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IDENTIFICATION OF A SERIES OF C_{25}- C_{40} ACYCLIC ISOPRENOID HYDROCARBONS IN CRUDE OILS

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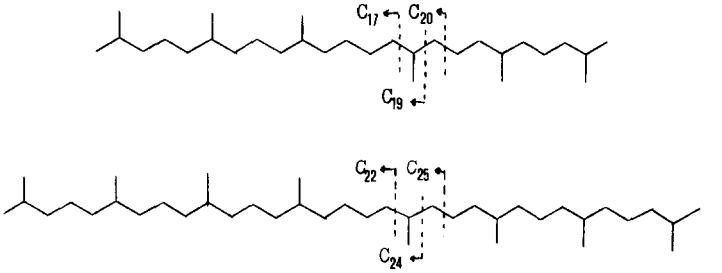
The identification of acyclic isoprenoid hydrocarbons in organic extracts of geological samples and particularly in petroleum deserves a great interest from the biological origin of the sedimentary organic matter and the understanding of geochemical processes.

Occurrence of the C_{10}- C_{20} isoprenoid series in geological settings is widely treated in the literature and its main formation through the degradation of phytol (II) commonly accepted (1). However the identification of C_{17} (2) and C_{22} (3) isoprenoid alkanes in shales and crude oils and more recently of linear C_{19}, C_{24} and anteiso C_{20}, C_{25} isomers (4) suggest that the rôle of C_{30} and C_{40} tail-to-tail isoprenoid compounds cannot be neglected.



Moreover, the detection of C_{21}- C_{25} homologs in a cretaceous shale (5) and in several crude oils (3,4) make evident a contribution of larger regular isoprenoid precursors. Among them natural polyprenols (I, n=6-22) have been proposed by Han and Calvin (3) but the absence of larger homologs than the regular C_{25} isoprenoid in an extract, induced Spyokerelle et al. (5) to consider the sesterterpenes (I, n=5) as an alternative source of those hydrocarbons. More recently Haug and Curry (6) have tentatively identified C_{26}, C_{28} and C_{30} isoprenoid alkanes in a seep oil so the hypothesis of polyprenols seems to be reinforced again.

$$H \leftarrow CH_2\text{-}\overset{CH_3}{\overset{|}{C}}\text{=}CH\text{-}CH_2 \rightarrow_n OH \qquad (I)$$

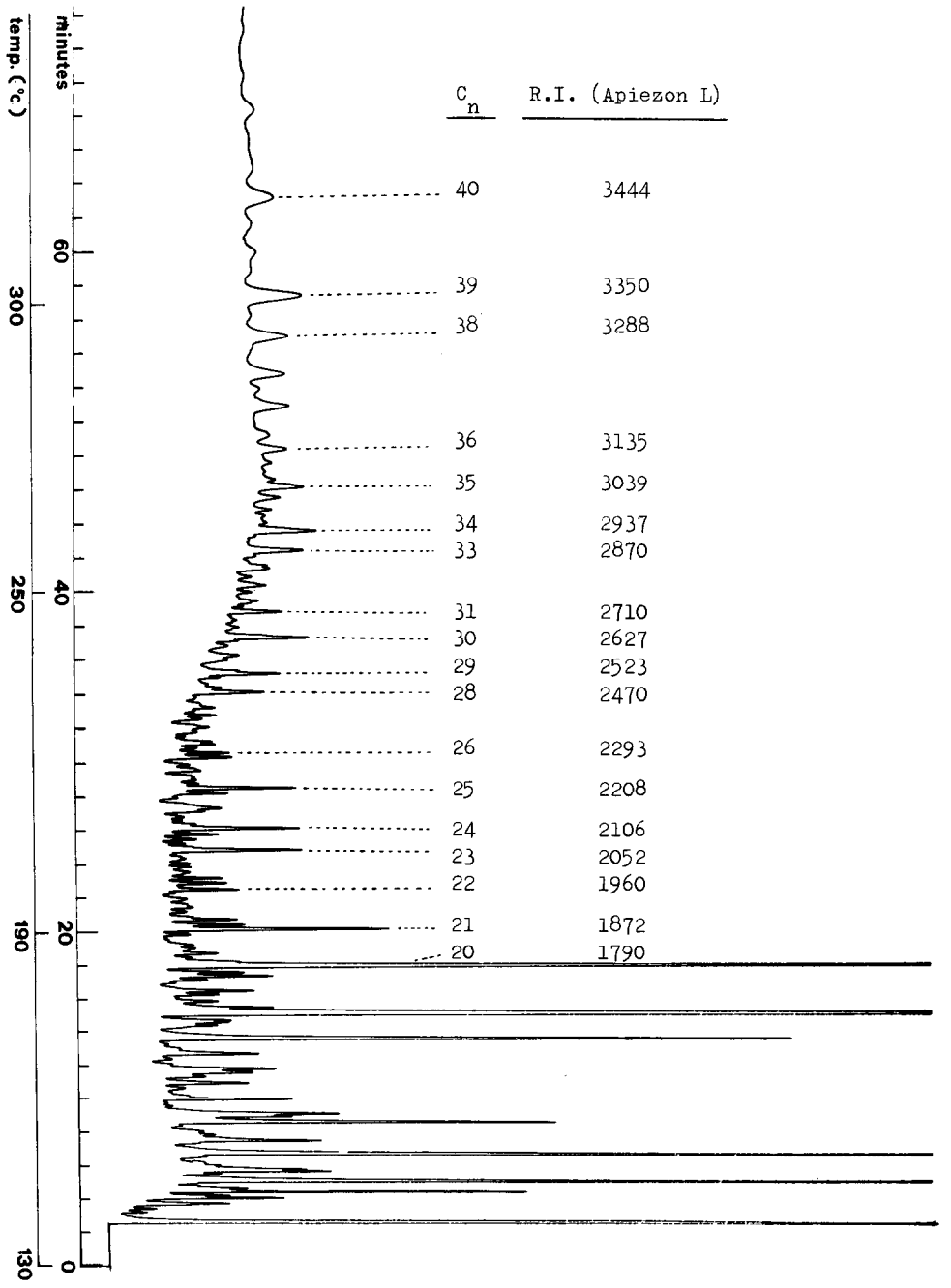
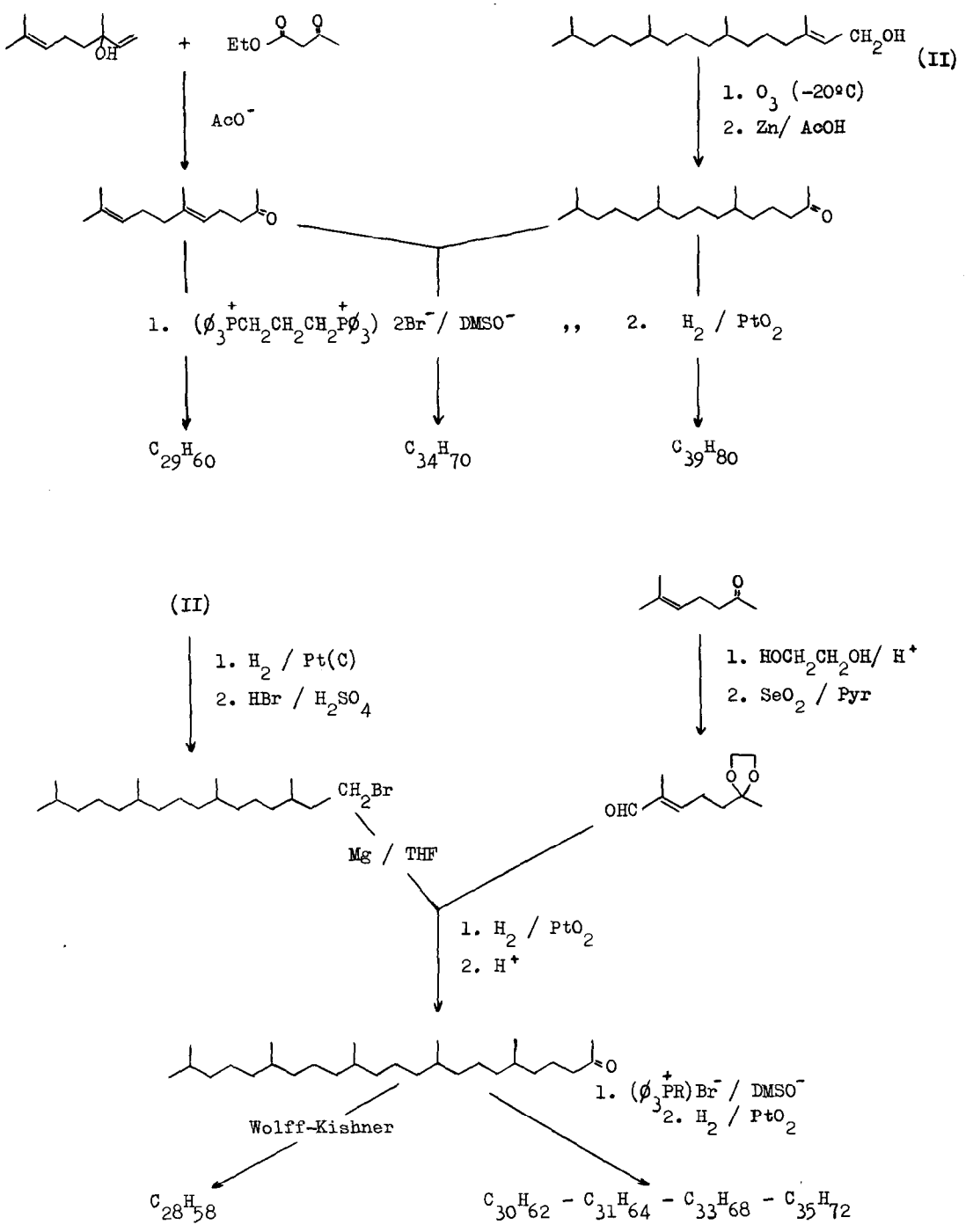

temp. (°c.)
minutes
300
250
190
130
60
40
20
0
C_n
R.I. (Apiezon L)
40 3444
39 3350
38 3288
36 3135
35 3039
34 2937
33 2870
31 2710
30 2627
29 2523
28 2470
26 2293
25 2208
24 2106
23 2052
22 1960
21 1872
20 1790

FIGURE 1



R = Et- ; Pr- ; Pent- ; 4-MeHex-

FIGURE 2

To gain insight into the presence and origin of these larger isoprenoid alkanes in oils we undertook a detailed examination of a Spanish crude oil (Castellón) reservoired in a miocene sedimentary formation.

Isolation of isoprenoid hydrocarbons from the oil was carried out by conventional thiourea adduction of the urea non-adduct residue of the crude oil saturated fraction. Figure 1 shows the corresponding GC profile. Further purification of the isoprenoids has been achieved by high efficiency column chromatography on alumina (n-pentane as eluent)(7). The fractions obtained were run on a GC-MS-COM system and the mass spectra of the suspected peaks registered, after that a mass-fragmentographic analysis for the significant ions (m/e 113, 183, etc ...) has been performed.

At the same time a set of isoprenoid alkanes were synthesized as reference compounds, according to the procedures outlined in figure 2. Mass spectra and GC retention indexes on two columns (Apiezon L and Dexsil) were obtained for all these hydrocarbons and compared with those previously acquired from the oil, affording the positive identification of the C_{26}- C_{35} and C_{39} members of the series. The remaining C_{36}, C_{38} and C_{40} regular homologs were also identified in the oil by their mass spectra, their retention indexes being in agreement with those calculated from the lower homologs (8).

Variable distributions of this series of regular isoprenoid hydrocarbons were further identified in several crude oils of different degree of maturity, the geochemical significance of which will be discussed elsewhere.

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