Isoprenoid and Dicarboxylic Acids

Isolated from Colorado Green River Shale (Eocene)

Abstract. *Isolation of the C_9 and C_{10} isoprenoid carboxylic acids, the C_{12} to $C_{18}\alpha,\omega$-dicarboxylic acids, and the 2-methyl 1,*n*-dicarboxylic acids (*n *is 13, 15, and 16) from organic extract of the Colorado Green River shale (Eocene) is reported. Separation was achieved by column and gas-liquid chromatographic techniques and structural identification of individual components, by mass spectrometry.*

The Colorado Green River shale, a sediment rich in organic matter of Eocene age, has been the object of several studies in organic geochemistry. The hydrocarbon material, which has been investigated most extensively, includes normal and isoprenoid alkanes, steranes, and triterpanes (see *1*).

Several reports have dealt with the fatty acids obtained from this sediment, and the presence of homologous series of normal fatty acids has been established (*2, 3*). More recent work by Leo and Parker (*4*) has dealt with the occurrence of iso- and anteiso-acids, whereas Eglinton and his collaborators (*5–7*) have reported isoprenoid fatty acids, ranging from C_{14} to C_{21}, with the exception of C_{18}, from this shale. We report here some of our results concerning the acid composition of extracts of the Colorado Green River shale, in particular the identification of two additional isoprenoid acids, as well as ten dicarboxylic acids.

The shale was obtained from Parachute Creek, 8 miles (13 km) northwest of Grand Valley, Colorado [108° 7′W; 39°37′N; elevation 7300 feet (2125 m)]. After pulverization, the sample (5.3 kg) was extracted ultrasonically with a mixture of benzene and methanol (4:1). From 55 g of hexane-soluble organic extract, 0.4 g of free acids was separated with 1*N* sodium hydroxide. Phenolic components were extracted from a saturated solution of sodium bicarbonate, and the remaining acids were esterified (BF_3 in MeOH). The esters were then separated by gas chromatography on a 3 percent SE-30 aeropack column (0.6 cm by 3 m), 80 to 100 mesh, programed at 4° per minute with a flow rate of 50 ml/min. Further purification of isolated fractions was accomplished on a 3 percent HIEPF 8 BP on a Gas Chrom column (0.6 cm by 2.5 m) (*8*), 80 to 100 mesh, under the same operating conditions.

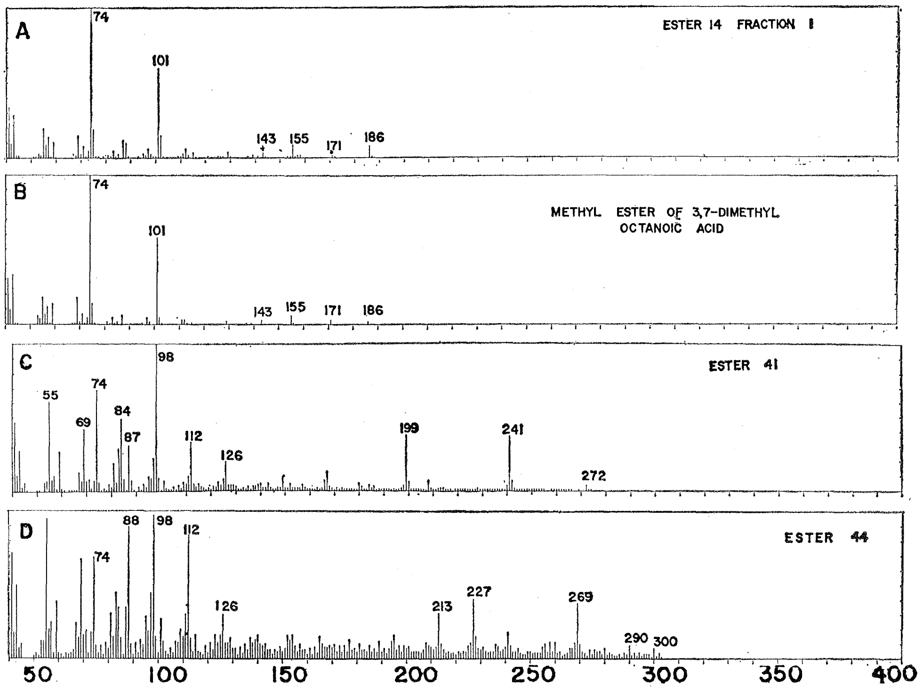
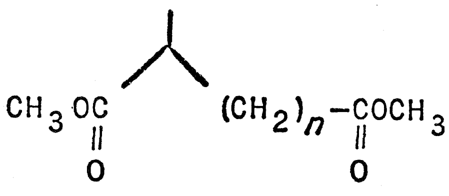


Fig. 1. Mass spectra of (A) Green River shale methyl 3,7-dimethyl octanoate; (B) authentic methyl 3,7-dimethyl octanoate; (C) Green River shale dimethyl tridecan-1, 13-dioate; and (D) Green River shale dimethyl 2-methyl tetradecan-1,14-dioate.

The C_9 and C_{10} isoprenoid acid methyl esters (2,6-dimethyl heptanoic acid and 3,7-dimethyl octanoic acids, respectively) were isolated and identified by mass spectrometry. Figure 1A gives the mass spectrum of the methyl ester of the C_{10} isoprenoid acid. Direct comparison of the spectrum with that of synthetic methyl 3,7-dimethyl octanoate (Fig. 1B) (*9*) established its identity. The structure of the C_9 acid was deduced from its mass spectrum [molecular weight, 172; base peak at mass-to-charge ratio (*m/e*) 88; peaks at *m/e* 101, 129, and 141].

A further interesting series is represented by the α,ω-dicarboxylic acids. The mass spectrum of the most abundant member of this series, dimethyl tridecan-1,13-dioate is given in Fig. 1C [compare with spectrum in Ryhage and Stenhagen (*10*)]. The mass spectra of dicarboxylic acids give rather characteristic fragmentation patterns (*10, 11*): the peaks at *m/e* 74 and 98, as well as the characteristic sequence M-31, M-64, and M-73, predominate in the mass spectra of these compounds. In addition to the C_{13} diacid (Fig. 1C), the C_{12}, C_{14}, C_{15}, C_{16}, C_{17}, and C_{18} dicarboxylic acids have been isolated and identified. The C_{19} dicarboxylic acid appears to be present in very small quantity. Also isolated in small quantity were three other dicarboxylic acids (C_{13}, C_{15}, and C_{16}), the methyl esters of which we assign structures I to III (dimethyl 2-methyl-1,13-dioate; dimethyl 2-methyl-1,15-dioate; and dimethyl 2-methyl-1,16-dioate) on the basis of their mass spectra.



I, *n* = 9

II, *n* = 11

III, *n* = 12

In the mass spectrum (Fig. 1D), prominent peaks at *m/e* 74, 88, 98, and 112 in the low mass region, as well as the series M-31, M-64, M-73, and M-87, are entirely in agreement with structure III. (There is also evidence for a monounsaturated C_{16} dicarboxylic acid of molecular weight 312.)

The C_7 to C_{12} normal fatty acids were also isolated and identified, but there was no indication of the higher homolog previously reported (*2–4*). Nor was there any evidence of the larger isoprenoid acids reported by Eglinton (*5*) or the iso- and anteiso-compounds reported by Leo and Parker (*4*). It is interesting to note that the C_{10} isoprenoid acid was not found in California petroleum by Cason and Khodair (*12*), even though their study included the search for this isomer. Although the absence of dicarboxylic acids in the naphthenic acid fraction of petroleum has been noted by Lochte (*13*), Douglas *et al.* (*7*) have recently reported the identification of C_8 to $C_{22}\alpha,\omega$-dicarboxylic acids from Carboniferous Scottish torbanite.

In this connection it is interesting to note that the C_{13}-diacid occurs as the major diacid component, determined by gas-liquid chromatography, in these studies, as is the case in torbanite (*7*). Long-chain dicarboxylic acids are rare in nature. Hilditch (*14*) noted the presence of C_{20} and C_{21} dibasic acids in the fruit coat fat, commonly known as Japan wax, of sumach berries; apparently, the dicarboxylic acids are rarely found in leaf waxes (*15*). Since microbial oxidation can lead to dicarboxylic acids (*16*), it has been suggested that the presence of these acids in sediments might be due to such transformations (*7*).

Reports of our detailed study of the acid composition of the Green River shale are in preparation [aromatic and cycloaromatic components (*17*), keto acids (*18*), saturated cyclic acids (*19*), and kerogen acids (*20*)].

PAT HAUG
H. K. SCHNOES*
A. L. BURLINGAME†

Department of Chemistry and *Space Sciences Laboratory, University of California, Berkeley 94720*

References and Notes

1. W. E. Robinson, J. J. Cummins, G. V. Dineen, *Geochim. Cosmochim. Acta* **29**, 249 (1965); J. J. Cummins and W. E. Robinson, *Chem. Eng. Data* **9**, 304 (1964); G. Eglinton, P. M. Scott, T. Belsky, A. L. Burlingame, M. Calvin, *Science* **145**, 263 (1964); A. L. Burlingame, P. Haug, T. Belsky, M. Calvin, *Proc. Nat. Acad. Sci. U.S.* **54**, 1406 (1965); I. Hills, E. Whitehead, D. Anders, J. Cummins, W. Robinson, *Chem. Commun.* (20 Nov. 1966), p. 752.
2. P. H. Abelson and P. L. Parker, *Carnegie Inst. Wash. Year Book* **61**, 181 (1962).
3. D. L. Lawlor and W. E. Robinson, *Abstr. Papers* (Div. of Petroleum Chemistry, American Chemical Soc., spring meeting, Detroit, Michigan, 1965), pp. 5–9.
4. R. F. Leo and P. L. Parker, *Science* **152**, 649 (1966).
5. G. Eglinton, A. G. Douglas, J. R. Maxwell, J. N. Ramsay, S. Ställberg-Stenhagen, *Science* **153**, 1133 (1966).
6. J. N. Ramsay, thesis, Univ. of Glasgow, Scotland (1966).
7. A. G. Douglas, K. Douraghi-Zadeh, G. Eglinton, J. R. Maxwell, J. N. Ramsay, in *Advances in Organic Geochemistry* (Pergamon, New York, in press). We thank Dr. Eglinton for sending us these results prior to publication.
8. Applied Science Labs, State College, Pennsylvania.
9. We thank Prof. James Cason for providing us with a sample of synthetic methyl 3,7-dimethyl octanoate.
10. R. Ryhage and E. Stenhagen, *Arkiv Kemi* **23**, 167 (1964).
11. ———, *ibid.* **14**, 497 (1959).
12. J. Cason and A. I. A. Khodair, *J. Org. Chem.*, in press.
13. H. L. Lochte and E. R. Littmann, *The Petroleum Acids and Bases* (Chemical Publishing Co., New York, 1955), p. 54.
14. T. P. Hilditch, *The Chemical Composition of Natural Fats* (Chapman and Hall, London, ed. 3, 1956), p. 121.
15. G. Eglinton and R. J. Hamilton, *Science* **156**, 1322 (1967).
16. A. S. Kester and J. W. Foster, *J. Bacteriol.* **85**, 859 (1963).
17. P. Haug, H. K. Schnoes, A. L. Burlingame, *Geochim. Cosmochim. Acta*, in press.
18. ———, *Chem. Commun.*, in press.
19. ———, unpublished results.
20. A. L. Burlingame and B. R. Simoneit, in preparation.

21. Supported by NASA grant NsG 101. We thank B. R. Simoneit for collecting the shale specimens and G. Zellweger for measuring the mass spectra.

* Present address: Department of Biochemistry, University of Wisconsin, Madison.

† Send correspondence concerning this report to Dr. Burlingame.

20 July 1967

Tree Ring Indices: A Circumpolar Comparison

Abstract. *A graphic and statistical comparison of major trends in tree ring indices representative of interior Alaska, northern Urals, northern Scandinavia, and Labrador indicates a highly significant correlation for most 50-year intervals between 1650 and the present. This is suggestive of similarities in trends of summer temperature on a circumpolar scale.*

Climatic changes, some of a rather large magnitude, have taken place in the past few hundred years on a worldwide scale. Although the most dramatic of these changes has been in the northern latitudes (*1, 2*) it is difficult to obtain a comprehensive view of the regional variation of climatic change, simply because instrumental records are short and stations are widely separated. Tree ring indices have provided supplementary information on some aspects of climatic change, for example, the occurrence of drought in the southwestern United States (*3, 4*), or relative summer temperatures in the north (*5–10*). In this paper, major fluctuations of tree ring indices representative of the northern timberline are compared and analyzed as indicators of climatic change.

The most important requirement for the construction of a climatically sensitive tree ring chronology is that the trees utilized be growing under some sort of climatic stress. The evidence for such a stress is the concomitant occurrence of similar patterns of wide and narrow rings in trees over local and regional areas. The systematic comparison of the sequence of patterns between trees and among groups of trees is termed cross dating, and permits the establishment of absolute dating for each ring. Chronologies developed in this manner may provide a reliable first approximation of the year-to-year variation of the stress-producing climatic parameter or parameters.

Tree ring indices are composed of a number of chronologies of individual or groups of trees and are representative of a regional area of uniformity with respect to the stress-producing climatic element. The direct comparison of chronologies by cross dating is limited to such regional areas. Other techniques must be employed for comparisons over greater distances, as between index groups. Hustich (*6*) compared minimal growth years only among tree ring indices representative of Alaska, Labrador, and Scandinavia, but with essentially negative results. Fritts (*4*) compared a large number of chronologies from the western United States in terms of relative 10-year departures from mean growth and was able to effectively show the historical and spatial pattern of drought in this large area from the year 1500 to the present. Adamenko (*9*) graphically compared indices representative of Scandinavia and the polar Urals which had been converted to 30-year running means, suggesting a strong resemblance of major tree growth trends between the two areas.

The present comparison is based on (i) a 300-year index composed of four groups totaling 32 trees (*Picea glauca*) representative of the Yukon-Tanana