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Manuscript received April 21, 1952.

Radiochemical Preparation of Heptadecene-8[1]

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During the course of studies concerned with the role of radioactivity in petroleum genesis, a highly purified sample of oleic acid was bombarded with 14 mev deuterons in the MIT cyclotron (*1*). Previous investigations (*2–4*) had shown that decarboxylation is a predominant reaction during the exposure of fatty or naphthenic acids to α-particles or to deuterons. Heptadecene-8 was, therefore, anticipated as a major product from the irradiation of oleic acid.

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH \rightarrow CH_3(CH_2)_7CH{=}CH(CH_2)_6CH_3 + CO_2$$

Following bombardment of 56.8 g of the purified oleic acid (free from stearic acid) for 2 hr with an average beam intensity of 9 μamp, using the gold-plated chamber described by Honig (*5*), the recovered viscous liquid was saponified by refluxing for 3 hr with alcoholic sodium hydroxide. The solution was then extracted with ether, and the extract was dried over sodium sulfate and evaporated on a steam bath. The yellow, viscous, nonsaponifiable residue amounted to 10% of the oleic acid originally bombarded. Part of this material (950 mg) was dissolved in 100 ml pentane and passed through a 12 × 800 mm column packed with a 5:1 Florosil-Celite 545 mixture. The effluent and wash pentane fluoresced deep blue under ultraviolet light. After the pentane was evaporated, a light, almost colorless liquid remained which had a melting point of 15°–20° C. On preliminary micro vacuum distillation using a simple U-type still, a solid residue remained. This material, which was not further investigated, amounted to about 0.5%, based on the original oleic acid, and had a melting point of 50°–60° C. Hydrogenation of a portion of the distillate (3% of the original oleic acid bombarded) indicated the liquid to contain 92% of mono-olefin based on the molecular weight (238) of the anticipated heptadecene.

Fractionation of a second portion of the chromatographed material (300 mg) in a micro still described by Craig (*6*) led to the recovery of a number of fractions, of which 5 had approximately the same boiling points and refractive indices. These 5 fractions were combined, and the physical properties of the resulting liquid are shown in Table 1.

An effort was made to establish the position of the double bond chemically. Approximately 75 mg of the material was ozonized in pentane at −30° C, and the resulting ozonides were hydrolized. The acids thus obtained were isolated and converted to the anilides with the intention of obtaining an x-ray powder pattern by which to identify the individual acids present (*7*). Unfortunately, impurities in the anilides caused a depression of the melting point so that the mixture could not be crystallized at room temperature. Attempts to purify the product further were not successful, and insufficient material was available for repetition of the work.

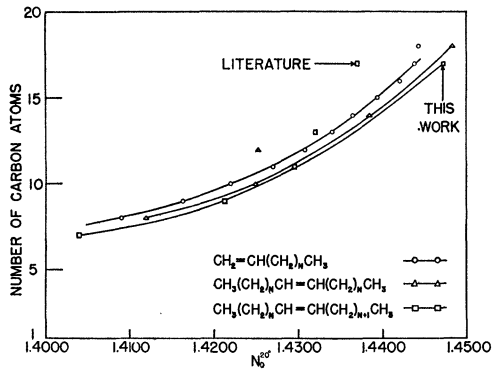

FIG. 1. Refractive indices of the isomeric normal monoolefins.

As indicated in Table 1, the refractive index and melting point of the unsaturated hydrocarbon obtained by radiochemical decarboxylation of oleic acid differ considerably from the values reported in the literature for heptadecene-8.

It has repeatedly been shown (*8–10*) that both the density and refractive index of an olefin increase as the double bond is shifted to the center of the molecule. Although heptadecene-1 has been reported as having n_D^{20} 1.4438 (*11*), the value for heptadecene-8 has been given as n_D^{20} 1.437 (*10*). The value for heptadecene-8

TABLE 1

PHYSICAL PROPERTIES OF HEPTADECENE-8

	Observed	Literature
D_4^{20}	0.802	0.795/25° (*13*)
N_D^{20}	1.472	1.437 (*11*)
Boiling point (corr), °C	297–298	173/16 mm (*13*)
Melting point (corr), °C	−12.5 to −11.5	−50 (*13*)
Double bonds/molecule (catalytic hydrogenation)	1.02 ± 0.05	1*
Carbon (%)	85.9	85.7*
Hydrogen (%)	14.1	14.3*

* Calculated.

[1] This paper is a contribution from American Petroleum Institute Research Project 43C, located at the Massachusetts Institute of Technology; W. L. Whitehead, director; Clark Goodman, physical director.
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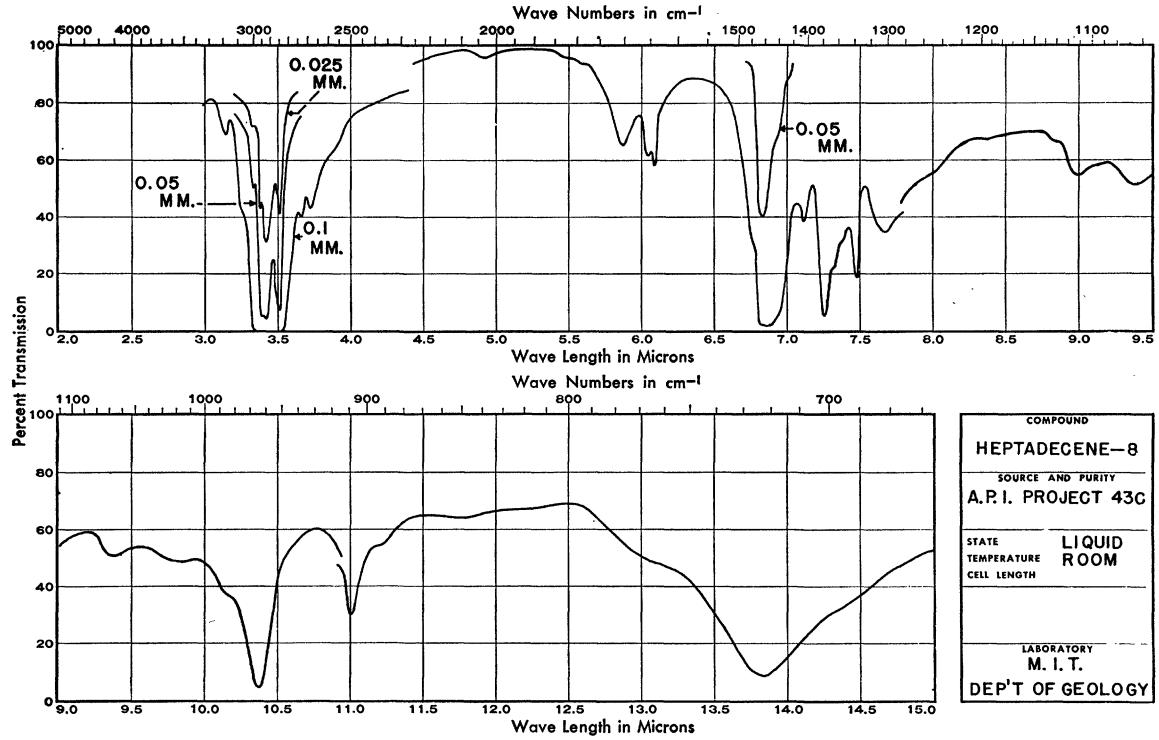

FIG. 2. Infrared spectrum of heptadecene-8 prepared by the radiochemical decarboxylation of oleic acid.

appears to be in error since, as indicated above, the compound with the internal double bond should have the higher refractive index. Fig. 1 was drawn to show the relationship between the refractive index of the hydrocarbon obtained in this work and of heptadecene-8 reported in the literature. One curve represents the indices of olefins having a terminal double bond; the second, the symmetrical compounds having the double bond in the center; and the third, the unsymmetrical compounds with the double bond occupying the linkage next to the center carbon atom. Discrepancies in the value for dodecene-6, tridecene-6, and heptadecene-8 are obvious from the figure. As indicated, the value for the hydrocarbon obtained in this work falls on the extrapolated curve of the unsymmetrical compounds.

Certain methods for the preparation of olefins are known to result in a mixture of isomers as a result of rearrangement of the double bond. Noorduyn (*12*) in his study of the constitution of olefins prepared by heating the barium salts of fatty acids with sodium ethoxide or sodium methoxide showed, by ozonolysis of the product, that the heptadecene-8 thus prepared from barium oleate was actually a mixture of isomers. No physical properties were given for this preparation. It is likely that the heptadecene-8 (Table 1) reported by Messer (*13*) is also a mixture, since it was prepared by distilling sodium oleate with sodium ethoxide.

Fig. 2 shows the infrared spectrum of the heptadecene obtained in this work. According to Rasmussen, Brattain, and Zucco (*14*), the strong band at 10.3 μ is characteristic of the *trans* form of RHC=CHR compounds, whereas the *cis* form has a weaker band of more variable position in the 10–11 μ region (*15*).[4] The *cis* form also has a strong band in the 14–16 μ region. From the absence of the latter band and from the shape and intensity of the 10.3 μ band, it appears that the heptadecene prepared in this work is at least predominantly of the *trans* form.

It appears from this work that heptadecene-8 of considerably higher purity than that previously reported has been prepared by the radiochemical decarboxylation of oleic acid. This study indicates the possibility of using high energy sources of radiation in the synthesis of organic compounds or their intermediates. In this case, the use of radiation has led to a practical method for the preparation of a high molecular weight olefin with an internal double bond. Compounds of this type have in the past been difficult to obtain in a satisfactory state of purity.

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Manuscript received April 23, 1952.

Frequency of Dicentric Bridges in Meiosis in the Grasshopper *Gesonia punctifrons,* Produced by Different Dosages of X-Rays[1]

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Experimental work on the effects of x-rays on the chromosomes of both animals and plants has been carried out mainly on the mitotic chromosomes. Similar studies on meiosis (*1–4*) have sometimes yielded contradictory results. In animals, especially, the studies on irradiated meiotic chromosomes (*5–11*) are not very numerous, and it seems desirable to have more quantitative data on the induced aberrations, obtained by direct cytological examinations conducted on the divisions immediately following treatment. We have, therefore, made a large-scale attempt to secure such data, as they seem to us to be essential not only for the understanding of the nature and causes of structural changes in the karyotype during evolution, but also for their special significance in relation to the effects of ionizing radiation. In the present paper we shall restrict ourselves to the presentation of the data of only one class of abnormality among several others found—namely, the frequency of dicentric bridges with fragments. These were detected at the first anaphase of meiosis by irradiating the testes of the grasshopper *Gesonia punctifrons,* a species with 23 acrocentric chromosomes in the males (Table 1).

Six experiments were carried out, with irradiations on the following dates: I, 5/12/48; II, 6/21/49; III, 4/3/50; IV, 5/9/50; V, 8/20/50; VI, 10/9/50. The grasshoppers to be treated with a particular dosage were put in separate muslin bags 4 × 5 cm in size. Two or three such bags, depending on the number of doses to be given in a particular experiment, were placed one upon another at a distance of 50 cm from the target. They were removed one by one at predetermined intervals. Radiation was carried out in the Radiology Department of the Calcutta Medical College, and the source of the x-rays was a G-E Maximar therapy tube. The voltage used was 200 kv, and the current was kept constant at 10 ma. The radiation was filtered through .5 mm copper and 1 mm aluminium filters. The dosages were varied by altering the time of exposure alone. It was not possible to measure the dosages in r-units in every experiment separately because the usual practice in this hospital is to calibrate the output of the tube at certain intervals of days. The various dosages indicated are therefore approximate, and errors of total dosages received in different experiments may be of the order of 4–5%.

The dosages used and the intervals between irradiation and treatment are shown for Expts I and II in Tables 2 and 3, respectively. In Expt III the only dosage was 80 r, the only interval 26 hr; in IV the doses were 40 r and 80 r, and the intervals 30 and 48 hr; in both V and VI the dosages were 40 r, 80 r, and 120 r, and the interval was always 30 hr.

G. punctifrons has been frequently used in our laboratory as experimental material and for the study of normal meiosis. Dicentric bridges were never observed in unirradiated material. It was therefore decided to have a single lot of grasshoppers to serve as controls, and the data for unirradiated material come from this lot alone.

TABLE 1

FREQUENCY OF DICENTRIC BRIDGES IN DIFFERENT EXPERIMENTS AT 30 HR AFTER IRRADIATION

Expt	40 r		80 r		120 r	
	Chromosomes	Bridges	Chromosomes	Bridges	Chromosomes	Bridges
I*	690	4			2,507	36
II	1,311	5	966	8		
IV	1,679	10	2,392	25		
V	1,794	7	2,093	16	4,278	47
VI	6,279	22	4,554	32	2,622	31
Sum	11,753	48	10,005	81	9,407	114
%		.41		.81		1.21
χ^2		2.50		2.36		1.53
P		.7		.5		.5

* Expt I, 280 r: 368 chromosomes, 17 bridges, 4.6%; Expt I, 320 r: 1,311 chromosomes, 47 bridges, 3.6%.

The frequencies of dicentric bridges accompanied by fragments in the first anaphase of meiosis, obtained in the different experiments when examined at 30 hr after irradiation, are shown in Table 1. It will be clear from the data that the frequencies found in the different experiments, with the same dosage, remain more or less constant, as the total χ^2 values indicate in each case. The corresponding value of P is not significant in any of the dosages, and therefore the slight deviations in the frequencies obtained during several repe-

[1] The authors record their deep sense of indebtedness to H. J. Muller for valuable suggestions incorporated in this paper. Thanks are also extended to S. Mukherji, professor of radiology, Calcutta Medical College, for providing facilities for x-raying in his hospital.

[2] The work was supported by a research fellowship offered to Ira Sarkar by the National Institute of Sciences of India.