



Stereochemistry, elution order and molecular modeling of four diaergostanes in petroleum



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ABSTRACT

Gas chromatography–mass spectrometry–mass spectrometry (GC–MS–MS) reveals four C₂₈ 13β,17α(H)-diasterane (diaergostane) peaks in petroleum from clay-rich source rocks, although only two diasterane peaks are commonly observed for each of the C₂₆, C₂₇, and C₂₉ diasteranes. Co-injection of two laboratory synthesized diaergostane standards having 5β(CH₃),13β(H),14β(CH₃),17α(H)-20S,24R and -20R,24R stereochemistry allowed assignment of the elution order for the four diaergostane peaks as follows: 20S,24R; 20S,24S; 20R,24S; 20R,24R. Partial least-squares regression analysis of 11 quantum chemical descriptors (e.g., molar volume, polarizability, torsion angles and surface area) determined by molecular modeling of the C₂₇–C₃₀ diasteranes, can be used to construct a model that validates the relative GC retention times of the stereoisomers of these compounds. Similar calculated Gibbs free energies for the lowest-energy conformers of the modeled C₂₈ 20S,24R versus 20S,24S and 20R,24S versus 20R,24R diasteranes explain why they occur in similar abundance.

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1. Introduction

Diasteranes have no direct precursors in living organisms (Ourisson, 1994). Diasterenes and diasteranes originate by “backbone rearrangement” of sterols or sterenes during diagenesis (Sieskind et al., 1979, 1989; Mackenzie et al., 1982; Brassell et al., 1984). Diasterenes were originally identified by Blunt et al. (1969) in acid catalyzed rearrangement products of cholest-4-ene or cholest-5-ene and they were isolated from bituminous shale by Rubinstein et al. (1975), who simulated their conversion from cholestanol by heating experiments on montmorillonite. Although most conversion of diasterenes to diasteranes is presumed to occur during catagenesis of clay-rich petroleum source rocks, a full spectrum of transformation products ranging from sterols and sterenes to thermally more stable diasteranes and triaromatic steroids occurs in some thermally immature sedimentary rocks (Melendez et al., 2013).

Diasteranes are of particular interest in crude oils from clastic source rocks (e.g., Requejo et al., 1997) because they are thermally

more stable and undergo biodegradation more slowly than steranes (Seifert and Moldowan, 1979). For this reason, many heavily biodegraded crude oils in which the steranes have been altered can still be evaluated in oil–oil and oil–source rock correlation studies by using diasteranes (e.g., Volkman et al., 1983; Peters et al., 2005 and references therein). The major diasterane isomers in crude oil have 13β,17α(H)-20S and -20R stereochemistry, although 13α,17β(H)-20S and -20R epimers also occur (Ensminger et al., 1978).

A peculiar pattern of four diaergostane peaks characterizes the gas chromatography–mass spectrometry–mass spectrometry (GC–MS–MS) traces of many crude oils and extracts from clay-rich source rocks (Fig. 1). The same pattern of peaks occurs in extracts from clay-poor source rocks and related crude oils, but is less pronounced due to lower relative concentrations of these compounds (Peters et al., 2005). Stereochemistry of each labeled peak in the figure is given in Table 1. Unlike the C₂₆, C₂₇, and C₂₉ homologs, which show only two diasterane peaks (peaks 2 and 3, 15 and 16, and 30 and 31 in Fig. 1, respectively), the C₂₈ trace shows four diaergostane peaks (23a, 23b, 24a and 24b). The C₃₀ diasteranes (peaks 36 and 37) occur as two broad peaks or as two partially resolved doublets, depending on gas chromatographic resolution. The purpose of this paper is to identify the four prominent

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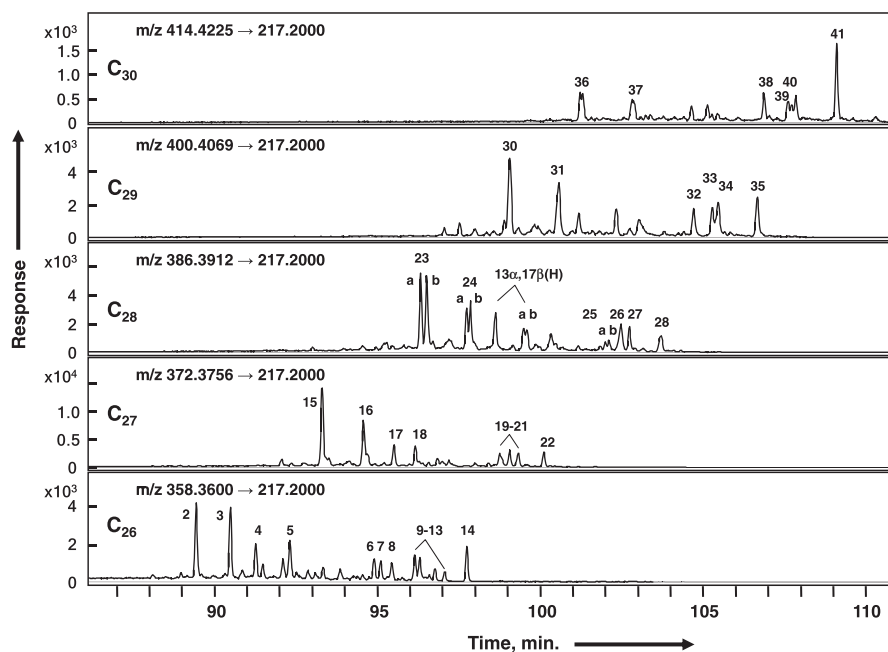


Fig. 1. GC–MS–MS analysis of a standard crude oil mixture (Stanford-1) dominated by oil from clay-rich petroleum source rocks. Peak identifications are in Table 1.

Table 1

Peak identifications for gas chromatography–mass spectrometry–mass spectrometry (GC–MS–MS) of steranes and diasteranes in Fig. 1. The internal standard (peak 1; not shown) was 5 β -cholane.

Peak	Epimer
2	C ₂₆ 13 β ,17 α -24-nordia-20S
3	C ₂₆ 13 β ,17 α -24-nordia-20R
4	C ₂₆ 13 β ,17 α -27-nordia-20S
5	C ₂₆ 13 β ,17 α -27-nordia-20R
6	C ₂₆ $\alpha\alpha\alpha$ -24-nor-20S
7	C ₂₆ $\alpha\beta\beta$ -24-nor-20R
8	C ₂₆ $\alpha\beta\beta$ -24-nor-20S
9	C ₂₆ $\alpha\alpha\alpha$ -24-nor-20R
10	C ₂₆ 21-nor $\alpha\alpha\alpha$ + $\alpha\beta\beta$
11	C ₂₆ $\alpha\alpha\alpha$ -27-nor-20S
12	C ₂₆ $\alpha\beta\beta$ -27-nor-20R
13	C ₂₆ $\alpha\beta\beta$ -27-nor-20S
14	C ₂₆ $\alpha\alpha\alpha$ -27-nor-20R
15	C ₂₇ 13 β ,17 α dia 20S
16	C ₂₇ 13 β ,17 α dia 20R
17	C ₂₇ 13 α ,17 β dia 20S
18	C ₂₇ 13 α ,17 β dia 20R
19	C ₂₇ $\alpha\alpha\alpha$ 20S
20	C ₂₇ $\alpha\beta\beta$ 20R
21	C ₂₇ $\alpha\beta\beta$ 20S
22	C ₂₇ $\alpha\alpha\alpha$ 20R
23	C ₂₈ 13 β ,17 α dia 20S (24S + 24R)
24	C ₂₈ 13 β ,17 α dia 20R (24S + 24R)
25	C ₂₈ $\alpha\alpha\alpha$ 20S
26	C ₂₈ $\alpha\alpha\alpha$ 20R
27	C ₂₈ $\alpha\beta\beta$ 20S
28	C ₂₈ $\alpha\alpha\alpha$ 20R
29	C ₂₈ 21-nor
30	C ₂₉ 13 β ,17 α dia 20S
31	C ₂₉ 13 β ,17 α dia 20R
32	C ₂₉ $\alpha\alpha\alpha$ 20S
33	C ₂₉ $\alpha\beta\beta$ 20R
34	C ₂₉ $\alpha\beta\beta$ 20S
35	C ₂₉ $\alpha\alpha\alpha$ 20R
36	C ₃₀ 13 β ,17 α dia 20S
37	C ₃₀ 13 β ,17 α dia 20R
38	C ₃₀ $\alpha\alpha\alpha$ 20S
39	C ₃₀ $\alpha\beta\beta$ 20R
40	C ₃₀ $\alpha\beta\beta$ 20S
41	C ₃₀ $\alpha\alpha\alpha$ 20R

diaergostane peaks and their stereochemistry and explain why only two peaks characterize most GC–MS–MS traces for C₂₆, C₂₇, and C₂₉ diasteranes. In addition, we used molecular mechanics in an attempt to validate the relative abundance and GC elution order of the diaergostanes.

Bauer et al. (1985) proved that the 13 β ,17 α (H)-20S epimers elute before the 13 β ,17 α (H)-20R epimers for the C₂₇, C₂₈ and C₂₉ diasterane homologs. Therefore, peaks 23a and 23b in Fig. 1 have 13 β ,17 α (H)-20S stereochemistry, whereas peaks 24a and 24b have 13 β ,17 α (H)-20R stereochemistry. The stereochemistry at C-24 must differ between peaks 23a and 24a and the corresponding 23b and 24b peaks, but it remains unclear which peaks have 24S versus 24R stereochemistry. An apparently analogous split into two peaks commonly occurs for the C₂₈ 5 α ,14 α ,17 α (H)-20S sterane (peaks 25a and 25b in Fig. 1), but not for the $\alpha\alpha\alpha$ 20R epimer (peak 28 in Fig. 1). The two 13 β ,17 α (H)-20S diasteranes (peaks 23a and b) are more abundant and better resolved than the 13 β ,17 α (H)-20R diasteranes (peaks 24a and b). This is directly analogous to the 5 α ,14 α ,17 α (H)-20S steranes (peaks 25a and b), which are more abundant and better resolved than the $\alpha\alpha\alpha$ 20R steranes (broad peak 28). The four diasteranes show higher concentrations and elute earlier than the corresponding steranes (Fig. 1), which is consistent with their comparatively better peak resolution.

Bauer et al. (1985) prepared two of the four diasteranes represented by peaks 23a, 23b, 24a, and 24b (Fig. 1). As discussed above, both of the prepared diaergostanes have 24R stereochemistry, but one is 20S and the other 20R. They referred to these compounds as (13R,17R,20S,24R)- and (13R,17R,20R,24R)-diasteranes, which we describe as 13 β ,17 α (H)-20S,24R and 13 β ,17 α (H)-20R,24R diaergostane, respectively. In addition, both of these diaergostanes have 5 β (CH₃)- and 13 β ,17 α (H)-stereochemistry based on the X-ray structure of a 20S ketone reaction intermediate (Fig. 1 in Bauer et al., 1985). Fig. 2 shows the stereochemistry of the 20S,24R diaergostane prepared by Bauer et al. (1985). The Bauer et al. (1985) standards should co-elute with two of the four diaergostane peaks. For example, if one standard co-elutes with 13 β ,17 α (H)-20R,24R, then, by elimination, the other peak in the doublet must be 13 β ,17 α (H)-20R,24S. In summary, our primary objective is to identify and characterize the 24R and 24S diastereomers of diaergostane (20S and 20R) that occur in petroleum.

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