Bicyclic naphthenic acids in oil sands process water: Identification by comprehensive multidimensional gas chromatography–mass spectrometry

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ABSTRACT

Although bicyclic acids have been reported to be the major naphthenic acids in oil sands process-affected water (OSPW) and a well-accepted screening assay indicated that some bicyclics were the most acutely toxic acids tested, none have yet been identified. Here we show by comprehensive multidimensional gas chromatography–mass spectrometry (GC × GC–MS), that >100 C_{8-15} bicyclic acids are typically present in OSPW. Synthesis or purchase allowed us to establish the GC × GC retention times of methyl esters of numerous of these and the mass spectra and published spectra of some additional types, allowed us to identify bicyclo[2.2.1]heptane, bicyclo[3.2.1]octane, bicyclo[4.3.0]nonane, bicyclo[3.3.1]nonane and bicyclo[4.4.0]decane acids in OSPW and a bicyclo[2.2.2]octane acid in a commercial acid mixture. The retention positions of authentic bicyclo[3.3.0]octane and bicyclo[4.2.0]octane carboxylic acid methyl esters and published retention indices, showed these were also possibilities, as were bicyclo[3.1.1]heptane acids. Bicyclo[5.3.0]decane and cyclopentylcyclopentane carboxylic acids were ruled out in the samples analysed, on the basis that the corresponding alkanes eluted well after bicyclo[4.4.0]decane (latest eluting acids). Bicyclo[4.2.1]nonane, bicyclo[3.2.2]nonane, bicyclo[3.3.2]decane, bicyclo[4.2.2]decane and spiro[4.5]decane carboxylic acids could not be ruled out or in, as no authentic compounds or literature data were available. Mass spectra of the methyl esters of the higher bicyclic C_{12-15} acids suggested that many were simply analogues of the acids identified above, with longer alkanoate chains and/or alkyl substituents. Our hypothesis is that these acids represent the biotransformation products of the initially somewhat more bio-resistant bicyclanes of petroleum. Although remediation studies suggest that many bicyclic acids can be relatively quickly removed from suitably treated OSPW, examination by GC × GC–MS may show which isomers are affected most. Knowledge of the structures will allow the toxicity of any residual isomers to be calculated and measured.

1. Introduction

'Naphthenic acids' occurring naturally in the oil sands of Alberta, Canada are concentrated by processing, resulting in oil sands process-affected water (OSPW) which, after much re-use, is stored in large tailings ponds or lagoons, awaiting final reclamation [1]. Undiluted OSPW has been shown to be somewhat toxic in numerous biological assays, but with time in storage the composition and toxicity changes, the latter usually reducing [2]. Nonetheless, residual toxicity remains and this has promoted numerous studies of treatment methods with oxidants or ozone, or by photocatalysis or bioremediation [3].

Numerous studies have shown that the major acids in different OSPW samples comprise, as a group, unknown alicyclic bicyclic compounds [2,4–7] and a well-accepted screening assay indicated that some synthetic alicyclic bicyclics were the most acutely toxic acids tested [8]. However, almost nothing is known about the identities, or even the numbers, of bicyclic acids present in OSPW.

Cyr and Strausz [9] isolated a C_{16} bicyclic acid from oil sands deposits in Alberta which had a mass spectrum similar to that of drimane or labdane bicyclanes, but these have not yet been reported in OSPW acids (cf [10–12]). Bowman et al. [13] recently identified

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bicyclic monoaromatic, indane and tetralin acids in a pore water sample from a composite tailings deposit, which combines fluid fine tailings from oil sands processing with gypsum to form a non-segregating deposit, but no alicyclic bicyclics were identified.

Elucidation of acid structures also has geochemical significance, providing an insight into the microbial degradation mechanisms of petroleum [14]. Some alicyclic bicyclic acids in crude oils and commercial naphthenic acids preparations derived from refining petroleum, have been identified [14–16], but several studies have noted the differences between the latter and OSPW acids, so perhaps nothing directly can be inferred from a comparison [17]. Furthermore, the few bicyclic acids identified in commercial naphthenic acids to date represent only a small fraction of those actually present, as the >100 compounds revealed by comprehensive multidimensional gas chromatography–mass spectrometry of the methyl esters (GC × GC–MS) of two commercial naphthenic acids mixtures attests [18].

Fortunately the bicyclic acids in OSPW seem to be quite prone to removal by ozone treatment and bacterial action [3]. Nonetheless, it is important to establish the identities of these acids so that the toxicity of relevant isomers can be measured, the mechanisms of remediation treatments better understood and the products of remediation treatment predicted.

In the present study we examined several methylated OSPW acidic extracts and a commercial acid mixture, by GC × GC–MS and identified several of the bicyclic acids present. Some bicyclics previously assumed to be representative of OSPW constituents, were not common.

2. Materials and methods

The naming of bicyclic compounds varies considerably throughout the literature. As an attempt to keep the naming of the compounds discussed consistent, the IUPAC nomenclature rules for polycyclic compounds based on the Von Baeyer system [19] have been used, with numbering of the carbons within the bicyclic core starting at a bridgehead carbon (Fig. 1A and B). Alternative names for compounds commonly used by chemical suppliers and search engines (e.g. decalin or octahydro-pentalene) are given alongside the systematic names.

Authentic bicyclo[2.2.1]heptane-2-ethanoic acid (Fig. 1A; Structure *Ib*), 2,6,6-trimethylbicyclo[3.1.1]heptane-3-carboxylic acid ((+)-3-pinanecarboxylic acid) (*IIa*), bicyclo[2.2.2]octane-2-carboxylic acid (*IVa*), 4-pentylbicyclo[2.2.2]octane-1-carboxylic acid (*IVc*), bicyclo[3.3.0]octane-2-carboxylic acid (*VIa*), 4-methyl-bicyclo[3.3.0]octane-2-carboxylic acid (3-methyl-octahydro-pentalene-1-carboxylic acid) (*VIb*) and bicyclo[3.3.1]nonane-1-carboxylic acid (*VIIIa*) were purchased from Sigma (Poole, UK). Authentic bicyclo[2.2.1]heptane-1-carboxylic acid (Ia), bicyclo[2.2.2]octane-1-carboxylic acid (*IVb*) and 5-methyl-bicyclo[3.3.1]nonane-1-carboxylic acid (*VIIIc*) were purchased from Molport (Riga, Latvia). Bicyclo[3.2.1]octane-6-carboxylic acid (*Va*) was synthesised from 2-hydroxybicyclo[3.2.1]octane-6-carboxylic acid (Sigma) by base catalysed dehydration followed by hydrogenation [20]. Bicyclo[3.3.1]nonane-3-carboxylic acid (*VIIIb*) was synthesised essentially by the methods of Sasaki et al. [21] as modified by Peters et al. [22]. Thus, reaction of adamantan-2-one in methanesulphonic acid in the presence of sodium azide produced the mesylate which was not isolated but heated with potassium hydroxide to give the unsaturated bicyclo[3.3.1]non-2-ene-7-carboxylic acid, obtained after extraction into acidified chloroform [21]. The corresponding saturated bicyclo[3.3.1]nonane-3-carboxylic acid (*VIIIb*) was obtained by hydrogenation [22] and the methyl esters by heating with BF$_3$/methanol. Bicyclo[4.3.0]nonane-3-carboxylic (*Xa*)

and 2-methylbicyclo[4.3.0]nonane-3-carboxylic acids (*Xb*) were obtained by catalytic hydrogenation (cf [15]) of the corresponding indane acids (Sigma). Bicyclo[4.4.0]decane-2-carboxylic (*XIVa*), 3-carboxylic acid (*XIVb*), 2-ethanoic (*XIVc*), 3-ethanoic (*XIVd*), and 2-propanoic acids (*XIVe*; numbers refer to position of alkanoate substituents on bicyclic core) were synthesised as described previously [15]. 7-methylbicyclo[4.2.0]octane-7-carboxylic acid (*VIIa*) was prepared by hydrogenating 1-methyl-1,2-dihydrocyclobutabenzene-1-carboxylic acid methyl ester over a Raney Nickel catalyst at 100 °C and 100 bar using a H-Cube® (ThalesNano Nanotechnology Inc., Budapest).

Four different OSPW samples and a commercial naphthenic acids mixture were analysed (Table 1). The OSPW included two samples (#1 and #2) from industry A described in two previous studies [23,24]. Briefly, sodium salt concentrates of #1 and #2 were acidified to pH < 2 and the acids extracted with ethyl acetate before derivatisation with BF$_3$/methanol [24]. Another OSPW (#3) was provided from industry B (Table 1) at a site with a high concentration of particulate matter. This water sample was filtered, acidified and then eluted through a 200 mg ENV+ SPE cartridge with acetonitrile before being dried under N$_2$ and derivatised with BF$_3$/methanol. A fourth OSPW acid extract (#4) from industry A was obtained by extracting a sample of raw OSPW, collected from a different tailings pond using the methods described previously [24]. The latter sample had undergone no pre-treatment/clean-up prior to extraction and derivatisation.

In addition to the above samples, a commercial naphthenic acids mixture (#5) was obtained from Merichem Co. for comparison (Table 1) and fractionated based on a method previously used [24–26]. Derivatisation of the acids with BF$_3$/methanol was followed by silver ion solid phase extraction (Ag$^+$ SPE). Analysis herein focused on fraction 3 obtained by elution through the argentation solid phase extraction column with hexane, since this contained the bicyclic acids (methyl esters).

Accurate mass measurements were made using a Thermofisher LTQ Orbitrap XL high resolution mass spectrometer with electrospray ionisation. The mass range was m/z 120–2000; mass accuracy <3 ppm RMS with external calibration. For negative ionisation the instrument was externally calibrated using the above, sodium dodecyl sulphate and sodium taurocholate. For loop-injections a Thermo Scientific Surveyor MicroLC was used to provide solvent flow at 20 μL min^{-1}., through a 2 μL sample loop. Solvents used were H$_2$O:MeOH (1:1). For nano-electrospray an Advion Triversa NanoMate was used to deliver samples diluted into MeOH ± 10% NH$_4$OAc at a flow of approximately 0.25 μL min^{-1}. API source settings: Infusion NanoMate source temperature 275 °C or 200 °C, sheath gas flow 3–7 (arb. units) 2 (arb. units), aux gas flow was not used capillary (ionising) voltage positive ionisation: +3.2 to 3.7 kV negative ionisation: −3.5 to −4.0 kV. Mass spectra were acquired at a minimum resolution of 30,000 (at m/z 400). Theoretical masses and mass accuracies were calculated using an online calculator tool [27].

Comprehensive multidimensional gas chromatography–mass spectrometry (GC × GC–MS) analyses were conducted as described previously [23,28], using an Agilent 7890A gas chromatograph (Agilent Technologies, Wilmington, DE) fitted with a Zoex ZX2 GC × GC cryogenic modulator (Houston, TX, USA) interfaced with an Almsco BenchTOFdx^{TM} time-of-flight mass spectrometer (Almsco International, Llantrisant, Wales, UK). The first-dimension column was a 100% dimethyl polysiloxane 60 m × 0.25 mm × 0.25 μm Rxi®-1ms (Restek, Bellefonte, USA), and the second-dimension column was a 50% phenyl polysilphenylene siloxane 2.5 m × 0.1 mm × 0.1 μm BPX50 (SGE, Melbourne, Australia). Helium was used as carrier gas and the flow was kept constant at 1.0 mL min^{-1}. Samples (1 μL) were injected at 300 °C splitless. The oven was programmed from 40 °C (hold for 1 min), then heated to 130 °C at 10 °C min^{-1} then at