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HR GC and GC-MS Study of Steroids in Northern Croatian Petroleum

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Since steranes might be of pharmaceutical utility, Northern Croatian petroleums were selected for a steroid study by HR GC: sample PI with a hilly elevated base of chromatograms at the heavy end (where steroids eluate) and with intensive *n*-alkanes; PII rich in *n*-alkanes with a comparatively flat heavy end; and PIII with a remarkably elevated heavy end, but poor in *n*-alkanes.

The fraction of saturates was studied for steranes by GC-MS, also the fraction of aromatics for MA and TA steroids. Mass spectra and mass fragmentograms m/z 217, m/z 253 and m/z 231, were used.

In 3 select samples (out of 43 petroleums), the steranes were determined in the range from norcholestanes up to *n*-propylcholestanes, making 3000––9000 ppm of saturates. So, it might be considered that there are Croatian petroleum samples which contain steranes in concentrations interesting for pharmaceutical purposes. Cholestanes, ergostanes and stigmastanes are dominant while the concentrations of diasteranes are low.

PIII is the sterane richest sample. Its characteristics are low epimerization of sterane skeletons, regarding H at C atoms in position 14, 17 and 20, as well as *n*-alkanes diminishing by biodegradation. PIII also contains the relatively highest TA steroid concentration.

The intensity proportion between TA steroids and MA steroids is highest for PII. This can be visualized by the thermal stress absorbed and it is in good agreement with the comparatively highest epimerization level.

INTRODUCTION

Steranes are thought[1] possibly to be curable constituents of petroleum (fractions). Since Northern Croatian petroleum is used for preparatives in skin treatment, it is found that steroids in Northern Croatian petroleum deserve to be studied.

In petroleums and other geochemical samples, steroids are ubiquitously present.[2] They are considered to be derived from biogenic steroids[3] which were, millions of years ago, incorporated into the biomass where they built together phospholipids, the lipid bilayer of the cell and nucleus membranes of eukaryots. When deposited at low

Eh (anoxic conditions) and pH higher than 7, steroids start converting[4] to steranes by losing the hydroxy group and by saturation of the 5,6 double bond. Steranes at the beginning conserve the biological stereoconfiguration 14α(H)17α(H)20*R*, which afterwards, by absorbing thermal stress, isomerize until the equilibrium 14α(H)17α(H)20*R* : : 14β(H)17β(H)20*R* : 14β(H)17β(H)20*S* : 14α(H)17α20(H)*S* $\approx$ 1:3:3:1, is reached.[2]

At lower pH under suboxic conditions, the angular methyl groups may rearrange from positions 10 and 13 to positions 5 and 14,[5] and diasteranes are generated.

Sterols might, in dependence on the original structure and on the conditions, convert to monoaromatic steroids[4] (MA-steroids), first by aromatizing the C-ring. By thermal stress, the A and B rings aromatize, generating triaromatic steroids (TA-steroids).

EXPERIMENTAL

Petroleum samples from 43 drilling wells in the Croatian Subbasin, Pannonian Basin, underwent investigation by high resolution gas chromatography (HR GC). Among 27 samples which generated gas chromatograms with heavy ends (exceeding 27 C atoms in molecules), 8 samples were submitted to fractionation. This included distillation at 200 °C; maltene separation by asphaltene precipitation in *n*-heptane; fractionation of maltenes by liquid column chromatography (LC) (Al_2O_3/SiO_2), using eluents of different polarity, into a mixture of normal+*iso*+cycloalkanes (saturates), into a mixture of compounds containing at least one aromatic ring (aromatics) and into a mixture of constituents with polar functional groups (polars).

According to gas chromatograms (GC conditions in Figure 1) and fractionation yields, 3 samples were selected for the study of steroids. For this purpose, their saturates and aromatics were subjected to high resolution gas chromatography – mass spectrometry (GC – MS). The identification of steroids was performed by full mass spectra taken for the peaks indicated by mass fragmentograms; m/z 217 for steranes (studied in saturates), m/z 253 for MA-steroids and m/z 231 for TA-steroids (aromatic steroids were studied in aromatics). (In literature[2,4,6], mass fragmentograms m/z 191 are often used in the studies of oligocyclic terpenoids.) For spectra interpretation, the published spectra[7] and a comparison of mass fragmentograms with published[2,4,7] and unpublished[12] fingerprints were used.

The fraction yields are expressed as weight percentages. The ratios between *n*-alkanes and *iso*+cycloalkanes were measured in gas chromatograms of saturates (according to peak areas with no correction factors). For comparison of the 3 select samples regarding sterane content, *ca.* 100 ppm (97 ppm in PI, 113 ppm in PII and 104 ppm in PIII) of β-cholane, as the internal standard, was added into the corresponding saturates. Peak heights compared with β-cholane in mass fragmentograms m/z 217 (with no correction factors) served for sterane intensity comparison between the samples. Due to lack of internal standards, for intensity comparison of the aromatic steroids, the absolute intensity response of the peak coeluating TA cholestane 20*R* + TA ergostane 20*S* (peak 2+3 in Figure 4) was taken. The 3 samples were injected one after another five times. The average values, normalized to the sample mass unit, were compared. In the same experiment, the relations of MA sterois to TA steroids are compared as the ratios of the absolute intensity of MA stigmastane 20*R* (peak 18 in Figure 3) to TA stigmastane 20*R* (peak 7 in Figure 4).

RESULTS

Gas chromatograms enabled a rough division of 27 petroleum samples into 3 groups which might be represented by the samples PI, PII and PIII (Figure 1A–1C).

The composition of the 3 petroleum groups is illustrated in Table I with fraction yields in the distillation residue (b.p. ≥ 220 °C in order to avoid the influence of evaporation losses). These are maltenes and their subfractions and asphaltenes (Table I).

The proportions of the *n*-alkane content to the *iso*+cycloalkane content obtained by HR GC, are also presented in the same table.

TABLE I

Composition of Northern Croatian petroleum samples

Sample	Maltenes: Asphaltenes	Saturates*			Aromatics*	Polars*
		mas. %	Alkanes** %n	HR GC % $\sum$i+cy		
PI	23 : 1	72.3	56.7	43.3	16.5	11.2
PIa	21 : 1	70.6	57.4	42.6	16.9	12.5
PIb	23 : 1	73.4	53.1	46.9	15.5	11.1
PII	26 : 1	76.1	60.6	39.4	17.8	6.1
PIIa	27 : 1	72.5	57.1	42.9	19.7	7.8
PIIb	28 : 1	72.2	59.8	40.2	19.9	7.9
PIII	20 : 1	51.8	19.5	80.5	26.3	21.9
PIIIa	18 : 1	47.6	16.3	83.7	29.3	23.1

* In maltenes
** In saturates

Mass fragmentograms for steranes (m/z 217) of samples PI, PII and PIII are shown in Figures 2A–2C. The peak numbers correspond to the related compounds in Table II.

24 Steranes in the range of norocholestanes up to *n*-propylcholestanes, including regular and rearranged ones, were determined. For most of the compounds, the stereoconfiguration might be drawn with the help of published and unpublished data[12] which were supported by full mass spectra.

Regardless of the fact that the proportions of sterane peak heights in mass fragmentograms do not exactly present their concentration ratios (no response correction factors used), normalization by means of β-cholane is applied in sterane intensity comparison of the 3 select samples. The proportion of specific steranes in each of the examined samples, is also given in Table III.

Mass fragmentograms of m/z 253, corresponding to MA steroids, and of m/z 231, corresponding to TA steroids, are shown in Figures 3 and 4, respectively, and the related compounds in Tables IV and V.

18 MA steroids and 7 TA steroids are determined.

The three samples studied might be arranged, according to the indicated intensity of TA steroids, as follows:

$$\text{PIII} > \text{PII} > \text{PI}$$

The ratio between the absolute intensity response of TA stigmastane (peak 7 in Figure 4) to MA stigmastane (peak 18 in Figure 3) (average over 5 experiments) is 1:0.19 for PI, 1:0.11 for PII, and 1:0.23 for PIII.

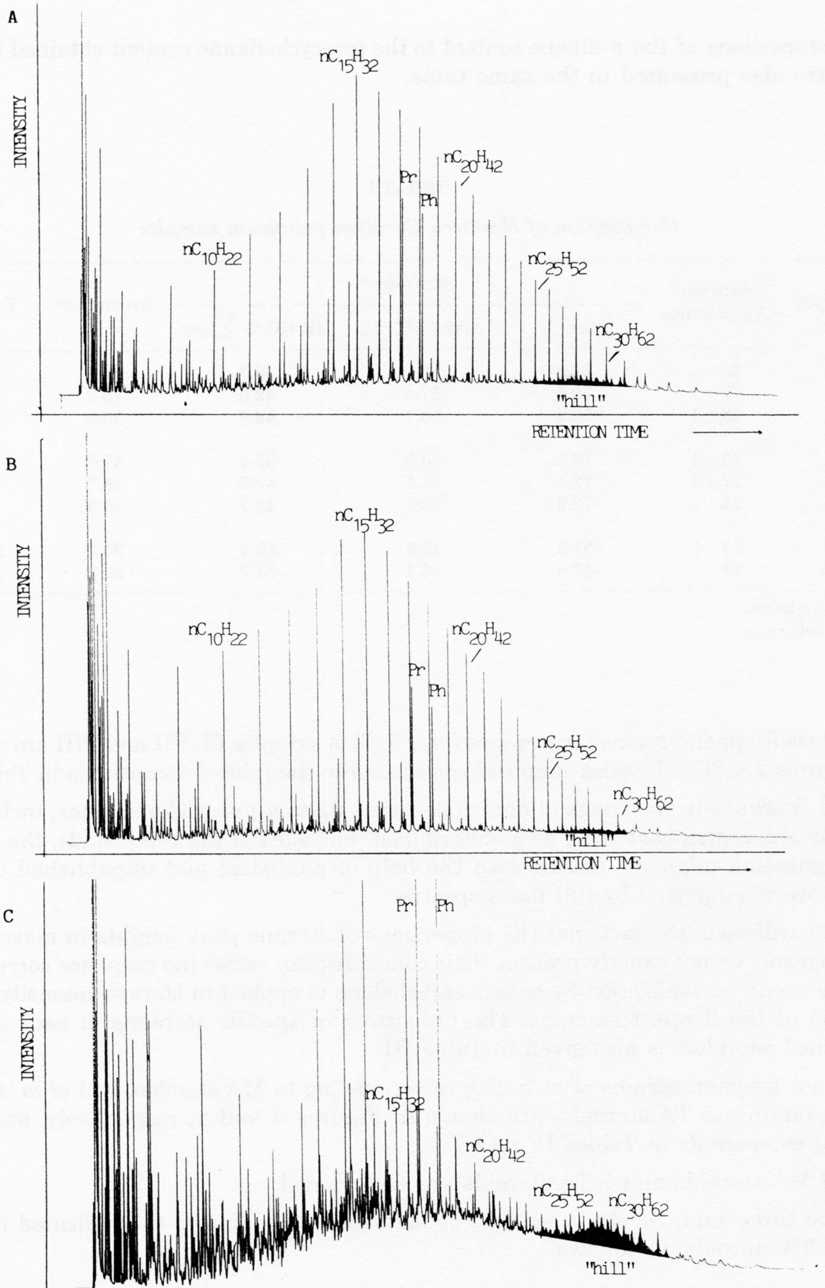


Figure 1. Gas chromatograms produced by non-polar fused silica capillary column (ø 0.25, length 25 m) at oven temperature of 50 °C $\xrightarrow{10\ °\mathrm{C\ min}^{-1}}$ 30 °C, A) sample PI, B) sample PII, and C) sample PIII. Intensive peaks in A) and B) present as a homologous range belong to *n*-alkanes. The »hill« at the heavy end is drawn in black.

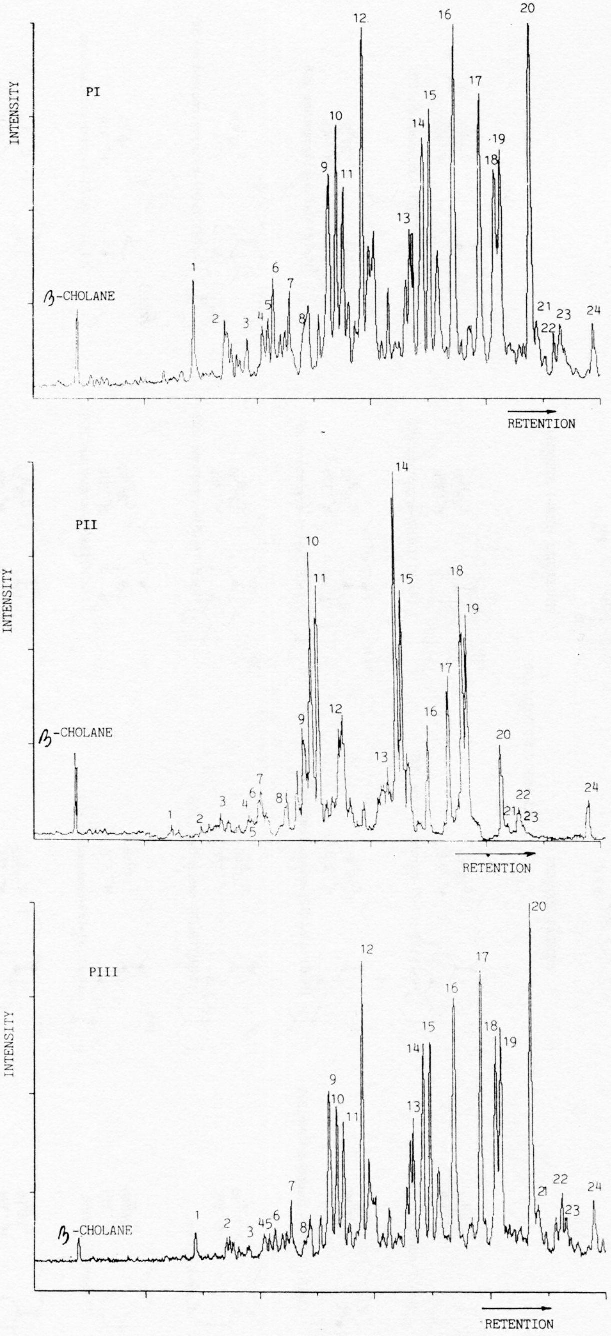
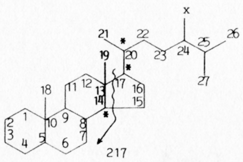
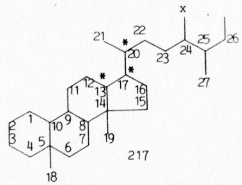


Figure 2. Mass fragmentograms m/z 217 for steranes: A) sample PI, B) sample PII and C) sample PIII. Peak numbers in mass fragmentograms correspond to the related compounds in Table II.

TABLE II *Steranes determined in mass fragmentogram* m/z *217.*

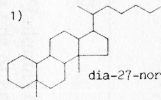


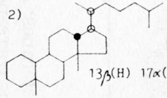
REGULAR STERANES

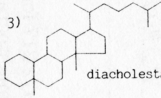


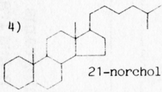
REARRANGED (DIA-) STERANES

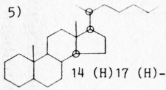
*EPIMERIZING POSITIONS

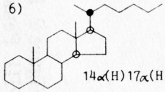
1)

$C_{26}H_{46}$
$M^{+\cdot}$ 358
dia-27-norcholestane

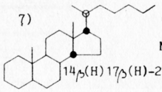
2)

$C_{27}H_{48}$
$M^{+\cdot}$ 372
13β(H) 17α(H)-diacholestane 20S

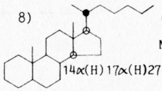
3)

$C_{27}H_{48}$
$M^{+\cdot}$ 372
diacholestane

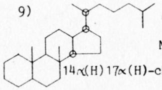
4)

$C_{26}H_{46}$
$M^{+\cdot}$ 358
21-norcholestane

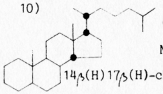
5)

$C_{26}H_{46}$
$M^{+\cdot}$ 358
14 (H)17 (H)-norcholestane 20S

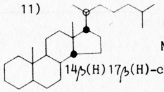
6)

$C_{26}H_{46}$
$M^{+\cdot}$ 358
14α(H)17α(H)27-norcholestane 20R

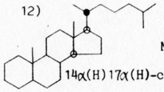
7)

$C_{26}H_{46}$
$M^{+\cdot}$ 358
14β(H)17β(H)-27-norcholestane 20S

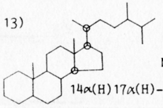
8)

$C_{26}H_{46}$
$M^{+\cdot}$ 358
14α(H)17α(H)27-norcholestane 20R

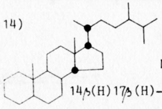
9)

$C_{27}H_{48}$
$M^{+\cdot}$ 372
14α(H)17α(H)-cholestane 20S

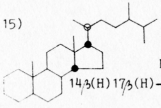
10)

$C_{27}H_{48}$
$M^{+\cdot}$ 372
14β(H)17β(H)-cholestane 20R

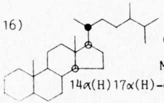
11)

$C_{27}H_{48}$
$M^{+\cdot}$ 372
14β(H)17β(H)-cholestane 20S

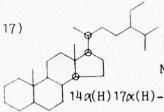
12)

$C_{27}H_{48}$
$M^{+\cdot}$ 372
14α(H)17α(H)-cholestane 20R

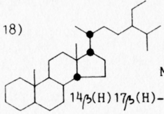
13)

$C_{28}H_{50}$
$M^{+\cdot}$ 386
14α(H)17α(H)-ergostane 20S

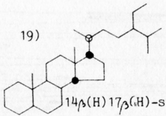
14)

$C_{28}H_{50}$
$M^{+\cdot}$ 386
14β(H)17β(H)-ergostane 20R

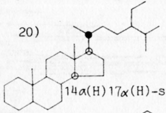
15)

$C_{28}H_{50}$
$M^{+\cdot}$ 386
14β(H)17β(H)-ergostane 20S

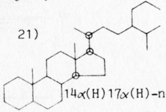
16)

$C_{28}H_{50}$
$M^{+\cdot}$ 386
14α(H)17α(H)-ergostane 20R

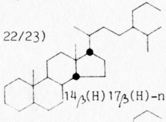
17)

$C_{29}H_{52}$
$M^{+\cdot}$ 400
14α(H)17α(H)-stigmastane 20S

18)

$C_{29}H_{52}$
$M^{+\cdot}$ 400
14β(H)17β(H)-stigmastane 20R

19)

$C_{29}H_{52}$
$M^{+\cdot}$ 400
14β(H)17β(H)-stigmastane 20S

20)

$C_{29}H_{52}$
$M^{+\cdot}$ 400
14α(H)17α(H)-stigmastane 20R

21)

$C_{30}H_{54}$
$M^{+\cdot}$ 414
14α(H)17α(H)-n-propylcholestane 20S

22/23)

$C_{30}H_{54}$
$M^{+\cdot}$ 414
14β(H)17β(H)-n-propylcholestanes

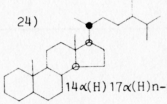
24)

$C_{30}H_{54}$
$M^{+\cdot}$ 414
14α(H)17α(H)n-propylcholestane 20R

TABLE III

Relative sterane intensity in the select samples of Northern Croatian petroleums.

Samples	^{1}Reg+^{2}Dia	$(\text{Reg+Dia})\times\frac{\%\ \text{saturates}}{100}$	$\frac{100\ ^{3}\text{ChES}}{\text{Reg+Dia}}$	$\frac{100\ \text{Dia}}{\text{Reg}}$	^{4}Ch : E : S	^{5}Epimerization
PI	4982	3602	80.5	5.5	1.0 : 1 : 1.1	1 : 0.7 : 0.8 : 1.3
PII	2943	2240	88.1	1.4	0.9 : 1 : 0.9	1 : 1.6 : 1.5 : 0.6
PIII	9211	4771	86.2	2.1	1.0 : 1 : 1.3	1 : 0.7 : 0.8 : 1.2

[1] Reg = summ of the peak heights of the steranes 4–24 (Figure 2, Table II) ($\sum\limits_{4-24} H_P$)

normalized to the peak heights equivalent to 1 ppm of β-cholane (H_{P1ppm}); $\frac{\sum\limits_{4-24} H_P}{H_{P1ppm}}$

$$^{2}\text{Dia} = \frac{\sum\limits_{1-3} H_P}{H_{P1ppm}} \qquad ^{3}\text{ChES} = \frac{\sum\limits_{9-20} H_P}{H_{P1ppm}} \qquad ^{4}\text{Ch : E : S} = \frac{\sum\limits_{9-12} H_P : \sum\limits_{13-16} H_P : \sum\limits_{17-20} H_P}{\sum\limits_{13-16} H_P}$$

[5] Epimerization = epimerization ratio among stigmastane peaks 17, 18, 19 and 20; normalized to peak 17

$$\text{Epimerization} = \frac{H_{P17} : H_{P18} : H_{P19} : H_{P20}}{H_{P17}}$$

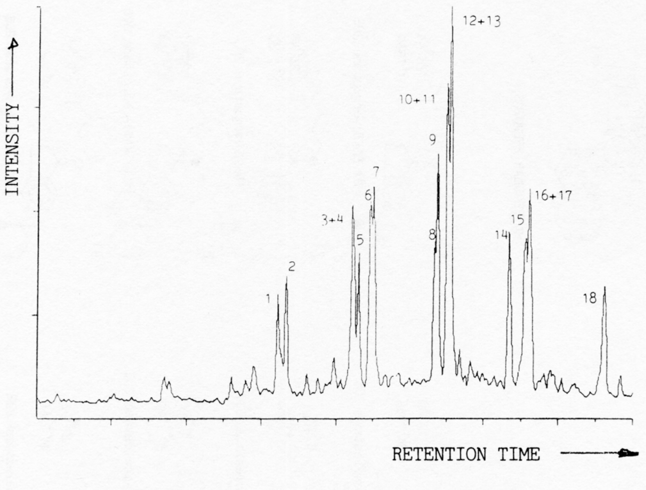
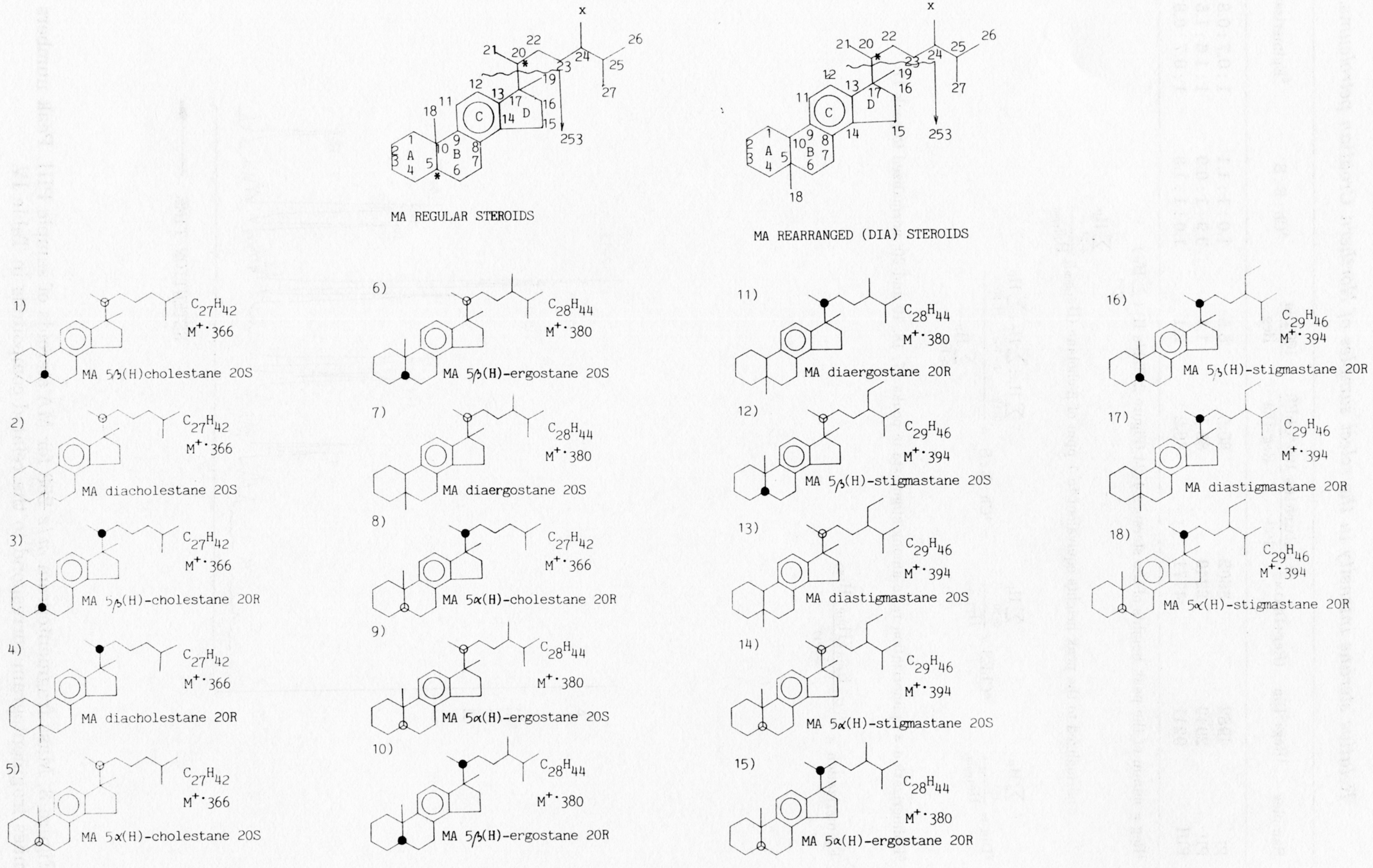


Figure 3. Mass fragmentogram m/z 253 for MA steroids of sample PIII. Peak numbers in the mass fragmentogram correspond to the related compounds in Table IV.

TABLE IV *Monoaromatic steroids determined in mass fragmentogram* m/z *253.*



MA REGULAR STEROIDS

MA REARRANGED (DIA) STEROIDS

1) $C_{27}H_{42}$ $M^{+\cdot}$ 366 MA 5β(H)cholestane 20S

2) $C_{27}H_{42}$ $M^{+\cdot}$ 366 MA diacholestane 20S

3) $C_{27}H_{42}$ $M^{+\cdot}$ 366 MA 5β(H)-cholestane 20R

4) $C_{27}H_{42}$ $M^{+\cdot}$ 366 MA diacholestane 20R

5) $C_{27}H_{42}$ $M^{+\cdot}$ 366 MA 5α(H)-cholestane 20S

6) $C_{28}H_{44}$ $M^{+\cdot}$ 380 MA 5β(H)-ergostane 20S

7) $C_{28}H_{44}$ $M^{+\cdot}$ 380 MA diaergostane 20S

8) $C_{27}H_{42}$ $M^{+\cdot}$ 366 MA 5α(H)-cholestane 20R

9) $C_{28}H_{44}$ $M^{+\cdot}$ 380 MA 5α(H)-ergostane 20S

10) $C_{28}H_{44}$ $M^{+\cdot}$ 380 MA 5β(H)-ergostane 20R

11) $C_{28}H_{44}$ $M^{+\cdot}$ 380 MA diaergostane 20R

12) $C_{29}H_{46}$ $M^{+\cdot}$ 394 MA 5β(H)-stigmastane 20S

13) $C_{29}H_{46}$ $M^{+\cdot}$ 394 MA diastigmastane 20S

14) $C_{29}H_{46}$ $M^{+\cdot}$ 394 MA 5α(H)-stigmastane 20S

15) $C_{28}H_{44}$ $M^{+\cdot}$ 380 MA 5α(H)-ergostane 20R

16) $C_{29}H_{46}$ $M^{+\cdot}$ 394 MA 5β(H)-stigmastane 20R

17) $C_{29}H_{46}$ $M^{+\cdot}$ 394 MA diastigmastane 20R

18) $C_{29}H_{46}$ $M^{+\cdot}$ 394 MA 5α(H)-stigmastane 20R

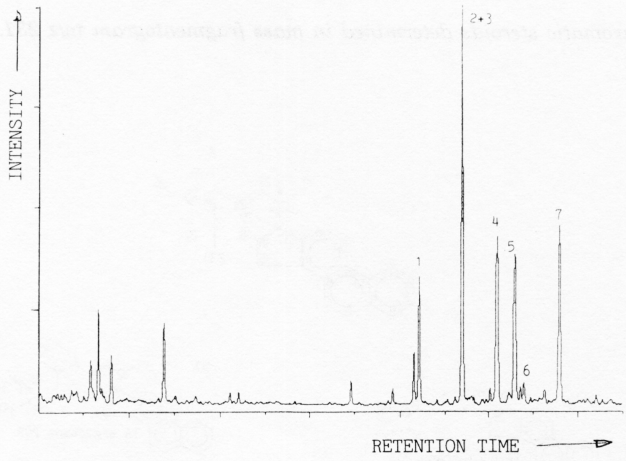


Figure 4. Mass fragmentogram m/z 231 for TA steroids in sample PIII. Peak numbers in the mass fragmentogram correspond to the related compounds in Table V.

DISCUSSION

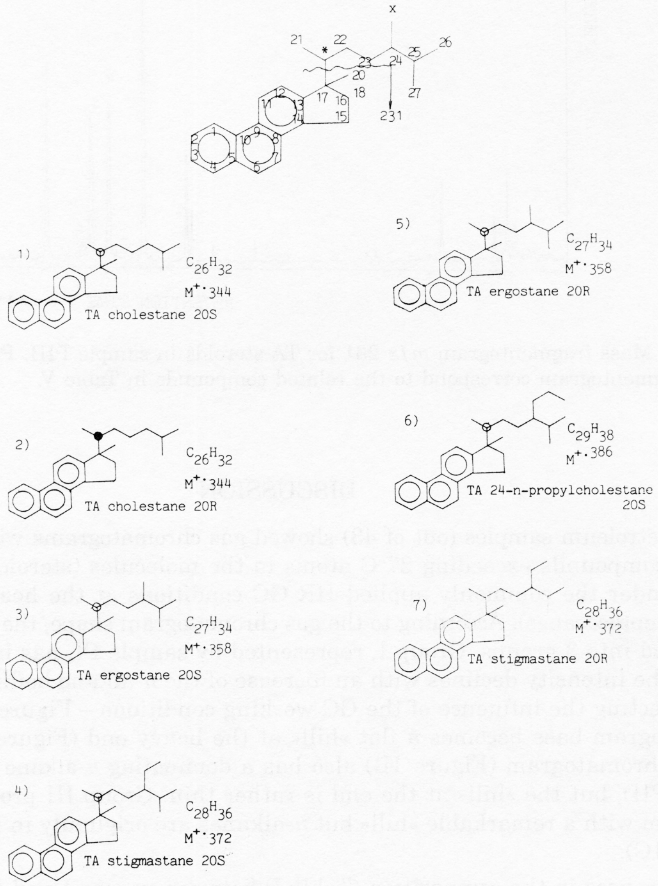
27 Petroleum samples (out of 43) showed gas chromatograms with heavy end containing compounds exceeding 27 C atoms in the molecules (steroids are known[2,6] to eluate under the commonly applied HR GC conditions at the heavy end – roughly around heptacosanes). According to the gas chromatogram shape, the 27 samples might be divided into 3 groups. Group I, represented by sample PI, has intensive *n*-alkane peaks. The intensity declines with an increase of the *n*-alkane boiling point, presumably reflecting the influence of the GC working conditions – Figure 1 (A and B). The chromatogram base becomes a flat »hill« at the heavy end (Figure 1A). The second type of chromatogram (Figure 1B) also has a dominating *n*-alkane content (group II, sample PII), but the »hill« at the end is rather thin. Group III produces a gas chromatogram with a remarkable »hill« but *n*-alkanes are originally in low concentration (Figure 1C).

Differences in the composition (Table I) between groups I and II are reflected in the polars and asphaltene content while no significant difference in saturates has been noticed. Group III is comparatively low in saturates, which possibly influences) the aromatics and polars to be relatively high. Also, *iso*+cycloalkanes dominate in the saturates of PIII.

The difference in the composition of petroleum samples, as mirrored in the gas chromatograms and fraction yields, should not be ascribed to different petroleum sources (a common, algal type source for all 43 examined Northern Croatian petroleum samples has been proved[8,9]). Theories of geogenic alteration might offer the explanation.[2,10] The algal type petroleum source produces, at an early stage of petroleum generation, the hydrocarbon mixture, reflected in the bimodal distribution and the »hill« at the end is remarkably expressed for example PI). By absorption of thermal energy, the source turns to a more mature stage when the »hill« flattens.[2]

TABLE V

Triaromatic steroids determined in mass fragmentogram m/z *231.*



Natural processes of *n*-alkanes diminishing (biodegradation) in the relatively cold geological petroleum traps are explained[10] by microbe activity when petroleum contistuents are consumed in a selective successive range starting with *n*-alkanes, then *iso*- and cycloalkanes, to aromatics and polars.[11] Sample PIII reflects a loss of *n*-alkanes by biodegradation.

Each of the three samples studied for steranes is found to contain all of the 24 steranes determined (Table II, Figures 2A–2C), by comparison with the published data, sterane intensity in Northern Croatian samples might be considered to be comparatively high. This information might serve as an encouragement for developing preparation a technology for a petroleum fraction rich in steranes (and low in aromatics) for pharmaceutical needs. The high sterane content might be explained by the algal (prokaryotic) origin of Northern Croatian petroleums.[8,9] PIII seems to be the richest sample by comparing the relative sterane intensity in saturates and in the whole distillation residue (b.p. ≥ 220 °C). Regarding the common origin, the reason seems to be the naturally diminished *n*-alkanes, increasing the concentration of the remaining constituents. Also, PIII is the sample with sterane epimerization ratio far too low to reach equilibrium, and so it mirrors a rather early maturation stage. Low mature geochemical samples are known[2] to contain a relatively high sterane concentration which decreases with maturation.

The PI sample with the epimerization ratio rather similar to PIII, is comparatively lower in sterane intensity, possibly because of a high *n*-alkane content. PII might be considered as the sample related to organic matter that suffered a comparatively highest thermal stress, as reflected in its highest epimerization ratio and lowest sterane intensity.

In all the three samples, regular steranes predominate while (identified) diasteranes are low. Among the regular ones, norcholestanes and *n*-propylcholestanes account for one fifth or less. The great majority (more than 80%) are cholestanes, ergostanes and stigmastanes, which are found to be in similar proportions in all samples.

The decrease in the peak number of mass fragmentograms *m*/*z* 253 and especially *m*/*z* 231, as compared to *m*/*z* 217, is not only due to the coeluation of components but might be also explained as a consequence of aromatization. C-ring aromatization causes a loss of the C atom chirality in position 14 for regulars or in position 13 for rearranged steroids, while in position 17 hydrogen is replaced by methyl.

Epimerization of MA steroids regarding H in positions 5 and 20 is reflected in the dominant peaks of fragmentogram *m*/*z* 253 (Figure 3, Table IV); 4 epimers of MA cholestanes, 4 of MA ergostanes and 4 of MA stigmastanes. 6 MA diasteroids epimerizing in position 20 have been determined.

Among the TA steroids, 7 compounds have been determined (Figure 4, Table V). They lost the angular methyl group in positions 10 or 5 for dia-isomers (affecting the number of C atoms so as to be different in TA steroids from those in its MA steroid and non-aromatic analogs and excluding dia-isomerization). Epimerization seems to be restricted to the H atoms in *exo*-radical (H attached to the C atom in position 20). As maturation products, TA steroids were expected to be highest in PII of the 3 select samples, but they were found to be highest in PIII. This might be due to the high aromatics content (Table I) found in PIII, which is explained as *n*-alkanes loss. Actually, the TA stigmastane to MA stigmastane ratio, which serves as a reliable maturation parameter, is the highest in PII confirming its relative maturity rank.

CONCLUSIONS

HR GC accompanied by MS was used to study complex mixtures, such as steroids, in Croatian petroleum samples. It enabled determination of 23 steranes, 18 MA steroids and 7 TA steroids in Northern Croatian petroleums.

The structure of the determined steranes varied:

- in the alkyl attached to position 24 (hydrogen, methyl, ethyl and *n*-propyl);
- in releasing methyl from *exo*-radical (C in positions 21 and 27);

– in the position of angular methyl groups (regular steranes with methyl groups in positions 10 and 13 and diasteranes with methyls in positions 5 and 14); and

– in epimerization connected to chiral C atoms in positions 14/13, 17 and 20.

The results indicate that Northern Croatian petroleum samples contain remarkable concentrations of steranes. This suggests that they might be considered to be potential raw materials for pharmaceutical purposes. The concentration of steranes depends on the maturity level and the biodegradation rank. Regular cholestanes, ergostanes and stigmastanes were in the majority of the steranes in each studied sample.

The results offer a base for developing a preparation technology for a petroleum fraction of saturates rich in steranes according to pharmaceutical needs.

MA steroids (when C ring is aromatized) are found to have a structure imposing a chirality loss in positions 14 and 13 for regular and rearranged steroids, respectively; and the C atom in position 17 loses hydrogen. The variety of MA steroids is influenced by methyl group rearrangement (from position 10 to position 5), by epimerization of H in position 20 and also by the length of the radical attached to C in position 24.

Trifold aromatization causes a loss of the angular methyl group. Variations are limited to the epimerization of H in position 20 (and in alkyl in position 24).

TA and MA steroids, being aromatics and so presumably undesirable constituents of a potential pharmaceutical raw material, are in concentrations dependent on the maturity and biodegradation of the petroleum sample. Since the low mature biodegraded samples seem to be a good choice for sterane concentration, the aromatic steroids in them should be taken out.

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SAŽETAK

Steroidi u nafti iz sjeverne Hrvatske

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Zbog farmakološkog interesa za sterane u sjevernohrvatskim naftama, 3 između 43 uzorka su odabrana s pomoću HR GC za istraživanje steroida: uzorak PI s brežuljkastim usponom osnovice kromatograma na teškom kraju (gdje se eluiraju steroidi), s mnogo *n*-alkana; PII bogat *n*-alkanima s relativno zaravnjenim teškim krajem; i PIII s istrazitim usponom na teškom kraju, ali siromašan *n*-alkanima.

S pomoću GC-MS sterani su istraživani u zasićenoj, a MA i TA steroidi u aromatskoj frakciji. Korišteni su cjeloviti spektri masa i fragmentogrami $m/z = 217$, $m/z = 253$ i $m/z = 231$.

U 3 odabrana uzorka utvrđeni su sterani u rasponu od norkolestana do *n*-propilkolestana koji su predstavljali *cca.* 3000 do 9000 ppm zasićene frakcije. Dominantni su kolestani, ergostani i stigmastani dok diasterana ima razmjerno malo.

PIII je steranima najbogatiji. Za taj uzorak je karakterističan nizak stupanj epimerizacije sterana s obzirom na H i C atom u položaju 14, 17 i 20, te osiromašenje na *n*-alkanima zbog geogene biodegradacije. PIII također sadržava razmjerrno najvišu koncentraciju TA steroida.

Odnos intenziteta TA steroida naprama MA steroidima najviši je za PII, što je zbog absorbiranoga termalnog stresa u suglasju s usporedno najvišom dosegnutom razinom epimerizacije.