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ISOLATION AND IDENTIFICATION OF AN ESTER FROM A CRUDE OIL

By Harry F. Phillips and Irving A. Breger

Trace Elements Investigations Report 704

UNITED STATES DEPARTMENT OF THE INTERIOR
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Chemistry

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by

Harry F. Phillips and Irving A. Breger

U. S. Geological Survey, Washington 25, D. C.

ABSTRACT

A dioctylphthalate has been isolated from a crude oil by means of adsorption column chromatography. The ester was identified by means of elemental analysis, refractive index, and its infrared absorption spectrum. Saponification of the isolate and examination of the resultant alcohol by means of infrared absorption spectra led to the conclusion that the ester is a branched chain dioctylphthalate. This is the first reported occurrence of an ester in crude petroleum.

INTRODUCTION

During a search for the occurrence of pigments in crude oil, an investigation was carried out on a sample from Flat Top Mesa, Duchesne County, Utah. This oil, light yellow in color, is very waxy and semisolid at room temperature. It is not known whether the oil was formed in the nonmarine Eocene Green River formation or in lower marine strata of Paleozoic age. Hunt, Stewart, and Dickey (1954) have discussed the general geology of the area from which the oil was collected as well as the relationship of the other naturally occurring carbonaceous substances of the region to the various strati-

graphic units present. Chromatographic separations followed by purification of the final isolate have led to the identification of a component of the oil as a dioctylphthalate. This is the first reported occurrence of an ester in crude petroleum.

EXPERIMENTAL

Sample preparation. The sample of oil (400 g) was dissolved in about 800 ml of cyclohexane by warming on a steam bath. The solution was allowed to cool overnight during which time a white wax precipitated. Centrifugation yielded a clear orange solution which was used for the chromatographic separations described below.

Chromatographic columns. Each column was constructed of Pyrex tubing to the top of which was sealed a sample reservoir. A Pyrex stopcock at the lower end of the tube was used to control the flow rate through the column. Adsorbent was retained by a small wad of glass wool above the stopcock. As shown in Table 1, relatively large columns were used in initial separations to permit handling the large sample charge. Later columns, in which only the concentrates were adsorbed, were usually smaller.

Adsorbents. All adsorbents were thoroughly mixed in a shell blender with equal parts by weight of Celite 545 as a filtering aid. Activated aluminum oxide; ignited aluminum oxide; Florisil, a synthetic magnesium silicate; and silica

Table 1.--Data for adsorption columns

Column no.	Column diameter (mm)	Column length (cm)	Adsorbent[1]	Solvent
1	34	78	Activated aluminum oxide[2]	Cyclohexane
2	34	80	do.	Do.
3	16	75	do.	Do.
4	12	85	do.	Do.
5	12	70	Ignited aluminum oxide[3]	N-heptane
6	12	64	Florisil[4]	Do.
7	9	30	Silica gel[5]	Do.
8	9	30	do.	Do.
9	12	75	do.	Do.

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[1] In each column adsorbent was mixed with equal parts by weight of Celite 545 (Johns-Manville Corp.).

[2] Alcoa F-20, 80-200 mesh, Aluminum Co. of America.

[3] Merck and Co., Inc.

[4] 100-200 mesh, Floridin Co.

[5] 60-200 mesh, Davison Chemical Co.

gel were used in the course of the separations. Each adsorbent-Celite mixture was dried at 110° C for 2 to 3 hours before use.

Solvents. Cyclohexane, which was found to be excellent for the separation of the wax from the original oil, was also used in initial experiments. Normal heptane was subsequently used in an attempt to improve the resolution of material on the column.

Chromatographic procedure. The adsorbent was introduced into a column as a thick slurry in the appropriate solvent after which solvent was eluted by applying pressure (4 to 5 psi) to the top of the column from a cylinder of nitrogen. The sample was adsorbed on the column and then developed using first pure solvent and later solvent containing 1 to 5 percent methanol. Adsorption of the sample resulted in the formation of a diffuse dark brown-orange band at the top of the column. Development was continued until a yellow band separated from this dark brown-orange area and moved down the column. The yellow band was recovered by extrusion or by cutting the column. As concentration increased with successive columns the recovered band of material darkened and became red in color. Adsorbent was stripped using a 20 percent solution of methanol in the solvent. The solution thus obtained was centrifuged to remove all traces of adsorbent and evaporated on a steam bath under a stream of helium to remove the methanol. The isolate was then dissolved in solvent and adsorbed on the next column of the series.

The final isolate was obtained after passing the sample through a series of nine columns. Table 1 shows the column dimensions, adsorbents, and solvents used during the separations. Changes in adsorbents and solvents were made in an effort to improve the resolution of the sample on the column. When n-heptane was used, the column was first filled with solvent and then the dry adsorbent mixture was sifted into it and allowed to settle by gravity. Pressure was then applied as when cyclohexane was used.

Five- or ten-ml fractions of eluant were taken from the columns during the separations. These fractions were evaporated on a steam bath under a stream of helium and infrared spectra were determined on the residues to eliminate any possible loss of significant colorless or nonfluorescent material.

A Perkin-Elmer infrared spectrophotometer, Model 21, was used to obtain all of the infrared spectra in this laboratory. Samples were prepared as films on sodium chloride plates. Spectra obtained from other sources are noted on Fig. 1.

The weight of the isolate from the final column was 0.610 g representing 0.15 percent by weight of the original oil. The isolate was quite viscous and very dark red in color. The infrared spectrum of the isolate (Fig. 1, Curve 1), when compared with card 98 of the National Research Council-National Bureau of Standards punched card series of infrared spectra (Fig. 1, Curve 4), indicated the isolate to be a dioctylphthalate.

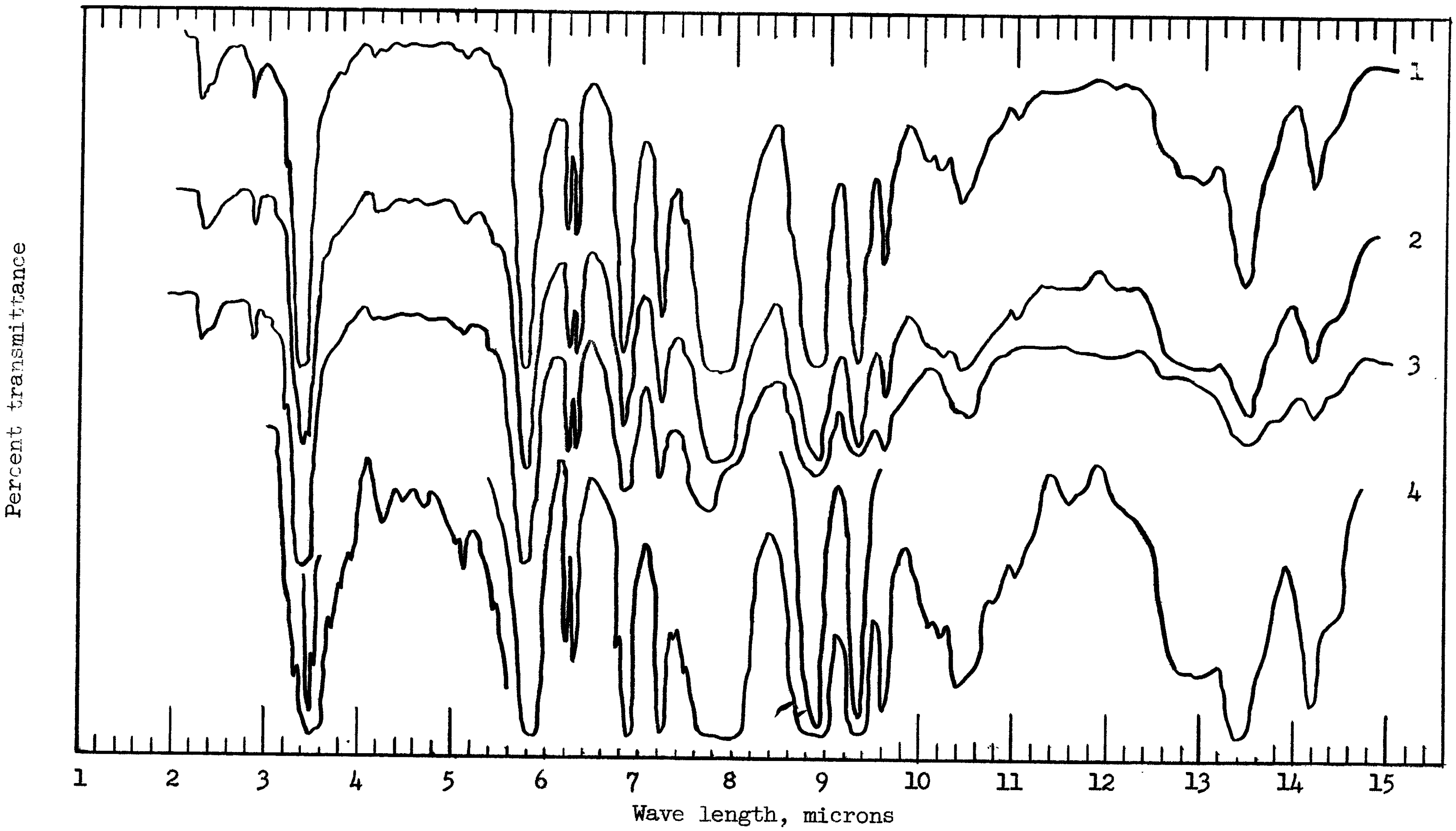

Figure 1.--Infrared absorption spectra. Curve 1, final column isolate; curve 2, distillate from final column isolate; curve 3, di-n-octylphthalate (product P6479, Eastman Kodak Co.); curve 4, dioctylphthalate, copy of card 98 furnished the National Research Council-National Bureau of Standards punched card series of infrared spectra by the U. S. Rubber Co.

Inasmuch as phthalic esters are colorless, the dark color of the material indicated the presence of an impurity.[1/]

Micro vacuum distillation. The final chromatographic isolate was purified by dissolving it in a few milliliters of n-heptane and transferring it to a micro vacuum distillation apparatus similar to that designed by Soltys (1936) but without the thermometer and capillary inlet. The distilling flask was placed in a copper heating block equipped with a thermometer; transferring solvent was removed from the sample by raising the block temperature to 65°C while passing a stream of nitrogen over the surface of the sample. The top of the flask was closed, the vacuum line connected, and the flask was then evacuated. The temperature of the block was raised slowly and a very pale yellow distillate was collected at a pressure of 0.03 to 0.05 mm Hg. It was thought likely that a small amount of the colored impurity was carried over imparting the slight color to the distillate.

The infrared spectrum of the distillate (Fig. 1, Curve 2) was almost identical to that for the impure, dark red, chromatographic isolate (Fig. 1, Curve 1). Removal of the highly colored impurity from the isolate had no visible effect on the

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[1/] The authors are indebted to Dr. Douglas Montgomery of the Canadian Bureau of Mines for pointing out the difficulty in separating porphyrins from oxygenated compounds by chromatography.

spectrum indicating the material to have been present in very small percentage. Analytical data for the distilled isolate are shown in Table 2.

Saponification. In an attempt to identify the dioctylphthalate further, the distilled ester was saponified using the micro method of Schneider (1946). The ester (10 mm^3) was absorbed on a small amount of ignited asbestos. This, with about 30 mm^3 of a solution of 0.1 N KOH in diethylene glycol was heated in a small distillation tube and the condensed ring of alcohol was collected in a capillary for identification. The small quantity of alcohol obtained (1-2 mg) made it desirable to attempt identification by means of infrared absorption spectra. The spectrum for the alcohol so isolated is shown in Fig. 2.

DISCUSSION

Comparison of the infrared spectra of Fig. 1 shows the isolate to be a dioctylphthalate. The triplet at 7.8, 8.95, and 9.35 microns is especially useful for this identification (Barnes, et al., 1944). R. R. Hampton of the U. S. Rubber Co. has noted (personal communication) that Curve 4 represents the 2-ethylhexyl isomer of dioctylphthalate. Further examination of the curves of Fig. 1, especially in the regions of 8.0-8.1, 9.85, 10.0-10.4, 11.05, and 11.9 microns, indicates the isolate to be more nearly similar in structure to the branched chain isomer (Curve 4) than to the straight chain isomer (Curve 3).

Table 2.--Analytical data for distilled isolate.

	Isolate	Di-n-octyl-phthalate	Di-iso-octyl-phthalate	Di-(2 ethylhexyl)-phthalate
Carbon, (percent)	74.07[1]	73.80[2]	73.80[2]	73.80[2]
Hydrogen, (percent)	9.96[1]	9.81[2]	9.81[2]	9.81[2]
n_D^{20}	1.4876	1.4845[3]		
n_D^{25}	1.4857	1.4826[3]		
n^{20}				1.4859[4]
n^{25}		1.482[4]	1.486[4]	1.484-1.485[4]

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[1] Analysis by Edward B. Brittin, U. S. Geological Survey

[2] Calculated.

[3] Product P6479, Eastman Kodak Co.

[4] "Modern Plastics Encyclopedia and Engineers Handbook", pp. 702-3, Plastics Catalogue Corp., New York, 1952.

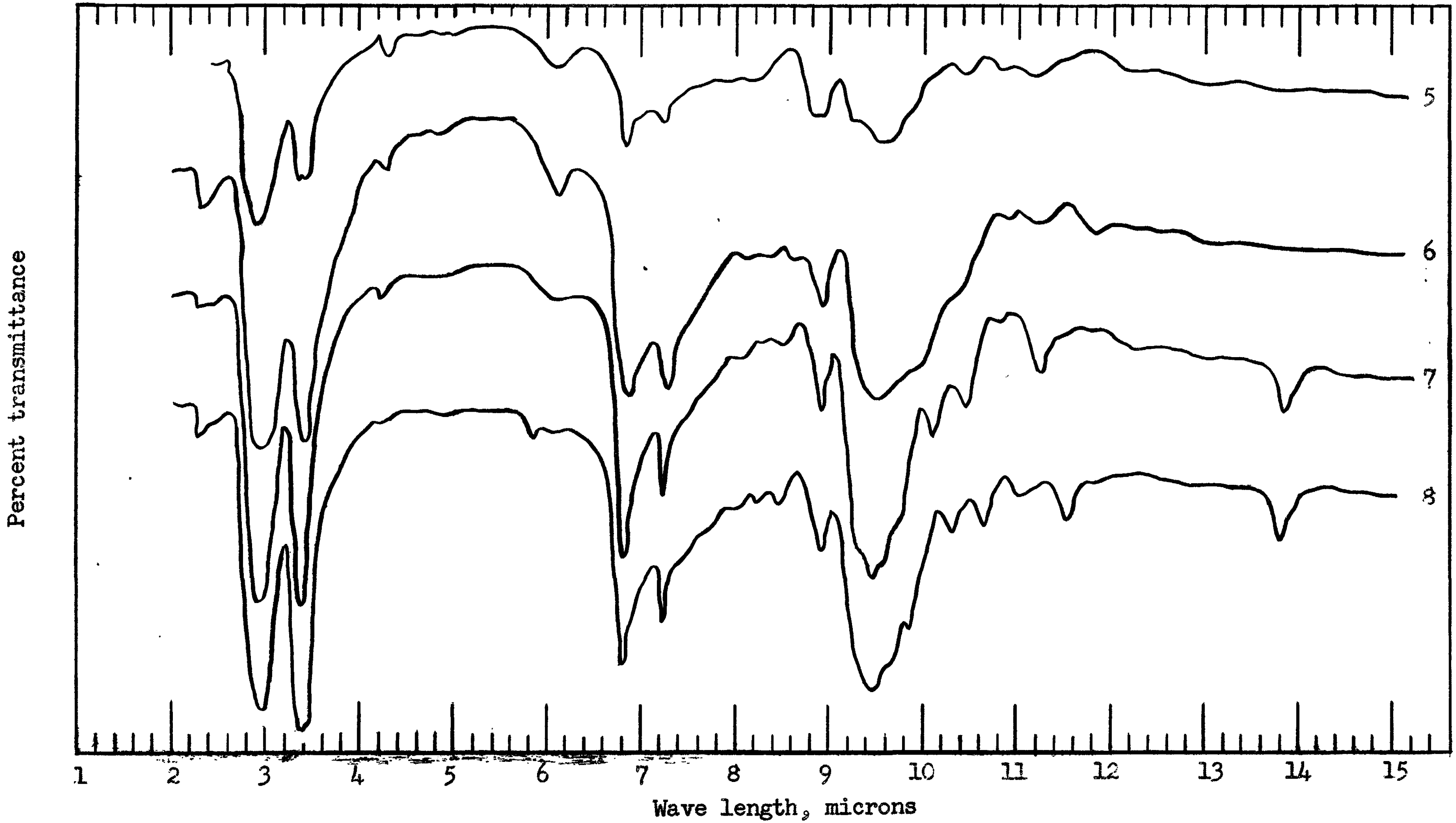


Figure 2.—Infrared absorption spectra. Curve 5, alcohol recovered by saponification of the isolated ester; curve 6, isooctyl alcohol (Gulf Oil Corp.); curve 7, n-octyl alcohol (product 871, Eastman Kodak Co.); curve 8, n-heptyl alcohol (product 381, Eastman Kodak Co.).

The spectra of Fig. 2 are for the alcohol recovered by saponification of the isolated ester (Curve 5), isooctyl alcohol (Curve 6), n-octyl alcohol (Curve 7), and n-heptyl alcohol (Curve 8). Curves 7 and 8 are for Eastman Kodak Co. products 871 and 381, respectively; the isooctyl alcohol, with the distribution of isomers shown below (A. Lewis, Jr., personal communication), was obtained through the courtesy of the Gulf Oil Corp.

Isomer	Percent by weight
4,5 dimethyl hexanol-1	30
3,5 dimethyl hexanol-1	30
5 methyl heptanol-1	15
3,4 dimethyl hexanol-1	15
5,5 dimethyl hexanol-1	5
Miscellaneous isomers	5

Curve 5, for the saponification product, is similar to the other spectra of Fig. 2 but appears to be more nearly similar to the spectra of the C_8 alcohols (Curves 6 and 7) than to the spectrum for the C_7 alcohol (Curve 8), especially at 5.8, 6.1, 10.85, 11.0, 11.2, and 11.5 microns.

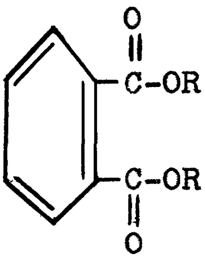
Examination of Curves 5, 6, and 7, moreover, shows variations at 10.0, 10.1, and 13.85 microns that indicate the alcohol isolated by saponification to be more nearly similar to the isooctyl alcohol than to the n-octyl alcohol.

SUMMARY

The ester isolated from the crude oil has been identified as a dioctylphthalate by means of elemental analysis, refractive index, and infrared absorption curves.

Consideration of infrared curves for various dioctylphthalates leads to the conclusion that the isolate is a branched chain dioctylphthalate. This conclusion has been supported by a comparison of infrared spectra for the alcohol recovered by saponification of the ester with other alcohols in the C_7-C_8 range.

Although the evidence supports the conclusion that the ester is a dioctylphthalate, the structure of the alcohol cannot be determined absolutely from the infrared spectra, nor can it be determined whether the compound is of one of the following structures where R and R′ are different isooctyl alcohol chains:



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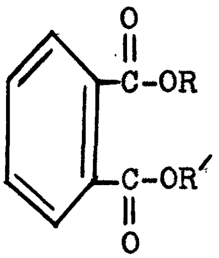

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The origin of the ester is unknown; it may be a preserved metabolic product or may have been formed during formation of the oil.

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