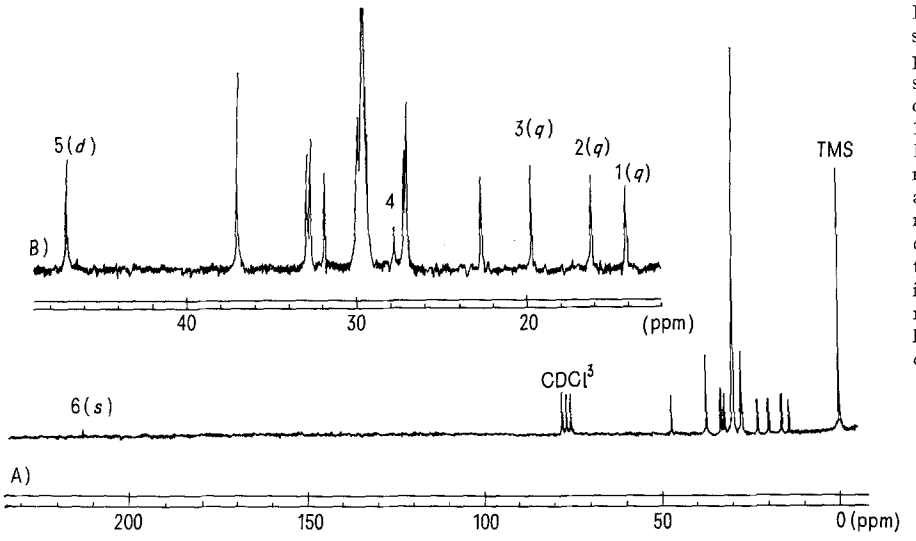

Fig. 2. ^{13}C-Nuclear magnetic resonance spectra of the active compound (38 mg per 0.5 ml $CDCl_3$) in Fraction A. The spectra were recorded in the following conditions: A) 4 sec pulse repetition, 10,000 times accumulation and 6,250 Hz frequency range; B) 2–1 sec pulse repetition, 5,000 times accumulation 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–CO–$CH(CH_3)$–CH_2– was concluded from the following spectral data; in the proton magnetic resonance (PMR) spectrum ($CDCl_3$) δ 2.10 (3H, CH_3–CO–, singlet), 1.04 (3H, –CO–CH(CH_3)–, doublet, J = 6.8 Hz) coupling with a signal at 2.49 (1H, –CO–C*H*(CH_3)–CH_2–, sextet, J = 6.8 Hz), and in the high resolution mass spectrum, a strong peak corresponding to the fragment CH_3–$C(\overset{+}{O}H)$=$\dot{C}H(CH_3)$ 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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Pesticide Research Institute, College of Agriculture, Kyoto University, Kyoto (Japan), 10 April 1974.

[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.

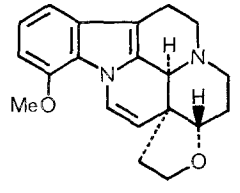
[6] Acknowledgements: We thank T. Ueno, K. Koshimizu and H. Ohigashi of Kyoto Univ. for measurements of mass spectra, PMR-spectra and ORD, respectively. We also thank Y. Kato and H. Hayakawa of Hitachi Co. Ltd. for measurements of high-resolution mass spectra, and K. Matsushita of JEOL Ltd. for CMR-spectra.

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,

4.46, 3.79, 3.90, 4.13, 414.), λ_{min} (MeOH) 230 and 312 nm (lg ε 4.35 and 4.06). The 100 MHz ^{1}H-NMR-spectrum in benzene – d_6 reveals a close similarity to that of cuanzine[2], an alkaloid co-occuring in the same plant and containing the vincamine skeleton with an additional tetrahydrofurane ring (**2**). In fact, **1** exhibits, beside an 1,2,3-hydrogen aromatic substitution pattern at δ 7.21 (dd, J_{ortho} 7.5, J_2 2 Hz), 7.09 (t, J_{ortho} 7.5 Hz), 6.52 (dd, J_1 7.5, J_2 2 Hz) and a methoxy group at δ 3.42, the signals of four protons at δ 4.33 (1H, bs), δ 3.63 (1H, dd, J_1 12, J_2 7 Hz) and δ 3.98–3.75 (2H, m), having the same pattern as the C-21, C-15 and C-18 protons of **2**, respectively. In comparison to cuanzine, the signals of the AB system due to the protons at C-17, of the carbomethoxy group and of the hydroxyl function, are missing. The absence of the two latter functional groups is confirmed by the IR spectrum which lacks of any CO and OH absorption. In addition, the ^{1}H-NMR-spectrum exhibits the presence of an AB system (δ_A 7.66, δ_B 5.05, J_{AB} 8 Hz) attributable to two olefinic protons, one of which strongly deshielded.

The above spectroscopic data and the mass spectrum, which contains only one important peak at *m/e* 237 (100%, ion *a*), are consistent with structure **1** for the new alkaloid (decarbomethoxy apocuanzine), the cis C/D ring fusion being deduced from the lack of Bohlmann bands in the 2800–2730 cm^{-1} region of the IR-spectrum and from the downfield resonance of the C-21 proton.



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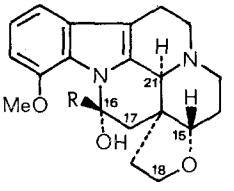
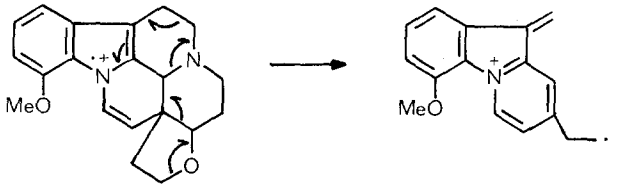
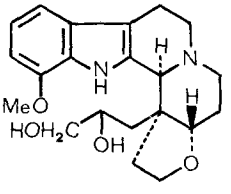


2 R = CO_2Me
3 R = H



a



4

Chemical confirmation of this supposition could be provided by correlation with cuanzine. Refluxing **1** in acetic acid yields the hydroxyderivative **3**, $C_{20}H_{24}N_2O_3$, M^+ = 340, OH stretching band at 3560–3440 cm^{-1} in the IR-spectrum, UV-maxima (MeOH) at 225, 270, 283 (infl.) and 292 nm (lg ε 4.60, 3.95, 3.86 and 3.73) characteristic of a methoxyindole chromophore.

In the ^{1}H-NMR-spectrum (100 MHz, $CDCl_3$) **3** exhibits, beside the C-15 proton at δ 5.47 (dd, J_1 10, J_2 7 Hz) and the C-21 proton at δ 4.25, an ABX system (δ_A 1.92, δ_B 2.56, δ^X 6.17, J_{AB} 15, J^{AX} 5, J^{BX} 2 Hz) which could be assigned to the geminal protons at C-17 and to an equatorial proton at C-16. Irradiation of the X proton transforms the signals at δ 1.92 and 2.56 into two doublets, the former displaying a slight broadening due to a long range W coupling with one of the protons at C-19 resonating at ca. 2.7 ppm. These data can be readily rationalized if the proton at C-17 resonating at δ 1.92 is placed in a β-axial position and the hydroxyl function at C-16 possesses an α-axial orientation.

Periodic acid cleavage of the diol **4** coming from the $NaBH_4$ reduction of cuanzine[2] yields the same hydroxyderivative **3**, thus establishing for the new alkaloid the absolute configuration shown in structure **1**.

Riassunto. Dalla corteccia della radice della *Voacanga chalotiana* è stata isolata la decarbometossi apocuanzina (**1**), un nuovo alcaloide indolico la cui struttura è stata definita per via spettroscopica e mediante correlazione chimica con la cuanzina (**2**).

Résumé. On a extrait de l'écorce des racines de *Voacanga chalotiana* un nouvel alcaloïde indolique, la décarbométhoxyapocuanzine. L'étude de son spectre de RMN et la corrélation chimique avec la cuanzine (**2**) permettent d'attribuer à cet alcaloïde la structure **1**.

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[1] B. GABETTA, E. M. MARTINELLI and G. MUSTICH, Fitoterapia *45*, 7 (1974).
[2] E. BOMBARDELLI, A. BONATI, B. DANIELI, B. GABETTA, E. M. MARTINELLI and G. MUSTICH, in press.
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Chemical Behavior of Conjugated Polyenoic Acids toward Sulfuric Acid. Acid-Catalyzed Cyclization and Successive Rearrangement of *Trans*-β-Ionylidene Crotonic Acid

In connection with our program[1] aiming at the elucidation of the chemical behavior of conjugated polyenoic acids, especially of vitamin A acid (I) homologues, toward H_2SO_4, we describe here the first example on the title reaction of the conjugated tetraenoic acid.

Methods and materials. Treatment of *trans*-β-ionylidene crotonic acid (II)[2] in $CHCl_3$ with 80–90% H_2SO_4 at room temperature for a few min, and extraction of the diluted aqueous acidic layer with ether, led to the almost exclusive formation of the 2 major products. Because of the great