FATTY ACIDS FROM EXPOSED ROCK SURFACES*

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Bear and Thomas[1] have given the name "petrichor" to the odour which is detectable when dry clays, rocks, and silicate minerals are moistened. It has been found that, after exposure in a dry atmosphere, an oily extract can be obtained from such material. However, the amount of oil is very small, amounting to 3 mg per square foot of tray area per month. Approximately one-third of the extracted oil consists of fatty acids, either free or esterified, and these have been separated and examined by gas chromatography. Of these acids, approximately 75% were free acids (fraction A); the remainder (fraction B) was obtained after hydrolysis. It can be seen from Table 1 that "A", the free acids, are much richer in C_8, C_9, and C_{10} than those obtained by hydrolysis.

The major components, as shown in Table 1, were palmitic and stearic acids, with a small amount of a monounsaturated C_{18} acid, probably oleic acid, and acids of lower molecular weights, n-nonanoic and lower homologues, which could possibly arise from oxidation of oleic acid.

There were also small amounts of acids which did not belong to the series of normal fatty acids, and these may be branched-chain fatty acids. The composition of the acids strongly suggests that they originate from partly decomposed fats, but whether the fat is of animal or vegetable origin, or whether it is produced on the rock surface or has been absorbed from the air, could not be determined. If absorbed from the air it might originate from airborne bacteria.

It seems unlikely that the higher molecular weight acids, mainly present as esters (probably glycerides), contribute significantly to petrichor, but the lower molecular weight free acids, presumably formed by autoxidation of fats, have a strong and persistent odour.

Experimental

General

The material for investigation was obtained by exposing clay in trays to the air for a prolonged period as described by Bear and Thomas,[1] extracting the oily material and recovering the acidic fractions. After the free fatty acids, and acids from hydrolysis, had been esterified, the esters in petroleum solution were washed several times with aqueous NaOH solution, and finally purified by column chromatography. Two of the esters were trapped at the column outlet and their structure established by their mass spectra.

* Manuscript received November 10, 1964.

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[1] Bear, I. J., and Thomas, R. G., *Nature*, 1964, **201**, 993.

Extraction

The oil could be obtained by steam distillation but it was found preferable to extract from the source material with ethanol. After evaporation of the solution, the oil was extracted from the residue with light petroleum, b.p. 30–40°. The acidic components, which generally represented about a third of the total extract, were separated from the oil in two stages. First, the light petroleum solution of oil was treated with cold NaOH (5%) in an ethanol/water mixture (40–60 v/v). After separation and acidification of the aqueous alcohol phase, mixed acids were extracted with light petroleum (fraction A). The petroleum was then evaporated from the residual non-acidic material, which was saponified for 30 min with 10% alcoholic KOH. The

TABLE 1

RELATIVE PERCENTAGES* OF CARBOXYLIC ACIDS IN PETRICHOR EXTRACTS

No. of Carbon Atoms in Chain	Relative Percentage		
	Solvent Extract Acid Fraction A	Solvent Extract Acid Fraction B	Steam Distillate Extract Acid Fraction A
4	n.d.	—	trace
5	—	—	trace
6	1·0	—	4·5
7	3·5	—	5·0
8	9·5	3·5	7·5
9	12·5	3·5	11·5
10	7·0	2·0	5·5
11	2·5	0·5	4·0
12	6·0	5·5	7·5
13	2·5	1·5	2·5
14	6·5	13·0	7·0
15	2·0	3·0	3·0
16	22·0	34·0	17·5
17	1·0	1·5	2·0
18†	3·5	3·0	1·5
18	15·0	26·0	8·0
19	trace	—	—
20	1·5	—	—
Total percentage of unidentified material	4·0	3·0	13·0

* To the nearest 0·5%. † Unsaturated acid.

solution was again treated with light petroleum to remove the unsaponified compounds, and the aqueous alcohol phase acidified and extracted with petroleum. This petrol phase was then treated with cold 5% NaOH in ethanol/water to recover the mixed acids (fraction B). The infrared spectra of the acids measured as films had absorption peaks at 3500–3560 cm^{-1} and 1700–1725 cm^{-1}.

Esterification of the Acids

The acid fractions A and B were esterified by refluxing for 5 min a methanolic solution containing 12·5% BF_3. After dilution with water, the esters were extracted with light petroleum, the solutions washed first with cold 1% NaOH and then with water, dried, and added to a column of

magnesium trisilicate which had been activated by drying for 4 hr at 250° and then adding 2% water. The esters were eluted from the column with light petroleum, followed by light petroleum/benzene, benzene/chloroform, and finally chloroform/methanol. The ester fraction which was eluted by light petroleum/benzene mixture (70 : 30 v/v) gave i.r. absorption peaks at 1735–1750 cm^{-1}.

Gas Chromatography

The methyl esters were chromatographed on both polar and non-polar columns using a gas density balance as detector. The non-polar column was 12 ft, o.d. $\frac{1}{4}$ in. copper tubing with 10% silicone elastomer E301 on Celite 545 60–85, the polar column an 8 ft o.d. $\frac{1}{4}$ in. copper tubing with 25% polypropylene sebacate on Celite 545 60–85. Nitrogen was used as carrier gas in all runs under the following conditions: non-polar column, 800 mm pressure, 35 ml/min flow rate, temperature 175°; polar column, 500 mm pressure, 35 ml/min flow rate, temperature 142°. Retention times were compared with those of reference samples of pure esters and the compounds so identified are listed in Table 1.

Two esters (methyl octanoate and methyl nonanoate) were identified by trapping in capillaries and examining their mass spectra.

The retention time of one minor component coincided with that of methyl oleate. This component was not present in the chromatogram of the hydrogenated oil, which showed a corresponding enhancement of the methyl stearate peak.

Acknowledgment is made to Dr. J. D. Morrison and the Division of Chemical Physics, CSIRO, for the mass spectrometric identification.