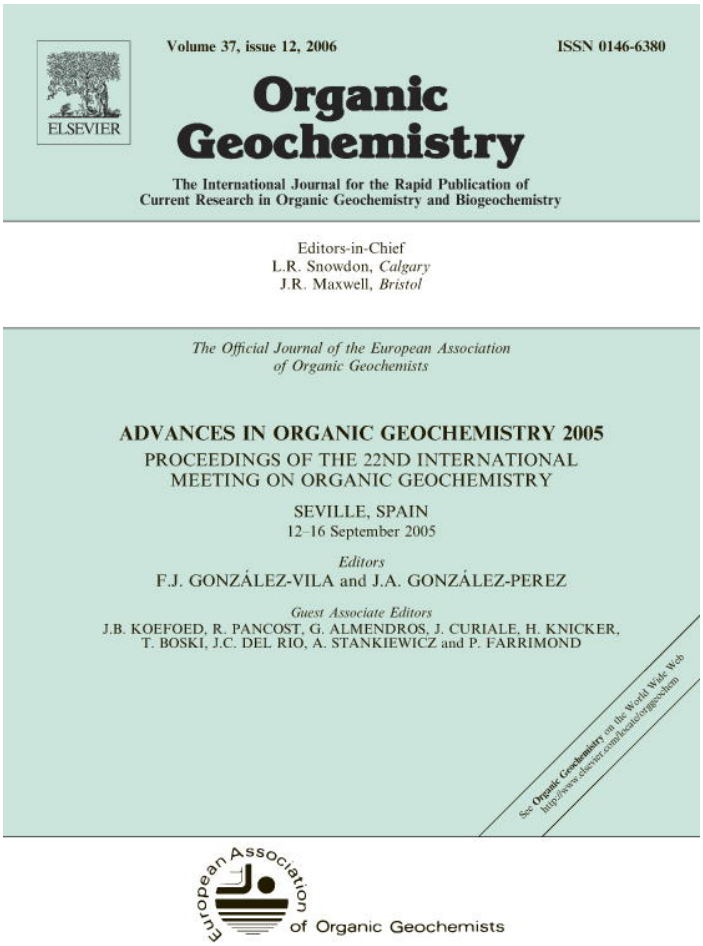

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The use of model compounds to investigate the release of covalently bound biomarkers via hydropyrolysis

Will Meredith [a], Chen-Gong Sun [a], Colin E. Snape [a,*], Mark. A. Sephton [b], Gordon D. Love [c]

[a] *Nottingham Fuel & Energy Centre, School of Chemical, Environmental and Mining Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK*
[b] *Department of Earth Science and Engineering, Imperial College, London SW7 2AZ, UK*
[c] *Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, USA*

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Abstract

This study describes the reduction of functionalised model compounds to their corresponding hydrocarbons by catalytic hydropyrolysis to provide information on the release of biomarkers from kerogens and asphaltenes covalently bound through the functional groups investigated. Five model compounds were investigated, the *n*-C_{18} carboxylic acids, stearic and oleic acids; the C_{24} steroidal acid, 5β-cholanic acid; and the saturated and unsaturated C_{27} sterols, 5α-cholestanol and cholesterol. The yield and distribution of the hydrocarbons generated were assessed for the model compounds adsorbed to silica and carbon substrates, and unsupported on a bed of catalyst. The *n*-C_{18} acids are shown to be reduced to the *n*-C_{18} alkane, with a selectivity of >95% for stearic acid, although due to its unsaturated structure, oleic acid is prone to cracking, with shorter chained *n*-alkanes also being formed. The conversion of these compounds, adsorbed to either silica or carbon is relatively low, even at hydropyrolysis temperatures significantly above their boiling point, suggesting that interactions between the acids and substrate leading to the formation of stable entities (Si–O–C linkages in the case of silica) significantly retard volatilisation. The yield can be increased by placing the compounds directly onto a bed of catalyst, but for low boiling compounds such as stearic acid this can result in volatilisation and cracking at temperatures below that of the activation point of the catalyst. This method produced improved yields of >95% pure product for higher boiling compounds such as 5β-cholanic acid. The presence of the functional group attached to the ring system of compounds such as 5α-cholestanol does not diminish the selectivity of the technique. The double bond in cholesterol resulted in more incomplete hydrogenation with sterenes being generated, and in addition to 5α and 5β-cholestane, diasteranes were also generated via migration of the double bond.

1. Introduction

The hydropyrolysis of coals and oil shales at high hydrogen pressures (>10 MPa), together with the use of a dispersed sulphided molybdenum catalyst, has been demonstrated to give rise to high yields (>65%) of dichloromethane (DCM) soluble oil, with conversions of organic matter >85% (Snape et al., 1994; Roberts et al., 1995). Further studies have shown that the use of a slow heating rate (8 °C min^{-1}) for the hydropyrolysis of organic-rich samples generates high yields of hydrocarbon

* Corresponding author. Tel.: +44 115 9514166; fax: +44 115 9514115.
E-mail address: colin.snape@nottingham.ac.uk (C.E. Snape).

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biomarkers such as hopanes and steranes, whilst minimising alteration of their isomeric distributions (Love et al., 1995, 1997). These characteristics make the bound biomarkers released by hydropyrolysis a powerful tool in tackling key problems in oil exploration; for example, in severely biodegraded crude oils and oil-contaminated drill cuttings, where the conventional approaches using free hydrocarbon biomarkers are limited (Murray et al., 1998; Russell et al., 2004). In addition to petroleum geochemistry, hydropyrolysis has recently been applied to the characterisation of organic matter in meteorites (Sephton et al., 2004), archaeological samples (Craig et al., 2004) and Archean bitumen (Brocks et al., 2003).

In order to exploit the hydropyrolysis technique to its full potential it is necessary to gain a better understanding of the efficiency and selectivity of the technique for releasing bound biomarkers from kerogens and oil asphaltenes. This study describes a series of experiments with functionalised model compounds including carboxylic acids (stearic acid, oleic acid and 5β-cholanic acid), and sterols (cholesterol and cholestanol), which allow for the selectivity of hydrogenation to their corresponding alkanes to be assessed. In addition, the extent of cracking and isomerisation undergone by *n*-alkanes and steranes upon formation from specific functionalities can be investigated.

Experiments with model compounds are commonly utilised to further our understanding of the efficiency and mechanisms involved in a variety of pyrolysis techniques (Smith et al., 1989; Rushdi et al., 2003). Many of the previous studies on the pyrolysis of carboxylic acids have investigated these compounds as a potential source of *n*-alkanes in the maturation of kerogen and generation of petroleum (Cooper and Bray, 1963; Shimoyama and Johns, 1971). Such studies have included the catalytic decarboxylation of carboxylic acid model compounds to generate hydrocarbons, using catalysts such as clays (Jurg and Eisma, 1964) and calcites (Shimoyama and Johns, 1972). In an attempt at determining the *n*-alkyl content of petroleum source rocks, a variety of model compounds, including *n*-hexadecanoic acid (*n*-C_{16}), were subjected to hydrous pyrolysis in the presence of brown coal (Smith et al., 1989). Further studies have included the use of carboxylic acids in order to understand the pathways of hydrocarbon formation, with the pyrolysis performed in an open system over activated alumina for dodecanoic acid (Leung et al., 1995) and octadecanoic acid (Billaud et al., 2003); while a similar experimental set up enabled the kinetics of octadecanoic acid catalytic cracking to be determined (Billaud et al., 2001). The closed system pyrolysis of eicosanoic (*n*-C_{20}) acid has been utilised to understand the origin of aliphatic hydrocarbons in brown coal liquefaction (Bongers et al., 1996), and the effect of clay and ammonium catalysts on the products of flash pyrolysis of stearic acid have been investigated (Nierop and Bergen, 2002).

Owing to their importance in biological processes, use as source tracers in biogenic material and the application of their diagenetic products as biomarkers in petroleum geochemistry (e.g. Gaskell and Eglinton, 1975), the thermal alteration of sterols has been studied under a variety of conditions (Falk et al., 1949; Rushdi et al., 2003). Most of these studies have attempted to understand the diagenetic transformation of steroids to steranes by the identification of reaction pathways and intermediates (Rushdi et al., 2003), rather than maximising the selective hydrogenation of the functionalised precursors to the reduced steranes. The thermal degradation of cholestane by hydrous and anhydrous pyrolysis has also been investigated (Abbott et al., 1995).

2. Methods

The fixed bed hydropyrolysis tests were conducted using the five model compounds, oleic acid (*cis*-9-octadecenoic acid – $C_{18}H_{34}O_2$), stearic acid (*n*-octadecanoic acid – $C_{18}H_{36}O_2$), 5β-cholanic acid (ursocholanic acid – $C_{24}H_{40}O_2$), cholesterol ($C_{27}H_{46}O$) and 5α-cholestanol ($C_{27}H_{48}O$), all obtained from Sigma (UK), with the apparatus and procedure that have been described in detail elsewhere (Snape et al., 1994; Roberts et al., 1995; Love et al., 1995). Briefly, the samples were pyrolysed with resistive heating from 50 °C to 250 °C at 250 °C min^{-1}, and then from 250 °C to 400 °C at 8 °C min^{-1}, under a hydrogen pressure of 15 MPa. A hydrogen sweep gas flow of 5 l min^{-1}, measured at ambient temperature and pressure ensured that the products were quickly removed from the reactor vessel. In order to assess the effect of temperature on the conversion of these model compounds, further tests were conducted with the same heating rate up to 500 °C, and also to 550 °C with the final temperature held for 10 min. The products were collected in a silica-filled trap, cooled by dry ice as described in a previous study (Meredith et al., 2004).

Prior to hydropyrolysis, the acid model compounds were adsorbed (~5 wt.%) onto both silica (35–70 mesh) and activated carbon (ground to a 50–250 μm powder), and loaded with a dispersed sulphided molybdenum catalyst as previously described (Love et al., 1995), to give a nominal molybdenum loading of 1 wt.% sample. To ensure that there was no contamination of the products, the sorbants and the trapping silica were pre-extracted in a soxhlet with *n*-hexane (24 h) and DCM/methanol (93:7 v/v; 48 h), and dried in a baffle furnace (600 °C 6 h). The products were desorbed from the trap silica by a short chromatographic column eluted with DCM, and the total yield determined by evaporation under a stream of dry nitrogen in pre-weighed vials.

Hydropyrolysis experiments were also performed with an aliquot of each model compound placed in the reactor directly onto a bed of sulphided molybdenum catalyst (250 mg), and heated as above to a final temperature of 400 °C and 500 °C for stearic acid and 400 °C, 500 °C and 550 °C for 5β-cholanic acid. Cholesterol and cholestanol were pyrolysed on a bed of catalyst with temperature programmes of 150 °C to 450 °C at 3 °C min^{-1}.

Quantification of the recovered products from the stearic and oleic acid experiments was achieved by the addition of *n*-decane as an internal standard, with analysis by gas chromatography–flame ionisation detection (GC–FID). Analysis was conducted before drying of samples, so no problems of evaporative losses were encountered. Since the products were largely composed of *n*-alkanes, and the response of these compounds to GC–FID is virtually identical (Tong and Karasek, 1984), a response factor of 1 was assumed. GC analyses were performed on a Chromopack CP9001 instrument, with separation achieved on a fused silica capillary column (25 m × 0.22 mm i.d.) coated with BPX5 phase (0.25 μm film thickness). Helium was employed as the carrier gas, with a temperature programme of 50 °C (1 min) to 300 °C (5 min) at 5 °C min^{-1}. Identification of the hydrocarbons generated was achieved by comparison with relative retention times and published mass spectra and for the hydropyrolysis products of 5β-cholanic acid by comparison to an authentic reference sample of 5β-cholane (Chiron, Norway). Gas chromatography–mass spectrometry (GC–MS) analyses were performed on a Fisons Instruments 8000 gas chromatograph interfaced to an MD 800 mass spectrometer (ionising energy 70 eV, source temperature 280 °C). Separation was achieved on a column similar to that used for the GC analyses, with helium as the carrier gas and an oven programme of 50 °C (2 min) to 300 °C (28 min) at 5 °C min^{-1}, with the data acquired in full-scan mode (mass range m/z 50–450).

3. Results and discussion

3.1. Stearic and oleic acids

Partial gas chromatograms of the products generated by the hydropyrolysis at 500 °C of silica and carbon supported oleic and stearic acids are shown in Fig. 1. The total product yields, expressed as weight % of the acid pyrolysed are shown in Fig. 2, with the proportion of the product represented by each of the *n*-alkanes for the experiments shown in Table 1. The hydrogenation of stearic acid when desorbed from a silica substrate is very selective at 400 °C and 500 °C with ~97% of the recovered pyrolysis product composed of *n*-octadecane, with minor amounts of *n*-C_{17} and *n*-C_{16} alkanes also generated. At 550 °C, a slightly greater degree of cracking is apparent with small amounts of alkanes from *n*-C_{12} to *n*-C_{17} generated. Owing to the presence of the double bond in oleic acid, this compound was more prone to cracking than the saturated stearic acid, with only ~75% of the initial acid reduced to *n*-octadecane. The remaining 25% of the alkanes were present as shorter chained homologues, which have a marked even/odd carbon number preference and are dominated by the *n*-C_{16}, *n*-C_{14} and *n*-C_{12} alkanes (Fig. 1). The degree of cracking of oleic acid and the distribution of the pyrolysis products remained fairly constant at all temperatures.

In contrast to previous studies where intermediates such as ketones were recovered in addition to the hydrocarbons (Shimoyama and Johns, 1971; Nierop and Bergen, 2002), the high hydrogen pressures and presence of the sulphided molybdenum catalyst in hydropyrolysis ensured complete hydrogenation of the acids at all pyrolysis temperatures. Furthermore, no polymerisation was apparent as has been reported in previous decarboxylation experiments (Shimoyama and Johns, 1972).

The yield of *n*-alkanes for both acids from the silica substrate is relatively low at 400 °C, with just 50 wt.% of the stearic acid and 34 wt.% of the oleic acid being recovered as hydrocarbons. With an increase in temperature the alkane yield increases significantly (Fig. 2), although it is not until

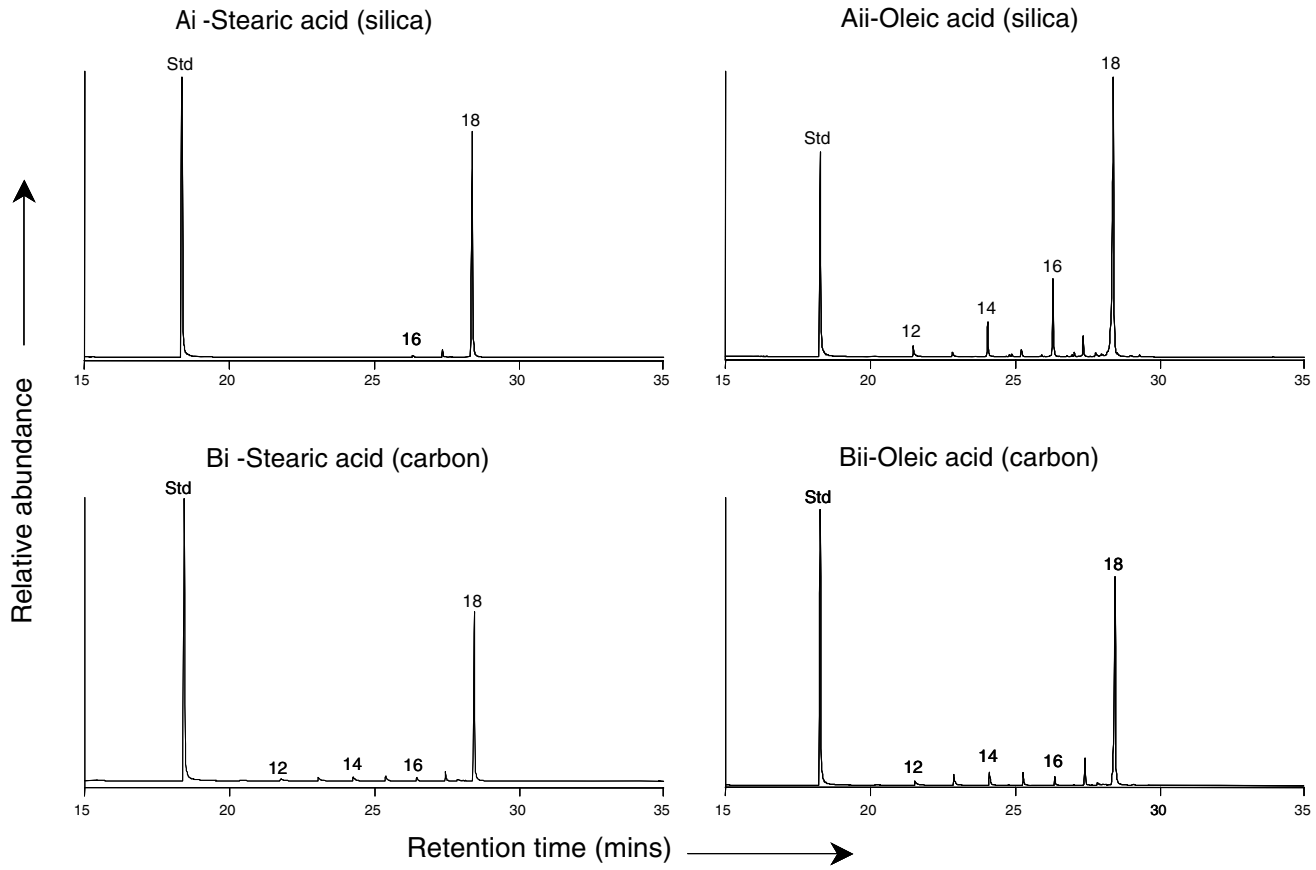

Fig. 1. Partial gas chromatograms of the products generated from the hydropyrolysis at 500 °C of (i) stearic acid; (ii) oleic acid, supported on a silica (A), and carbon (B) substrate. Numbers refer to the carbon number of the generated *n*-alkanes; Std = *n*-decane.

550 °C, a temperature greatly in excess of the boiling point of these acids, that the product yield for both compounds is ~70 wt.%. Bearing in mind that 500 °C is usually a sufficiently high temperature to achieve maximum conversions for relatively immature kerogens, this suggests that relatively stable bonds are formed between the silica surface and carbonyl groups of the model compounds. In comparison, it is interesting to note that, when adsorbed on silica, asphaltenes typically give conversions of only 400–500 mg/g C (Meredith et al., 2004) compared to over 900 mg/g C for immature kerogens (Love et al., 1995). Although interactions among relatively large aromatic clusters could contribute to high char yields, complex formation between asphaltenes and surface oxygen functional groups may again be a contributory factor to the suppression of yields. Such retarded volatilisation of carboxylic acids adsorbed to silica, due to the strong adsorption of the carbonyl groups onto the polar silica, has previously been reported (Park et al., 2000; Hudson et al., 2001). Indeed, studies with silica-immobilised substrates have indicated that the Si–O–C surface linkage is stable to hydropyrolysis up to temperatures approaching 600 °C (Mitchell et al., 1993), suggesting the formation of such bonds is occurring in silica substrate experiments.

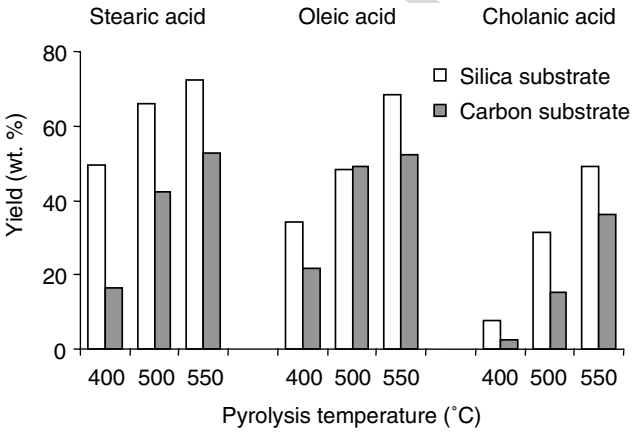

Fig. 2. Effect of pyrolysis temperature on the total yield (wt.% of starting acid recovered) of products generated from the hydropyrolysis of stearic, oleic and 5β-cholanic acids from the two substrates.

Table 1
Proportion of product comprised of each *n*-alkane (%) from the hydropyrolysis of stearic and oleic acids adsorbed to silica and carbon substrates at different pyrolysis temperatures

n-Alkane	Silica substrate						Carbon substrate					
	Stearic acid (°C)			Oleic acid (°C)			Stearic acid (°C)			Oleic acid (°C)		
	400	500	550	400	500	550	400	500	550	400	500	550
n-C_{11}	–	–	–	–	–	–	0.1	0.4	5.1	–	–	–
n-C_{12}	–	–	0.6	1.3	2.5	2.5	0.1	2.3	5.7	–	2.4	2.5
n-C_{13}	–	–	0.9	–	0.7	0.2	0.1	2.9	5.3	–	3.8	4.0
n-C_{14}	–	–	1.0	4.3	6.4	4.9	0.3	3.4	4.4	–	3.9	3.8
n-C_{15}	–	–	1.0	0.9	1.4	1.1	0.6	3.1	3.6	–	3.1	3.3
n-C_{16}	0.9	0.5	1.0	11.6	13.7	12.9	1.1	2.2	2.5	1.2	2.2	2.3
n-C_{17}	2.3	2.4	3.0	4.3	13.3	3.7	5.1	4.0	4.8	6.4	5.5	6.2
n-C_{18}	96.8	97.1	92.6	77.6	72.0	74.7	92.6	81.7	68.6	92.3	79.0	77.8

Adsorption to the carbon substrate appeared to influence both the yield and distribution of *n*-alkanes generated from the two acids. Stearic acid appeared to be more susceptible to cracking at all temperatures. As with the silica substrate, the degree of hydrocracking was heavily influenced by the pyrolysis temperature, with the proportion of *n*-octadecane generated decreasing from 93% at 400 °C, to 69% at 550 °C. Conversely, adsorption to the carbon substrate appeared to reduce the degree of cracking of oleic acid at lower temperatures, with the pyrolysis product at 400 °C composed of 92% of *n*-octadecane, in contrast to 78% from the silica substrate. This may not be of great significance as the product yield at this temperature was relatively low, especially for the carbon substrate (~20 wt.%). At 500 and 550 °C with greater yields generated the degree of hydrocracking was similar to that seen for the silica substrate, although the distribution of products was significantly different, with no dominance of even-numbered shorter chained homologs observed. The high temperature formation of much of the *n*-octadecane would suggest that stable bonds are being formed with the activated carbon, as with the silica where a variety of surface oxygen functionalities exist. However, activated carbon is highly microporous in character compared to the silica, so physical occlusion in small pores could also be a contributory factor.

In an attempt to increase the yield of octadecane at lower temperatures, the experiments were repeated with the stearic acid placed directly onto a bed of sulphided molybdenum catalyst. While the total product yield was marginally higher than for the silica adsorbed sample at 400 °C (56 wt.% of the acid pyrolysed is recovered as hydrocarbons compared to 49%), analysis of this product showed it to be highly cracked, with a large proportion of *n*-alkenes generated (Fig. 3). Furthermore, only ~60% of the total yield was composed of hexane-soluble alkenes and alkanes, with the remainder comprised of partially hydrogenated octadecenol. Such intermediates were not present in the substrate-adsorbed experiments, with only the fully reduced alkanes being formed. This is thought to be due to the volatilisation of the stearic acid at temperatures below that of the activation point of the catalyst (~250 °C).

3.2. 5β-Cholanic acid

The selectivity of the hydrogenation of the polycyclic 5β-cholanic acid was similar to that observed for stearic acid, with the product being >95% 5β-cholane (Fig. 4). Owing to the significantly higher boiling point of the C_{24} cholanic acid compared to the C_{18} acids, a higher pyrolysis temperature is required before significant yields of products are generated. As illustrated in Fig. 2 there is a low yield at 400 °C, only ~30% of the initial acid is recovered as hydrocarbons from the silica substrate at 500 °C, and it is not until the final temperature of 550 °C that a yield of >50 wt.% is achieved, with the silica again yielding a higher proportion of product than the carbon substrate. Co-injection with, and comparison to the spectra generated from the analysis of an authentic reference sample of 5β-cholane demonstrates that no significant isomerisation of the cholane occurs during hydropyrolysis. The other products formed, which are highlighted in the expanded part of Fig. 4, include small amounts of unsaturated cholenes, which were separated from the cholane on Ag-impregnated silica to produce a highly pure single compound

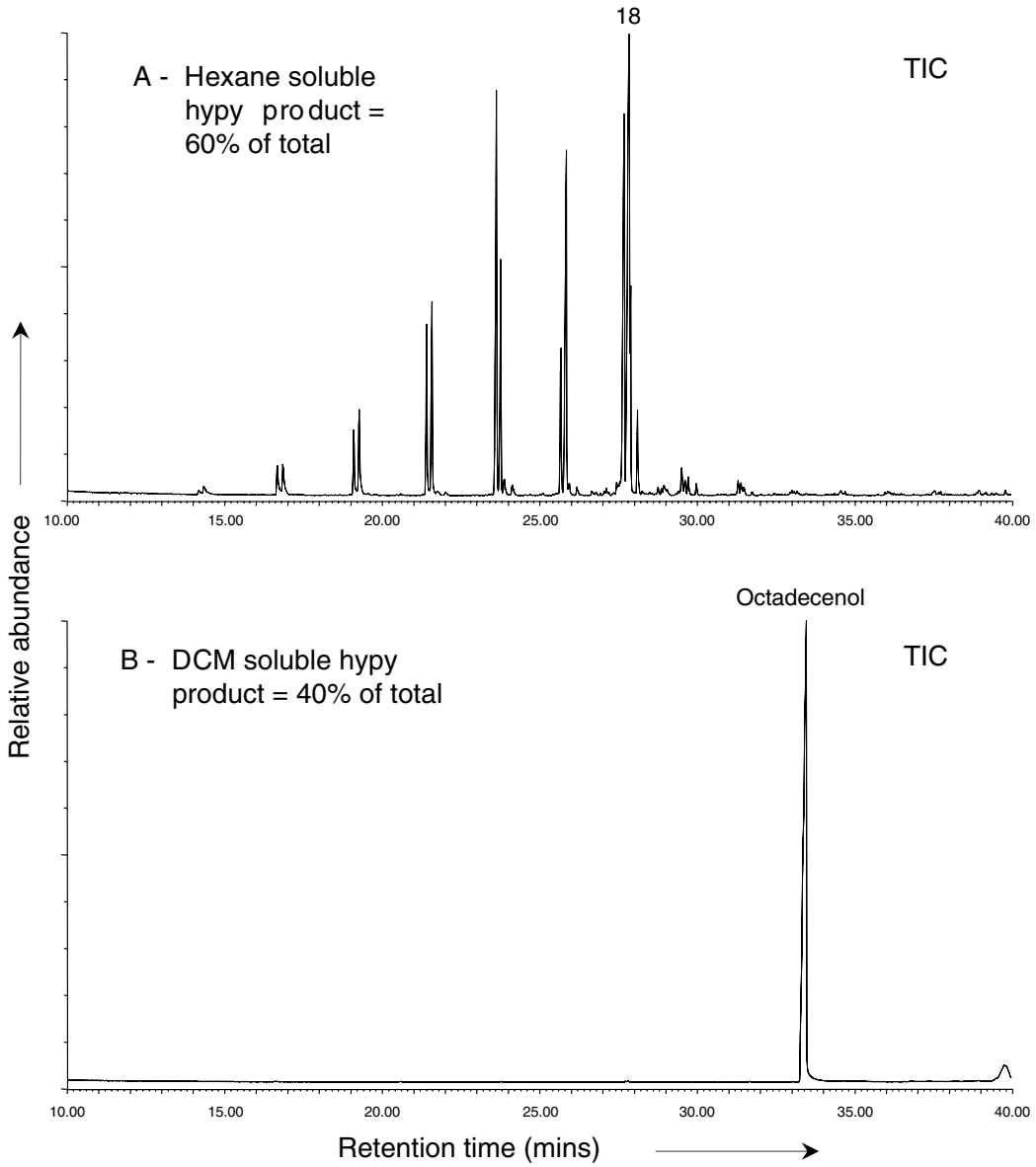

Fig. 3. Partial total ion chromatograms (TIC) of the products generated from the hydropyrolysis of stearic acid supported on a bed of catalyst at 500 °C: (A) hexane-soluble product; (B) dichloromethane-soluble product.

sample (not illustrated). Adsorption to the carbon substrate did not result in significantly different product distribution than that from the silica substrate (not illustrated).

Experiments similar to those performed on the stearic acid with the sample placed on a bed of catalyst resulted in a product similar to that generated from cholanic acid adsorbed on silica, although the product was more fully hydrogenated with fewer cholenes generated. There was no evidence of increased hydrocracking or the recovery of partially reduced compounds as seen for stearic acid, and this configuration of the reactor resulted in significantly improved yields, especially at lower temperatures. The total yield at 500 °C increased from 31 to 67 wt.%, and from 49 to 69 wt.% at 550 °C.

The highly selective hydrogenation of 5β-cholanic acid demonstrates that the selectivity of defunctionalisation of model compounds by hydropyrolysis is not influenced by the compound having a polycyclic structure, provided that the functional group is located on the side chain. The presence of a functional group attached to the ring system was tested by experiments with the saturated and unsaturated alcohols, cholesterol and 5α-cholestanol.

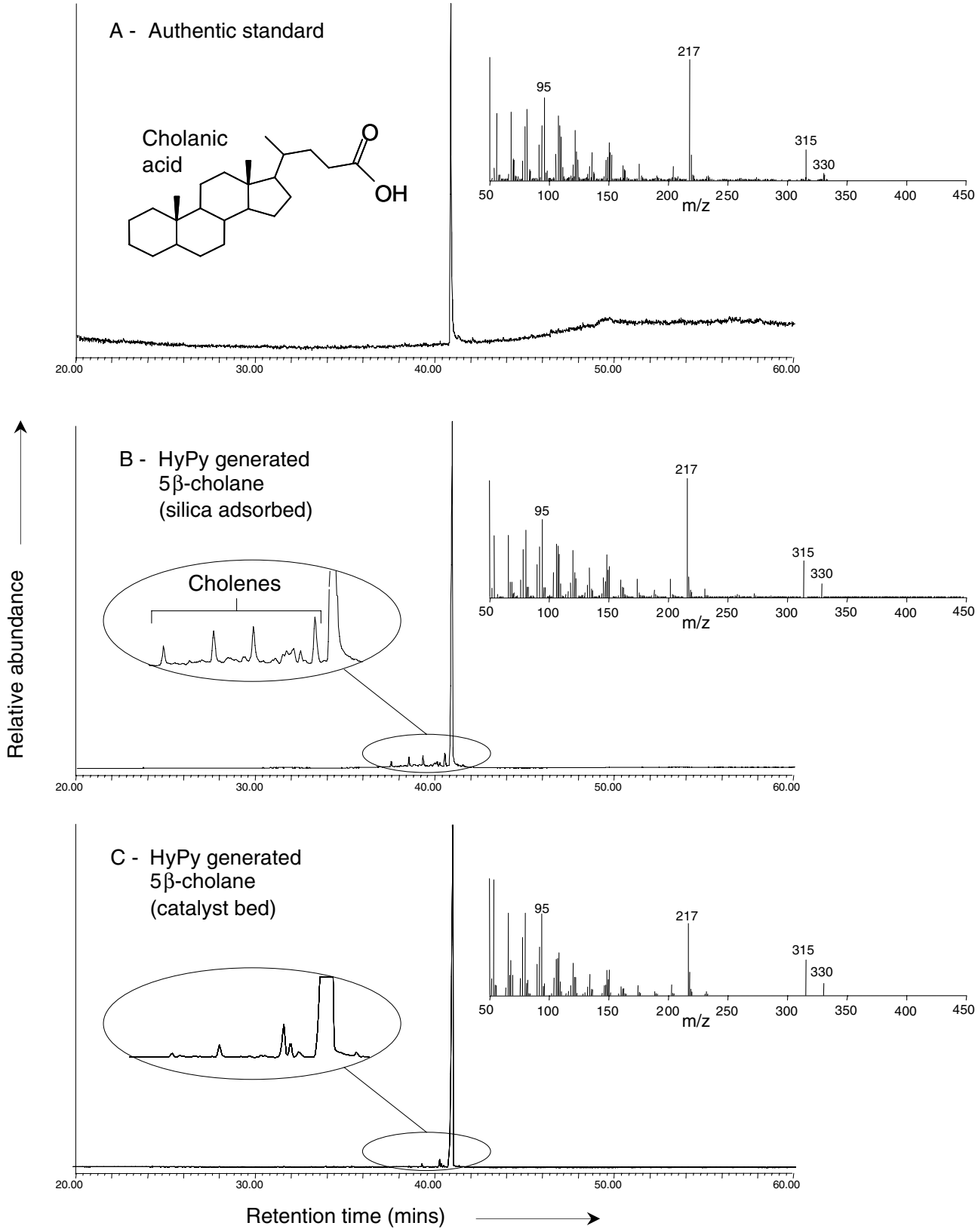

Fig. 4. Partial TIC, together with the spectra of the dominant peak of (A) authentic reference sample of 5β-cholane; (B) hydropyrolysis generated 5β-cholane from silica substrate supported 5β-cholanic acid; (C) hydropyrolysis generated 5β-cholane from catalyst bed supported 5β-cholanic acid.

3.3. Cholestanol and cholesterol

The products of the hydropyrolysis of cholestanol are shown in Fig. 5, and the presence of the functional group on the ring system of this compound appears to have no influence on the selectivity of hydrogenation when compared to the products generated from the hydropyrolysis of 5β-cholanic acid. With a relatively slow heating rate of 3 °C min^{-1} to 450 °C the overall yield is ~60 wt.%, with the product composed largely (>90%) of 5α(H)-cholestane, with minor quantities of unsaturated cholestenes also generated. A minor amount of isomerisation is apparent for the C-5 hydrogen at the junction of the A and B rings, resulting in the formation of small amounts of 5β(H)-cholestane (coprostane). The unsaturated cholestenes probably arise during the reduction of the alcohol group and the subsequent migration of the double bond within the ring system. The presence of a bed of catalyst beneath the sample during hydropyrolysis has been previously shown to fully hydrogenate the alkenes generated during the pyrolysis of immature oil shales (Meredith et al., 2003). The occurrence of cholestenes in the cholestanol hydropyrolysis product suggests that double bond migration can occur after volatilisation of the model compounds at temperatures below the activation point of the sulphided molybdenum catalyst at approximately 250 °C. Therefore, it may be necessary to investigate composite catalyst systems that, in addition to the sulphided molybdenum catalyst, also contain Group VIII noble metals, particularly palladium and platinum, which are known to be active for hydrogenation from room temperature.

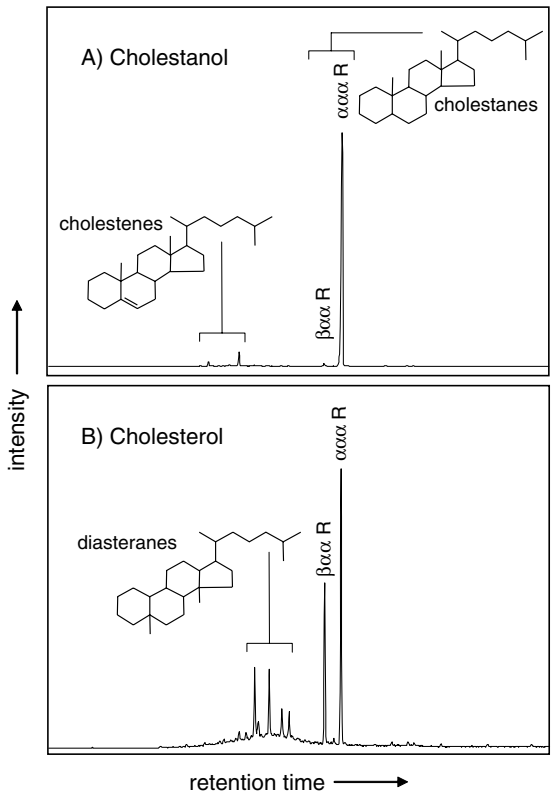

Fig. 5. Partial TIC of the products generated from the hydropyrolysis at 500 °C of (A) cholestanol; (B) cholesterol.

The products generated from the hydropyrolysis of cholesterol (Fig. 5) demonstrate that the presence of the double bond within the structure significantly decreases the selectivity of the defunctionalisation. As the double bond in cholesterol is adjacent to a ring-junction position it is apparent that the formation of two isomers of cholestane is inevitable upon hydrogenation. Of the total cholestane product (~70 wt.% of the initial cholesterol was recovered), approximately 60% was composed of 5α(H)-cholestane and 40% of 5β(H)-cholestane. Furthermore, in addition to the dominant cholestane product and minor amounts of cholestenes as seen in the hydropyrolysis of saturated cholestanol, significant quantities of diasteranes are also generated from cholesterol. These arise from rearrangement of the structure, which further studies will attempt to eliminate by optimising the catalyst system and experimental conditions employed.

The highly selective defunctionalisation of model compounds demonstrated in this study will potentially allow for hydropyrolysis to be employed as a preparative method for the compound-specific carbon isotope analysis of important biological compounds, as recently described for carboxylic acids by Sephton et al. (2005).

4. Conclusions

The selectivity towards hydrogenation of single functionalised saturated carboxylic acids and sterols by hydropyrolysis to their corresponding alkanes is extremely high with >90% being achieved for stearic acid, 5β-cholanic acid and cholestanol, with negligible hydrocracking and isomerisation being observed. Unsaturated model compounds such as oleic acid and cholesterol show lower selectivity, with minor cracking and structural rearrangement being apparent.

The choice of substrate on which the model compounds are supported has a major influence on both the yield and product distribution, with silica generating higher yields of more selectively

reduced products than the carbon substrate. The most selective results for high boiling point compounds are obtained by placing the model compounds directly onto a bed of sulphided molybdenum catalyst.

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