

REARRANGED STERANES IN SEDIMENTS AND CRUDE OILS.

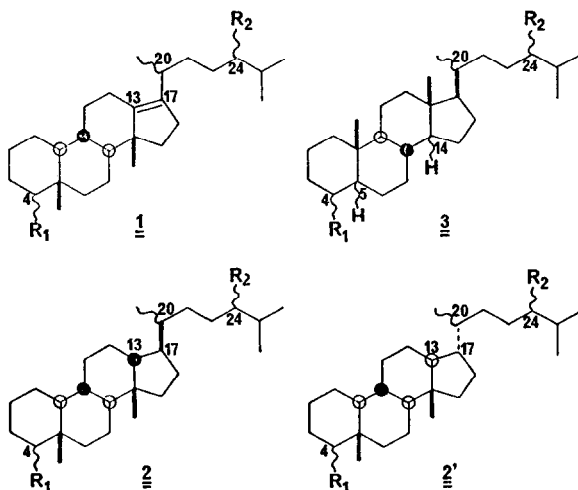
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One of the aims of organic geochemistry is to get a better knowledge of the structural changes undergone by biological molecules during and after their burial in the sedimentary environment. Some of these changes already appear during diagenesis in the recent sediments and probably result from microbial influence ¹. In a later stage the concomitant effects of temperature and catalytic activity of minerals induce further changes, such as defunctionalisation, isomerisations and cracking of carbon-carbon bonds. That the carbon skeleton of complex molecules, such as steroids, can still be preserved far into an advanced stage of maturation is evident from the presence of various steranes in ancient sediments and crude oils ². However the steroid skeleton does undergo structural changes, under mild geological conditions, one of these being the backbone rearrangement of sterenes which leads to $\Delta^{13(17)}$ rearranged sterenes 1 ³.

We would now like to report the identification of a series of steranes with a backbone rearranged skeleton 2 and 2' in sediments and crude oils of various origins where they occur along with normal steranes 3 and triterpanes of the hopane type 4 (table 1). In order to simplify the nomenclature we propose to call these new compounds "diasteranes", the stereochemistry of the hydrogens at C-13 and C-17 being referred to as α or β . E.g. the $13\beta,17\alpha(H)$ rearranged cholestane will be called $\beta\alpha$ -diacholestane 2a.



- a. $R_1 = R_2 = H$
- b. $R_1 = H, R_2 = CH_3$
- c. $R_1 = H, R_2 = C_2H_5$
- d. $R_1 = CH_3, R_2 = H$
- e. $R_1 = R_2 = CH_3$
- f. $R_1 = CH_3, R_2 = C_2H_5$

20R and 20S

TABLE 1 : Samples analyzed for rearranged steranes *

	- Seven marine oil shales from various locations and depths in the Lower Toarcian formation of the Paris basin (180×10^6 years)
<u>Sediments</u>	- Two continental oil shales : Messel and Stockstadt (W. Germany ; Eocene ; 50×10^6 years)
	- One shale from the Upper Cretaceous of Gaboon.
	- Three oils ranging from Triassic to Upper Cretaceous in the Paris basin
<u>Crude oils</u>	- Several oils from Tunisia (Eocene)
	- One oil from the Upper Cretaceous of Gaboon.

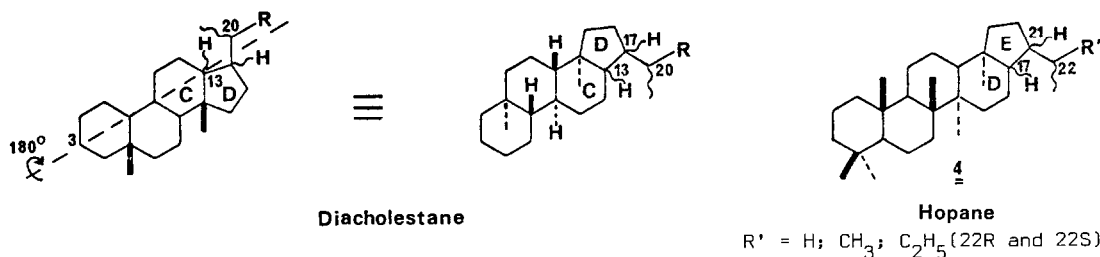
* All the samples contain significant amounts of diasteranes, except the very immature Messel shale where no trace could be detected.

The analytical procedure used has been described in detail previously³. Stainless steel capillary columns were coated with Apiezon L or OV 101. Large use has been made of mass fragmentography with GC-MS-computer coupling in order to elucidate complex mixtures.

More than fifty peaks were separated from the complex mixture of branched and cyclic alkanes of a marine oil shale from the Lower Toarcian formation of the Paris basin (180×10^6 years) as seen on figure 1 which only shows the part of the chromatogram corresponding to steranes. The more volatile part mainly contains acyclic isoprenoids and the less volatile part C_{32} - C_{35} triterpanes of the hopane type⁴. Peak numbers refer to table 2.

Four diasteranes were identified by co-elution with authentic standards on two capillary columns (OV 101 and Apiezon L) and comparison of their mass spectra : $\beta\alpha$ -diacholestanes 20S ($\underline{2a}$, peak 3) and 20R ($\underline{2a}$, peak 4)⁵, 4-methyl- $\beta\alpha$ -diacholestanes 20S ($\underline{2d}$, peak 12) and 20R ($\underline{2d}$, peak 13). The latter two compounds were synthesised by backbone rearrangement of the corresponding 4 α -methyl-cholest-5-ene under usual conditions⁶, separation of the 20R and 20S diasterenes, followed by reduction of the $\Delta^{13(17)}$ double bond (PtO₂, AcOH, trace HClO₄).

The structure of eight other homologous diasteranes was deduced from their relative retention times and their mass spectral fragmentation patterns as compared with the compounds $\underline{2a}$ and $\underline{2d}$: 24-methyl- $\beta\alpha$ -diacholestanes 20S ($\underline{2b}$, peak 9) and 20R ($\underline{2b}$, peak 11), 24-ethyl $\beta\alpha$ -diacholestanes 20S ($\underline{2c}$, peak 14) and 20R ($\underline{2c}$, peak 16), 4,24-dimethyl- $\beta\alpha$ -diacholestanes 20S ($\underline{2e}$, peak 22) and 20R ($\underline{2e}$, peak 26), 4-methyl-24-ethyl- $\beta\alpha$ -diacholestanes 20S ($\underline{2f}$, peak 31) and 20R ($\underline{2f}$, peak 37). The methyl group at C-4 is most probably α .



Further conclusions can be obtained from the close structural analogy of the C-D rings in diasteranes and the D-E rings in hopanes. Since hydrogenation under acidic conditions (PtO₂, AcOH, trace HClO₄) of hop-17(21)-ene mainly yields 17 α ,21 β (H)-hopane and small amounts of $\beta\alpha$ -hopane⁷, we can assume that the minor products obtained by hydrogenation of the 20S and 20R $\Delta^{13(17)}$ diacholestenes and eluted after 20S and 20R $\beta\alpha$ -diacholestanes are the $\alpha\beta$ -diacholestanes 20S and 20R ($\underline{2'a}$). Co-elution of these two $\alpha\beta$ -diacholestanes (20S and 20R)

enhanced peaks 6 and 7. The two 20S and 20R 4-methyl- $\alpha\beta$ -diacholestanes ($\underline{2}'a$) obtained as minor products by hydrogenation of the 4-methyl- $\Delta^{13(17)}$ -diacholestenes (20S and 20R) enhanced peaks 19 and 21. These results are further confirmed by the identical mass spectral fragmentation patterns. Peaks 27, 32 and 35 were tentatively identified as homologous compounds, respectively : 24-ethyl- $\alpha\beta$ -diacholestane (20R or 20S) ($\underline{2}'c$) and 4,24-dimethyl- $\alpha\beta$ -diacholestanes 20R and 20S ($\underline{2}'e$) from their mass spectra and their relative retention times.

It can be assumed at this stage that the rearranged steranes which we have identified arise by hydrogenation under geochemical conditions of the precursor diasterenes $\underline{1}$ which are still present as such in the more immature part of the Lower Toarcian formation of the Paris basin ³. This new class of biological markers reflects the complexity of the changes undergone by steroids in the geological environment. Furthermore diasteranes can also be useful as correlation markers among crude oils or between crude oils and their source rocks ⁸⁻¹⁰.

N° of compound	Formula	STRUCTURE	N° of compound	Formula	STRUCTURE
1, 2	C ₂₇ H ₄₈	Rearranged steranes	28, 33	C ₂₈ H ₅₀	Methylcholestanes
3	C ₂₇ H ₄₈	* $\beta\alpha$ -diacholestane 20S	31	C ₃₀ H ₅₄	4-methyl-24-ethyl- $\beta\alpha$ -diacholestane 20S
4	C ₂₇ H ₄₈	* $\beta\alpha$ -diacholestane 20R	32	C ₂₈ H ₅₂	4,24-dimethyl- $\alpha\beta$ -diacholestane 20S or 20R
5,8	C ₂₈ H ₅₀	Rearranged steranes	35	C ₂₉ H ₅₂	4,24-dimethyl- $\alpha\beta$ -diacholestane 20R or 20S
6	C ₂₇ H ₄₈	$\alpha\beta$ -diacholestane 20S or 20R	36	C ₂₈ H ₅₀	*4 α -methylcholestane
7	C ₂₇ H ₄₈	$\alpha\beta$ -diacholestane 20R or 20S	37	C ₃₀ H ₅₄	4-methyl-24-ethyl- $\beta\alpha$ -diacholestane 20R
9	C ₂₈ H ₅₀	24-methyl- $\beta\alpha$ -diacholestane 20S	38,41	C ₃₀ H ₅₄	Rearranged 4-methylsteranes
10	C ₂₉ H ₅₂	Rearranged sterane	39	C ₂₈ H ₅₀	*24-methylcholestane
11	C ₂₈ H ₅₀	24-methyl- $\beta\alpha$ -diacholestane 20R	42	C ₂₈ H ₅₀	*4 β -methylcholestane
12	C ₂₈ H ₅₀	*4-methyl- $\beta\alpha$ -diacholestane 20S	43	C ₂₉ H ₅₂	*24-ethyl-5 β -cholestane
13	C ₂₈ H ₅₀	*4-methyl- $\beta\alpha$ -diacholestane 20R	44, 45	C ₃₀ H ₅₄	Rearranged 4-methylsteranes
14	C ₂₉ H ₅₂	24-ethyl- $\beta\alpha$ -diacholestane 20S	47	C ₂₈ H ₅₀	4 α ,24-dimethylcholestane
15	C ₂₇ H ₄₈	*5 β -cholestane (coprostane)	48	C ₂₉ H ₅₂	*24-ethylcholestane
16	C ₂₉ H ₅₂	24-ethyl- $\beta\alpha$ -diacholestane 20R	50,54,55	C ₃₀ H ₅₄	Methylsteranes
19	C ₂₈ H ₅₀	4-methyl- $\alpha\beta$ -diacholestane 20S or 20R	51	C ₂₉ H ₅₀	*C ₂₉ $\alpha\beta$ -hopane
20	C ₂₉ H ₅₂	Rearranged 4-methylsterane	52	C ₂₈ H ₅₂	4 β ,24-dimethylcholestane
21	C ₂₈ H ₅₀	4-methyl- $\alpha\beta$ -diacholestane 20R or 20S	56	C ₃₀ H ₅₄	4 α -methyl-24-ethylcholestane
22	C ₂₉ H ₅₂	4,24-dimethyl- $\beta\alpha$ -diacholestane 20S	60	C ₃₀ H ₅₂	*C ₃₀ $\alpha\beta$ -hopane
23,24,29,34	C ₃₀ H ₅₄	Rearranged 4-methylsteranes	64	C ₃₀ H ₅₂	*C ₃₀ $\beta\alpha$ -hopane
25	C ₂₇ H ₄₈	*5 α -cholestane	67	C ₃₁ H ₅₄	*C ₃₁ $\alpha\beta$ -hopane
26	C ₂₉ H ₅₂	4,24-dimethyl- $\beta\alpha$ -diacholestane 20R	68	C ₃₁ H ₅₄	*C ₃₁ $\alpha\beta$ -hopane
27	C ₂₉ H ₅₂	24-ethyl- $\alpha\beta$ -diacholestane 20S or 20R			

TABLE 2 : Diasteranes and methyl-diasteranes from shales and crude oils (some hopane triterpanes are also included). Compounds marked with * have been identified by direct comparison with authentic standards.

Mass spectral data :

$\beta\alpha$ -diacholestanes (20R or 20S) : m/e = 372 (M⁺, 35 %), 357 (15 %), 315 (5 %), 287 (10 %), 259 (43 %), 217 (66 %), 203 (12 %), 189 (38 %), 177 (20 %), 163 (38 %), 149 (53 %), 95 (100 %).

4-methyl- $\beta\alpha$ -diacholestanes (20R or 20S) : m/e = 386 (M⁺, 66 %), 371 (40 %), 315 (100 %), 301 (8%), 273 (35 %), 231 (34 %), 203 (36 %).

$\alpha\beta$ -diacholestanes (20R or 20S) : m/e = 372 (M⁺, 36 %), 357 (22 %), 315 (3 %), 287 (5 %), 259 (28 %), 232 (46 %), 217 (80 %), 203 (12 %), 189 (82 %), 177 (18 %), 163 (56 %), 149 (47 %), 95 (100 %).

4-methyl $\alpha\beta$ -diacholestanes (20R or 20S) : m/e = 386 (M⁺, 60 %), 371 (86 %), 315 (57 %), 301 (8 %), 273 (34 %), 246 (38 %), 231 (34 %), 203 (57 %), 95 (100 %).

DONTRIEN

Steranes and diasteranes

Apiezon L 50m x 0.5mm

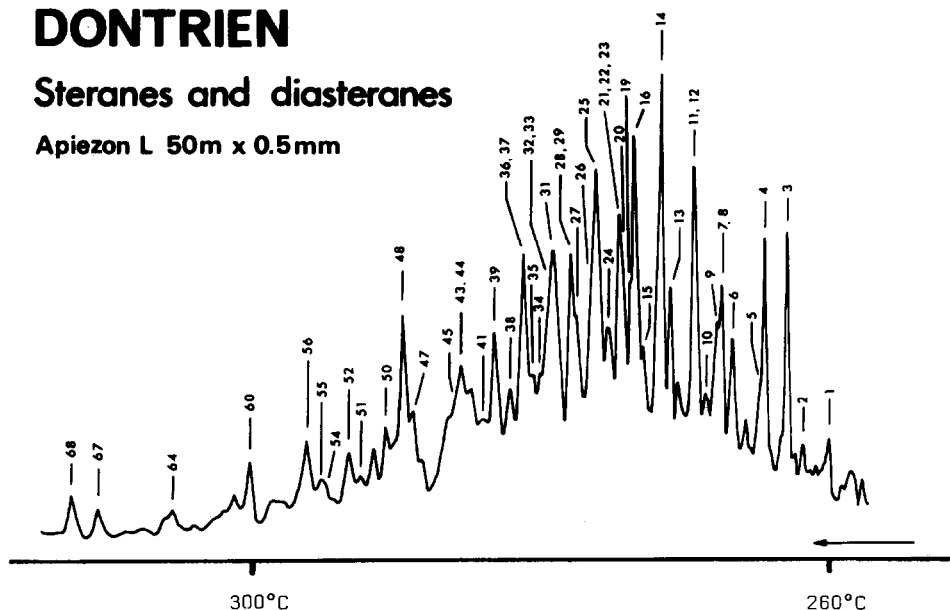


FIGURE 1 : Gas chromatogram of the branched and cyclic alkanes of DONTRIEN shale (depth : 1325 m)¹¹. Apiezon L, 50 m : 0.5 mm ; 160-300°C, 3°/min. Peak numbers refer to table 2. Missing numbers correspond to very minor peaks often present in greater amounts in other samples.

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