Keto-carboxylic Acids isolated from the Colorado Green River Shale (Eocene)

By PAT HAUG, H. K. SCHNOES, and A. L. BURLINGAME*

(*Department of Chemistry and Space Science Laboratory, University of California, Berkeley, California* 94720)

THE isolation and identification of organic compounds from ancient sediments has received considerable attention in recent years, and the Green River Formation (Eocene) is perhaps the most extensively investigated carbon-rich deposit in this respect. Here we record the interesting finding of methylketo-acids in Green River oil shale extracts.

Details of the extraction and isolation of the non-phenolic acidic components from the powdered oil shale have been described.[1] The esterified acids ($MeOH-BF_3$) were separated by g.l.c. (10 ft. × ¼ in. column of 3% SE-30, followed by a 6 ft. × ¼ in. 3% HIEPF), and the esters thus isolated were examined by mass spectrometry. Two fractions were obtained which from their low and high resolution mass spectra† could be identified as saturated keto-esters. One of these showed a molecular ion at *m/e* 214 and strong peaks at *m/e* 183 ($M - 31$; $C_{11}H_{19}O_2$), 157 ($M - 57$; $C_9H_{17}O_2$), 125 ($M - 57 - 32$; $C_8H_{13}O$), 97, 87, 74, 69 and 58 (C_3H_6O; base peak). The second compound had a molecular ion at *m/e* 256 and peaks at 225 ($M - 31$), 199 ($M - 57$; $C_{12}H_{23}O_2$), 167 ($M - 57 - 32$; $C_{11}H_{19}O$), 149 (167-18; $C_{11}H_{17}$) 87, 74 and 58 (C_3H_6O; base peak). These data

† Conventional and high resolution mass spectra were obtained on a CEC 21-110 mass spectrometer. High resolution mass spectra were recorded on a photoplate.

clearly identify the compound with $M = 214$ as methyl 10-oxoundecanoate (I) and the compound with $M = 256$ as methyl 13-oxotetradecanoate (II).

$$CH_3O—\overset{O}{\overset{\|}{C}}—[CH_2]_n—\overset{O}{\overset{\|}{C}}—CH_3 \quad \begin{matrix}(I),\ n = 8;\\ (II),\ n = 11.\end{matrix}$$

The mass spectra of keto-esters have been studied[2] and their fragmentation patterns are characteristic of aliphatic diketo-functionalisation;[3] in particular, the sequence $M - 31$, $M - 57$ and $M - 57 - 32$, together with the intense peak at m/e 58 (resulting from the McLafferty rearrangement involving the keto-grouping), identify these compounds as methylketo-esters. An impure sample of the keto-acid corresponding to M 242 was obtained and the presence of the remaining isomer at M 228 is indicated by our data.‡

The finding of methylketo-acids in an ancient sediment is of some interest, since these long-chain terminal keto-acids are relatively rare in nature.[4] Long-chain methyl ketones (C_{17}—C_{37}) have been isolated from soil.[5] Since it is known that certain micro-organisms, *e.g.*, *Penicillium* species, can metabolise fatty acids up to C_{14} to methyl ketones,[6] it is possible that keto-acids represent intermediates of microbial degradation of n-fatty acids. The isolation of such minor components from ancient sediments is thus of significance with respect to any speculations or deductions on the history of a given sediment and the original diagenetic transformation of organic material.

Support of this work through grants from the National Aeronautics and Space Administration is acknowledged. The authors thank Mr. B. R. Simoneit for collection of shale specimens from Parachute Creek, 8 miles NW of Grand Valley, Colorado (long. W 108° 7′; lat. 39° 37′; el. 7300′).

(*Received, August* 31*st.* 1967; *Com.* 926.)

‡ High-resolution mass-spectral data obtained on the total acid fraction liberated upon demineralisation (HF) of pulverized, exhaustively extracted (benzene–MeOH) shale indicate a series of keto-acids in amounts comparable to the normal acids (Burlingame and Simoneit, unpublished results).

[1] P. Haug, H. K. Schnoes, and A. L. Burlingame, *Science*, in the press; *Geochim. Cosmochim. Acta*, in the press.
[2] R. Ryhage and E. Stenhagen, *Arkiv. Kemi*, **1960**, **15**, 545.
[3] A. L. Burlingame, D. H. Smith, and W. J. Richter, *J. Amer. Chem. Soc.*, in preparation.
[4] G. Eglinton and R. J. Hamilton in "Chemical Plant Taxonomy", ed. T. Swain, Academic Press, New York, 1965, ch. 8.
[5] R. I. Morrison and W. Bick, *Chem. and Ind.*, **1966**, 596.
[6] M. Starkle, *Biochem Z.*, 1924, **151**, 371; W. Franke and W. Heinen, *Arch. Mikrobiol.*, 1958, **31**, 50.