Phytochemistry, Vol 23, No 9, pp 2064–2065, 1984
Printed in Great Britain

0031–9422/84 $3 00 + 0 00

REVISED STRUCTURES FOR THE BEJAROLS FROM *SANTOLINA OBLONGIFOLIA*

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(*Received* 22 *November* 1983)

Key Word Index—*Santolina oblongifolia*; Compositae; bejarols; dihydropyrannerolidols

Abstract—The ^{13}C NMR spectra of the bejarols isolated from *Santolina oblongifolia* suggest they are nerolidol derivatives with a 2,6-dialkyldihydropyranose structure.

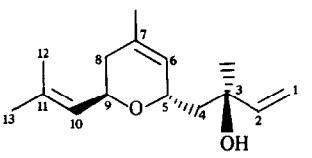
We have recently reported [1] the isolation of three sesquiterpene alcohols related to nerolidol, from the essential oil of *S. oblongifolia* Boiss., proposing for them the furanic structures *β-trans*-bejarol (**1**), *α-trans*-bejarol (**2**) and *cis*-bejarol (**3**).

Further new evidence, especially the ^{1}H NMR spectra at 200 MHz (Table 1) and comparison of the ^{13}C NMR spectra of the bejarols with that of the 'rose oxide' (Table 2) now show that the structures of the bejarols must be as depicted (**1**–**3**).

In the ^{13}C NMR spectra of the bejarols, the chemical shifts due to C-5 through C-14 were practically identical to those reported for the 'rose oxide' [2], showing that they all must have the same partial structure. The signals due to the five remaining carbon atoms identified the substituent group as 2-methyl-2-hydroxybut-2-enyl, because the chemical shifts of the signals were comparable with those shown by compounds with this partial structure, such as linalol and related substances [2, 3].

The stereochemistry of the bejarols was easily deduced from their ^{1}H NMR spectra and with the help of Dreiding models. The coupling constants for the signal due to H-9 of **1** and **2** ($J_{9,8e}$ = 5 Hz and $J_{9,8a}$ = 6 Hz) were evidence for its pseudoequatorial disposition in both compounds [4], while the coupling constant $J_{5,6}$ = 1.5 Hz, agreed with an H-5:H-6 dihedral angle of about 80°, from which the axial disposition of H-5 followed. All these facts allowed us to assign to compounds **1** and **2**, the *trans* relative position for the substituents at C-5 and C-9 in the pyranose ring.

Relative configurations at C-3 and C-5 were deduced from the chemical shifts of the signals due to the methyl group at C-3 in the ^{1}H NMR and ^{13}C NMR spectra, compared with those exhibited by known similar compounds [5]. The spectral signals at δ1.33 and 26.84 and 1.23 and 29.59 in the ^{1}H NMR and ^{13}C NMR spectra of **1** and **2**, respectively, allowed us to assign them the *erythro* and *threo* relative configurations, respectively. The presence of intramolecular H-bonds was evident by the non-equivalence of the H-4 protons in the ^{1}H NMR spectra.



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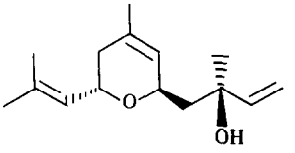

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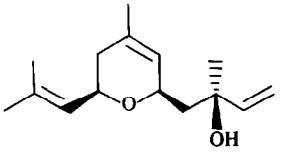

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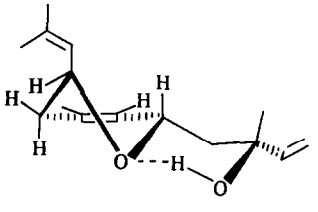
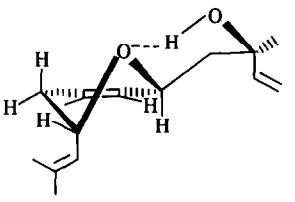
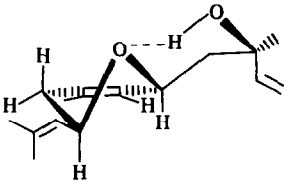


1a



2a



3a

Table 1. ^{1}H NMR spectral data for compounds 1–3 (200 MHz, $CDCl_3$, TMS; values in parentheses are coupling constants)

Proton	1	2	3
H-1$_c$	4.97 *dd* (2, 10.8)	5.10 *dd* (1.5, 10.8)	5.10 *dd* (2, 10.8)
H-1$_t$	5.22 *dd* (2, 17)	5.35 *dd* (1.5, 17)	5.35 *dd* (2, 17)
H-2	5.90 *dd* (10.8, 17)	5.88 *dd* (10.8, 17)	5.90 *dd* (10.8, 17)
H-4	1.88 *dd* (10.8, 16)	1.49 *dd* (2, 15)	1.90 *dd* (10.8, 15)
H-4'	1.51 *dd* (2, 16)	1.93 *dd* (11.5, 15)	1.48 *dd* (2, 15)
H-5	4.52 *ddd* (1.5, 2, 10.8)	4.42 *ddd* (1.5, 2, 11.5)	4.42 *ddd* (15, 2, 10.8)
H-6	5.29 *br s*	5.39 *br s*	5.24 *br s*
H-8	1.70 *dd* (5, 18)	2.10 *dd* (5, 13)	1.75 *dd* (3.3, 18)
H-8'	2.00 *dd* (6, 18)	1.80 *dd* (6, 13)	2.10 *dd* (10.8, 18)
H-9	4.48 *ddd* (5, 6, 8)	4.48 *ddd* (5, 6, 8)	4.30 *ddd* (3.3, 8, 10.8)
H-10	5.21 *br d* (8)	5.17 *br d* (8)	5.29 *br d* (8)
Me-15	1.33 *s*	1.23 *s*	1.23 *s*
Me-12	1.73 *d* (1.4)	1.72 *d* (1.4)	1.72 *d* (1.4)
Me-13	1 72 *d* (1.4)		
Me-14	1.70 *d* (1.4)	1.70 *d* (1.4)	1.70 *d* (1.4)

Table 2. ^{13}C NMR spectral data for compounds 1–3, 'rose oxide' and linalol*

C-atom	1	2	3	'Rose oxide'	Linalol
C-1	111.05	112.66	112.34	—	111.3
C-2	146.05	144.61	144.51	—	145.0
C-3	72.58	73.57	73.41	—	72.7
C-4	44.34	44.07	46.15	—	41.8
C-5	65.78	66.65	70.93	65.5	—
C-6	123.32	123.11	123.42	119.9	—
C-7	137.13	137.05	137.00	135.6	—
C-8	35.39	35.36	35.42	36.1	—
C-9	69.75	70.55	72.29	70.7	—
C-10	124.85	124.73	125.12	126.1	—
C-11	131.81	131.89	132.02	131.7	—
C-12	18.43	18.39	18.37	18.3	—
C-13	25.81	25.72	25.52	25.7	—
C-14	23.24	23.13	22.75	23.0	—
C-15	26.84	29.59	29.51	—	27.2

*^{13}C NMR spectra were recorded at 50.3 MHz in a Bruker WP 200 SI instrument in $CDCl_3$ using TMS as internal standard. To differentiate between CH_3, CH_2, CH and C, the DEPT sequence was used

From all these data, the configuration for this pair of diastereomers followed as *RSR/SRS* for **1**, and *RRS/SSR* for **2**, so that the most probable conformations are as depicted by structures **1a** and **2a**.

For compound **3**, the multiplicity (Table 1) and chemical shifts of the ^{1}H NMR signals due to H-9 and H-5 (δ4.30 and 4.42) and the ^{13}C NMR signals due to C-9 and C-5 (δ72.29 and 70.93) suggested the *cis*-relative configuration for the substituents at C-9 and C-5, and similar considerations to those stated for compounds **1** and **2**, allowed us to deduce for **3**, a *threo*-relative configuration (*RRR/SSS*) and the most probable conformation is depicted by structure **3a**.

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