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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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.

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

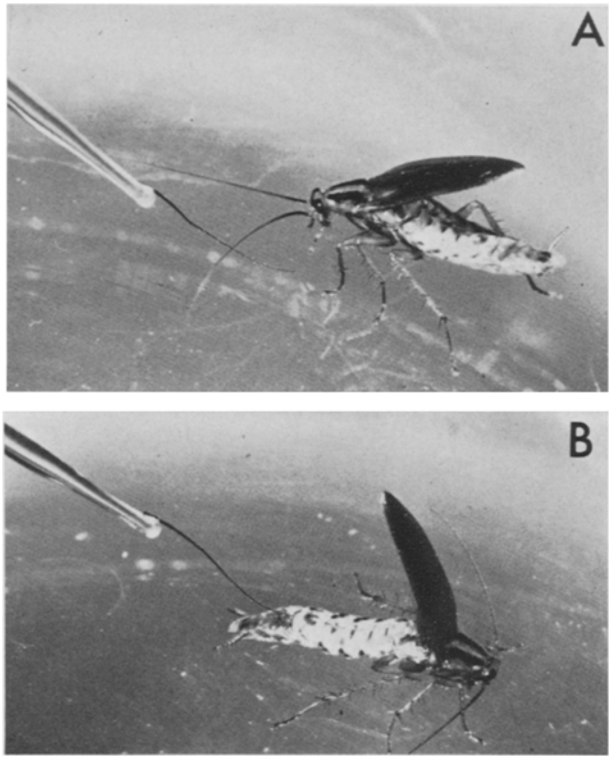

Fig. 1. Bioassay of the active substance to *Blatella germanica* adult male. A) The male responded by contact with his antennae to the isolated male antenna treated with the active substance. B) He turned around and raised his wings.

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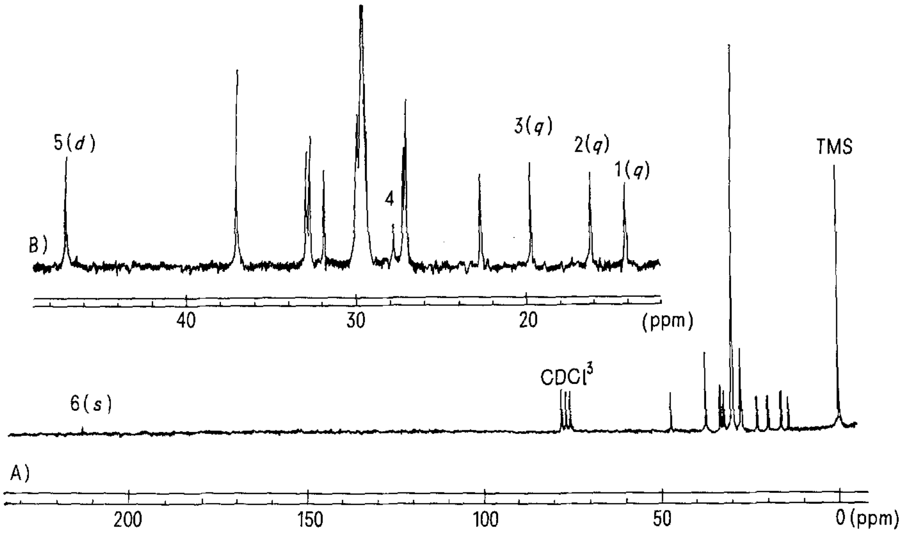

Fig. 2. ${}^{13}C$-Nuclear magnetic resonance spectra of the active compound (38 mg per 0.5 ml $CDCl_3$) in Fraction A. The spectra were recorded in the following conditions: A) 4 sec pulse repetition, 10,000 times accumulation and 6,250 Hz frequency range; B) 2–1 sec pulse repetition, 5,000 times accumulation and 1,000 Hz frequency range. The numbers given in the peaks of spectra correspond to the assignment in the text. Each letter code in parentheses indicates the information from off-resonance decoupled spectra. The letters *s*, *d* and *q* represent singlet, doublet and quartet, respectively.

(7.5 g). The crystalline mass (67.6 mg) from the active eluate was recrystallized twice from ethanol to yield colourless fine needles (46.5 mg), m.p. 45–46°. The high resolution mass spectra of the substance and its 2,4-dinitrophenylhydrazone (m.p. 55–56°) indicated a molecular ion peak at *m/e* 450.4803 (calculated value for $C_{31}H_{62}O$, 450.4797), and 630.5066 (calcd. value for $C_{37}H_{66}N_4O_4$, 630.5080), respectively. These spectral data suggest that the substance may be a saturated aliphatic carbonyl compound.

The structural moiety of $CH_3\text{–}CO\text{–}CH(CH_3)\text{–}CH_2\text{–}$ was concluded from the following spectral data; in the proton magnetic resonance (PMR) spectrum ($CDCl_3$) δ 2.10 (3H, $CH_3\text{–}CO\text{–}$, singlet), 1.04 (3H, $\text{–}CO\text{–}CH(C\mathit{H}_3)\text{–}$, doublet, $J = 6.8$ Hz) coupling with a signal at 2.49 (1H, $\text{–}CO\text{–}C\mathit{H}(CH_3)\text{–}CH_2\text{–}$, sextet, $J = 6.8$ Hz), and in the high resolution mass spectrum, a strong peak corresponding to the fragment $CH_3\text{–}C(\overset{+}{O}H)\text{=}CH(CH_3)$ at *m/e* 72.0540 (calcd. value 72.0574) resulted from the McLafferty rearrangement of the methyl ketone having an α-methyl branch. Other signals in the PMR-spectrum indicated the presence of a long alkyl chain (δ around 1.22, 49H) with a methyl branch (δ 0.82, 3H, doublet, $J = 6.5$ Hz) and of a terminal methyl (δ 0.84, 3H triplet, $J = 6.5$ Hz).

The foregoing assignment of the PMR signals was consistent with the information from ${}^{13}C$-nuclear magnetic resonance (CMR) spectrum. As shown in Figure 2, signals were observed derived from the following carbon atoms; a terminal methyl (δ 14.13, 1), a branched methyl (δ 19.74, 3), a carbonyl (δ 212.59, 6) which is attached both by a methyl (δ 27.92, 4) and a methine (δ 47.26, 5) having a methyl (δ 16.19, 2), besides another methine and 24 methylenes. These assignments of the CMR-signals were based upon empirical chemical shifts as to alkanes and carbonyl compounds[3], and the result of off-resonance decoupling experiment.

The methyl branch on the long alkyl chain was presumed to be attached to the carbon atom at 11th position from the methyl ketone terminal, because the high-resolution mass spectrum showed a significant peak at *m/e* 197.1910 (calcd. value for $C_{13}H_{25}O$, 197.1916), and also the mass spectrum[4] of the Wolff-Kishner reduction product showed 2 strong peaks at *m/e* 183 ($C_{13}H_{27}$) and 281 ($C_{20}H_{41}$).

From the above-mentioned data, the structure of the active principle in Fraction A was determined to be 3,11-dimethyl-2-nonacosanone[5]. This compound showed a distinct activity at the concentration of 50 µg/ml when assayed by the method described above.

Isolation and characterization of the active principle(s) in Fraction B are now under investigation.

Zusammenfassung. Aus Cuticularwachs geschlechtsreifer Weibchen von *Blattella germanica* (L.) wurde 3,11-Dimethyl-2-nonacosanon isoliert, das erwachsene Männchen der Art zum Balzverhalten anregt, wenn sie es mit ihren Antennen berühren.

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[3] J. B. Stothers, *Carbon-13 NMR-Spectroscopy* (Academic Press, New York, 1972), and G. C. Levy and G. L. Nelson, *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists* (Wiley-Interscience, New York 1972).

[4] Mass spectrum was measured with a Hitachi RMS-4 mass spectrometer attached with a Hitachi K-53 gas chromatograph (5% OV-17).

[5] In spite of the presence of 2 possible asymmetric carbons, no optical rotation was observed in *n*-hexane solution ($c = 1.85$) in the range 240–600 nm.

[6] Acknowledgements: We thank T. Ueno, K. Koshimizu and H. Ohigashi of Kyoto Univ. for measurements of mass spectra, PMR-spectra and ORD, respectively. We also thank Y. Kato and H. Hayakawa of Hitachi Co. Ltd. for measurements of high-resolution mass spectra, and K. Matsushita of JEOL Ltd. for CMR-spectra.

Decarbomethoxy Apocuanzine, a New Indole Alkaloid from *Voacanga chalotiana*

Benzene extraction of the root bark of *Voacanga chalotiana*, collected in Angola, afforded a complex mixture of tertiary bases from which four new indole alkaloids have been isolated[1]. The present communication is concerned with the elucidation of structure ***1*** for one of the new bases, $C_{20}H_{22}N_2O_2$ (M = 322), m.p. 196° (from AcOEt), $[\alpha]_D^{22}$ –132° ($CHCl_3$), λ_{max} (MeOH) 218, 247, 276 (infl.), 297 (infl.), 307 and 318 nm (lg ε 4.45,