

Identification of a Cycloalkyl Ketone in Wilmington Petroleum Through use of Chromatography and Spectroscopy

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An acetyl-isopropyl-methyl cyclopentane, the first cycloalkyl ketone to be found in petroleum, has been identified in Wilmington, Calif., petroleum as part of the work of API Research Project 52. The cycloalkyl ketone was isolated from the virgin petroleum by a combination of distillation, liquid-solid chromatography, and gas-liquid chromatography. The compound, which is present in the crude oil to the extent of at least 5 p.p.m., was identified by interpretation of medium and high resolution mass, infrared, and nuclear magnetic resonance spectra.

A CYCLOALKYL KETONE has been isolated from Wilmington petroleum and was identified by a combination of mass, infrared, and nuclear magnetic resonance spectroscopy as an acetyl-isopropyl-methyl-cyclopentane. This compound was isolated by distillation, liquid-solid chromatography, and gas-liquid chromatography. The compound was present to the extent of at least 5 p.p.m. in the crude oil.

This identification was made as a part of the work of American Petroleum Institute Research Project 52b from an adsorption fraction that had been prepared for a study of the nitrogen compounds present in the 130°-250° C. fraction of Wilmington crude oil. The concentration of nitrogen compounds for the work of Project 52 resulted in the concentration of other polar compounds, including many oxygen compounds.

Acetyl-isopropyl-methyl-cyclopentane is the first cycloalkyl ketone to be identified in a virgin petroleum. A review of the literature (1) shows that fatty acids, naphthenic acids, and phenol are present in petroleum. In addition, Latham, Ferrin, and Ball (5) identified fluorenones from petroleum, and Barton, Carruthers, and Overton (2) identified a triterpenoid lactone. Lochte and Littman (6) reported the identification of several aliphatic ketones from a gas-well condensate.

EXPERIMENTAL

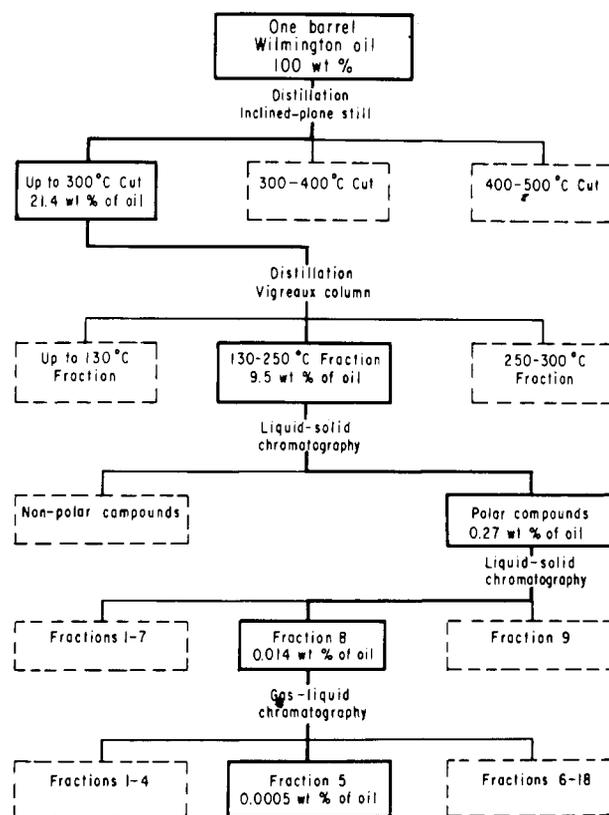
A 21-barrel sample of the Wilmington petroleum was obtained for study under various API fundamental research projects. This sample was protected from oxidation by blanketing it with specially purified nitrogen gas containing less than two p.p.m. of oxygen. In all subsequent handling, the fractions of this oil were protected from exposure to oxygen.

The procedure used to isolate the cycloalkyl ketone from Wilmington oil is outlined in Figure 1. One barrel of the Wilmington oil was distilled in a specially designed inclined-plane still (4). This distillation was carried out at about 0.1 mm. of Hg pressure and with approximately one minute contact time of the oil with the heated inclined plane of the still. The oil, while in the still, came in contact with only gold or stainless steel surfaces. Three cuts with boiling ranges of up-to-300° C., 300°-400° C., and 400°-500° C. were collected by successive passes of the oil over the inclined plane which was heated to 100° C., 175° C., and 225° C., respectively.

The cut boiling to 300° C., which amounted to 21.4 weight-per cent of the crude, was distilled through a 2.5-foot Vigreux column under reduced pressure so that maximum

pot temperature was 195° C. Three fractions were collected with boiling ranges of up-to-130° C., 130°-250° C., and 250°-300° C. The 130°-250° C. fraction amounted to 9.5 weight per cent of the oil.

The polar compounds in the 130°-250° C. fraction were concentrated by liquid-solid chromatography. A glass adsorption column, 203 by 2.75 cm., had a free liquid volume of 800 ml. when packed with 100-200 mesh Alcoa F-20 Alumina. This alumina was washed with methanol and activated at 300° C. under total vacuum and packed into the column under protection of a nitrogen atmosphere. The alumina adsorbent bed was prewet with pentane, and a portion of the 130°-250° C. fraction was precolated through the column (adsorbent-to-sample ratio of 0.7). After all of



NOTE—Broken-line boxes not pertinent to this paper

Figure 1. Isolation procedure

the sample passed through the column, 800 ml. of pentane was added to the column to displace the unadsorbed non-polar compounds. The adsorbed polar compounds then were desorbed with 10 liters of a solution of 40 volume per cent methanol in benzene. Using a batchwise procedure, 8,139 grams of the 130°–250° C. distillate were processed to yield 231 grams of the polar compound concentrate, equivalent to 0.27 weight per cent of the original oil.

The concentrate of polar compounds was separated by a liquid-solid chromatography procedure using the column and adsorbent previously described but with an adsorbent-to-sample ratio of 21. The concentrate was eluted from the column by a series of solvents with increasing polarity as shown in Table I.

Fraction 8, which was eluted with 1 per cent methanol in benzene, represented 0.014 weight per cent of the crude oil. This fraction was separated into 18 fractions by gas-liquid chromatography using a 25-foot by 1/4-inch aluminum column packed with 25 per cent Apiezon L on Gas-Chrom-P at 190° C. A portion of the chromatogram of fraction 8 is shown in Figure 2. Repeated trapping of the material that emerged under the shaded peak (GLC fraction 5 in Figure 2,) resulted in the isolation of 40 mg. of material, equivalent to 5 p.p.m. of the original crude oil.

Table I. Separation of Polar Compound Concentrate by Liquid-Solid Chromatography

Fraction No.	Eluant	Eluant Vol. (ML.)	Recovery of Concn. (Wt. %)
1	Pentane	1,400	24.9
2	Pentane	5,600	32.6
3	1% benzene in pentane	7,000	8.8
4	5% benzene in pentane	7,000	2.9
5	25% benzene in pentane	7,000	4.0
6	Benzene	7,000	3.3
7	1% methanol in benzene	7,000	7.0
8	1% methanol in benzene	2,000	5.2
9	40% methanol in benzene	7,000	1.9
	Total		90.6

The medium resolution mass spectrum of fraction 5 was obtained using a modified Consolidated Mass Spectrometer Model 21-103; and the high resolution mass spectrum was obtained through the courtesy of Esso Research and Engineering Co. The nuclear magnetic resonance spectrum was obtained with a Varian Associates A-60 instrument; and the infrared spectrum was obtained with a Perkin-Elmer Model 21 infrared spectrophotometer.

RESULTS AND DISCUSSION

Identification of the material in GLC fraction 5 was based on the information gained from mass, infrared, and nuclear magnetic resonance spectra. Correlation of results from the three spectral methods led to the identification of the compound as an acetyl-isopropyl-methyl-cyclopentane.

The low-voltage medium resolution mass spectrum of fraction 5 showed that this material contained over 90 per cent of a compound with a mass-to-charge ratio of 168. There were no significant peaks at higher mass-to-charge ratios at either high or low ionizing voltage. Hence, 168 was assumed to be the molecular weight. The empirical formula of this compound was determined by comparing the measured isotope abundance ratios of the parent ion with theoretical ratios for various compounds with molecular weights of 168 (3), as shown in Table II. This comparison shows that the empirical formula of fraction 5 is $C_{11}H_{20}O$.

Table III presents data and assignments for some of the more intense ions in the medium resolution high voltage mass spectral fragmentation of fraction 5. The m/e 125 ion could correspond to the loss of either an isopropyl or an acetyl group. Proof that the m/e 125 ion results from the loss of an acetyl group from the parent compound was obtained by use of high resolution mass spectrometry which showed that this ion had a mass of 125.173 (theoretical for C_9H_{17}) rather than 125.136 (theoretical for $C_8H_{13}O$).

The m/e 83 ion, a loss of 85 mass units from the parent molecule, is typical of cyclic hydrocarbons. It corresponds to either an ionized cyclohexyl radical or a methyl cyclopentyl radical.

The m/e 43 ion could correspond to an acetyl group, a propyl group, or both. In the high resolution mass spectrum,

Table II. Observed and Theoretical Isotope Abundance Ratios

Intensity Ratios for m/e 's 168,	Ratios				
	Observed	Theoretical for $C_{11}H_{20}O$	Theoretical for $C_{10}H_{16}O_2$	Theoretical for $C_{12}H_{24}$	Theoretical for $C_{13}H_{12}$
169, 170					
169/168	0.1222	0.1225	0.1114	0.1335	0.1424
170/168	0.00909	0.00886	0.00963	0.00821	0.00938
169/170	13.44	13.82	11.57	16.26	15.18

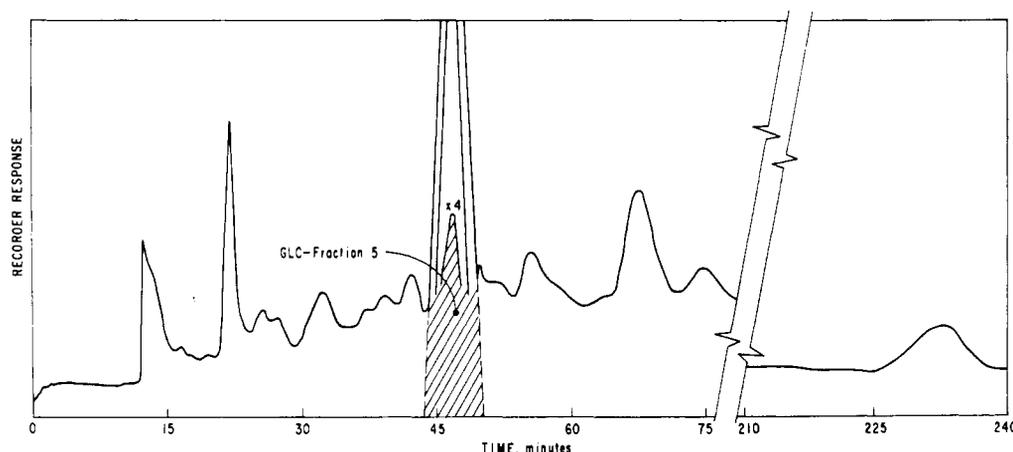


Figure 2. Gas-liquid chromatogram of adsorption Fraction 8

the m/e 43 peak was resolved into two peaks—one due to acetyl ions and the other, propyl ions. The presence of the propyl ion does not in itself prove that the parent compound contained a propyl group, because this ion could result from a geminal dimethylcyclohexane type compound by breakage of two ring bonds and a hydrogen rearrangement. This type of process would be expected to be of higher energy than the loss of an isopropyl or acetyl group from a five-membered ring. Thus a change in ionizing voltage should change the ratio of the intensities of the two ions if the propyl group resulted from the dimethylcyclohexane configuration. Measurements of the ratio at several ionizing voltages in the low energy range showed no such change and thus support the argument that the parent molecule contains both an acetyl and an isopropyl group.

The locations of some of the more definitive bands in the infrared spectrum of fraction 5 are shown in Table IV. Proof of an aliphatic carbonyl group was provided by the strong band at $1,712\text{ cm}^{-1}$. The band at $1,451\text{ cm}^{-1}$ corresponds to symmetrical deformation of hydrogens on a saturated ring. The band at $1,355\text{ cm}^{-1}$ corresponds to the symmetrical deformation expected for a methyl group bonded to a carbonyl group. Strong bands in the $990\text{--}910\text{ cm}^{-1}$ region suggest an aliphatic ring. A band at 804 cm^{-1} is probably an isopropyl skeletal vibration. Bands which could be assigned to olefinic or aromatic compounds are absent from the infrared spectrum.

Table III. High Voltage Mass Spectral Fragmentation

m/e	Relative Intensity ^a	Loss of	Probable Ion
168	793	...	$\text{C}_{11}\text{H}_{20}\text{O}^+$
153	239	CH_3	$\text{C}_{10}\text{H}_{17}\text{O}^+$
125	1,414	$\text{CH}_3\text{C}(=\text{O})$	$\text{C}_8\text{H}_{17}^+$
83	2,545	85	$\text{C}_8\text{H}_{11}^+$
43	19,353	125	$\text{C}_2\text{H}_3\text{O}^+$ and C_3H_7^+

^aTotal ionization adjusted to 10^5 units.

Table IV. Significant Bands in the Infrared Spectrum of Fraction 5

Band Location, Cm^{-1}	Assignment
1712	Aliphatic carbonyl vibration.
1451	Symmetrical deformations of hydrogens on a saturated ring.
1355	Symmetrical deformations of a methyl group bonded to a carbonyl group.
990-910	Aliphatic ring.
804	Isopropyl skeletal vibrations.

Table V. Observed and Theoretical Values of integrated NMR Spectrum

Hydrogen	Chemical Shift from TMS in p.p.m.	Number of Hydrogens	
		Observed	Theoretical ^a
a	2.07	2.95	3
b	1.92	1.02	1
c	1.77	1.06	1
d	1.65-1.12	5.01	5
e	1.05	1.03	1
f	0.90	6.01	6
g	0.73	2.99	3

^a Assuming empirical formula $\text{C}_{11}\text{H}_{20}\text{O}$.

Table VI. Summary of Spectral Data

Presence of	Spectral method
M.W. 168	Mass
Formula $\text{C}_{11}\text{H}_{20}\text{O}$	Mass, Isotope abundance ratios
Aliphatic ring	Mass, IR, and NMR
Methyl group	Mass and NMR
Acetyl group	NMR and I.R.
Isopropyl	Mass, NMR, and I.R.

Band assignment

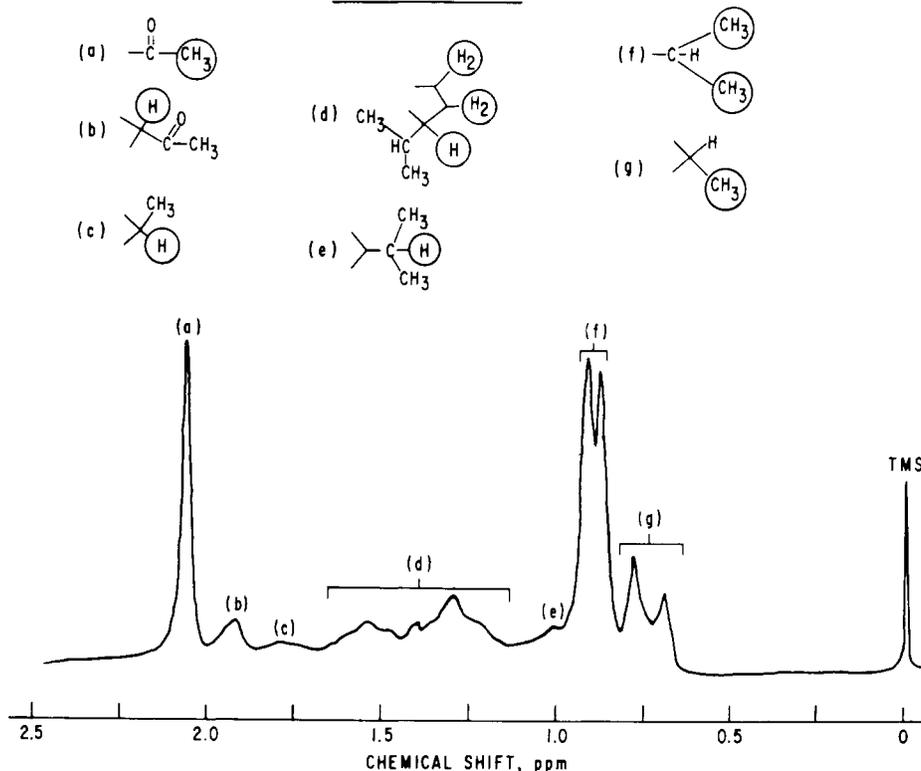


Figure 3. NMR spectrum of Fraction 5

The 60-megacycle nuclear magnetic resonance spectrum of fraction 5 is shown in Figure 3, with chemical shifts given in parts per million relative to tetramethylsilane which was used as an internal standard. The relative areas of the various peaks are shown in Table V. The signal at 2.07 p.p.m. (a), equivalent to 3 hydrogens, corresponds to the hydrogens of a methyl group bonded to a keto group; the signal at 1.92 p.p.m. (b), equivalent to 1 hydrogen is assigned to a single ring hydrogen at the junction of an acetyl group and an aliphatic ring; and signal (c) at 1.77 p.p.m., equivalent to 1 hydrogen, is assigned to a single ring hydrogen at the junction of a methyl group and an aliphatic ring. The multiplet from 1.65 to 1.12 p.p.m. (d), equivalent to 5 hydrogens, has been assigned to hydrogens bonded to an aliphatic ring. The signal at 1.05 p.p.m. (e), equivalent to 1 hydrogen, has been assigned to the single hydrogen of an isopropyl group. The doublet at 0.90 p.p.m. (f), equivalent to 6 hydrogens, has been assigned to the methyl hydrogens of an isopropyl group. The doublet at 0.73 p.p.m. (g), equivalent to 3 hydrogens corresponds to the splitting of a methyl group attached to a carbon with 1 hydrogen attached.

The spectral data are summarized in Table VI. Although the data do not reveal the positions of the substituent groups, they show that the compound in fraction 5 is an acetyl-isopropyl-methyl-cyclopentane, the first compound of this type to be identified in a virgin petroleum.

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Reference to specific commercial materials or models of equipment in this paper is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.