

## LIPIDS OF RECENT SEDIMENTS, PART II. BRANCHED AND CYCLIC ALKANES AND ALKANOIC ACIDS OF SOME TEMPERATE LACUSTRINE AND SUB-TROPICAL LAGOONAL/TIDAL-FLAT SEDIMENTS

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### ABSTRACT

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Analyses of the branched and cyclic alkane and alkanolic acid fractions from three temperate lacustrine and three sub-tropical lagoonal/tidal-flat sediments parallel earlier evidence from the corresponding straight-chain saturated and unsaturated fractions that the soluble organic material originates from both autochthonous and allochthonous sources.

Among the lacustrine examples, that are thought to receive the highest contribution from blue-green algae occurs the highest relative abundance of 7- and 8-methylheptadecanes. In contrast, these components were not detected in the bottom sediment of the lake of lowest productivity. Varying concentrations of *iso*- and *anteiso*-alkanoic acids were found in the fractions studied in most detail. For example, the low concentrations of these components, obtained by solvent extraction alone of two of the sediments, parallel the distributions of the corresponding *n*-alkanoic acids in that they do not reflect a high bacterial and/or fungal contribution.

The hydrocarbon fractions are, in general, characterised by an envelope of unresolved components and by triterpanes of the hopane type. The unresolved envelope probably originates from pollution of the sediments by fossil fuel products. The distribution of the triterpanes indicates that at least some of these components do not arise from contamination by petroleum products.

Triterpenoid acids of the hopane type are present in certain of the sediments, indicating that these geolipids can be formed at the earliest stages of diagenesis.

### INTRODUCTION

The importance of studying the lipids in recently deposited sediments in relation to biological input, diagenesis of these lipids and the origin of geo-

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lipids was described in Part I of this series (Brooks et al., 1976). The discussion centred round the distributions of straight-chain hydrocarbons and fatty acids observed in six surface sediments. The most significant findings were:

(1) Carbon-number distributions of both the hydrocarbons and the fatty acids were, in most cases, similar to those typically found in organisms.

(2) Bimodal distributions of hydrocarbons and fatty acids were observed in almost all of the samples. The presence of a higher carbon-number maximum ( $> C_{20}$ ) was taken to be indicative of a higher plant contribution, and a lower carbon-number maximum ( $< C_{20}$ ) taken to be indicative of an autochthonous contribution (algae and/or bacteria).

(3) Variations in the relative abundances of these two groups of lipids were thought to arise from differences in the sedimentary environments.

(4) Differences were observed in the carbon-number distributions of straight-chain lipids extracted before and after hydrolysis of the sediments. This effect is partially explicable in terms of an increased bacterial contribution to the lipids obtained by hydrolysis of the sediment residue and is thought to result from degradation of bacterial cell-walls.

(5) In general, the observed carbon-number distributions were consistent with those which have been observed in some ancient, but relatively unaltered sediments.

In the present study the corresponding branched/cyclic alkane and alkanolic acid fractions of the same sediments have been examined. An attempt has again been made to compare the compositions of these fractions among the sediments and to correlate them with possible contributors (Poltz, 1972; Cranwell, 1973, 1974).

A preliminary report of this work has been given elsewhere (Eglinton et al., 1974), as have descriptions of the environments from which the samples were collected (Brooks, 1974; Eglinton et al., 1974; Gaskell and Eglinton, 1974; Brooks et al., 1976). No further details of the environments are given here except to list areas from which the samples were collected: Esthwaite Water, Rostherne Mere, Grasmere (all temperate, lacustrine, freshwater lakes in the U.K.), Port Moresby (New Guinea), Virgin Islands (U.S.) and Rockhampton (Australia) (tropical, saline environments).

## RESULTS

Table I lists approximate concentrations of the branched and cyclic alkanes and alkanolic acids; these correlate with those of the corresponding straight-chain components as follows:

(1) The relative abundances in the temperate lacustrine sediments are higher than those in the lagoonal/tidal-flat sediments.

(2) The relative abundances of alkanes obtained after hydrolysis of the sediment residue are lower than those in the extract before hydrolysis.

(3) In the Grasmere and Virgin Islands samples, the relative abundances of

TABLE I

Concentrations of branched and cyclic (B/C) alkanes and alkanolic acids in sediments

Sediment	B/C alkanes* <sup>1</sup> (ppm)	B/C alkanolic acids* <sup>1</sup> (ppm)
Rostherne	63 (16)* <sup>2</sup>	20 (7)
Esthwaite	133 (33)	62 (130)
Grasmere	47 (5)	28 (2)
Virgin Islands	19 (5)	1 (7)
Rockhampton	n.d. (2)	1.5 (2)
Port Moresby	n.d. (1)	1 (1)

\*<sup>1</sup> Dry weight of sediment.\*<sup>2</sup> First figure is concentration obtained by extraction of the sediment before hydrolysis; figure in parentheses is concentration obtained after hydrolysis of the sediment residue. n.d. = not detected by weighing.

branched and cyclic alkanolic acids in the extracts before and after hydrolysis of the sediment parallel those of the *n*-alkanoic acids. In contrast, the abundances in Rostherne Mere and Esthwaite of branched and cyclic acids obtained before and after hydrolysis of the sediment are reversed with respect to the *n*-alkanoic acids.

The concentrations of the branched and cyclic fractions from the Rockhampton and Port Moresby sediments were very low and are not discussed below in any detail.

#### *Branched and cyclic alkanes (B/C alkanes) from solvent extraction alone*

Fig.1 shows the distributions of the B/C alkane fractions isolated by solvent extraction of the sediments from Esthwaite, Rostherne, Grasmere and Virgin Islands. These distributions have been shown elsewhere (Eglinton et al., 1974) and are reproduced here to allow further discussion of components which have been identified since the earlier study. With the exception of the fraction from Grasmere, the distributions can be divided into three sections to facilitate discussion.

The first region includes compounds with retention times of less than approximately 45 min, excluding the pronounced envelope of unresolved components in the chromatograms of the Esthwaite, Rostherne and Virgin Islands fractions. The unresolved envelope is included in the second region described below. The compounds identified in the first region, from GC (gas chromatography) and C-GC-MS (computerised-gas chromatography-mass spectrometry) analyses, include a mixture of 7- and 8-methylheptadecanes (I and II; peak 3), an acyclic alkane (peak 1; C<sub>18</sub>H<sub>38</sub>) with a mass spectrum similar to that of peak 3, pristane (III; peak 2), phytane (IV; peak 4) and an unidentified C<sub>24</sub> tetracyclic alkane (peak 5). Mass spectra of the components marked with circled numbers were not obtained and these components are

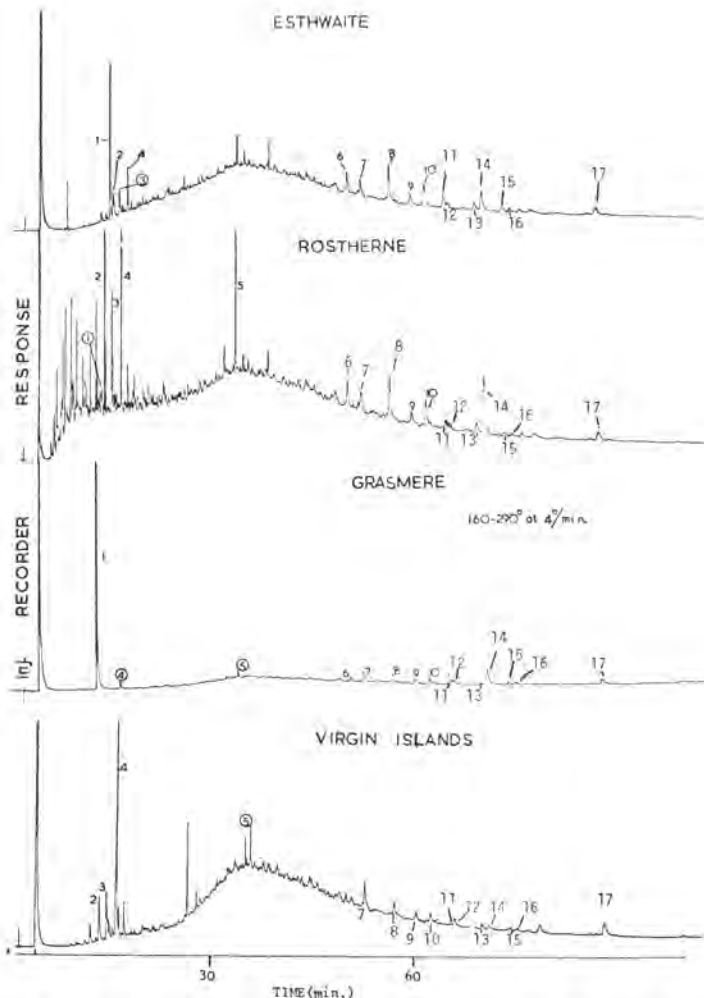


Fig.1. Gas chromatograms of the branched and cyclic alkanes (by solvent extraction alone) from surface sediments. Peak identifications are given in Table II. Conditions: stainless-steel column (50 m  $\times$  0.25 mm) coated with Dexsil 300; temperature programmed from 160 to 290°C at 4°C/min; He carrier at 40 psi.

tentatively assigned only on the basis of comparison of retention data. Very small quantities of this fraction were obtained from the Port Moresby and Rockhampton samples and no mass-spectral data could be obtained.

The unresolved mixture of 7- and 8-methylheptadecanes (I and II), a major constituent of Rostherne sediment, is present only in minor concentrations in the Esthwaite and Virgin Island samples, and is absent from the Grasmere sediment. The Grasmere and Esthwaite fractions are dominated by the unidentified branched C<sub>18</sub> alkane, which is possibly also present in Rostherne but is

absent from the Virgin Islands fraction. Pristane (III) and phytane (IV) are relatively abundant components in Rostherne and are present in lower concentrations in Esthwaite. Phytane is particularly abundant in the Virgin Island sediment, possibly together with a significant contribution of pristane.

The second region, which overlaps the first, includes the unresolved envelope (also present in Port Moresby) and extends from approximately 20 to 60 min in retention time (Fig.1). Although the individual components could not be resolved with the use of capillary columns, the mixture was examined by mass fragmentography (Hites and Biemann, 1970). Fig.2 shows the com-

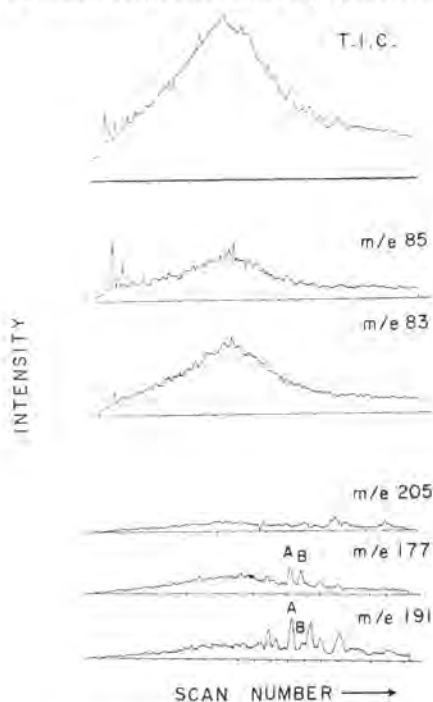


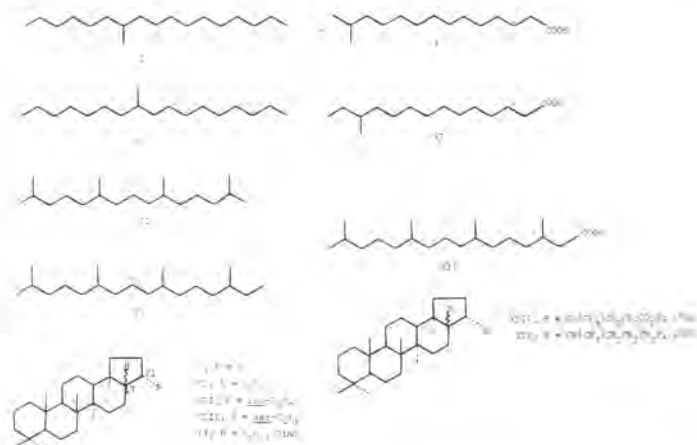
Fig.2. Total ion current record and specific ion plots for  $m/e$  85, 83, 205, 177 and 191 from the C-GC-MS analysis of the pre-hydrolysis branched and cyclic alkane fraction from Esthwaite surface sediment.

Conditions: stainless-steel column (3 m  $\times$  1.5 mm i.d.) packed with 3% OV17 on Gas Chrom Q; temperature programmed from 140 to 280°C at 8°C/min.

puter-reconstructed total ion current trace (TIC) from a packed column GC-MS analysis of the B/C alkanes from Esthwaite sediment. Also shown are specific ion plots for  $m/e$  values 83 and 85 which are prominent fragment ions in the spectra of cyclohexyl alkanes and acyclic alkanes, respectively. Although the plot of  $m/e$  85 emphasises the presence of the lower-molecular-weight alkanes listed in Table II, the remainder follows the TIC distribution. The ion plot for  $m/e$  83 also follows the envelope, but more closely than  $m/e$  85. Similar trends were observed for the specific ion plots for  $m/e$  69,

TABLE II

Branched and cyclic hydrocarbons present in Recent sediments from Esthwaite\*<sup>1</sup>, Rostherne\*<sup>1</sup>, Grasmere\*<sup>2</sup> and the Virgin Islands



Peak No. (Fig.1)	Structure No.	Formula	Structure
1	—	$C_{18}H_{36}$	unknown
2	III	$C_{19}H_{40}$	pristane
3	I, II	$C_{18}H_{36}$	7- and 8-methyl heptadecanes
4	IV	$C_{20}H_{42}$	phytane
5	—	$C_{24}H_{52}$	tetracyclic alkane
6	V; 17 $\alpha$ H	$C_{27}H_{46}$	17 $\alpha$ H-22, 29,30-trisnorhopane
7	V; 17 $\beta$ H	$C_{27}H_{46}$	17 $\beta$ H-22, 29,30-trisnorhopane
8	VI; 17 $\alpha$ H	$C_{29}H_{50}$	17 $\alpha$ H-30-norhopane
9	IX; 17 $\beta$ H	$C_{29}H_{50}$	30-normoretane
10	VII; 17 $\alpha$ H	$C_{30}H_{52}$	17 $\alpha$ H-hopane
11	—	$C_{30}H_{50} + C_{30}H_{52}$	$C_{30}$ -triterpane/triterpane
12	—	$C_{29}H_{50}$	$C_{29}$ -triterpane
13	VIII; 17 $\alpha$ H	$C_{31}H_{54}$	17 $\alpha$ H-homohopane, 22R or S
14	VIII; 17 $\alpha$ H	$C_{31}H_{54}$	17 $\alpha$ H-homohopane, 22R or S
15	—	—	triterpane?* <sup>3</sup>
16	—	—	triterpane?* <sup>3</sup>
17	VIII; 17 $\beta$ H	$C_{31}H_{54}$	17 $\beta$ H-homohopane

\*<sup>1</sup> Identified by capillary GC-MS (Dexsil) and co-chromatography with authentic standards.

\*<sup>2</sup> Identified from mass spectral comparison (capillary GC-MS) with authentic standards and by relative retention time.

\*<sup>3</sup> No molecular ion observed but abundant ion at  $m/e$  191 present.

97 and 111, indicating a greater contribution to the unresolved envelope from cyclic alkanes [or alkenes not separated from alkanes by  $Ag^+$  TLC (thin-layer chromatography)] than acyclic alkanes. Thus, mass fragmentography is of limited use in assigning types of compounds present in the envelope.

The third region of the chromatograms in Fig.1, which also overlaps the second, covers retention times greater than ca. 45 min and is dominated by pentacyclic triterpenoids. A number of components in this region which were previously recognised by mass spectrometry (Eglinton et al., 1974) have now been assigned by comparison with authentic standards and capillary GC-MS. Thus, the region is dominated in the lacustrine sediments by a series of triterpanes of the hopane type. From relative retention data alone, it appears that this is also true in the case of the Virgin Islands and Port Moresby (not shown) sediments. Components present include members of the  $17\beta$ H-hopane series (V,  $17\beta$ H and VIII,  $17\beta$ H; peaks 7 and 17), the  $17\alpha$ H-hopane series (V-VIII,  $17\alpha$ H; peaks 6, 8, 10, 13 and 14, respectively) and 30-normoretane (IX,  $17\beta$ H; peak 9). Smaller concentrations of unidentified triterpenoid alkanes and alkenes are also present (Table II). Further information on the triterpenoid components of the Esthwaite and Rostherne fractions was obtained by mass fragmentography. The mass spectra of alkanes of the hopane type are well documented (Ensminger et al., 1974; Kimble et al., 1974a, b; Van Dorsselaer, 1974) and it has been shown that the ions of  $m/e$  values 149 and 191, 177 and 191, 191, 191 and 205 are abundant in the spectra of  $C_{27}$ ,  $C_{29}$ ,  $C_{30}$  and  $C_{31}$  triterpanes of this type, respectively. Thus, from a comparison of the ion plots of  $m/e$  191 and  $m/e$  177, for example, it is possible to infer the presence of  $C_{29}$  triterpenoid alkanes in a complex mixture (Fig.2, peaks A and B). Further, a comparison of the intensity ratios of these characteristic ions (or the corresponding ions in  $C_{27}$  and  $C_{31}$  triterpanes) can provide information about the stereochemistry of a particular component (Van Dorsselaer, 1974). Peak A (Fig.1, peak 8) corresponds to  $17\alpha$ H-30-norhopane (VI) and peak B (Fig.1, peak 9) to 30-normoretane (IX). As expected on the basis of these independent assignments  $m/e$  191 >  $m/e$  177 in peak A, and  $m/e$  177 >  $m/e$  191 in peak B.

#### *Branched and cyclic alkanes from hydrolysis of sediment residues*

The fractions from Esthwaite, Rostherne and the Virgin Islands were analysed by GC (not shown). That from Esthwaite was also analysed by GC-MS. The Rostherne sample is the only one in which the complexity of the fraction approaches that of the pre-hydrolysis fraction and, unlike Esthwaite and the Virgin Islands, it retains the complex unresolved envelope of components. It seems likely that its presence in this fraction from Rostherne sediment is a result of incomplete extraction prior to hydrolysis of the residual sediment (see below).

The triterpenoids in the Esthwaite fraction had a very similar distribution to that (Fig.1) in the corresponding fraction obtained before hydrolysis of the sediment. This also appeared to be the situation for the Rostherne and Virgin Islands fractions.

*Branched and cyclic alkanolic acids from solvent extraction alone*

Fig.3 shows the distributions of the B/C alkanolic acids (methyl esters) from the three lacustrine sediments and the Virgin Islands sample. Again, these chromatograms have been shown elsewhere (Eglinton et al., 1974) but are reproduced here for discussion purposes. The chromatograms can be conveniently divided into two sections.

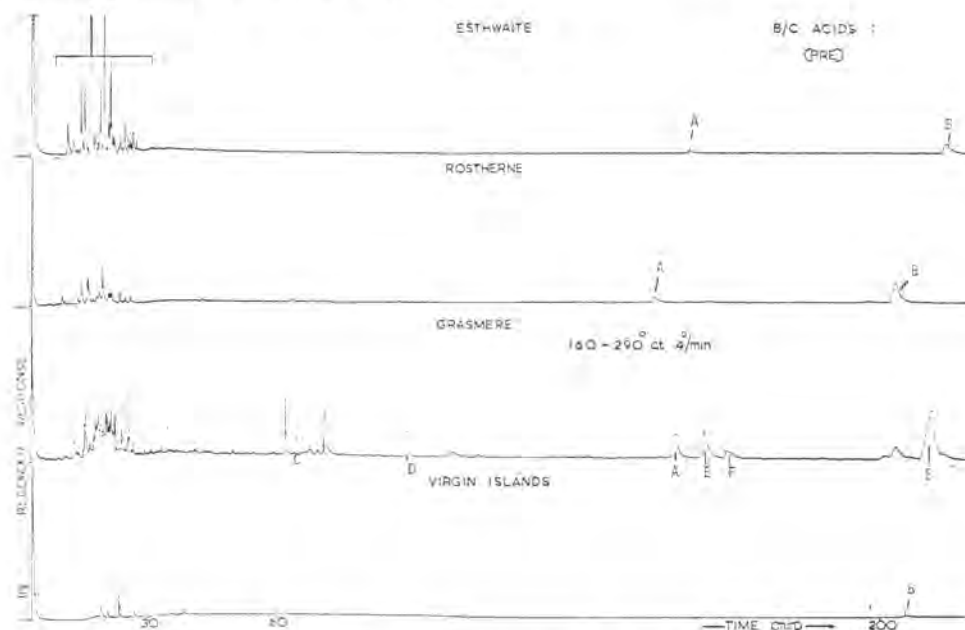


Fig.3. Gas chromatograms of the branched and cyclic alkanolic acids (as methyl esters) from sediments (by solvent extraction alone). Conditions as for Fig.1.

The components of the lower-molecular-weight region fall into the same pattern as that described by Eglinton (1973) for B/C carboxylic acids in other Recent sediments and the Green River shale, and by Cranwell (1973) in a study on the Blelham Tarn, England. The distributions of B/C alkanolic acids for the three lacustrine samples are complex (Table III) and not all of the components in this region could be identified by GC-MS. It is clear, however, that the distribution in Grasmere differs from those of Esthwaite and Rostherne (Fig.3). A  $C_{19}$ -cyclopropanoid acid is the major component in this region of the Grasmere distribution but, if present in Esthwaite and Rostherne, only occurs in very low abundance. The Rostherne and Esthwaite fractions are dominated by a series of *iso*-carboxylic acids (maximising at *iso*- $C_{15}$ , X), and *anteiso*-carboxylic acids (maximising at *anteiso*- $C_{15}$ , XI).

The major acid in this region of the Virgin Islands fraction is phytanic acid (XII) (Table III), present with significant amounts of an unidentified  $\gamma$ -lactone.



TABLE III

Low-molecular-weight branched and cyclic alkanolic acids in sediments

Component <sup>*1</sup>	Esthwaite		Rostherne		Grasmere		Virgin Islands		Port Moresby	
	extract <sup>**2</sup>	hydrolysate <sup>**3, **4</sup>	extract <sup>**2</sup>	hydrolysate <sup>**2</sup>	extract <sup>**2</sup>	hydrolysate <sup>**2</sup>	extract <sup>**2</sup>	hydrolysate <sup>**2</sup>	extract <sup>**2</sup>	hydrolysate <sup>**2</sup>
Iso-C <sub>14</sub>	×	×	n.d.	×	×	×	n.d.	×	n.m.	×
Iso-C <sub>15</sub>	×	×	×	×	×	×	n.d.	×	n.m.	×
Anteiso-C <sub>18</sub>	×	×	×	×	×	×	n.d.	×	n.m.	×
γ-lactone	n.d.	n.d.	×	n.d.	n.d.	n.d.	×	n.d.	n.m.	n.d.
Iso-C <sub>16</sub>	×	×	n.d.	×	×	×	n.d.	×	n.m.	×
Pristanic	×	×	n.d.	×	×	×	n.d.	×	n.m.	×
Iso-C <sub>17</sub>	×	×	×	×	×	×	n.d.	×	n.m.	×
Anteiso-C <sub>17</sub>	×	×	×	×	×	×	n.d.	×	n.m.	×
Phytanic	×	×	n.d.	×	×	×	×	×	n.m.	×
C <sub>19</sub> -cyclopropane	n.d.	n.d.	n.d.	n.d.	×	×	n.d.	×	n.m.	×

<sup>\*1</sup> In order of elution in Fig. 3.<sup>\*\*2</sup> Packed column GC-MS; ECL values on butanediol succinate (100 m) and co-injection of iso-C<sub>16</sub>, anteiso-C<sub>18</sub> and C<sub>17</sub> on Dexsil (50 m).<sup>\*\*3</sup> Fraction from hydrolysis of residual sediment.<sup>\*\*4</sup> ECL values on butanediol succinate (100 m).<sup>\*\*5</sup> Packed column GC-MS and relative retention times on Dexsil (50 m).<sup>\*\*6</sup> Capillary GC-MS on Dexsil (50 m).

n.d. = not detected; n.m. = not measured; × = present.

The higher-molecular-weight regions which have been examined are characterised by the presence of triterpenoid acids, although the mixtures are simpler in each case than the corresponding alkanes. Components *A* and *B* (Fig.3) in Rostherne and Esthwaite were assigned as the methyl esters of 17 $\alpha$ H- and 17 $\beta$ H-bishomohopanoic acid, respectively (XIII and XIV) since their mass spectra (packed GC-MS) were virtually identical to those of the authentic standards and they cochromatographed with the standards (Dexsil, 50 *m*). Grasmere contains a wider variety of triterpenoid acids (methyl ester peaks *A-F* in Fig.3), ranging in molecular formula from C<sub>31</sub>H<sub>52</sub>O<sub>2</sub> to C<sub>32</sub>H<sub>54</sub>O<sub>2</sub> (Eglinton et al., 1974). The major components (*A* and *B*) have now been assigned as the methyl esters of 17 $\alpha$ H- and 17 $\beta$ H-bishomohopanoic acids by comparison of their mass spectra (Dexsil capillary GC-MS) with those of authentic standards.

#### *Branched and cyclic alkanolic acids from hydrolysis of sediment residues*

The branched and cyclic alkanolic acids released by hydrolysis of residual sediments have not been studied in the same detail as the corresponding fractions obtained by solvent extraction alone. The fractions from Esthwaite and Rostherne are similar in composition to those from the pre-hydrolysis fractions in that they show high relative abundances of *iso*- and *anteiso*-acids (Table III). The sample from Port Moresby also shows a high relative abundance of *iso*- and *anteiso*-acids in contrast to that obtained by solvent extraction alone, since the latter contained insufficient material for analysis. No data are available on the sample from Rockhampton, again due to the low concentration of the fraction. The distribution of components in the Virgin Islands fraction shows a remarkable similarity to that in the Port Moresby sample (Eglinton et al., 1974, and Table III), in contrast to the fraction from solvent extraction alone, which contained a  $\gamma$ -lactone and phytanic acid (XII) as the most abundant components (Fig.3). The high-molecular-weight components of only Rostherne sediment have been examined. In this case the 17 $\alpha$ H- and 17 $\beta$ H-bishomohopanoic acids were both present but in lower relative abundance to the branched acids than in the corresponding fraction obtained by solvent extraction alone.

## DISCUSSION

#### *Branched and cyclic alkane fractions*

The occurrence in sediments of an unresolved mixture of 7- and 8-methylheptadecanes is likely to indicate a contribution of organic matter from blue-green algae (Han et al., 1968; Gelpi et al., 1970). The relative abundance of this mixture in the distributions shown in Fig.1 broadly correlates with the *n*-alkane distributions (Brooks et al., 1976), which indicate that Rostherne sediment has the highest blue-green algal contribution. This observation is in

agreement with the present domination of the standing algal crop by *Microcystis aeruginosa* (Reynolds and Rogers, 1976). The 7- and 8-methylheptadecanes have also been isolated from *M. aeruginosa* collected from the lake itself (Gaskell, 1974). Both the Esthwaite and Virgin Islands sediments appear to have lower algal contributions than Rostherne sediment on the basis of this criterion. The significance of the unidentified branched C<sub>18</sub> alkane (Fig.1, peak 1), in relation to biological input is not known. Its presence has not been reported in living organisms. The absence of 7- or 8-methylheptadecanes from Grasmere is in agreement with the absence of the *n*-C<sub>17</sub> alkane and the known lower productivity of Grasmere than Esthwaite or Rostherne Mere (Brooks et al., 1976).

The significance of the differences in the relative abundances of pristane and phytane in the sediments is at present unknown, except that they may in part represent contamination from petroleum sources (Powell and McKirdy, 1973). This is in agreement with the absence of these two components in the B/C alkane fraction obtained after hydrolysis of residual Esthwaite sediment, since the unresolved envelope of presumed pollution origin (see below) was also absent. Significant quantities of pristane and phytane have also been found in Dead Sea sediments (Nissenbaum et al., 1972). Phytane may be a product of the diagenesis of the phytol side chain of chlorophyll, although Nissenbaum et al. have suggested the lipids of halophilic bacteria as an alternative source.

The unresolved envelope of hydrocarbons (Fig.1) has been observed in the chromatograms of several other Recent sediments (e.g. Arpino et al., 1973) and its origin has yet to be unequivocally established. Tissier and Oudin (1974) have reported these envelopes in marine muds collected off the northwest coast of France. Contamination of the sediments by industrial or domestic wastes is the most likely explanation (Farrington and Quinn, 1973; Zafiriou, 1973; Cooper et al., 1974).

Depth studies with sediment cores would be expected to provide more evidence about the origin of these envelopes. Such studies have shown that in Rostherne the envelope decreases in relative abundance with increasing sediment depth and is absent at a depth of 18 cm (Gaskell, 1974). This indicates an origin in contamination. It appears, therefore, that the surface sediment of Grasmere is less polluted than those of the other sediments in Fig.1, especially when the concentrations of alkanes (Table I) are considered.

The pentacyclic triterpanes of the hopane type in Esthwaite, Rostherne, Grasmere and Virgin Islands sediments are of particular interest because these compounds occur widely in ancient sediments and petroleum (Ensminger et al., 1974; Kimble et al., 1974a; Van Dorselaer et al., 1974; Whitehead, 1974; Allan et al., 1976). The presumed presence of pollutants from petroleum products in the Recent sediments (see above) indicates that the triterpanes could also arise from the same source. Contamination from such a source can certainly account for a number of the triterpanes but it cannot, however, account for all of them (Fig.1 and Table II), as follows:

- (1) All of the hopanes identified in petroleum have the more stable 17 $\alpha$ H-

configuration (Ensminger et al., 1974; Van Dorsselaer et al., 1974; Whitehead, 1974; Pym et al., 1975). No hopanes with the less stable  $17\beta\text{H}$ -configuration have been detected.

(2) In petroleum, the  $17\alpha\text{H}$ -hopanes with  $> 30$  C atoms each occur as mixtures of two diastereoisomers at  $\text{C}_{22}$  in the side chain with the earlier eluting isomer in slightly higher abundance (Ensminger et al., 1974; Van Dorsselaer et al., 1974; Whitehead, 1974; Pym et al., 1975). Indeed, this distribution has been used as a criterion of pollution of surface sediments (Dastillung and Albrecht, 1976). This contrasts with the sediments examined here; Rostherne mere, for example, shows the two isomers of  $17\alpha\text{H}$ -homohopane (VIII;  $17\alpha\text{H}$ ) in a ratio of ca. 1:5 (Fig.1).

(3) The unresolved envelope of hydrocarbons was virtually absent from the alkane fraction obtained by hydrolysis of the Esthwaite residual sediment but the same triterpanes were present as those in the extract obtained before hydrolysis.

(4) Depth studies of Rostherne sediment (Gaskell, 1974) have shown that the unresolved envelope does not appear to be associated with the triterpanes since these are still present when the envelope is not apparent in gas chromatograms of the B/C alkanes.

It appears, therefore, that at least some of the triterpanes are syngenetic with the sediments although it is possible that they could arise from pre-existing sedimentary formations or from eolian transportation (Simoneit, 1975).

The origin of the hopane-type triterpanes in sediments and petroleum has been discussed previously (Ensminger et al., 1974; Kimble et al., 1974a,b; Van Dorsselaer et al., 1974). The available evidence suggests that their precursors may arise mainly from blue-green algae and/or bacteria.

#### *Branched and cyclic alkanolic acids*

The presence of *iso*- and *anteiso*-acids is thought to indicate a bacterial contribution to a sediment (Leo and Parker, 1966; Cranwell, 1973) although the presence of the *iso*- and *anteiso*- $\text{C}_{15}$  acids has also been reported in an aquatic fungus, *Sphaerulina pedicellata* (Schulze and Quinn, 1973). In the samples described herein the abundance of *iso*- and *anteiso*-alkanoic acids in the fractions obtained by hydrolysis of residual sediment correlate with the corresponding *n*-alkanoic and alkenoic acid distributions which suggested a high contribution of bacterial lipids released by hydrolysis (Brooks et al., 1976). The low concentrations of *iso*- and *anteiso*-acids obtained by solvent extraction alone of the Grasmere and Virgin Islands sediments (Table I and Fig.3) parallel the distributions of the corresponding *n*-alkanoic acids which do not reflect a high bacterial and/or fungal contribution (Brooks et al., 1976). Such a contribution is apparent, however, in both the *n*-alkanoic (Brooks et al., 1976) and B/C alkanolic acids obtained by hydrolysis of residual Virgin Islands sediment (Eglinton et al., 1974, and Table III). The latter fraction shows a

remarkable similarity to the corresponding fraction from Port Moresby sediment (Eglinton et al., 1974) and probably reflects similarities in the two environments of deposition.

Cyclopropanoid acids are also thought to be indicative of a bacterial contribution and have been found in abundance in Recent sediments (Cranwell, 1974; Cardoso et al., 1975). In view of the lower productivity of Grasmere (Brooks et al., 1976) it is surprising that the sediment contains a relatively high abundance of a  $C_{19}$  cyclopropanoid acid. This contrasts with the low relative abundances of  $n-C_{16:0}$  and  $n-C_{18:0}$  obtained by solvent extraction of the Grasmere sediment. The distributions of the low-molecular-weight branched and cyclic alkanoid acids obtained by solvent extraction alone of the three lacustrine sediments, are markedly different from those in the corresponding fraction of the Virgin Islands sample (Fig.3) and presumably reflect the marked differences in the depositional environments.

The reason for the very high relative abundance of phytanic acid in the Virgin Islands sediment is not clear, although it has been reported as a constituent of ruminant fats and sera (Hansen et al., 1966) and of rumen bacteria (Hansen, 1966). It has also been demonstrated that phytanic acid arises, in part, from phytol (Brooks, 1974). A more detailed discussion of possible origins for phytanic acid has been given recently by Boon et al. (1975).

The triterpenoid acids of the hopane skeleton which have been found in the very young sediments examined herein are also present in ancient sediments of both marine and lacustrine origin (Van Dorsselaer et al., 1974). Their presence has not been reported in living organisms, so it appears that they can be formed at the earliest stages of diagenesis. It has been suggested that these compounds originate from a  $C_{35}$ -tetrahydroxyhopane precursor (Van Dorsselaer, 1974) which has been detected in a variety of bacteria and blue-green algae (Förster et al., 1973; Rohmer, 1975). The  $17\beta$ H-bishomohopanoic acid present in the three lacustrine samples and probably also in the Virgin Islands sediment (Fig.3, peak B), has also been found in a JOIDES marine core by Simoneit and Burlingame (1974).

#### EXPERIMENTAL

The extraction and fractionation procedures are described in Part I of this series (Brooks et al., 1976). The branched and cyclic fractions were obtained by urea adduction of total hydrocarbon or fatty acid fractions. The conditions used for GC and C-GC-MS are also described earlier (Brooks et al., 1976).

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