

# 青海湖现代沉积物中三种新结构烯烃化合物 及其地球化学意义

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**提 要** 笔者首次在地质体中检出了三种新结构三环二萜烯,  $\Delta^{11}$  山达海松二烯、二氢芮木泪柏烯、13-异海松二烯, 探讨了其生源母质及其在地质体中的演化过程。这种结构的烯烃化合物可以作为陆源高等植物的示踪剂, 反映了青海湖中有机质来源除了湖中浮游生物和底栖生物外, 陆源高等植物的贡献是不可忽视的。

**关键词** 新结构三环二萜烯 生源母质 演化过程 地化意义

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青海湖是我国最大的内陆高原微咸水湖泊。为了研究青海湖沉积物中有机质的来源、分布及演化规律, 笔者选取了湖区不同地点如湖中心、湖湾、河流入湖口处以及青海湖子湖——耳海和尕海等地的现代沉积物淤泥柱样品, 做了有关 GC-MS 分析。研究结果表明: 青海湖现代沉积物中有机质含量高, 属于营养型湖泊, 生物标志物种类丰富, 包括二至五环萜烷、萜烯类化合物、甾烷、甾烯等。本文仅详细讨论在青耳海样品中检出的三种尚未见报道的三环萜烯化合物。

## 1 样品采集与分析

中科院兰州地质所与青海盐湖所共同合作于 1989 年 8 月在青海湖用重力管采样器采集了湖底沉积物岩心和表层沉积物样品 (图 1)。本文重点研究青耳海样品。采样点水深 4m, 表层沉积物均为黑色淤泥。样品冷冻干燥后粉碎至 80 目, 称取适量用氯仿和甲醇抽提, 铜片脱硫。抽提物用正己烷沉淀青质后, 过柱(三氧化二铝与硅胶)分离。获得的饱和烃馏分进行 GC-MS 分析。

所用仪器及分析条件: 色-质分析仪是 HP-5988A 型四极矩质谱仪, 色谱柱为石英



图 1 青海湖采样点位图

Fig. 1 Sampling sites in Qinghai Lake

毛细管柱(50m×0.32mm),固定液SE54,载气:高纯氮,程序升温80℃~200℃,6℃/min,再由200℃~300℃,3℃/min。质谱离子源温度200℃,电离电压70eV,EI源。

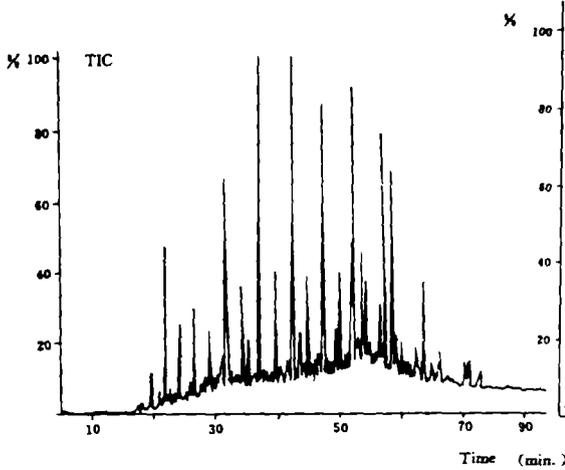


图2 青耳样品饱和烃馏分的总离子流图

Fig. 2 TIC chromatogram of aliphatic fraction of ginger samples

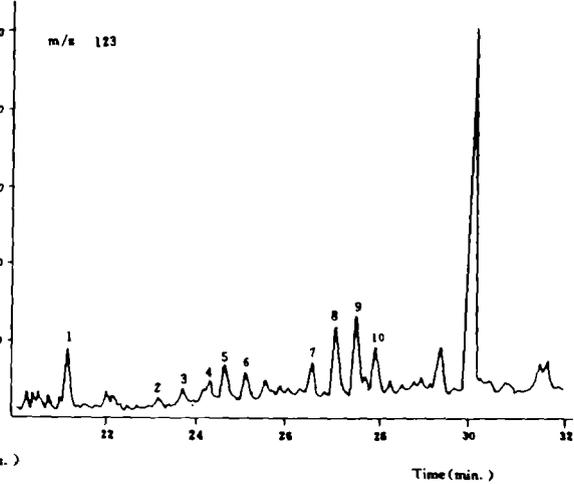


图3 二环萜与二萜类化合物 m/z 123 质量色谱图

Fig. 3 m/z 123 fragmentogram of terpanes and terpenes

## 2 气相色谱分析和色谱质谱鉴定

图2和图3分别是青耳样品饱和烃总离子流图和 m/z 123 质量色谱图,其中7、8、9号峰的棒图示于图4左。7号峰分子离子峰  $M^+ = 272$ ,基峰 257(M-15);8号峰分子离子峰  $M^+ = 274$ ,基峰 259(M-15);9号峰  $M^+ = 272$ ,基峰 137,特征碎片峰 257(M-15)。主要断裂碎片的结构分析见图5。这些峰流出于  $C_{20}$ -长侧链二环萜烷之后,但见于四环萜烷之前(图3中各峰的命名列于表1),推测属于三环萜类化合物,通过查阅大量合成标样化合物的谱图数据,鉴定结果与 Weaver, Wenkert 等(1965)所分析的几种三环萜烯化合物合成标样谱图(图4右)相吻合,且碎片断裂机理合理。因此,检出于青耳样品中的这几种化合物定名为  $\Delta^{8,9}$ 山达海松二烯、二氢芮木泪柏烯、13-异海松二烯。

表1 二环萜烷与二萜类化合物鉴定结果

Table 1 Analysis results of terpanes and terpenes

峰号	$M^+$	基峰	定名与结构
1	208	109	4 $\beta$ (H)-桉叶油烷
2	278	123	$C_{20}$ -长侧链二环萜烷
3	278	123	$C_{20}$ -长侧链二环萜烷
4	278	123	$C_{20}$ -长侧链二环萜烷
5	278	123	$C_{20}$ -长侧链二环萜烷
6	278	123	$C_{20}$ -长侧链二环萜烷
7	272	257	$\Delta^{8,9}$ 山达海松二烯
8	274	259	二氢芮木泪柏烯
9	272	137	13-异海松二烯
10	274	245	13-异海松烯
11	274	123	16 $\alpha$ (H)-贝壳松烷

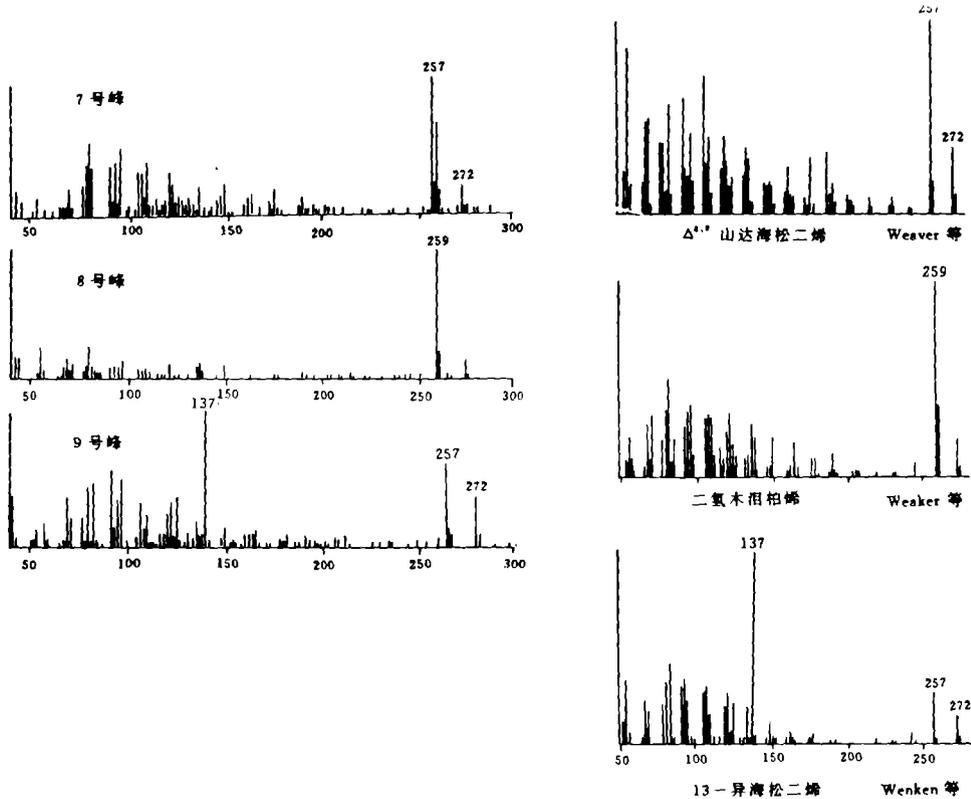


图 4 三种新结构萜烯化合物质谱图 左图:检出于地质体中;右图:合成标样  
 Fig. 4 Mass spectrum of terpenes left: compounds detected in geological body  
 right: synthesized standard samples

### 3 问题讨论

#### 3.1 三种新结构萜烯化合物的生源母质及演化过程

已有文献报导在树脂、生油岩中检出了山达海松烷、海松烷(Snowdon, 1978),有关天然有机高分子化合物研究文献中,有的亦涉及到了海松二烯酸(Pimaradiene acid),即海松酸,山达脂海松酸(Sandaracopimaric acid)的资料,海松酸和异海松酸可从松香中分离得到,而松香是松脂用水蒸汽蒸馏后的不挥发玻璃状脆性物质(约占松脂的 70%),主要由三环二萜酸组成(约占松香的 90%)。因此,从生物体中的酸类化合物到地质体中烃类化合物的演化过程如图 5。

#### 3.2 上述几种萜烯化合物的地球化学意义

海松酸、山达脂海松酸是树脂酸的重要组成部分,树脂酸最初是从松树树干割口流出的粘稠液体中分离出来的。上述几种检出于地质体中的萜烯化合物是树脂酸脱羧的产物。因此,青海湖中有机质来源除了湖中浮游生物和底栖生物外,亦有由河流带入的陆源高等植物的贡献。

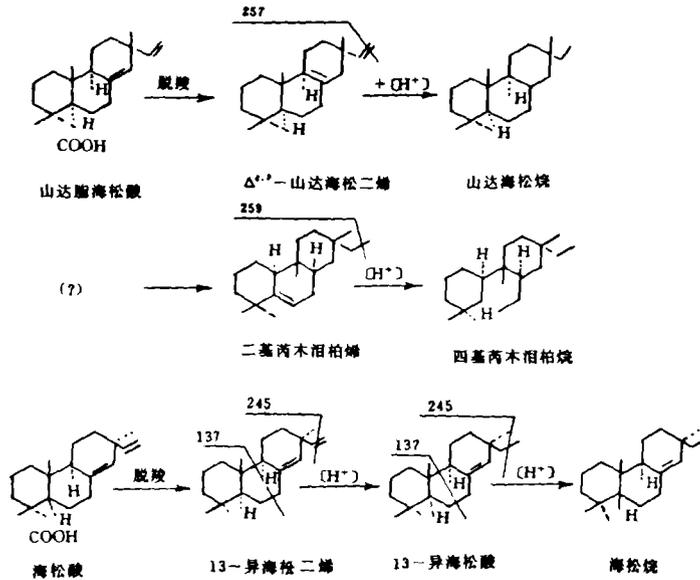


图5 几种萜类化合物从生物体到地质体演化示意图

Fig. 5 Evolution Model of terpenes from organisms to geological bodies

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### Three New Structural Terpenes and Their Geochemical Significance in Recent Sediment of Qinghat Lake

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## Absract

Three new structural tricyclic diterpenes are first reported in this paper. They are examined in the recent sediments of Qinghai Lake and their eluting time is between bicyclic terpanes of long chain and tetracyclic diterpanes of m/z 123 mass chromatogram. They are

named as  $\Delta^{8,9}$ -sandaracopimaradiene, dihydrorimuene, 13-isopimaradiene through the analysis of broken mechanism of fragments in mass spectrum and the contrast study of synthesized standard spectrum made by Weaver and Wenkert, their molecular ion peaks  $m/e$  are 272, 274, 272, respectively, and correspond abundant peaks  $m/z$  are 257, 259, 137, respectively.

The studied information about natural organic high molecular compounds shows that sandaracopimaric acid and pimaradiene acid had been isolated from resin acid and their structures had been identified. The authors deduce that sandaracopimaric acid and pimaradiene acid are the precursors of  $\Delta^{8,9}$ -sandaracopimaradiene, 13-isopimaradiene. In addition, many literatures have reported that sandaracopimaradiene and pimaradiene have been detected in oil and source rock. Therefore, the three new structural tricyclic diterpenes studied in this paper are the middle transfer products from the acids in high plants to alkanes in geologic body, the evolution process is that acid is transferred into alkene through dehydroxylation and then transferred into alkane through hydrogenation. The detection of  $\Delta^{8,9}$ -sandaracopimaradiene, dihydrorimuene, 13-isopimaradiene not only enriched the types of biomarkers but also provided the proof for the transfer process of organic matter from organisms to geological body. These three new structural compounds examined in the recent sediment of Qinghai Lake reflects the information that organic matter in Qinghai Lake is not only derived from the organisms of the lake, but also has the input of terrigenous high plants.