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Hydrocarbons from Australian Oil, 200 Million Years Old

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### Authors

Van Hoesen, William

Haug, Pat

Burlingame, A L

et al.

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**University of California**  
**Ernest O. Lawrence**  
**Radiation Laboratory**

HYDROCARBONS FROM AUSTRALIAN OIL,  
200 MILLION YEARS OLD

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HYDROCARBONS FROM AUSTRALIAN OIL,  
200 MILLION YEARS OLD

William Van Hoesen, Pat Haug, A. L. Burlingame,  
and Melvin Calvin

July 19, 1966

HYDROCARBONS FROM AUSTRALIAN OIL, 200 MILLION YEARS OLD

William Van Hoesen, Pat Haug, A. L. Burlingame, and  
Melvin Calvin, F. R. S.

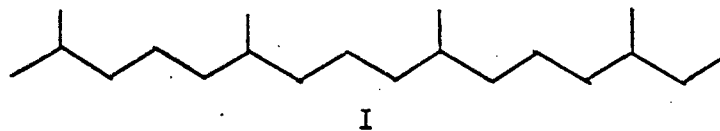
Department of Chemistry and Space Sciences Laboratory,  
University of California, Berkeley, California

In an attempt to extend our investigation of the organic components of ancient sediments<sup>1, 2, 3, 4</sup> to another continent and presumably a separate origin, we have extensively studied the hydrocarbons present in the Moonie Crude Oil from Queensland, Australia.<sup>5</sup> It is believed that the oil had its source in Permian rocks, probably sedimentary, and later migrated along an unconformity at the bottom of the reservoir basin into Jurassic and Triassic sandstone, dated on the basis of spores.<sup>6, 7, 8</sup> A wide spectrum of sediment analyses varying the parameters of time and geographic location can be expected to have considerable importance relative to the question of when and how life evolved on earth and possibly even in extraterrestrial environments. Eventually such an approach may also shed some light on the ecology of a particular locale at a given geologic period.

The experimental procedure, previously explained in detail,<sup>1</sup> involved the use of column chromatography (TLC grade neutral  $\text{Al}_2\text{O}_3$ -elution with n-heptane) to separate from 3.89 g of crude oil, the "total" hydrocarbon fraction (1.46 g). Using this "total" fraction, the "normal" (straight chain) hydrocarbons were separated by means of a 5 Å molecular sieve, from the "branched-cyclic" hydrocarbons, the latter representing approximately 42% of the "total" hydrocarbons. Individual compounds of the "branched-cyclic fraction" were separated on a 3% SE-30 gas-liquid chromatography column (10 ft. x 1/4 in.) and purified successively on (25 ft. x 1/4 in.) 2 1/2% 7-ring metapolyphenylether and 3% tetracyanoethylated pentaerythritol chromatographic phases. A modified C.E.C. 103 mass spectrometer was used to elucidate the structures of isolated compounds.

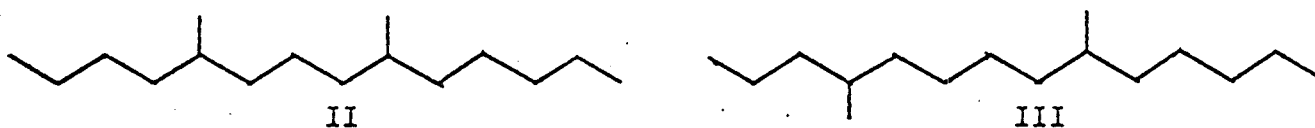
In Figures I-III the original mass spectra of the first three compounds isolated from the Moonie Oil are presented. These are sample spectra illustrating the purity attained by the above isolation procedures and proper mass spectrometric handling techniques. In Figure V-VII the bar graphs drawn from these originals are presented. (Relative intensities for all peaks which are off scale due to the choice of the base peak are given in Table I.) All spectra published in this and preceding papers have been handled in the same manner.

The gas chromatograms (packed column, 10 ft x 1/16 in. 3% SE-30-program rate 6°/min.) of the "total", "branched-cyclic" and "normal" fractions are presented in Figure IX. The normal alkanes can be seen to run from C<sub>9</sub> to C<sub>29</sub> with maxima at C<sub>12</sub> and C<sub>18</sub> and negligible odd over even predominance. Particularly indicative of life processes are the isoprenoid alkanes, which possess a high degree of structural specificity. The isolated C<sub>15</sub>, C<sub>16</sub>, C<sub>18</sub>, C<sub>19</sub> (pristane) and C<sub>20</sub> (phytane) isoprenoids, whose mass spectra are given in Figures IV-VIII, appear to have a regular isoprenoid structure corresponding to that of phytane, Structure I.



Evidence was also obtained for the existence of a C<sub>21</sub> isoprenoid but it was not separable from other components. Also identified were representatives of three other homologies; Figure X gives the mass spectrum of C<sub>15</sub> iso-alkane (2-methyltetradecane), Figure XI that of

$C_{18}$  anteiso-alkane (3-methylheptadecane), and Figures XII and XIII those of  $C_{15}$  and  $C_{16}$  n-alkyl-cyclohexane. Possible biological origins of these compounds have previously been discussed.<sup>4</sup> Figures XIV-XVII give the mass spectra of four (relatively pure by gas chromatographic as well as by mass spectrometric standards) unidentified compounds,  $X_1$ ,  $X_2$ ,  $Y_1$ , and  $Y_2$ . Compounds  $X_1$  and  $X_2$  are branched  $C_{16}$  alkanes and were collected from the region marked X in the gas chromatogram in Figure IX;  $Y_1$  and  $Y_2$  are branched  $C_{17}$  alkanes and are from the region marked Y. An interpretation of the mass spectrum of compound  $X_1$  suggests Structure II (5,9-dimethyl-tetradecane).



Similarly, a possible interpretation of compound  $X_2$  is given by Structure III (4,9-dimethyltetradecane). The formation of such compounds might be possible by cracking of squalane. Table II presents the relative retention times of Compounds  $X_1$ ,  $X_2$ ,  $Y_1$  and  $Y_2$  on gas chromatographic phases. High resolution mass spectrometric studies verify that these are saturated branched hydrocarbons.<sup>9</sup> Figure XVIII, a gas chromatogram on a 3% SE-30 (150 ft. x 0.010 in. - program rate 1<sup>o</sup>/min.) capillary column reveals the actual complexity of these regions. A thorough mass spectrometric analysis of the  $C_{17}$  isoprenoid region (as determined by coinjection of the synthetic 2,6,10-trimethyltetradecane)<sup>10</sup> indicates that this compound is not present



in significant amounts. Mass spectrometric ambiguities in the identification of the exact structure of the  $C_{19}$  isoprenoid<sup>4</sup> have been eliminated (and pristane established as definitely present) by coinjection of pristane.<sup>11</sup> An investigation of the high mass region has given no evidence of steranes or triterpanes although high molecular weight unsaturated compounds are present.

Hydrocarbons from the Australian Moonie Oil, age 200 million years, therefore, resemble very strongly the hydrocarbons found in other sediments varying in age from 30 million to 2.7 billion years. Since we have found indications of isoprenoids, iso-alkane, anteiso-alkane, n-alkyl cyclohexane, and normal alkane series in the oils and sediments examined, as indicated in Table III, it is becoming increasingly evident that among biogenic sediments, variations due to individual sediment history and ecology are to be found primarily in the relative amounts of these compounds present, and possibly in the hydrocarbons present only in small quantities, and not in the types of <sup>hydrocarbons</sup> ~~compounds~~ present.

### ACKNOWLEDGMENTS

We would like to express our thanks to Professor R. B. Johns and Dr. H. K. Schnoes for many helpful discussions and to the National Aeronautics and Space Administration, grant NsG 101-61, and to the U. S. Atomic Energy Commission for supporting this research.

- <sup>1</sup>Eglinton, G., Scott, P. M., Belsky, T., Burlingame, A. L., Richter, W., and Calvin, M., Advances in Organic Geochemistry, Vol. 2, 1964 ed by G. D. Hobson & M. C. Louis /Pergamon Press, 1966. pp. 41-74.
- <sup>2</sup>Belsky, T., Johns, R. B., McCarthy, E. D., Burlingame, A. L., Richter, W., and Calvin, M., Nature, 206, 446 (1965).
- <sup>3</sup>Burlingame, A. L., Haug, Pat, Belsky, Theodore, and Calvin, Melvin, The Proceedings of the National Academy of Sciences, 54, 1406 (1965).
- <sup>4</sup>Johns, R. B., Belsky, T., McCarthy, E. D., Burlingame, A. L. Haug, Pat, Schnoes, H. K., Richter, W., and Calvin, M., Geochimica et Cosmochimica Acta (in press).
- <sup>5</sup>We thank A. S. Keller, Resident Geologist, Union Oil Development Corporation, Toowomba, Queensland, Australia, for generously providing us with a sample of the Moonie Crude Oil.
- <sup>6</sup>Keller, A. S. (1965) Personal Communication.
- <sup>7</sup>McLaughlin, R. C., University of Melbourne, Victoria, Australia (1964) Personal Communication.
- <sup>8</sup>Milner, H. B., Nature, 202, 959 (1964).
- <sup>9</sup>We thank Dennis Smith for running the high resolution mass spectra of these compounds.
- <sup>10</sup>We thank Eugene D. McCarthy for providing us with a sample of synthetic, C<sub>17</sub> Isoprenoid, 2,6,10-trimethyltetradecane.
- <sup>11</sup>McCarthy, Eugene D., and Calvin, Melvin, to be presented at the 151st National Meeting of the ACS, Petroleum Division, New York, 1966.

TABLE I  
OFF SCALE MASS SPECTRAL INTENSITIES

M/E	IV	V	VI	VII	VIII	X	XI	XIV	XV	XVI	XVII	M/E
40			210	160	180	121	670	120	120	840		40
41	770	420	2000	770	710	2140	1000	1200	2500	2300	1040	41
42	220	134	500	220	170	820	800	300	550	630	256	42
43		1070	3300	1800	1400	3570	6000	2600	4000	5000	1930	43
44			131	260	150	157	3300		116	170		44
53			101									53
55	335	230	900	450	420	515	600	640	580	110	655	55
56	400	194	660	460	370	393	260	470	400		375	56
57		950	3400	2400	1720	1790	500	2600	1800	5200	2620	57
58			170					120		180	109	58
60							400					60
61							3500					61
62							150					62
69	120		285	200	270	179	250	250	230	380	336	69
70	180	147	230	140	280	150	110	280	200	370	304	70
71		820	1300	1300	910	800	250	1300	790	2000	1100	71
72										110		72
83							130	131	190	136		83
84									125			84
85		250		410	410	672	113	500			120	85
97							210	120	125	220	110	97
98			140					160		200	160	98
99			130			143	190		160			99

TABLE II  
Relative Retention Times

Compound	10' x 1/4", SE-30 Program rate 4°/min.	25' x 1/4", 2 1/2% PPE Isothermal 136° C
C <sub>16</sub> Isoprenoid	22.7 min.	10.8 min.
X <sub>1</sub>	23.5 "	11.9 "
X <sub>2</sub>	24.2 "	12.8 "
Y <sub>1</sub>	26.7 "	19.0 "
Y <sub>2</sub>	28.2 "	20.8 "
C <sub>18</sub> Isoprenoid	28.6 "	23.1 "

TABLE III

Approximate Relative Abundance of Alkanes\*

Sample	Age	Isoprenoids						
		C <sub>15</sub>	C <sub>16</sub>	C <sub>17</sub>	C <sub>18</sub>	C <sub>19</sub>	C <sub>20</sub>	C <sub>21</sub>
Soudan Shale	2.7 x 10 <sup>9</sup>		0.08		0.6	1	0.6	0.1
Nonesuch Oil	1 x 10 <sup>9</sup>	0.4	1.2			1	0.3	0.1
Nonesuch Calcite Vein	1 x 10 <sup>9</sup>	0.2	0.8			1	0.3	
Antrim Shale	265 x 10 <sup>6</sup>			0.2	1.3	1	0.6	
Moonie Oil	200 x 10 <sup>6</sup>	0.3	0.9			1	0.3	<0.05
Green River Shale	50 x 10 <sup>6</sup>		0.4	<0.1	0.2	1	5.5	
San Joaquin Oil	30 x 10 <sup>6</sup>				0.9	1	0.9	
Abbott Seep Oil	3 x 10 <sup>6</sup>					1	0.3	
Abbott Rock Oil	3 x 10 <sup>6</sup>				0.4	1	0.5	

\* Determined from gas chromatographic peak heights

TABLE III (Con't.)

Sample	Age	Steranes			Triterpane
		C <sub>27</sub>	C <sub>28</sub>	C <sub>29</sub>	C <sub>30</sub>
Soudan Shale	2.7 x 10 <sup>9</sup>	0.03			1.2
Green River Shale	50 x 10 <sup>6</sup>	0.05	0.5	0.8	1.2

TABLE III (con't.)

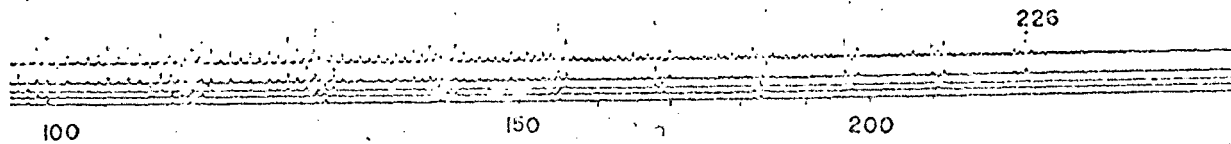
Sample	Age	<u>Iso-Alkane</u>				<u>Anteiso-Alkane</u>			<u>n-alkyl-Cyclohexanes</u>					X <sub>1</sub>	X <sub>2</sub>	Y <sub>1</sub>	Y <sub>2</sub>
		C <sub>15</sub>	C <sub>16</sub>	C <sub>17</sub>	C <sub>18</sub>	C <sub>16</sub>	C <sub>17</sub>	C <sub>18</sub>	C <sub>15</sub>	C <sub>16</sub>	C <sub>17</sub>	C <sub>18</sub>	C <sub>19</sub>	C <sub>16</sub>	C <sub>16</sub>	C <sub>17</sub>	C <sub>17</sub>
Nonesuch Oil	1 x 10 <sup>9</sup>		<0.1	0.2	0.07	<0.1	0.2	0.05		0.1	0.1	<0.1	0.1				
Moonie Oil	200 x 10 <sup>6</sup>	0.1						0.1	0.2	0.3				0.1	<0.1	0.05	0.1



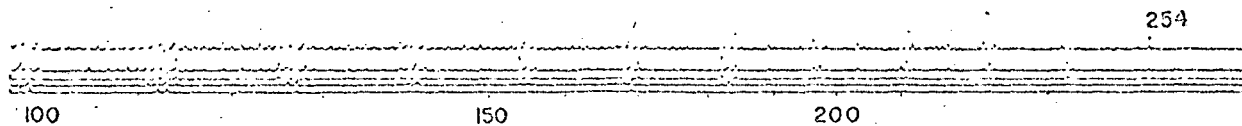
TABLE III (con't.)

Sample	Normal Alkane																										
	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>14</sub>	C <sub>15</sub>	C <sub>16</sub>	C <sub>17</sub>	C <sub>18</sub>	C <sub>19</sub>	C <sub>20</sub>	C <sub>21</sub>	C <sub>22</sub>	C <sub>23</sub>	C <sub>24</sub>	C <sub>25</sub>	C <sub>26</sub>	C <sub>27</sub>	C <sub>28</sub>	C <sub>29</sub>	C <sub>30</sub>	C <sub>31</sub>	C <sub>32</sub>	C <sub>33</sub>	C <sub>34</sub>	
Soudan Shale						0.01	0.07	0.5	1	0.9	0.5	0.9															
Nonesuch Oil				0.01	0.05	0.3	0.7	0.95	1	0.9	0.75	0.55	0.4	0.3	0.2	0.1	0.09	0.07	0.05	0.04	0.03	0.02	0.01	0.01	0.01		
Nonesuch Calcite Vein			0.2	0.1	0.3	0.4	0.6	0.8	1	1.2	1.35	1.35	1.30	1.2	1.1	1.0	0.8	0.7	0.6	0.4	0.3	0.2	0.1	0.08	0.05	0.03	
Antrim Shale		0.005	3.0	5.0	5.0	4.0	3.0	1.5	1	0.5	0.2	0.005															
Moonie Oil	0.03	0.3	0.2	0.4	0.3	0.5	0.7	0.8	1	1.04	1.03	0.9	0.8	0.7	0.65	0.4	0.3	0.1	0.06	0.01	0.005						
Green River Shale					0.01	0.02	0.05	0.04	1	0.06	0.1	0.02	0.08	0.25	0.1	0.01	0.15	0.01	0.25	0.02	1.1	0.02	1.1	0.01	0.09		
San Joaquin Oil		0.2	1.3	2.0	2.4	2.2	1.8	1.4	1	0.6	0.4	0.2	0.1	0.05													
Abbott Seep Oil							0.1	0.7	1	0.4	0.2	0.08	0.06	0.05	0.04	0.025	0.025	0.025	0.06	0.04	0.07	0.08	0.3	0.1	0.05	0.03	
Abbott Rock Oil					0.01	0.05	0.2	0.6	1	1.2	1.3	1.0	0.8	0.5	0.3	0.2	0.15	0.1	0.08	0.01							

MOONIE C<sub>13</sub> ISOPRENOID



MOONIE C<sub>13</sub> ISOPRENOID



MOONIE C<sub>19</sub> ISOPRENOID

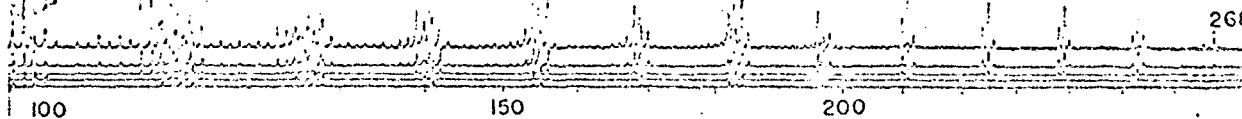


Figure I Original Mass Spectrum of Moonie Oil C<sub>16</sub> Isoprenoid

Figure II Original Mass Spectrum of Moonie Oil C<sub>18</sub> Isoprenoid

Figure III Original Mass Spectrum of Moonie Oil C<sub>19</sub> Isoprenoid

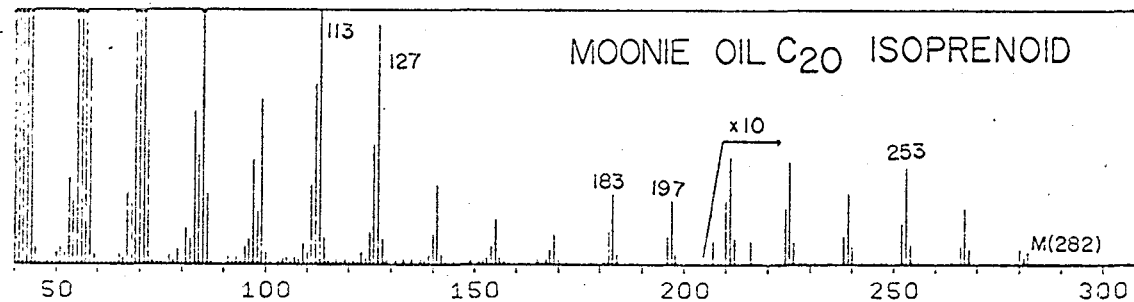
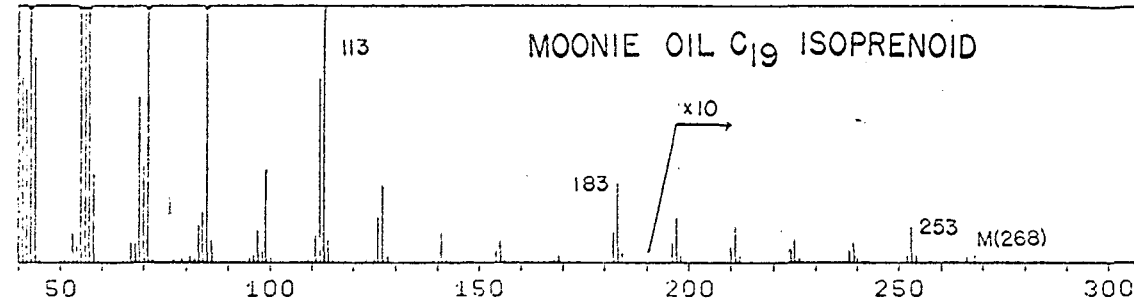
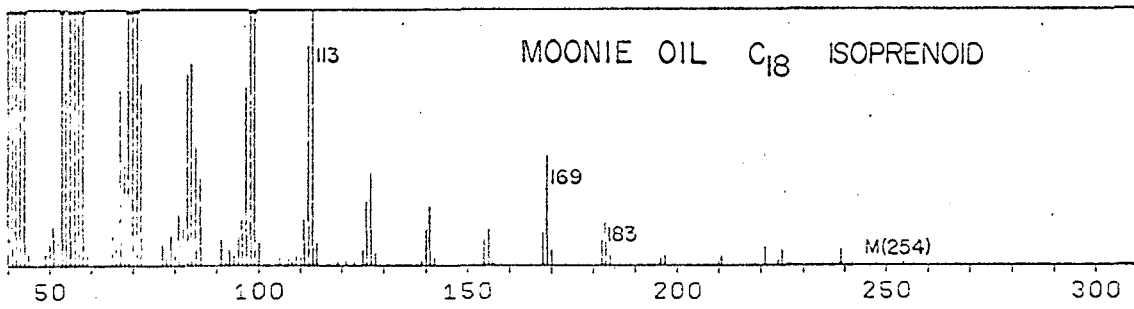
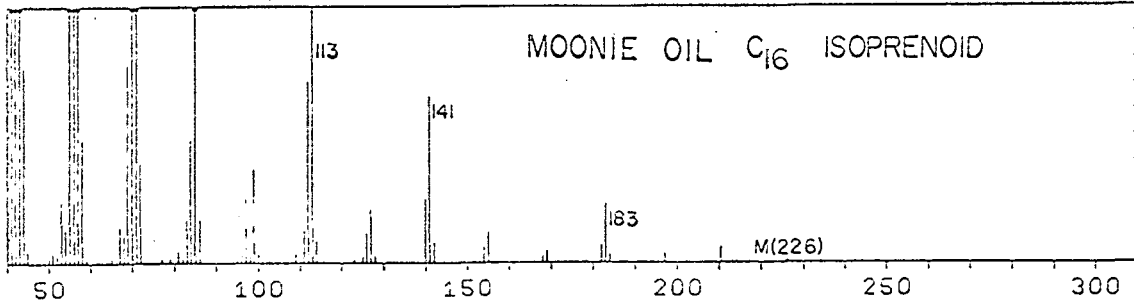
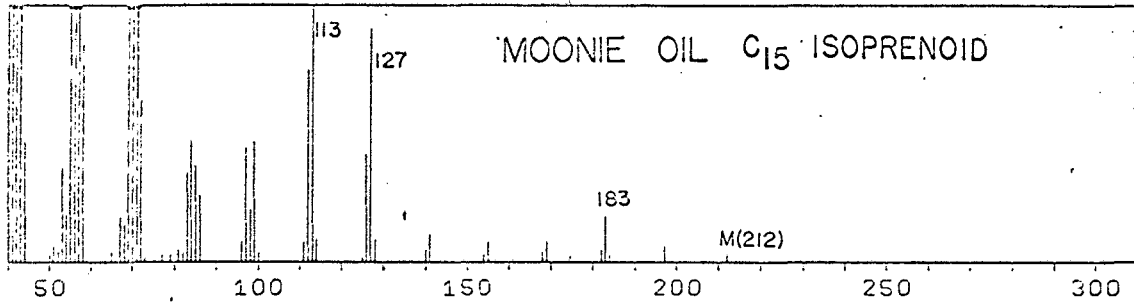


Figure IV Mass Spectrum of Moonie Oil C<sub>15</sub> Isoprenoid

Figure V Mass Spectrum of Moonie Oil C<sub>16</sub> Isoprenoid

Figure VI Mass Spectrum of Moonie Oil C<sub>18</sub> Isoprenoid

Figure VII Mass Spectrum of Moonie Oil C<sub>19</sub> Isoprenoid

Figure VIII Mass Spectrum of Moonie Oil C<sub>20</sub> Isoprenoid

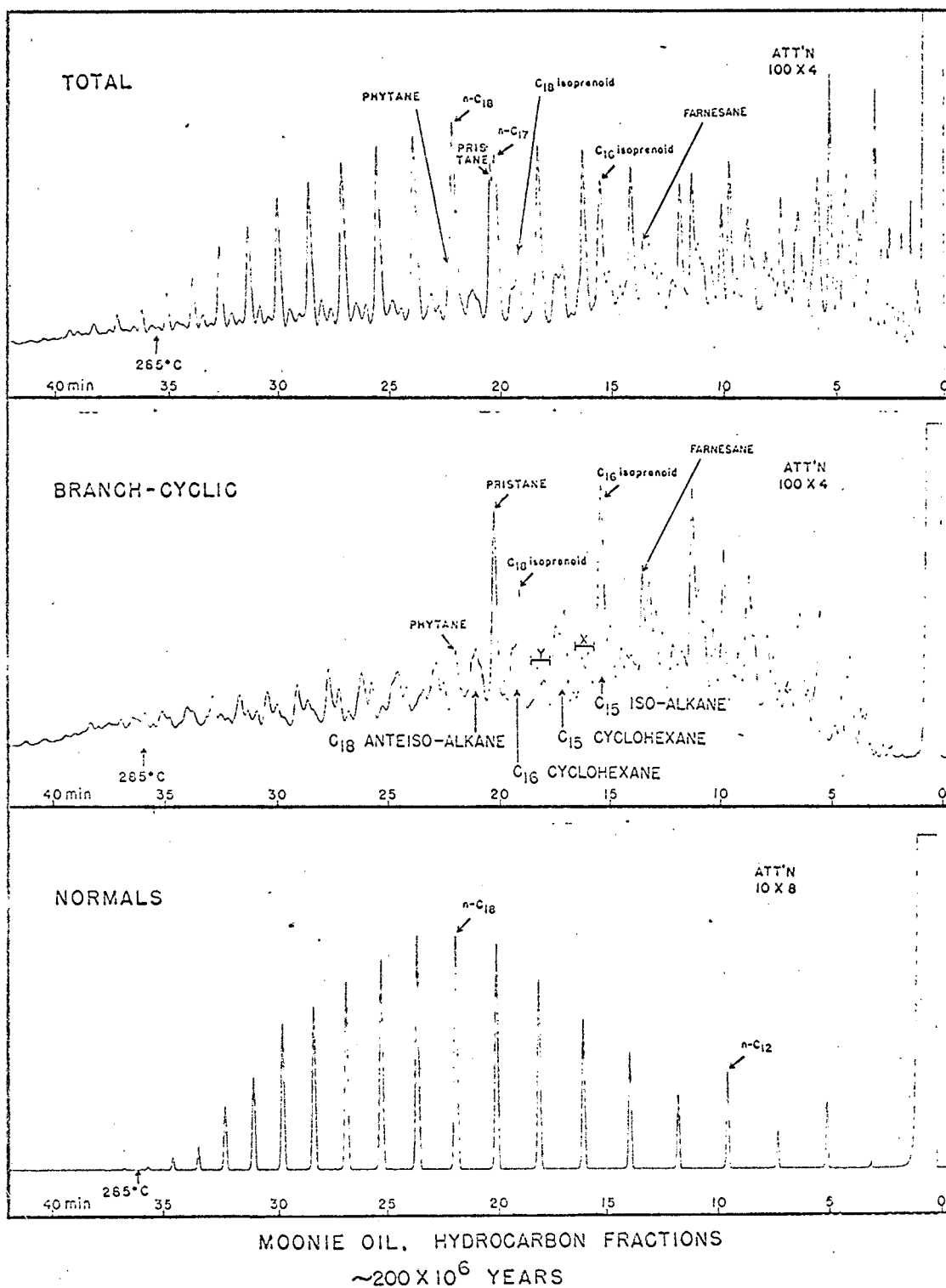


Figure IX Gas Chromatograms of "Total", "Branched-Cyclic" and "Normal" Hydrocarbon Fractions of the Moonie Oil

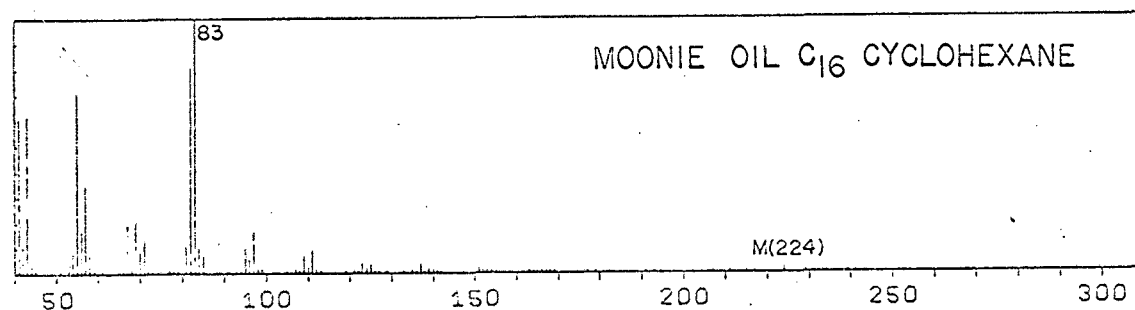
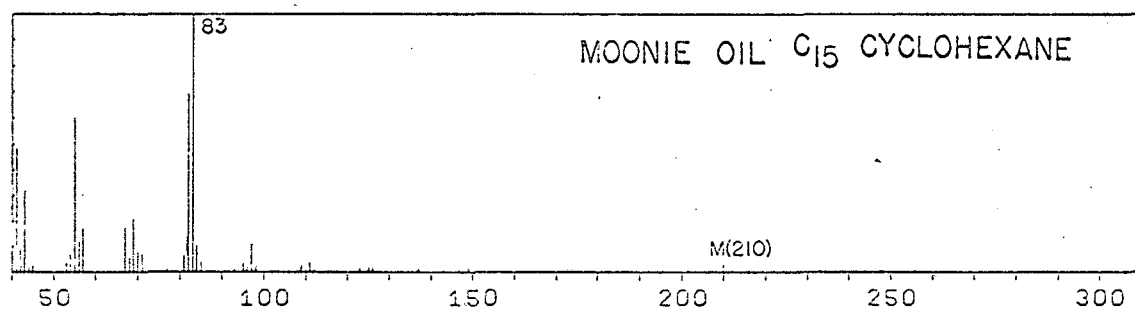
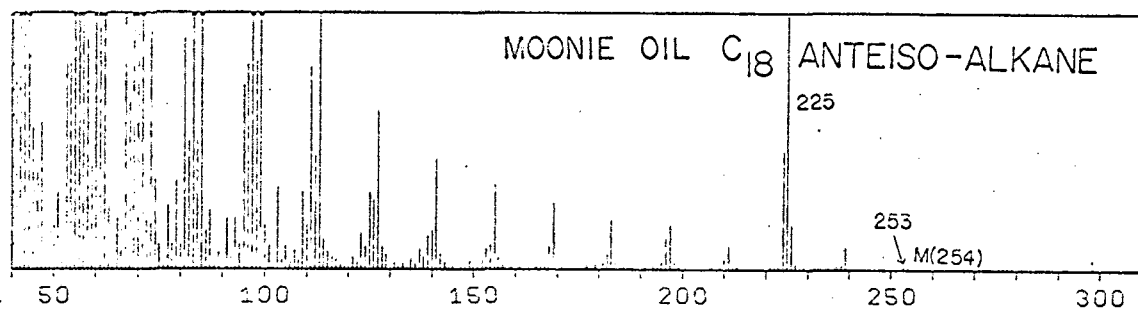
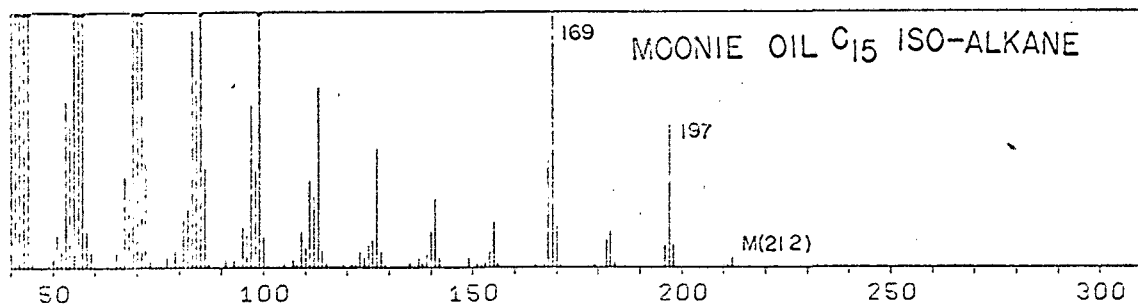


Figure X Mass Spectrum of Moonie Oil C<sub>15</sub> Iso-Alkane

Figure XI Mass Spectrum of Moonie Oil C<sub>18</sub> Anteiso-Alkane

Figure XII Mass Spectrum of Moonie Oil C<sub>15</sub> n-Alkyl-Cyclohexane

Figure XIII Mass Spectrum of Moonie Oil C<sub>16</sub> n-Alkyl-Cyclohexane

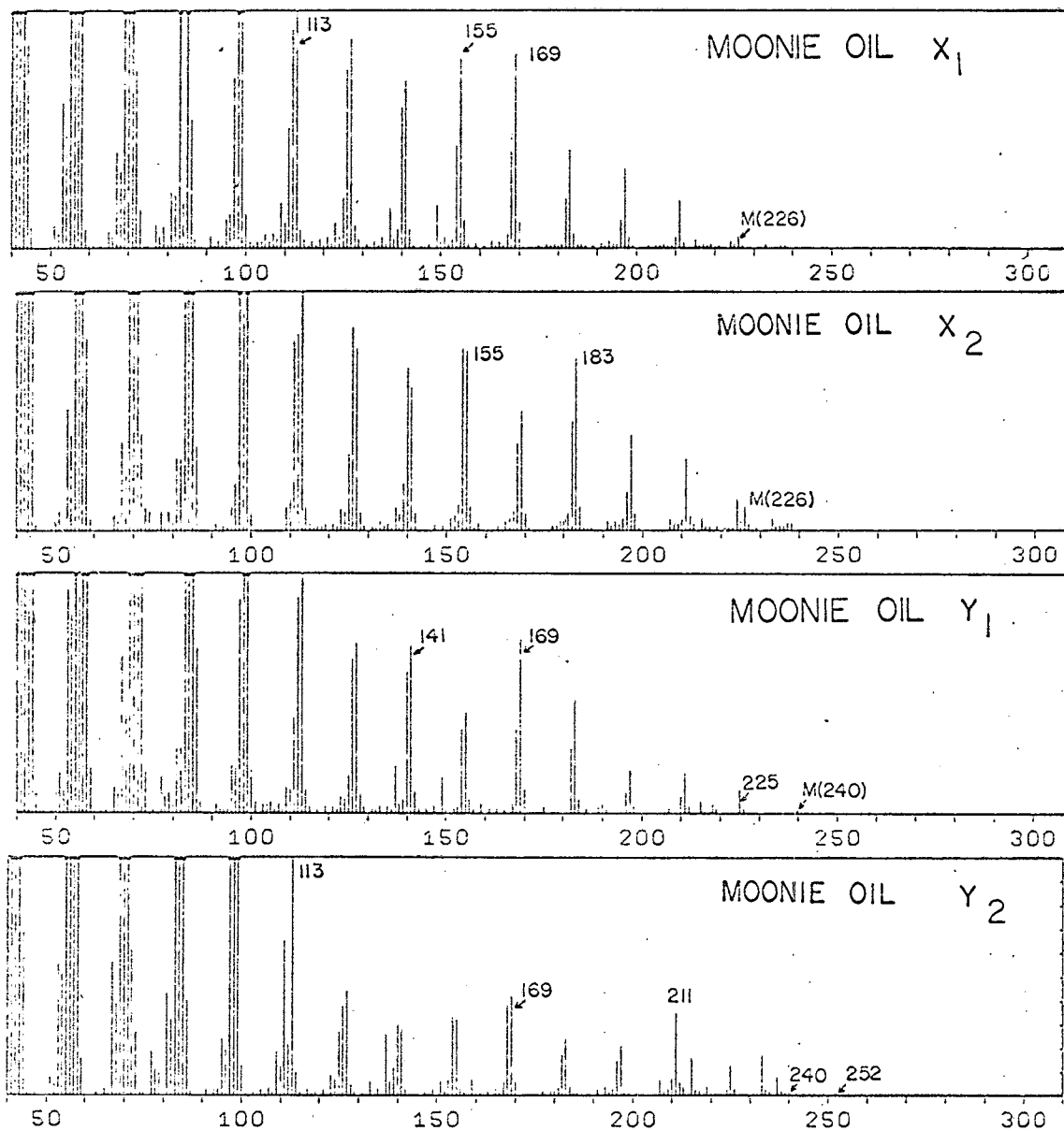


Figure XIV Mass Spectrum of Moonie Oil X<sub>1</sub>

Figure XV Mass Spectrum of Moonie Oil X<sub>2</sub>

Figure XVI Mass Spectrum of Moonie Oil Y<sub>1</sub>

Figure XVII Mass Spectrum of Moonie Oil Y<sub>2</sub>

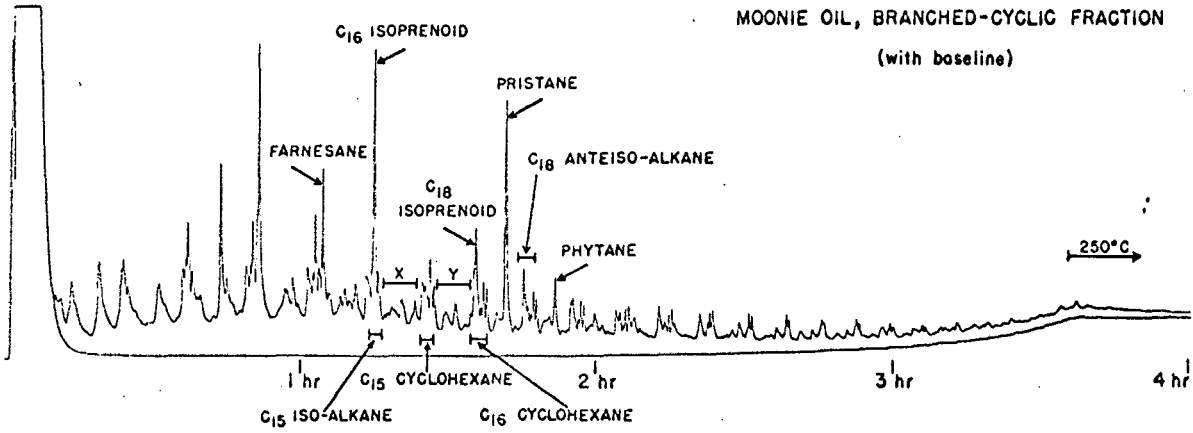


Figure XVIII Capillary Column Gas Chromatograph of Moonie Oil  
"Branched-Cyclic" Hydrocarbon Fraction

