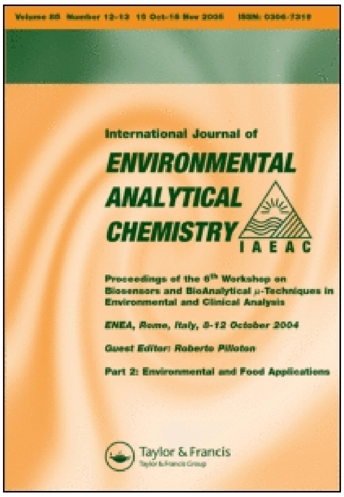

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Identification by GC/MS of Acidic Compounds Produced During the Photosensitized Oxidation of Normal and Isoprenoid Alkanes in Seawater

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IDENTIFICATION BY GC/MS OF ACIDIC COMPOUNDS PRODUCED DURING THE PHOTOSENSITIZED OXIDATION OF NORMAL AND ISOPRENOID ALKANES IN SEAWATER

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Experiments carried out *in vitro* in the presence of anthraquinone allowed to simulate the photosensitized oxidation of linear and isoprenoid alkanes in the marine environment. The main acidic photoproducts formed after solar irradiation were identified by gas chromatography and gas chromatography/mass spectrometry and different mechanisms were proposed in order to explain their production. The detection of most of these photoproducts among the acidic compounds formed during the photodegradation of a petroleum fraction proved the suitability of anthraquinone as a model sensitizer for studies of the photochemical degradation of petroleum saturated hydrocarbons in water.

KEY WORDS: Petroleum, photodegradation, photosensitized oxidation, alkanes, hexadecane, pristane, acidic photoproducts.

INTRODUCTION

Previous studies have demonstrated that photooxidation processes may have considerable importance in the long-term weathering of oil spills in the marine environment.[1,2] Recently, during the study of the photochemical degradation of a crude oil hydrocarbon fraction, we showed that the photosensitized oxidation of alkanes results in the production of significant quantities of non acidic photoproducts.[3] We also observed the formation of an acidic fraction, which proportion increased with irradiation time.

Different authors have already analysed seawater extracts obtained after irradiation of spilled crude oils, and detected several fatty acids derived from the photodegradation of alkanes.[4,5] However, the mechanisms leading to the formation of such compounds were not clearly established.

The aim of the present work was to study more precisely the production of acidic compounds during the photosensitized oxidation of alkanes, particularly of normal and isoprenoid components. The study was carried out using hexadecane and pristane as model hydrocarbons and anthraquinone as sensitizer. This sensitizer has been found well suited for studies of the photosensitized degradation of petroleum saturated hydrocarbons by solar light.[3,6]

EXPERIMENTAL

Substrates Hexadecane (98%) and pristane (95%) were obtained respectively from Fluka and Sigma. The total hydrocarbon fraction of a crude oil (Asthart, Gabes Gulf) was separated on a wet packed (*n*-hexane) column filled with silica gel (20 cm × 1.5 cm I.D., Fluka 60 + 5% H_2O) and eluted with *n*-hexane.[7]

Photooxidation experiments These manipulations were carried out in Pyrex flasks containing 50 ml of sterile synthetic seawater[8] and 200 μl of substrate. The mixture was irradiated by natural sunlight for two months. Traces of anthraquinone (few mg) were added in the case of hexadecane and pristane.

Isolation of the acidic fractions After irradiation of pristane or hexadecane, the medium was acidified with hydrochloric acid (pH 1) and extracted with chloroform (3 × 20 ml). The combined extracts were dried on $CaCl_2$, filtered, concentrated and chromatographed on a wet packed (*n*-hexane) column filled with silica gel (20 cm × 1.5 cm I.D., Fluka 60).

Three fractions were eluted respectively with 100 ml of hexane (F_1) 100 ml of chloroform (F_2) and 50 ml of methanol (F_3). F_1 contained residual hydrocarbons, F_2 contained non-acidic photoproducts and F_3 contained the acidic photoproducts.

The strong acidic photoproducts produced after irradiation of the Asthart crude oil total hydrocarbon fraction were isolated after extraction at pH 9 of the aqueous solution with chloroform, subsequent acidification of the aqueous phase at pH 1 and further extraction with chloroform.

These different acidic fractions were esterified with BF_3/methanol or BF_3/propanol before gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) analyses.[9]

Instrumental analysis GC was performed on a Delsi series 30 chromatograph equipped with a split injector and a FID detector. The following conditions were employed: 25 m × 0.3 mm (I.D.) capillary column coated with SE-52; temperature programmed from 70°C to 270°C at 3°C/min., helium carrier gas pressure, 0.9 bar; detector temperature, 280°C; injector temperature, 290°C.

GC/MS analyses were carried out on a HP 5985 spectrometer (electron energy, 70 eV; source temperature, 120°C).

The identification of photoproducts involved the comparison of their retention times and mass spectra with those of commercial or synthesized reference substances. The mass spectra for which standard compounds were not available were interpreted according to established rules.[10]

Synthesis of reference compounds The synthesis of 2,6-dimethyl-heptanoic acid required hydrogenation of commercial 2,6-dimethyl-5-heptenal in methanol with Raney nickel catalyst and oxidation of the resulting 2,6-dimethyl-heptanol with $KMnO_4$ in acetone.[11] 3,7-dimethyl-octanoic and 3,7,11-trimethyldodecanoic acids were obtained in a similar way from commercial geraniol and farnesol respectively. 4,8,12-trimethyltridecanoic acid was synthesized from isophytol according to a previously described procedure.[12] 2,6,10,14-tetramethylpentadecanoic acid (pristanic acid) was produced from phytol.[11]

RESULTS AND DISCUSSION

Photosensitized oxidation of n-hexadecane

After irradiation of the model compound, the analysis of the F_3 fraction allowed to demonstrate the photochemical production of straight chain fatty acids with carbon atom numbers lower or equal to 16 (Figure 1). In order to explain the formation of

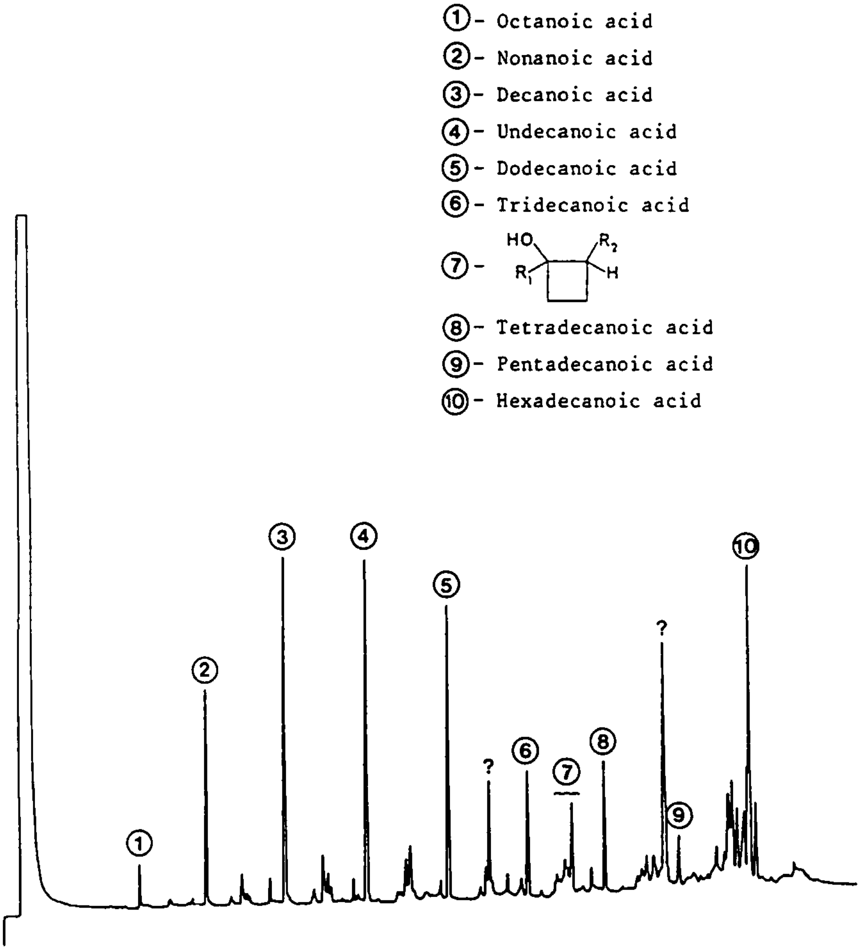


Figure 1 Gas chromatogram of hexadecane acidic photoproducts (after methylation).

hexadecanoic acid ⑩, we propose different mechanisms involving the initial abstraction of H˙ by the excited sensitizer from the terminal carbon of hexadecane (Eq. 1)

$$R{-}CH_3 + X \longrightarrow R{-}CH_2^{\cdot} + HX^{\cdot} \tag{1}$$

$R- = CH_3{-}(CH_2)_{14}{-}$
X = anthraquinone at the triplet state

The primary radical thus formed can react with molecular oxygen forming a peroxy radical[5,13] (Eq. 2), which stabilizes itself as hydroperoxide by abstraction of a hydrogen atom on a molecule of reduced sensitizer (Eq. 3) or on another molecule of substrate (Eq. 4)

$$R{-}CH_2^{\cdot} + O_2 \longrightarrow R{-}CH_2{-}O{-}O^{\cdot} \tag{2}$$

$$R{-}CH_2{-}O{-}O^{\cdot} + HX^{\cdot} \longrightarrow R{-}CH_2{-}O{-}OH + X \tag{3}$$

$$R{-}CH_2{-}O{-}O^{\cdot} + SH \longrightarrow R{-}CH_2{-}O{-}OH + S^{\cdot} \tag{4}$$

SH = substrate

Homolytic cleavage of the O—O bond[14] results in the formation of a primary alkoxy radical (Eq. 5), which can react with molecular oxygen affording hexadecanal (Eq. 6)

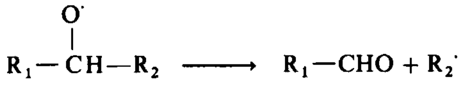
$$R{-}CH_2{-}O{-}OH \xrightarrow{h\nu} R{-}CH_2{-}O^{\cdot} + HO^{\cdot} \tag{5}$$

$$R{-}CH_2{-}O^{\cdot} + O_2 \longrightarrow R{-}CHO + HO_2^{\cdot} \tag{6}$$

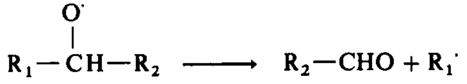
In the presence of peroxides or molecular oxygen, this aldehyde can be easily oxidized to the corresponding carboxylic acid.[4,15]

Fatty acids with carbon atom numbers lower than 16 can be formed through the corresponding aldehydes, by:

a) a β cleavage[16] of the secondary alkoxy radicals produced (according to the mechanisms previously described)[6] after hydrogen abstraction on the secondary carbons of hexadecane (Eqs. 7 and 8)



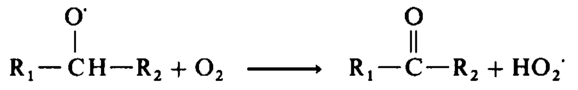
$$R_1{-}\overset{\overset{\displaystyle O^{\cdot}}{|}}{C}H{-}R_2 \longrightarrow R_1{-}CHO + R_2^{\cdot} \tag{7}$$



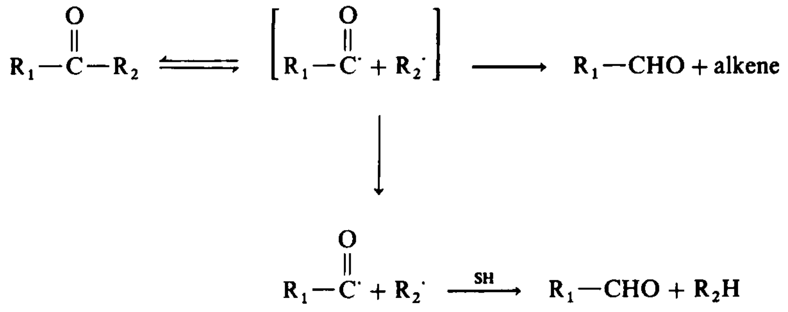
$$R_1{-}\overset{\overset{\displaystyle O^{\cdot}}{|}}{C}H{-}R_2 \longrightarrow R_2{-}CHO + R_1^{\cdot} \tag{8}$$

b) A Norrish type I cleavage of the isomeric hexadecanones resulting from the reaction of these secondary alkoxy radicals with molecular oxygen[6] (Eq. 9), followed by cage disproportionation[17] or diffusion and hydrogen abstraction reactions (Eqs.

10 and 11)



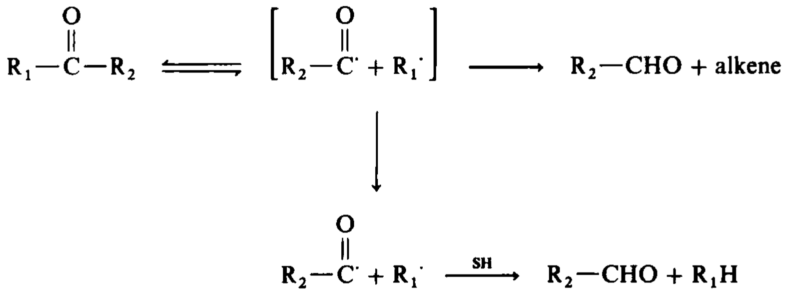
$$R_1-\overset{O^\bullet}{\overset{|}{C}}H-R_2 + O_2 \longrightarrow R_1-\overset{O}{\overset{\|}{C}}-R_2 + HO_2^\bullet \qquad (9)$$



$$R_1-\overset{O}{\overset{\|}{C}}-R_2 \rightleftharpoons \left[R_1-\overset{O}{\overset{\|}{C}}{}^\bullet + R_2^\bullet\right] \longrightarrow R_1-CHO + \text{alkene}$$

$$\downarrow$$

$$R_1-\overset{O}{\overset{\|}{C}}{}^\bullet + R_2^\bullet \xrightarrow{SH} R_1-CHO + R_2H \qquad (10)$$

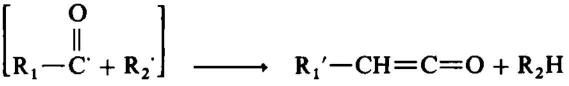


$$R_1-\overset{O}{\overset{\|}{C}}-R_2 \rightleftharpoons \left[R_2-\overset{O}{\overset{\|}{C}}{}^\bullet + R_1^\bullet\right] \longrightarrow R_2-CHO + \text{alkene}$$

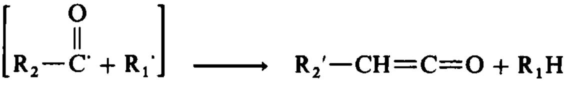
$$\downarrow$$

$$R_2-\overset{O}{\overset{\|}{C}}{}^\bullet + R_1^\bullet \xrightarrow{SH} R_2-CHO + R_1H \qquad (11)$$

We can note that the cage disproportionation reactions can also afford ketenes (Eqs. 12 and 13), labile compounds which can react easily with water giving carboxylic acids (Eqs. 14 and 15)



$$\left[R_1-\overset{O}{\overset{\|}{C}}{}^\bullet + R_2^\bullet\right] \longrightarrow R_1'-CH{=}C{=}O + R_2H \qquad (12)$$



$$\left[R_2-\overset{O}{\overset{\|}{C}}{}^\bullet + R_1^\bullet\right] \longrightarrow R_2'-CH{=}C{=}O + R_1H \qquad (13)$$

$$R_1'-CH{=}C{=}O + H_2O \longrightarrow R_1-COOH \qquad (14)$$

$$R_2'-CH{=}C{=}O + H_2O \longrightarrow R_2-COOH \qquad (15)$$

Photodegradation of *n*-nonadecan-10-one allowed to confirm the production of fatty acids arising from Norrish type I cleavage of ketones. Indeed, after a ten days

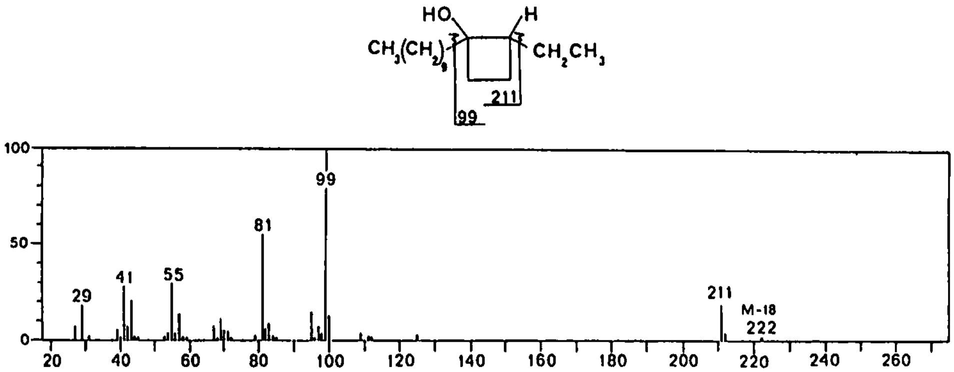


Figure 2 Electron impact mass spectrum of one of the isomeric cyclobutanols produced during the photosensitized oxidation of hexadecane.

irradiation of this ketone, we detected decanoic acid among its photoproducts. Small amounts of cyclobutanols ⑦ were also identified in fraction F_3 (Figure 1). The mass spectrum of one of these isomers is shown in Figure 2. These compounds can be produced from isomeric hexadecanones by classical photocyclization reactions.[18,19]

Photosensitized oxidation of pristane

The gas chromatogram of the methylated acidic photoproducts is shown in Figure 3. The main components were identified by comparison of their retention times and mass spectra with those of the available standards (Figure 3). In the case of branched methyl esters, fragment ions at m/z:74, 87, 88 and 101 allow an easy recognition of methyl substitution at positions 2 or 3 (Table 1).

The different acyclic isoprenoid acids identified can be produced according to the mechanisms previously described for hexadecane. The presence in fraction F_3 of 6,10-dimethylundecan-2-one ⑭ (Figure 3), which is one of the main non-acidic pristane photoproducts,[20] is probably due to a lack of efficiency of the chromatographic separation.

Table 1 Mass spectrometric data of acidic compounds produced during the photosensitized oxidation of pristane.

Compound (identified as methyl ester)	*Code*	*Molecular ion*	*Relative percentages of the ions at m/z*			
			74	*87*	*88*	*101*
2,6-DMH	11	172	2	9	100	34
3,7-DMO	12	186	100	6	1	68
4,8-DMN	13	200	55	100	11	1
2,6,10-TMUD	15	242	—	7	100	41
3,7,11-TMDD	16	256	68	3	1	100
4,8,12-TMTD	18	270	30	100	7	1
2,6,10,14-TMPD	19	312	—	4	100	35

⑪- 2,6-dimethylheptanoic acid (2,6-DMH)

⑫- 3,7-dimethyloctanoic acid (3,7-DMO)

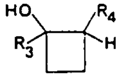
⑬- 4,8-dimethylnonanoic acid (4,8-DMN)

⑭- 6,10-dimethylundecan-2-one

⑮- 2,6,10-trimethylundecanoic acid (2,6,10-TMUD)

⑯- 3,7,11-trimethyldodecanoic acid (3,7,11-TMDD)

⑰-



⑱- 4,8,12-trimethyltridecanoic acid (4,8,12-TMTD)

⑲- 2,6,10,14-tetramethylpentadecanoic acid (2,6,10,14-TMPD)

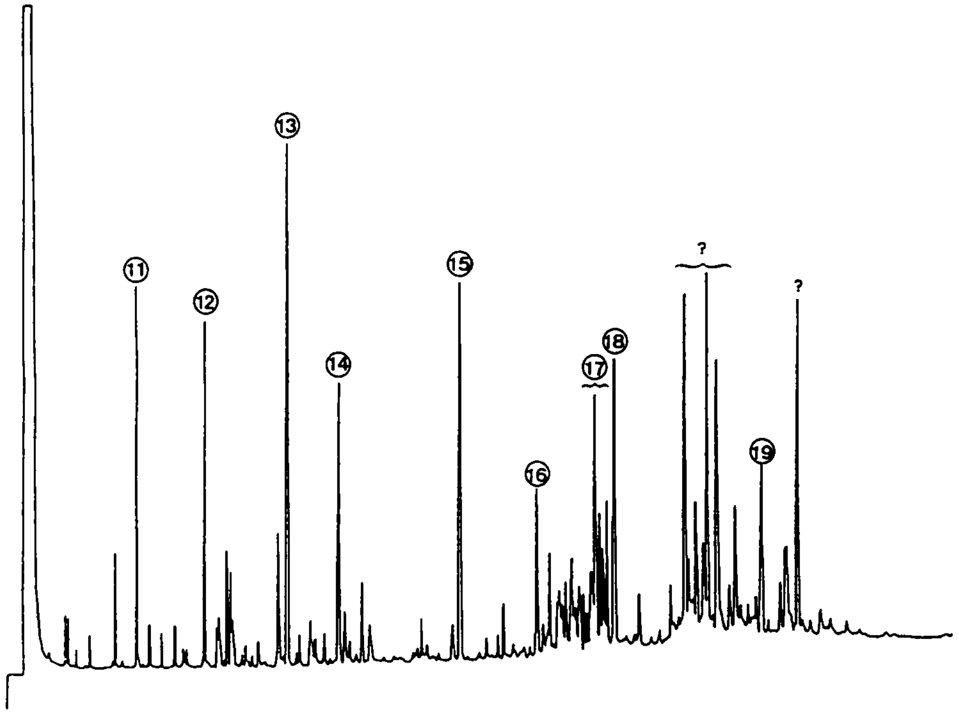


Figure 3 Gas chromatogram of pristane acidic photoproducts (after methylation).

Comparing the quantitative results obtained after photodegradation of hexadecane and pristane (Table 2), we may realise that pristane exhibit a stronger photo-reactivity than hexadecane (which is in good agreement with the results previously obtained),^{4,20} and affords a higher proportion of acidic photoproducts. This last observation can be explained by thermodynamic factors. Indeed, during the photosensitized oxidation of branched alkanes, β cleavages of secondary alkoxy radicals (Eqs. 7 and 8) or Norrish type I cleavages of ketones (Eqs. 10 and 11) can be thermodynamically favoured by the presence of a methyl branching in the β position

Table 2 Quantitative results obtained after sunlight irradiation of pristane and hexadecane for two months.

	Pristane	*Hexadecane*
% of residual hydrocarbon	80.1	92.3
% of non-acidic photoproducts	10.6	5.5
% of acidic photoproducts	9.3	2.2

relative to the alkoxy radical, or in the α position relative to the carbonyl group. Both mechanisms enable the formation of relatively stable secondary radicals.

Photodegradation of the Asthart crude oil total hydrocarbon fraction

Several of the above identified alkane photoproducts were also identified among the acidic compounds produced after a two month solar irradiation of the Asthart crude oil total hydrocarbon fraction (Figure 4).

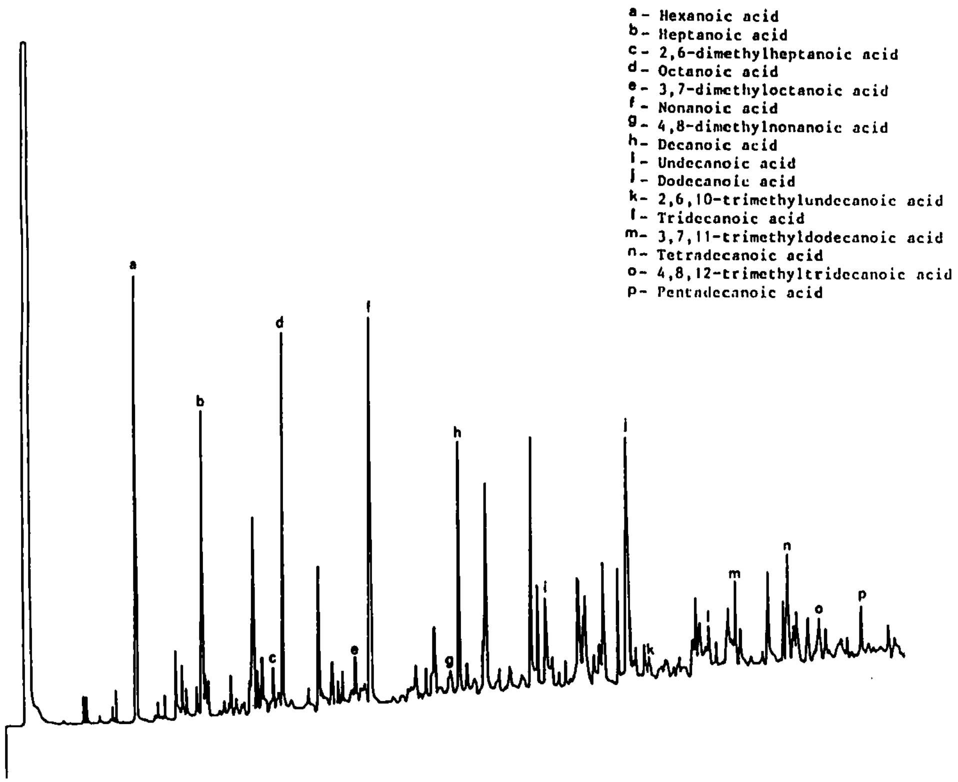


Figure 4 Gas chromatogram of the main acidic photoproducts obtained after irradiation of the Asthart crude oil hydrocarbon fraction for two months.

Therefore, we may conclude that during the photodegradation of petroleum in the marine environment, besides the production of significant amounts of non-acidic photoproducts,[3] relatively high quantities of acidic compounds can be produced by the photosensitized oxidation of alkanes present. These processes, which contribute to the dispersion of spilled oils in the marine environment, may constitute a non-negligible source of acyclic isoprenoid fatty acids often detected in the sediments.[21–23]

This work supports also the suitability of anthraquinone as model sensitizer for studies of the photosensitized oxidation of petroleum alkanes in the marine environment.

References

1. S. S. Miller, *Environ. Sci. Technol.*, **17**, (1983), 568.
2. J. R. Payne and C. R. Phillips, *Environ. Sci. Technol.*, **19**, (1985), 569.
3. J.-F. Rontani and P. J.-P. Giral, *Int. J. Environ. Anal. Chem.*; **42**, (1990), 61.
4. H. P. Hansen, *Rapp. P. V. Reun. Cons. Int. Explor. Mer* **171**, (1977), 101.
5. H. P. Gesser, T. A. Wildman and Y. B. Tewori, *Environ. Sci. Technol.*, **11**, (1977), 605.
6. M. Ehrhardt and G. Petrick, *Mar. Chem.*, **16**, (1985), 227.
7. J.-F. Rontani, J.-C. Bertrand, F. Blanc and G. Giusti, *Mar. Chem.*, **18**, (1986), 1.
8. P. Baumann and L. Baumann. In: *The Prokaryotes: A Handbook on Habitats, Isolation and Identification of Bacteria* (P. S. Mortimer *et al.*, eds.) (Springer Verlag, New York, 1981) p. 1302.
9. L. D. Metcalfe and A. A. Schmitz, *Anal. Chem.*, **33**, (1961), 363.
10. F. W. McLafferty. In: *Interpretation of Mass Spectra* (N. J. Turro, ed.) (University Science Books, 1980) p. 201.
11. J. Cason and D. W. Graham, *Tetrahedron* **21**, (1965), 471.
12. J.-F. Rontani, G. Baillet and C. Aubert, *J. Photochem. Photobiol., A: Chem.* (in press).
13. A. E. Klein and N. Pilpel, *J. Chem. Soc. Faraday Trans.*, **69**, (1973), 1729.
14. R. G. Zika. In: *Marine Organic Chemistry* (E. K. Duursma and R. Dawson, eds.) (Elsevier, Amsterdam, 1981) p. 299.
15. L. G. Durham and H. S. Mosher, *J. Am. Chem. Soc.*, **84**, (1962), 2811.
16. B. Ranby and J. F. Rabek. In: *Photodegradation, Photooxidation and Photostabilization of Polymers* (Wiley, New York, 1975) p. 100.
17. F. D. Lewis and J. G. Magyar, *J. Am. Chem. Soc.*, **95**, (1973), 5973.
18. P. J. Wagner, *J. Am. Chem. Soc.*, **89**, (1967), 5898.
19. F. D. Lewis and T. A. Hilliard, *J. Am. Chem. Soc.*, **94**, (1972), 3842.
20. J.-F. Rontani and G. Giusti, *J. Photochem. Photobiol., A: Chem.*, **40**, (1987), 107.
21. M. Blumer and W. J. Cooper, *Science*, **158**, (1967), 1463.
22. R. F. Leo and P. L. Parker, *Science*, **152**, (1966), 649.
23. P. A. Cranwell, *Chem. Geol.*, **14**, (1974), 1.