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NOVEL TERPENOID SULFOXIDES AND SULFIDES IN PETROLEUM

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Abstract: Homologous series of novel and unexpected biological markers, bicyclic and tetracyclic terpenoid sulfoxides and sulfides, have been identified in the Athabasca bitumen.

The Northern Alberta heavy oils have recently been shown to contain a homologous series of all head to tail tricyclic hexaprenoids ranging from C_{20} to C_{30} with the C_{23} member as the most abundant.[1,2] Their structure was identified as the 4,4,8,10,13-pentamethyl, 14-alkyl 13β(H), 14α(H)-perhydrophenanthrane, where the alkyl varies from CH_3 to 3,7-dimethylnonyl.[2] They represent a new sester and/or triterpane class of biological markers in petroleum of unestablished origin.[3] We wish to report here the isolation and identification in the same oil of two novel homologous series of terpenoid sulfoxides and sulfides. One of them has a bicyclic and the other a tetracyclic structure, and it is shown that the latter is related to the above tricyclic terpanes. The presence of several other naphthenic sulfoxides was also detected.

Terpenoid sulfoxides in nature are rare but a few, all in highly functionalized form, have been reported recently.[4] On the detection of sulfoxides in petroleum there is only one detailed study due to Okuno, Latham and Haines[5] who in 1967 isolated mixtures of naphthenic sulfoxides from six different crude oils. They were able to determine the elemental formula of the main component as $C_{13}H_{24}SO$ and to conclude that "saturated heterocyclic sulfoxides with two condensed rings of dicycloalkyl sulfoxides would be included in this molecular weight". These authors stressed that the sulfoxides were absent in the virgin crudes and were formed from their sulfide precursors only when the oils were exposed to aerial oxidation.

Using silica gel column chromatography, vacuum distillation, diazomethane treatment to esterify carboxylic acids followed by silica gel chromatography, we were able to isolate a pale yellow oil from the deasphalted Alberta heavy crudes in yields ranging from 0.1 to 1.0%. The i.r. spectrum of this oil, Figure 1, features the characteristic intense absorption band of the sulfoxide group at 1040 cm^{-1}. Its overall appearance is rather similar to the one reported by Okuno et al.[5] The entire fraction was found by field ionization mass spectrometry to consist of materials having the molecular formula $C_nH_{2n+z}SO$, where n varies from 10 to 30 with maxima occurring at 12-15 and 23. The value of z varies from 0 to -6 with a maximum at -2. The elemental formulae were confirmed by high resolution mass spectrometry, Table 1.

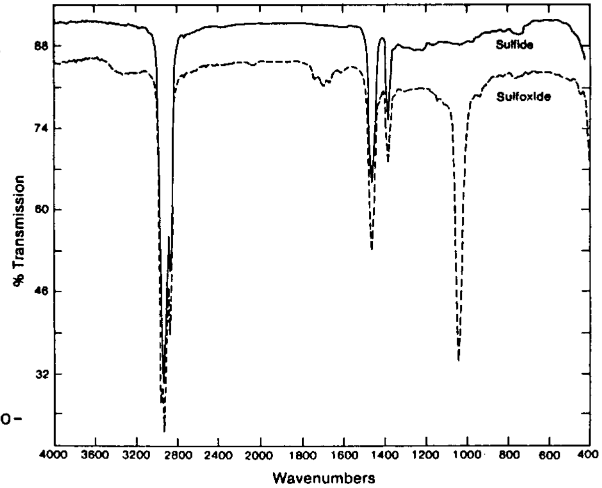


Fig.1. I.r. spectrum of sulfoxide fraction and corresponding sulfides.

Table 1. Mass Measurements of Sulfoxides[1]

Formula	Measured	Difference$\times10^{-4}$ [2]	z[3]
$C_{10}H_{18}SO$	186.1074	- 4	-2
$C_{10}H_{20}SO$	188.1232	- 3	0
$C_{11}H_{20}SO$	200.1230	- 5	-2
$C_{13}H_{24}SO$	288.1545	- 3	-2
$C_{14}H_{28}SO$	244.1864	+ 3	0
$C_{15}H_{28}SO$	256.1865	+ 5	-2
$C_{17}H_{30}SO$	282.2012	- 6	-4
$C_{17}H_{32}SO$	284.2181	+ 8	-2
$C_{18}H_{32}SO$	296.2170	- 4	-4
$C_{19}H_{36}SO$	312.2494	+ 7	-2
$C_{23}H_{40}SO$	364.2807	+ 7	-6

[1] Obtained on a Kratos MS-50 high resolution ms.
[2] Obs. - calc. [3] Value of z in $C_nH_{2n+z}SO$.

Sulfoxides, being highly polar molecules, cannot be readily analyzed by gas chromatography. On the other hand, the sulfides or hydrocarbons to which they can be reduced are amenable to gc analysis. For this reason the sulfoxides were converted to sulfides by $LiAlH_4$ treatment at 65°C in 53% yield leaving an unconverted sulfoxide residue of 32 wt%. Capillary gc analysis of this sulfide fraction revealed an unresolved complex mixture. Treatment of the residual unconverted sulfoxides with $LiAlH_4$ at 100°C led to the corresponding sulfides in 40% yield. By contrast, these sulfides appeared as a series of discrete peaks in the gc-mass chromatogram (60 m x 0.35 mm OV-101) displayed as the total ion current in Figure 2, and as the characteristic m/z 183 fragmentogram in Figure 3.

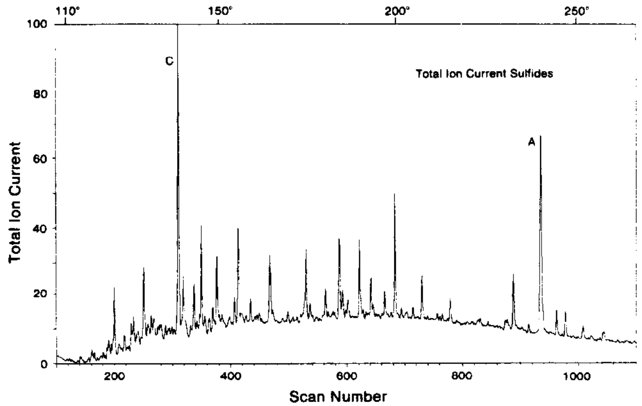


Fig.2. gc-mass chromatogram of sulfides

Reduction of the sulfoxides or sulfides with Raney nickel gave the corresponding hydrocarbons. The complete mass spectra of the two most prominent peaks in the sulfide spectrum, 'A' and 'C' in Figure 2, are presented in Figure 4 along with that of the hydrocarbon, 'B' from 'A'.

The structural assignment of sulfide 'A' is based on its mass spectrum and the structure of the hydrocarbon product 'B'. The tetracyclic sulfides comprise a homologous series as manifested by their characteristic m/z 319 fragmentogram ranging from C_{22} to C_{31} in relative concentrations very similar to their hydrocarbon counterparts, the tricyclic terpanes.[1] In all cases the C_{23} member is the most abundant. Also, the C_{23} hydrocarbon from the oil and from the reduction of the sulfides or sulfoxides coelute on the gc column and give identical mass spectra; consequently they should be identical molecules. The structure of the C_{23} member of the hydrocarbon series, has been previously assigned.[1,2]

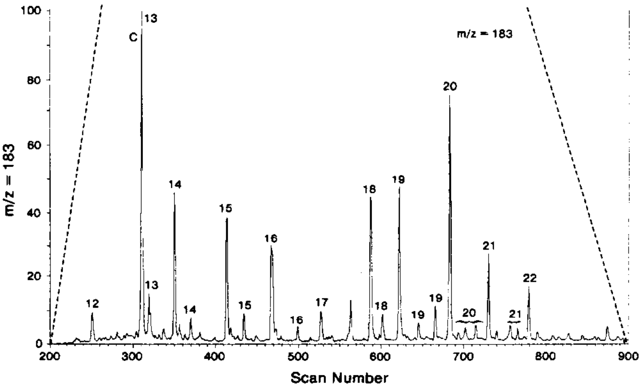


Fig. 3. m/z 183 mass fragmentogram of sulfides

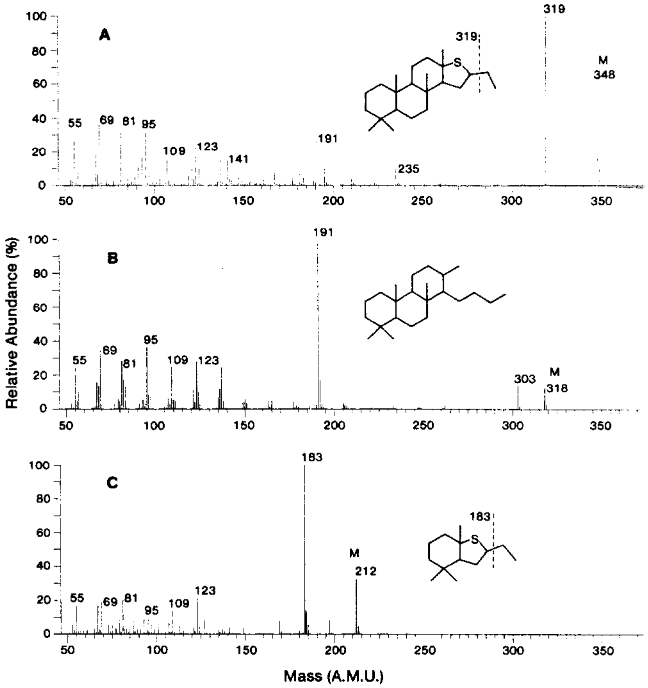
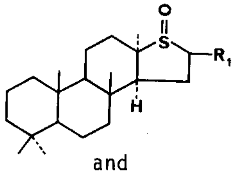


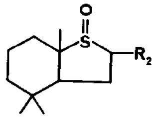
Fig.4. Mass spectra of compounds A, B, and C.

The dicyclic sulfides, Figures 3 and 4C, also comprise a homologous series extending from C_{12} to C_{22} with an isoprenoid side chain from CH_3 to 6-methyldec-2-yl and the mass spectra of their reduced hydrocarbon products are in good agreement with the available mass spectra for 2-alkyl-1,1,3-trimethylcyclohexanes.

On this basis the most probable structures for the two homologous series of sulfoxides detected in the Northern Alberta heavy oils are:



and



where R_1 is a CH_3 to a 3,7-dimethylnonyl and R_2 a CH_3 to a 6-methyldec-2-yl.

A fraction from the deasphalted oil containing cyclic sulfides was isolated by column chromatography. Gc-ms analysis revealed that two of the three principal members are the same as the two principal ones obtained from the $LiAlH_4$ reduction of the sulfoxides, namely C and A. In addition a hexacyclic sulfide with elemental formula $C_{31}H_{52}S$ also appeared but its structure has not yet been determined.

As far as could be ascertained, neither of these molecules nor any similar simple terpane derived sulfoxides or sulfides have been reported before. The terpenoid sulfides and hydrocarbons are likely to have a biological product-precursor relationship, but the sulfide and sulfoxide series may be linked either biogenically[6] or abiogenically.[5,7] Bacterial oxidation of dibenzothiophene to the sulfoxide dibenzothiophene-5-oxide for instance, has been observed.[6] The facile aerial oxidation of sulfide to sulfoxide is also well known.

We find that contrary to the conventional oils studied by Okuno et al.[5], which reportedly contained no sulfoxides in their virgin state, the five different samples of Alberta oil sand oils we examined all contained sulfoxides. In order to confirm this beyond doubt, we have taken one of our samples ourselves from a depth of ∿ 30 m below the surface. It was immediately placed in a glass container, purged with argon and sealed air-tight. The extraction of the bitumen from this sample was done under an argon atmosphere and the entire analysis was completed without delay. This sample gave 0.1% sulfoxides based on the deasphalted oil.

Therefore we are forced to conclude that sulfoxides are present in the virgin oil and they are a manifestation of the mildly oxidative post-depositionary conditions that have prevailed in the Alberta oil sand reservoirs. Thus, the terpenoid sulfides and sulfoxides represent a novel, valuable series of biomarkers, which are linked to the ubiquitous tricyclic terpanes and other cyclic terpanes present in most petroleums and appear to point to some hitherto unrecognized microbial activities responsible for their formation. They are also useful to establish redox conditions in crude oil deposits.

The close structural relationship of these terpenoid sulfides and sulfoxides to aromatic thiophenes suggests them as one of the principal precursors of aromatic thiophenes present in most crude oils and one of the precursors of the tricyclic terpanes which evolve during the mild thermolysis of the resin fraction of the Alberta oil sand bitumens.[1]

Further studies are in progress.

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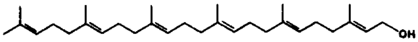
3. Aquino Neto, F.R., Restle, A., Connan, J., Albrecht, P. and Ourisson, G., *Tetrahedron Lett.*, 2027 (1982). These authors established the stereochemistry of the C_{20} members of the series and suggested the all head to tail hexaprenol,  a cell constituent, as a possible precursor.
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