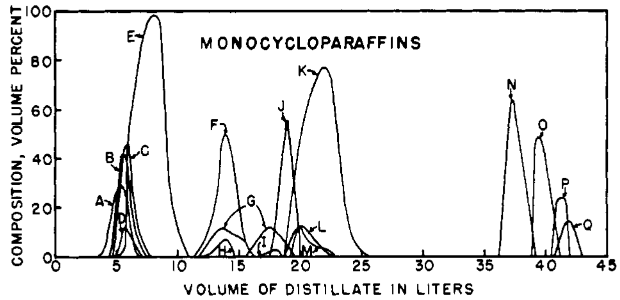


Figure 4. Amounts of the individual monocycloparaffins as a function of the volume of distillate

A. 1,*trans*-2-*cis*-3-Trimethylcyclohexane
B. 1-Methyl-*trans*-2-*n*-propylcyclopentane
C. 1-Methyl-3-*n*-propylcyclopentane
D. 1,1,2-Trimethylcyclohexane
E. 1-Methyl-*cis*-3-ethylcyclohexane
F. 1-Methyl-*trans*-2-ethylcyclohexane
G. 1-Methyl-1-ethylcyclohexane
H. 1,*cis*-2-*trans*-3-Trimethylcyclohexane
I. 1,1,3-*cis*-5-Tetramethylcyclohexane
J. Isopropylcyclohexane
K. *n*-Propylcyclohexane
L. 1-Methyl-*cis*-2-ethylcyclohexane
M. *n*-Butylcyclopentane
N. 1-Methyl-*trans*-2-*n*-butylcyclopentane
O. 1-Methyl-*trans*-4-*n*-propylcyclohexane
P. 1-Methyl-*cis*-3-*n*-propylcyclohexane
Q. 1-Methyl-*trans*-3-*n*-propylcyclohexane

presence of a bridgehead methyl group and by comparing its C^{13} NMR spectrum with that of a number of model bicycloparaffins (7). The identity was confirmed by comparison of its infrared spectrum with that reported by Knotnerus and Schilling (*6*). *exo*-2-Methyl-*cis*-bicyclo[3.3.0]-octane and *endo*-2-methyl-*cis*-bicyclo[3.3.0]octane were identified by direct comparison of their infrared and NMR spectra with those of the synthetic compounds. *exo*-3-Methyl-*cis*-bicyclo[3.3.0]octane was isolated from fractions boiling near 153.7° C. A comparison of the infrared and NMR spectra with those of the 1-, *exo*-2, and *endo*-3-methyl isomers indicated that it was not one of these. The infrared spectrum showed some features similar to those which appear in the spectrum of the 40% *exo*-3-methyl and 60% *endo*-3-methyl mixture. These features near 7.65 and near 9.7 microns do not occur in the *endo*-3-methyl compound and are attributable to the *exo*-3-methyl compound. On this basis the compound from petroleum was identified as *exo*-3-methyl-*cis*-bicyclo[3.3.0]octane. The relative retention times obtained by Knotnerus and Schilling on a squalane column and the boiling points for the samples from petroleum are in accord with this interpretation. These are as follows:

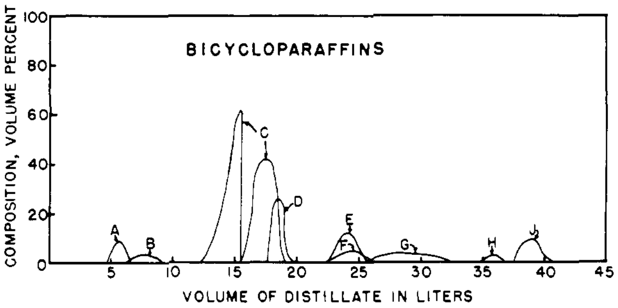


Figure 5. Amounts of the individual bicycloparaffins as a function of the volume of distillate

A. 1-Methyl-*cis*-bicyclo[3.3.0]octane
B. 1-Methyl-*trans*-bicyclo[3.3.0]octane
C. *exo*-2-Methyl-*cis*-bicyclo[3.3.0]octane
D. *exo*-3-Methyl-*cis*-bicyclo[3.3.0]octane
E. *endo*-2-Methyl-*cis*-bicyclo[3.3.0]octane
F. Unidentified C_9 bicycloparaffin
G. *trans*-Bicyclo[4.3.0]nonane
H. *cis*-Bicyclo[4.3.0]nonane
J. Bicyclo[3.3.1]nonane

Table I. Hydrocarbons Isolated[a]

No.	Name	B.P. at 760 Mm., ° C.	Amount in Original Crude, Vol. %
1	3-Ethylheptane	143	0.05
2	1,*trans*-2,*cis*-3-Trimethylcyclohexane	145.66	0.11
3	1,1,2-Trimethylcyclohexane	146.07	0.03
4	1-Methyl-*trans*-2-*n*-propylcyclopentane[b]	146.37	0.12
5	1-Methyl-*cis*-bicyclo[3.3.0]octane	146.7	(0.06)
6	2,4,6-Trimethylheptane	147.6	0.01
7	1-Methyl-3-*n*-propylcyclopentane[b]	148	0.14
8	2,2,3,5-Tetramethylcyclohexane[b]	148.4	0.01
9	1-Methyl-*trans*-bicyclo[3.3.0]octane[b]	148.4	0.01
10	1-Methyl-*cis*-3-ethylcyclohexane	148.79	0.58
11	1,*cis*-2,*trans*-3-Trimethylcyclohexane	151	0.02
12	1-Methyl-*trans*-2-ethylcyclohexane	151.76	0.22
13	1,1,3,*cis*-5-Tetramethylcyclohexane	151.96	0.007
14	1-Methyl-1-ethylcyclohexane	152.06	0.13
15	*exo*-2-Methyl-*cis*-bicyclo[3.3.0]octane	152.46	0.40
16	*exo*-3-Methyl-*cis*-bicyclo[3.3.0]octane	153.7	0.07
17	2,5-Dimethyl-3-ethylhexane[b]	154.1	0.03
18	Isopropylcyclohexane	154.76	0.16
19	2,4-Dimethyloctane	155.9	0.09
20	1-Methyl-*cis*-2-ethylcyclohexane	155.99	0.06
21	2-Methyl-4-ethylheptane	156.2	0.08
22	*n*-Butylcyclopentane	156.6	0.05
23	*n*-Propylcyclohexane	156.72	0.61
24	4,4-Dimethyloctane	157.5	0.10
25	*endo*-2-Methyl-*cis*-bicyclo[3.3.0]octane	158.5	0.05
26	Unidentified C_9 bicycloparaffin	158.5	0.01
27	2,5-Dimethyloctane	158.5	0.15
28	4-Isopropylheptane	158.9	0.02
29	2,6-Dimethyloctane	160.38	0.55
30	*trans*-Bicyclo[4.3.0]nonane	161.02	0.03
31	2-Methyl-3-ethylheptane	161.2	0.64
32	4,5-Dimethyloctane	162.13	0.02
33	3,4-Dimethyloctane	163.14	0.08
34	*cis*-Bicyclo[4.3.0]nonane	167.65	0.004
35	1-Methyl-*trans*-2-*n*-butylcyclopentane[b]	169.4	0.23
36	Bicyclo[3.3.1]nonane	170	0.06
37	1-Methyl-*trans*-4-*n*-propylcyclohexane[b]	172.2	0.15
38	1-Methyl-*cis*-3-*n*-propylcyclohexane[b]	174.2	0.09
39	1-Methyl-*trans*-3-*n*-propylcyclohexane[b]	175	0.04
		Total	5.271

[a] Spectra used to identify these hydrocarbons are given in a thesis by Zalman Ronen entitled "Compositon of the Branched Paraffin-Cycloparaffin Portion of Petroleum, 140° to 180° C." While available, copies may be obtained from the Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa. [b] Identification tentative.

cis-Bicyclo[3.3.0]octanes	Boiling Point at 760 Mm., ° C.	Relative Retention Time
1-Methyl	146.7	100
endo-3-Methyl	...	114.7
exo-2-Methyl	152.46	116.0
exo-3-Methyl	153.7	120.4
endo-2-Methyl	158.5	137.5

The cis- and trans- isomers of bicyclo[4.3.0]nonane were identified by comparison of their infrared spectra with those given by Lindeman and LeTourneau (*8*) and their NMR spectra with those available in the API catalog (*2*). Bicyclo[3.3.1]nonane was tentatively identified from its boiling point, 170° C., and melting point, 130° C. The corresponding values reported for a synthetic sample are 170° and 145–46° C. (*13, 14*). This identification was confirmed by direct comparison of its NMR spectrum with that of a synthetic sample.

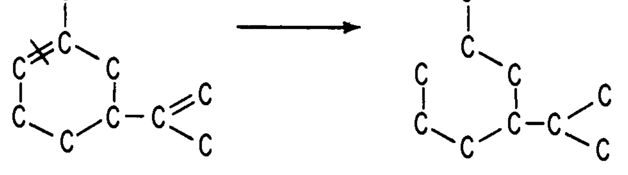
A C_9 bicycloparaffin, isolated from fractions boiling near 148° C. with refractive index n_D at 25° C. of 1.4538, was tentatively identified as 1-methyl-*trans*-bicyclo[3.3.0]-octane. The NMR spectrum showed that the compound contained a bridgehead methyl group. The infrared spectrum showed that this compound was not the cis isomer which boils only 1.3° C. lower. 1-Methyl-*cis*-bicyclo[3.2.1]-octane was considered as another possibility. However, a comparison of its mass spectrum (parent peak to base peak ratio) with those of other bicycloparaffins suggests that the compound has two five-membered rings. This leads to its tentative identification as 1-methyl-*trans*-bicyclo[3.3.0]octane.

In addition to the foregoing, a C_9 bicycloparaffin, with refractive index n_D at 25° C. of 1.4655, was isolated from fractions boiling near 158.5° C. Infrared and NMR spectra were obtained, but it was not possible to establish the identity.

Summary of Results. The amounts of the individual hydrocarbons in the crude petroleum which were isolated and identified together with their normal boiling points are given in Table I. These hydrocarbons amount to 5.27% of the original crude petroleum, and the 10 hydrocarbons isolated in previous work account for another 4.95% of the crude. Since the paraffin-cycloparaffin portion normally boiling from 140° to 180° C. constitutes 12.2% of the crude, approximately 84% of this portion is now accounted for.

DISCUSSION

Six dimethyloctanes out of the 12 dimethyloctanes possible were identified. Those not detected, the 2,2-, 2,3-, 2,7-, 3,3-, 3,5-, and 3,6-isomers, are believed to be present only in relatively small amounts. Two of the branched paraffins—2,6-dimethyloctane and 2-methyl-3-ethylheptane—are present in unusually large amounts. The probable genesis of 2,6-dimethyloctane from the acyclic terpenoids and of 2-methyl-3-ethylheptane from limonene has been reported (*12*). 4-Isopropylheptane, though present to a much smaller extent, may possibly be formed from the monocyclic terpenoid sylvestrene by a reaction analogous to that of 2-methyl-3-ethylheptane from limonene:



Sylvestrene 4-Isopropylheptane

Ten out of a possible 18 C_9 cyclohexanes boiling in this range were identified. Very few of the large number of C_9 and C_{10} cyclopentanes and C_{10} cyclohexanes were identified. In part, this is due to a lack of good physical and spectrometric data for the pure compounds.

Though many bicycloparaffins are theoretically possible in the range from 140° to 180° C., nine compounds account for almost the entire bicycloparaffin content. All of the bicycloparaffins, which were identified in this investigation, are of the bicyclo[3.3.0]octane, bicyclo[4.3.0]nonane, and bicyclo[3.3.1]nonane series. No evidence was found for the presence of bicyclo[2.2.1]heptanes, bicyclo[2.2.2]octanes, or bicyclo[3.2.1]octane found in lower boiling fractions by Lindeman and LeTourneau (*8*). Also, bicyclo[3.2.1]octane was found in this petroleum in a previous investigation (*10*). All of the bicycloparaffins isolated from this petroleum as well as those isolated by Lindeman and LeTourneau (*8*) are in accord with the prediction (*11*) that only those bicycloparaffins with five- or six-membered rings would be found in petroleum.

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