yielded yellow crystals of **6,7-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)naphthalene-2,3-dicarboxylic anhydride**, m.p. 220–228°, with infrared spectrum identical with an authentic specimen.

**Acknowledgment.**—The award of a research grant (G-14528) from the National Science Foundation is gratefully acknowledged.

---

# Characterization and Synthesis of a Monocyclic Eleven-Carbon Acid Isolated from a California Petroleum*,[1]

JAMES CASON AND KOEI-LIANG LIAUW

*Chemical Laboratories, University of California, Berkeley, California*

*Received July 29, 1964*

A $C_{11}$ monocyclic acid has been isolated from a California petroleum by methods involving fractional distillation, a sequence of gas chromatographies, and crystallization of the amide. The structure, deduced largely from application of physical methods, was established by comparison with a synthetic sample as *trans*-2,2,6-trimethylcyclohexylacetic acid. Both *cis* and *trans* isomers of this structure were synthesized from ionone. Interesting features of the n.m.r. spectra of these isomers are discussed, as are certain unexpected features of the mass spectrum. 5-Cyclopentylhexanamide was synthesized, and its mass spectrum was determined for comparison purposes.

Although the acidic components of petroleum, commonly termed naphthenic acids, have been the subject of intensive investigation by several highly competent chemists,[2] the number of component acids that have been identified remains small. Lochte and co-workers[2] succeeded in isolating and identifying several acyclic and monocyclic acids containing less than ten carbon atoms; however, in the range of greatest abundance of naphthenic acids, the $C_{10}$ to $C_{20}$ level, the only acids identified, other than normal isomers, are the two $C_{10}$ isomers, *cis*- and *trans*-2,2,6-trimethylcyclohexanecarboxylic acid. The chief deterrent to these investigations has been the formidable task of separating the remarkably complex mixture which comprises the naphthenic acids. The two $C_{10}$ acids just cited were separated by virtue of the severe hindrance at the carboxyl group.

A current surge of interest in the nature of components of petroleum appears to be especially concerned with theories of the origin of petroleum. The evolution of petroleum, more or less directly, from plants has received considerable support, especially by recent reports[3] of the isolation of isoprenoid hydrocarbons from petroleum. It has been suggested that a major source of the petroleum hydrocarbons consists of carboxylic acids[4]; however, in the molecular weight range above ten carbons only the normal fatty acids had been isolated prior to our current investigations. We have reported[5] the separation and identification of acyclic isoprenoid acids at the $C_{14}$, $C_{15}$, $C_{19}$, and $C_{20}$ molecular weights. The present report is concerned primarily with isolation and identification of a cyclic $C_{11}$ acid which also proves to have an isoprenoid structure.

The acids used for this investigation were extracted, prior to cracking, from middle distillates of a San Joaquin Valley naphthenic-type crude.[6] A sample of these acids which had been separated from phenols by esterification of the acids, followed by saponification, showed a significant absorption in the ultraviolet [$\lambda_{\max}$ 197 m$\mu$ ($\epsilon$ 2920) based on an average mol. wt. of 214]; however, this is probably owing to aromatic acids rather than alkenoic acids. There is an additional smaller maximum or shoulder at about 223 m$\mu$ ($\epsilon$ ~700), which is characteristic of aromatic acids; furthermore, the acids recovered after vigorous oxidation with potassium permanganate showed an ultraviolet absorption similar to that observed before oxidation. There were present no significant amounts of severely hindered acids. Direct acid-catalyzed esterification for 4 hr. at 30°, with a large excess of methanol, left only 4% of acids unesterified, and a second esterification of the surviving acids in refluxing methanol left only 0.5% of the original acids unesterified. Gas chromatography of the esters from the second esterification gave a tracing very similar to that obtained from the esters from the first esterification. The presence of significant quantities of acid-sensitive molecules was contraindicated by examination of samples of methyl esters prepared by acid-catalyzed esterification, from the silver salt and methyl iodide, or by use of diazomethane. Gas chromatography, and in some instances rechromatography of collected fractions, failed to reveal significant differences in these lots of esters.

Gas chromatography of the methyl naphthenates on various partitioning agents gave a continuum extending over 0.5 hr. or longer, with only a few broad peaks projecting in the region representing esters with more than ten carbons. Separation was improved somewhat and waiting for elution of higher molecular weight material was eliminated by gas chromatography of cuts from a rather rough fractional distillation. The complexity of the mixture is illustrated by gas chromatography (Figure 1) of the fraction of b.p. 130–135° (13 mm.). When cut C, Figure 1, was rechro-

---

* To Professor Louis F. Fieser.

(1) This investigation was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

(2) The earlier investigations of naphthenic acids, as well as the modern investigations at the University of Texas, are described by H. L. Lochte and E. R. Littmann, "The Petroleum Acids and Bases," Chemical Publishing Co., New York, N. Y., 1955.

(3) (a) R. A. Dean and E. V. Whitehead, *Tetrahedron Letters*, **No. 21**, 768 (1961); (b) J. G. Bendoraitis, B. L. Brown, and L. S. Hepner, Sixth World Petroleum Congress, Frankfort, section V, Paper 15, June 1963; (c) J. J. Cummins and W. E. Robinson, *J. Chem. Eng. Data*, **9**, 304 (1964).

(4) J. E. Cooper and E. E. Bray, *Geochim. Cosmochim. Acta*, **27**, 1113 (1963).

(5) J. Cason and D. W. Graham, *Tetrahedron*, in press.

(6) We wish to express our appreciation to Dr. A. H. Batchelder of the California Research Corporation for his assistance in arranging for us to receive a generous supply of these naphthenic acids from the Standard Oil Co. of California.

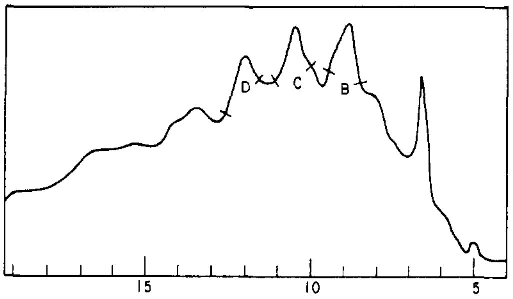

Figure 1.—Tracing from gas chromatography of a 160-$\mu$l. sample of methyl naphthenates, b.p. 130–135° (13 mm.) (column 10 ft. × $^3/_8$ in., packed with 20% silicone SE-30 dispersed on 30–60-mesh Chromosorb P; temperature 193°; helium flow rate 120 cc./min.). Fractions were collected as indicated by cross lines on the tracing.

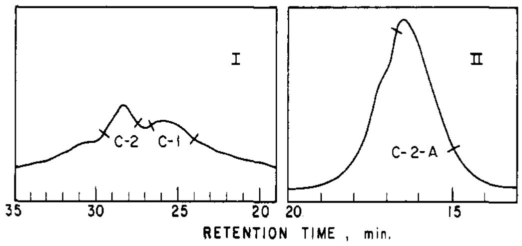

Figure 2.—Gas chromatography of cuts of methyl naphthenates: tracing I, 50-$\mu$l. sample of cut C, Figure 1 (column 10 ft. × $^3/_8$ in., packed with 20% NPGS on 30–60-mesh Chromosorb P; temperature 158°; helium flow rate 110 cc./min.); tracing II, 20-$\mu$l. sample of cut C-2, tracing I (column 10 ft. × $^3/_8$ in., packed with 30% silicone GE SF-96 on 30–60-mesh Chromosorb P; temperature 180°; helium flow rate 150 cc./min.). On silicone SE-30 as partitioning agent, the tracing was essentially identical to tracing II.

matographed on the same column (silicone), a single symmetrical peak was observed; however, when this cut was rechromatographed on neopentyl glycol succinate[7] (NPGS), a minimum of eight components was demonstrated (Figure 2, tracing I). Still a third chromatography (Figure 2, tracing II) of cut C-2,[7] again on silicone, suggests the presence of at least three components. In reality, subsequent investigation, as discussed below, of cut C-2-A showed the presence of at least two components in this cut from the chromatography shown in tracing II.

It is worthy of note that the chromatography on silicone shown in tracing II reveals the heterogeneity of the material applied, whereas chromatography in the same column of the once-chromatographed cut C (Figure 1), containing no less than 12 compounds, gave a single symmetrical peak. This difference in behavior is presumed to arise from the fact that rechromatography of cut C on silicone was actually a chromatography on silicone in which was dissolved some dozen methyl naphthenates, including the seven or more removed by the second chromatography on NPGS (Figure 2, tracing I). This type of phenomenon has been observed regularly during separations of the naphthenates. On some occasions it has proved profitable to chromatograph a fourth time on the same partitioning agent used for the second chromatography.

Two subsequent gas chromatographies of cut B, Figure 1, gave separations similar to those shown in Figure 2, and cut B-1-B was finally collected. Ammonolysis of this ester fraction with methanol in ammonia resulted in crystallization of a 10% yield (based on ester in this cut) of pure *n*-decanamide. Identification rested on n.m.r. spectrum and comparison with an authentic sample. Although the use of urea adduction is probably more nearly quantitative, only the normal amides have been observed to crystallize from ammonolysis in methanol of a mixture of methyl naphthenates.

Treatment of cut D in the manner described for cut B yielded cut D-1-B, from which was obtained a 27% yield of *n*-hendecanamide, identified by n.m.r., mass spectrum, and comparison with an authentic sample. The mass spectrum of this amide showed only a single molecular ion, at *m/e* 185. The methyl ester (cut D-1-B) from which the amide was prepared showed a major peak for a molecular ion at *m/e* 200 (ester of $C_{11}$ acid); however, there were also significant molecular ion peaks at *m/e* 212 (monocyclic $C_{12}$ acid) and 224 (bicyclic $C_{13}$ acid). The possibility of isolation of these components has not yet been explored further.

The mass spectrum of cut C-2-A showed a major molecular ion (4.5% of base peak) at *m/e* 198 (ester of monocyclic $C_{11}$ acid); however, there was also present a nearly equal (4%) molecular ion at *m/e* 196 (ester of bicyclic $C_{11}$ acid). This fraction gave no crystalline amide on ammonolysis in methanol, but saponification and preparation of amide *via* the acid chloride gave a 13% yield of recrystallized amide, m.p. 112–113°, single molecular ion at *m/e* 183 (monocyclic $C_{11}$ amide) in the mass spectrum. The complete mass spectrum is shown in Figure 3 since it contains certain features which led to erroneous initial deductions concerning structure. There appears to be a paucity of data on the fragmentation patterns of substituted monocyclic compounds.

The base peak at *m/e* 59, in the spectrum in Figure 3, is the rearrangement fragment $CH_2{=}C(OH)NH_2$, which has been reported[8] as the characteristic base peak for an amide with no $\alpha$ substituent and with at least one $\gamma$-hydrogen. This criterion proved reliable, but the prominent peak at *m/e* 69 compared with a rather minor peak at *m/e* 71 proved misleading. Since this ratio is so large compared with that at *m/e* 41 and 43 ($C_3$) and at 55 and 57 ($C_4$), it was suspected that there might be present an unsubstituted cyclopentyl ring or a disubstituted cyclopropyl ring. Furthermore, the prominent peak at *m/e* 72 was taken as good evidence for no substitution at the $\beta$ position, since this peak must be ascribed[9] to the fragment $CH_2\text{-}CH_2\text{-}CONH_2$. The analogous peak at *m/e* 89 is prominent in the fragmentation pattern from the ester, cut C-2-A. The prominent peak at *m/e* 168 (M − 15) is expected only when loss of methyl is encouraged by substitution at a quaternary carbon[10] or in a ring[11];

---

[7] Of the various partitioning agents tried, the best were silicone fluid and NPGS. Cuts collected from a silicone chromatography were given letters, while those collected from an NPGS chromatography were given numbers. Thus, cut C-2-A is obtained by collecting the third cut from a silicone chromatography and rechromatographing on NPGS, then collecting the second cut from this chromatography and rechromatographing on silicone, and finally collecting the first cut from this third chromatography.

[8] J. A. Gilpin, *Anal. Chem.*, **31**, 935 (1959).

[9] Of the various places where fragmentation patterns of acid derivatives have been discussed, perhaps the most informative and authoritative is that by R. Ryhage and E. Stenhagen in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., London, 1963, p. 399.

[10] R. Ryhage and E. Stenhagen, *Arkiv Kemi*, **15**, 333 (1960).

[11] R. I. Reed, ref. 9, p. 641.