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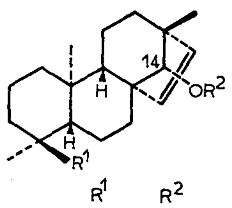
Tartessol, a New Diterpene from *Sideritis grandiflora* Salzm.[1]

Continuing our investigations on diterpenes from *Sideritis* species (Labiatae) endemic to the Iberian Peninsula[2–4], we have studied *S. grandiflora* Salzm. collected near Paterna (Cádiz) last spring. From the aerial part we have isolated two compounds already described: sideridiol (*ent*-15-kaurene-7α, 18-diol)[5] and SP-2 (*ent*-7α-acetoxy-15-beyerene-14β, 18-diol)[6–8], plus a new diterpene[9], tartessol (**1**), $C_{22}H_{34}O_3$, m.p. 193–4° (from *n*-hexane), $[\alpha]_D^{22°}$ + 19.1° (*c*, 0.61, EtOH).

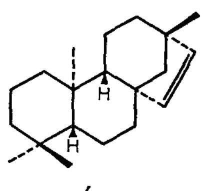
The last compound has IR-absorptions indicative of hydroxyl, 1,2-disubstituted *cis*-olefin and acetoxy functions (3480; 3080, 3050, 730; 1710, 1250 cm^{-1} in KBr). Its NMR-spectrum ($CDCl_3$, 60 MHz) shows the following signals: at δ 5.55 an AB quartet (*J* 6 Hz) due to the vinyl protons of a 1,2-disubstituted *cis*-olefin attached to fully substituted carbon atoms, at δ 4.51 a singlet originated by a proton geminal to a secondary acetoxy group, and at δ 3.23 an AB quartet (*J* 10.6 Hz) assignable to a $-\overset{|}{\underset{|}{C}}-CH_2OH$ grouping possibly in equatorial configuration[10]. The upper region of the NMR-spectrum shows the methyl singlet corresponding to the acetoxy group at δ 2.03 and three C-Me singlets at δ 0.95, 0.81 and 0.78.

As expected, acetylation of compound **1** gave the corresponding derivative **2** (a syrup). The NMR-spectrum of **2**, a diacetate, indicates a paramagnetic shift for the signal due to the primary alcohol which now appears at δ 3.76, a value fully consistent with an equatorial configuration for this grouping[10].

The above data present close analogies with previously described products[6–8] and suggest formula **1** for tartessol. This structural hypothesis was confirmed as follows:



	R^1	R^2
1	CH_2OH	Ac
2	CH_2OAc	Ac
3	CH_2OH	H
5	CO_2H	Ac
6	CO_2H	H
7	CO_2Me	H



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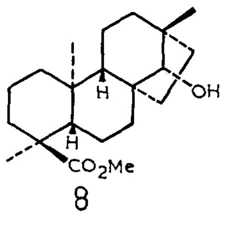

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Treatment of **1** with 5% ethanolic KOH at room temperature gave the diol **3** [m.p. 184–6° (acetone: *n*-hexane), $[\alpha]_D^{22°}$ + 58.3° (*c*, 0.30, EtOH)], which was oxidized with CrO_3/Py to yield a ketoaldehyde derivative extremely sensitive to air oxidation. Without further purification, the ketoaldehyde was subjected to the Huang-Minlon reduction under N_2 atmosphere, affording a new product (**4**) [m.p. 29–31° (spontaneously on cooling,) $[\alpha]_D^{22°}$ + 37.7° (*c*, 1.2, $CHCl_3$)] identical in all respects with *ent*-15-beyerene (stachene)[4, 11]. The structure and absolute stereochemistry of the carbon skeleton is thus established.

Compound **1** was transformed to the carboxylic acid **5** [m.p. 240–2° (acetone:*n*-hexane), $[\alpha]_D^{22°}$ + 7.9° (*c*, 0.43, EtOH)] by Jones oxidation and this was readily hydrolized to the hydroxy acid **6** [m.p. 228–230° (acetone:*n*-hexane), $[\alpha]_D^{22°}$ + 56.6° (*c*, 0.35, EtOH)]. Treatment of **6** with CH_2N_2 in ethereal solution gave the methyl ester **7** [m.p. 136–8° (acetone:*n*-hexane), $[\alpha]_D^{22°}$ + 39.6° (*c*, 0.51, $CHCl_3$)] and the ester was then reduced (Pd/C, EtOH) to the dihydroderivative **8** [m.p. 167–9° (*n*-hexane), $[\alpha]_D^{22°}$ + 10.1° (*c*, 0.66, $CHCl_3$)].

It is well known[12] that hydrogenation of the olefin bond of an *ent*-15-beyerene causes a paramagnetic shift of the C-20 methyl group and a simultaneous slight shielding of the C-17 methyl. Both effects are noticed comparing the NMR-spectra of compounds **7** and **8** (δ 1.18, 1.05, 0.80 and 1.16, 0.98, 0.97 respectively). This observation practically excludes both positions as a location for the primary hydroxyl group. It must be attached to C-4.

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[1] Part XVIII in the series 'Studies on diterpenes from genus *Sideritis*'. For Part XVII see T. G. DE QUESADA, B. RODRÍGUEZ and S. VALVERDE, *Phytochemistry*, in press.

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[9] Satisfactory elemental analysis have been obtained for all the products here described.

[10] A. GAUDEMER, J. POLONSKY and E. WENKERT, Bull. Soc. chim. Fr. *1964*, 407.

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The equatorial configuration of this group was already suggested by the chemical shifts of the AB quartets originated by this group in compounds **1** and **2**[10] (vide supra) and further confirmed because compounds **7** and **8** exhibit IR-absorptions at 1250 cm^{-1} in agreement with what is postulated[13] for $-CO_2Me$ group on C-4 and equatorial configuration.

Finally the location of an acetoxy group on C-14 follows from the NMR data which consistently shows the geminal proton of the acetoxy group as one proton singlet, pointing to the C-14 carbon of an *ent*-15-beyerene skeleton. The configuration has been assigned on bases of IR data. The C-14 OH absorption frequencies at the IR-spectra (c, 6.10^{-4}, CCl_4) of **7** and its dihydroderivative **8** are 3580 and 3637 cm^{-1} respectively, indicating an intramolecular interaction[14] of the π-orbitals and the OH group in the case of **7**.

Résumé. Un nouveau diterpène tartessol (**1**) a été isolé de la *Sideritis grandiflora* Salzm. (Labiées) est sa structure est proposée comme étant *ent*-14β-acétoxy-15-beyèren-18-ol.

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[15] The authors thank Dr. J. BORJA, Botany Department, Faculty of Pharmacy, Madrid, for the collection and botanical classification of the plant material and Dr. JUANA BELLANATO, Institute of Optics, C.S.I.C., Madrid, for the high resolution IR spectra.

Sex Pheromone of the German Cockroach (*Blattella germanica* L.) Responsible for Male Wing-Raising: 3,11-Dimethyl-2-nonacosanone

When an adult male of the German cockroach, *Blattella germanica* (L.), comes in contact with a sexually matured female of the same species, he shows a characteristic sequence of courtship behavior involving 'fencing' with antennae, turning his direction around 180° and simultaneous wing-raising, secreting from his tergal glands for the female to lick, and eventually copulating. Both ROTH and WILLIS[1] and ISHII[2] have postulated that communication through their antennal contact plays a decisive role for adult males to discriminate between females and males, and that the discrimination is principally due to contact chemoreception of the antennae of males with the substance(s) which is found in cuticular wax of sexually matured females.

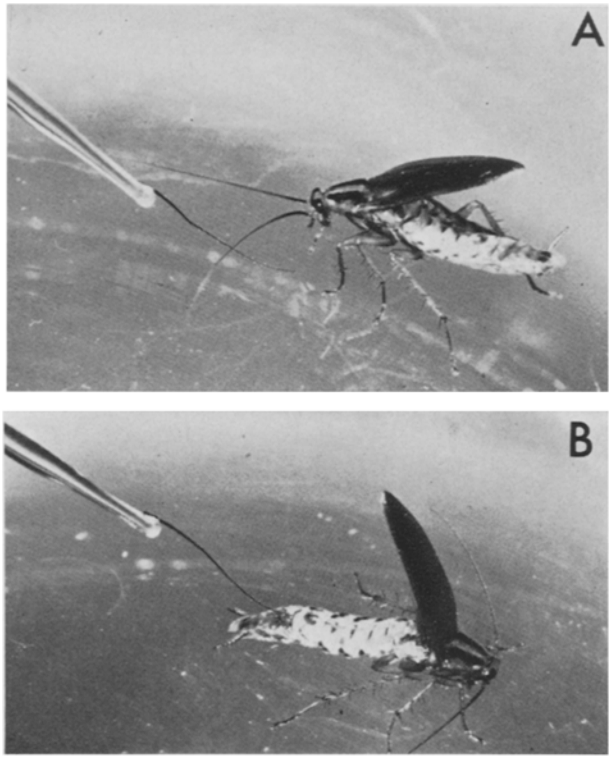

Fig. 1. Bioassay of the active substance to *Blatella germanica* adult male. A) The male responded by contact with his antennae to the isolated male antenna treated with the active substance. B) He turned around and raised his wings.

We now report here that the courting response of adult *B. germanica* males is elicited by contact of their antennae with each of two components which are extracted from the body surface of sexually matured females, and one of them is isolated in crystalline form and characterized as 3,11-dimethyl-2-nonacosanone.

Material and methods. Bioassay for *B. germanica* male to be stimulated was carried out as follows; an antenna was cut off close to the base from an adult male, attached to a small glass rod, and dipped into a carbon tetrachloride solution containing the test material in a definite concentration for 2–3 sec. After allowing it to dry, the male antenna was brought in contact with antennae of 10 test males one after another which had been sexually isolated for 1–2 weeks after their adult emergence. Positive response was evaluated by wing-raising and turning the direction of the test males within 30 sec at about 25 °C (Figure 1).

Females to be extracted were segregated from males immediately after adult emergence and reared at 25–28 °C for 1–2 weeks until their sexual maturation.

Results and discussion. The females (1,600) were washed repeatedly with several portions of *n*-hexane within 3 min to extract only the wax from the surface of their bodies. The combined *n*-hexane solution (1,600 ml) was evaporated to give an active oily material (404 mg), from which the active neutral fraction (381 mg) was separated by the conventional procedure. The neutral fraction was chromatographed on a column of silicic acid (16 g, Mallinckrodt, 100 mesh) to give active 2 fractions, tentatively termed Fraction A and Fraction B, which were eluted with a mixture of *n*-hexane and ether 100:1 and 100:50 respectively. They showed independently the activity for eliciting response of wing-raising from males.

To isolate and characterize the active substance(s) from Fraction A, the similar procedure was repeated starting with about 36,000 sexually matured females. The Fraction A (71.7 mg) thus obtained was subjected again to chromatographic purification on a column of silicic acid

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