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SESQUITERPENE HYDROCARBONS FROM THE ROOTS OF *OTANTHUS MARITIMUS*

J. DE PASCUAL TERESA, A. SAN FELICIANO, A. F. BARRERO, M. MEDARDE and F. TOMÉ

Dptº Química Orgánica, Fac Ciencias y Farmacia, Salamanca, Spain

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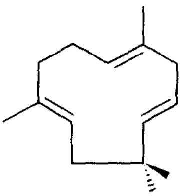
Key Word Index—*Otanthus maritimus*; Anthemideae; Compositae; sesquiterpenes.

Following our work on the composition of *Otanthus maritimus* (L.)* Hoffmanns & Link [1, 2], we have identified the sesquiterpene hydrocarbons from the roots that were not studied by Bohlmann *et al.* [3] in their previous paper. Khafagy *et al.* [4] have also studied this plant and have isolated 7-*O*-neohesperidosyl acacetin.

By chromatographic separation we have isolated α-humulene (**1**) and (−)-β-cariophyllene (**2**), which were identified by comparison with authentic samples, and four other sesquiterpenes with tripentagonal-tricyclic skeletons.



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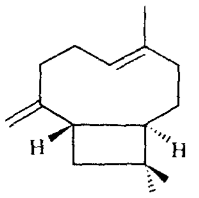

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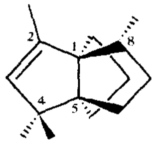

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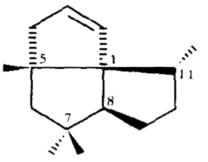

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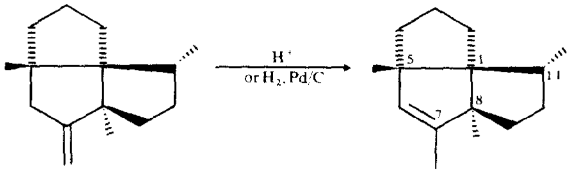

5　**3**

(−)-Isocomene (**3**), (−)-modephene (**4**), (−)-β-isocomene (**5**) (mp 100°, $[\alpha]_D = -63.2°$) and (−)-silphinene (**6**) (oil, $[\alpha]_D = -46.7°$) had the same spectroscopic and physical properties as those described by Zalkow *et al.* [5–7] and Bohlmann *et al.* [8, 9].

The stereochemistries depicted for **3**, **4**, **5** and **6** are based on the probable biogenetic pathway [7, 9] and the absolute configuration of (−)-β-cariophyllene (**2**) which is considered to be their precursor.

EXPERIMENTAL

IR: film. ^{1}H NMR: CCl_4 with TMS as internal reference. MS: 70 eV. $[\alpha]_D$: $CHCl_3$ (conc g/100 ml).

The plant was collected from the beach of Santa Eugenia de Riveira (Coruña. Spain). Roots (900 g) of *Otanthus maritimus* (L.) Hoffmanns & Link, extracted in a Soxhlet with hexane gave 37.7 g of extract that after dry CC afforded 12.9 g of hydrocarbon fraction (less polar). By CC of this fraction over Si gel and Si gel–$AgNO_3$ the following substances were isolated: **3** (3.475 g), **4** (847 mg), **6** (360 mg), **5** (1.392 g), **2** (1.197 g) and **1** (136 mg).

(−)-*Isocomene* (**3**). Mp 59–60°, $[\alpha]_D = -85.2°$ (1.38%). IR ν_{max}^{film} cm^{-1}: 3020, 1675, 1190, 1020, 1005, 940, 845. ^{1}H NMR (60 MHz): δ 0.84 (3H, *d*, $J = 7$ Hz, Me-11); 1.04 (6H, *s*, Me-5, Me-8); 1.55 (3H, *d*, $J = 2$ Hz, Me-7); 4.80 (1H, *q*, $J = 2$ Hz, H-6). MS *m/e* (rel. int.): M^+ 204 (12) $C_{15}H_{24}$, 189 (12), 175 (10), 162 (100), 147 (55), 134 (26), 119 (41), 105 (27), 91 (22).

(−)-*Modephene* (**4**). Colourless oil. $[\alpha]_D = -20.5°$ (1.22%). IR ν_{max}^{film} cm^{-1}: 3010, 1670, 1385, 1365, 1140, 1095, 950, 845. ^{1}H NMR (60 MHz): δ 0.94 (6H, *s*, Me-4) 0.95 (3H, *d*, $J = 6$ Hz, Me-8); 1.56 (3H, *d*, $J = 2$ Hz, Me-2); 4.75 (1H, *q*, $J = 2$ Hz, H-3). MS *m/e* (rel. int.): M^+ 204 (21) $C_{15}H_{24}$, 189 (100), 175 (7), 161 (48), 147 (46), 133 (38), 119 (54), 105 (39), 91 (30).

(−)-*Silphinene* (**6**). Colourless oil. $[\alpha]_D = -46.7°$ (0.86%). IR ν_{max}^{film} cm^{-1}: 3050, 1635, 1380, 1370, 1200, 1008, 990, 917, 850, 732. ^{1}H NMR (90 MHz): δ 0.82 (3H, *d*, $J = 7$ Hz, Me-11); 0.92 (3H, *s*, Me-7); 0.99 (3H, *s*, Me-7); 1.09 (3H, *s*, Me-5); 1.67 (2H, *s*, H-6); 2.31 (2H, *qt*, $J = 18$, 2 Hz, H-4); 5.49 (2H, *qt*, $J = 6.5$, 2 Hz, H-2 and H-3). MS *m/e* (rel. int): M^+ 204 (49) $C_{15}H_{24}$, 189 (68), 175 (20), 161 (46), 148 (68), 147 (100), 133 (69), 119 (65), 105 (82), 91 (76).

(−)-*β-Isocomene* (**5**). Mp 100°. $[\alpha]_D = -63.2°$ (0.95%). IR ν_{max}^{film} cm^{-1}: 3080. 1665, 1120, 1100, 1035, 1020, 890, 820. ^{1}H NMR (90 MHz): δ 0.92 (3H, *d*, $J = 7$ Hz, Me-11); 0.97 (3H, *s*, Me-5); 1.08 (3H, *s*, Me-8); 2.10 (1H, *dt*, $J = 14$, 1 Hz, H-6); 2.29 (1H, *dt*, $J = 14$, 2.5 Hz, H-6); 4.59 (2H, *s.a.*, H-13). MS *m/e* (rel. int.): M^+ 204 (29) $C_{15}H_{24}$, 189 (60), 175 (15), 161 (46), 147 (71), 134 (35), 133 (68), 120 (40), 119 (60), 108 (100), 105 (75), 91 (66).

Isomerization of (−)-*β-isocomene* (**5**). 138 mg of **5** in refluxing H_2SO_4 (0.3 ml)–EtOH (2.5 ml)–C_6H_6 (2.5 ml) after 5 min gave

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* We thank Professor Dr. Bartolomé Casaseca Mena (Botany Department, Fac. Sciences, Salamanca) for the plant classification. This plant has also been called *Diotis maritima* (L.) and *Diotis candidissima* Desf.

103 mg of (−)-isocomene (**3**) identical with a natural sample. Compound **5** (40 mg) in Et_2O (2 ml) and H_2 atmosphere (room temp. and pres.) with 10% Pd/C afforded 37 mg of **3**.

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CARBON-13 NMR SPECTRA OF SOME *ENT*-ROSANE DITERPENOIDS

MARÍA C. GARCÍA-ALVAREZ,* BENJAMÍN RODRÍGUEZ,* SERAFÍN VALVERDE,* BRAULIO M. FRAGA† and ANTONIO G. GONZÁLEZ†

* Instituto de Química Orgánica, CSIC., Juan de la Cierva 3, Madrid-6, Spain and † Instituto de Productos Naturales Orgánicos, CSIC, Tenerife, Spain

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Key Word Index—Diterpenoids; *ent*-rosa-5,15-diene; *ent*-8,5-*friedo*-pimara-5,15-diene derivatives; ^{13}C NMR analysis.

Abstract—The ^{13}C NMR signals of the parent hydrocarbon *ent*-rosa-5,15-diene (*ent*-8,5-*friedo*-pimara-5,15-diene) and some of their oxygenated derivatives have been assigned.

INTRODUCTION

^{13}C NMR spectroscopy is an excellent tool for the structural elucidation of natural substances. In the diterpene field there is already a considerable amount of information which confirms this view. Podocarpanes [1], labdanes [2,3], primaranes [4,5], abietanes [6], *ent*-kauranes [7], *ent*-beyeranes [8,9], *ent*-atisanes [10–12], *ent*-trachylobanes [13,14] and *ent*-clerodanes [15–17] have been studied among others.

The availability of a series of *ent*-rosane derivatives and our continued interest [8–11] in the applications of ^{13}C NMR spectroscopy has prompted us to carry out this study. Until now, only ^{13}C NMR data of rosenonolactone and some of its derivatives [18], jesromotetrol [19], and partial results on rimuene [20] (the epimer at C-13 of compound **1**) have been reported. This paper presents the ^{13}C NMR data for the parent hydrocarbon *ent*-rosa-5,15-diene (**1**) and the C-11 and/or C-15 and C-16 oxygenated derivatives (**2**–**8**), many of which are natural diterpenoids [21, 22].

RESULTS AND DISCUSSION

The assignments for the ^{13}C NMR chemical shifts of the diterpenoids (Table 1) were made with the aid of off-resonance decoupled spectra and selective decoupling experiments, and further based on comparison of pairs of compounds, consideration of β, γ and δ substituent effects, general chemical shift arguments and literature data on related structures [4, 5, 18–20].

In general we have detected no unusual effects in this type of hydrocarbon skeleton. The presence of an 11-keto group (**8**), the different stereochemistry of the C-11