units and, at the same time base pairing and stacking. Thus, even a single α-nucleotide in a β-nucleotide chain is very likely to represent a serious 'mistake' in the chain.

Discussion. This investigation of molecular models demonstrates that the principles of base pairing and helix formation, which are essential for the propagation of the genetic information, are not exclusively possible with β-nucleotides. α-Nucleotides seem to be capable of exhibiting similar secondary structures. Thus one can assume that the replication of genetic material should proceed also with α-nucleotides. But such a replication appears to be possible only with nucleotides of uniform glycosidic configuration, since α- and β-nucleotides within the same strand interfer with helix formation.

Thus we are dealing with a similar phenomenon as is encountered for the amino acids and proteins: of two equally suitable stereoisomers, nature has chosen one, which thereafter is applied uniformly and consequently[21].

α-Oligonucleotides can prove to be useful tools for the investigation of enzymes related to the nucleic acid metabolism and protein biosynthesis with respect to their specificity to the α-glycosidic linkage. In an earlier paper of this series[22], it was shown that certain α-nucleoside 5'-phosphates are resistent to crude *Crotalus adamanteus* venom (acting as a 5'-nucleotidase). However, HOLÝ[14] observed, using a purified preparation of 5'-nucleotidase from *Crotalus adamanteus* venom, that the 5'-phosphates of α-uridine, 2'-deoxy-α-uridine and 2'-deoxy-α-cytidine were hydrolyzed.

The synthesis of oligonucleotides containing α-nucleoside units, their physical and chemical properties and their behaviour towards various enzymes are under investigation.

Zusammenfassung. Studien anhand von DREIDING Stereomodellen zeigen, dass die Bildung von helixartigen Sekundärstrukturen durch Basenpaarung und Basenstapelung nicht auf Polynucleotide mit β-ständig angeordneten Basen (Konfiguration wie sie in den Nukleinsäuren gefunden wird) beschränkt ist. Auch Polymere aus lauter α-Nucleotideinheiten scheinen dazu befähigt zu sein.

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18 June 1973.

[21] Note that D- and L-amino acids are enantiomers, whereas α- and β-nucleosides are diastereomers.

[22] U. SÉQUIN and CH. TAMM, Helv. chim. Acta *55*, 1196 (1972).

[23] Acknowledgments. The author thanks Prof. CH. TAMM for his continuous interest and for encouraging discussions. The investigation was supported by the 'Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung' (project Nr. 2.460.71).

The Structure of a New Phytoecdysone Kaladasterone: an Application of ^{13}C Magnetic Resonance Spectroscopy to Structural Problems

In the course of our investigation of family Convolvulaceae, we also studied constituents of several Indian Ipomoea species. From the seeds of one of them, which is locally known as Kaladana, we isolated together with previously known phytoecdysones (ecdysone, ecdysterone, makisterone A) also new compounds, muristerone A[1] (II), calonysterone[2], and kaladasterone. The determination of the structure of the last mentioned compound as I is reported herewith, and it is based on evidence from variety of spectroscopic as well as chemical data. We wish, however, to report some ^{13}C magnetic resonance studies which proved to be of importance in determining locations of functionalization of ecdysones.

Kaladasterone (I), $C_{27}H_{42}O_7$ (M^+ at m/e 478.2941, calc. 478.2930), m.p. 242–243° (methanol/acetone), $[\alpha]^{24}$ + 79.3° (metanol), shows in the IR- region absorptions at 1605, 1652, and 3200–3600 cm^{-1} (KBr), and an UV- absorption at λ_{max} (methanol 298 nm (ε 10800) characteristic for a doubly conjugated keto group. The PMR- and CMR- spectra closely resemble spectra of other phytoecdysones[3–5]. (The NMR-spectra were taken in deuterio-pyridine unless stated otherwise; δ_H as well as δ_C are given in ppm from TMS).

In fact, the PMR- spectrum in DMSO-d_6 exhibits signals of 5 methyl groups at δ 0.73; δ 0.86 (d, J ≃ 7 Hz); δ 0.96, and δ 1.06, and of the usual olefinic proton at H_7

[1] L. CANONICA, B. DANIELI, I. WEISZ-VINCZE and G. FERRARI, Chem. Commun. (*1972*), 1060.

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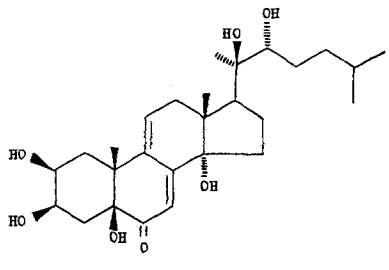
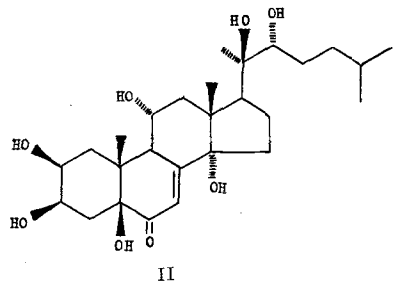
[3] D. H. S. HORN, in *Naturally Occurring Insecticides*, (Eds. M. JACOBSON and D. G. CROSBY; M. Dekker, New York 1971).

[4] P. BEYNON, B. DANIELI, G. FERRARI, J. KREPINSKY, S. MURAKAMI, and G. RAINOLDI, Tetrahedron, in preparation.

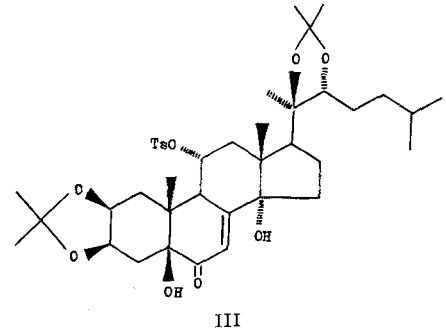
[5] G. LUKACS and C. R. BENNETT, Bull. Soc. chim. Fr. (*1972*), 3996.



I



II



III

(s, δ 5.65). In addition to this, a signal of still another olefinic proton on a six membered ring is present in the spectrum at δ 6.18 ($W_{12} \simeq 10$ Hz).

Kaladasterone forms a 2,3,22-triacetate, a 2,3;20,22-diacetonide, and 20,22-monoacetonide-2,3-diacetate. The PMR-spectra in $CDCl_3$ of these derivatives lack any signal due to H_9 indicating that the double bond must be located in C_9–C_{11} (H_{11} appears as a doublet of a doublet in the range of δ 6.18–6.42, $J_1 \simeq 6$, and $J_2 \simeq 2$ Hz) thus excluding the alternative location of the double bond in C_{14}–C_{15}.

The CMR-spectrum gives conclusive enough information about the complete structure of kaladasterone. The spectrum strongly resembles that of muristerone A[4], as far as the chain carbons signals are concerned (these signals have been bound non-sensitive to structural changes in the tetracyclic part of the molecule[4,5]): C_{20} 76.5 and C_{22} δ 76.8; C_{21} δ 22.4; C_{23} δ 23.2; C_{24} δ 37.1; C_{25} δ 28.2 and C_{26} and C_{27} δ 21.2 and δ 21.5. This spectrum further confirms the presence of the usual OH-bearing carbons C_{14} (δ 83.2), C_2 and C_3 (δ 69.9 and δ 67.9), and C_5 (δ 79.7), and also of C_6 carbonyl group (δ 201.2), at the same fields as in muristerone A.[4]

The CMR-spectrum also exhibits 4 signals due to sp^2 carbons (C_8 δ 155.9; C_{11} δ 132.9; C_9 δ 137.3; C_7 δ 116.8) and as C_8 and C_7 are located differently than is usual in other phytoecdysones containing C_6–C_7–C_8 conjugated system (C_7 δ 120.3; C_8 δ 165.0), it presents proof that kaladasterone contains the other double bond in conjugation with Δ^7 and located between C_9–C_{11}.

On the basis of the above, the only possible structure of kaladasterone seems to be that expressed by the formula I and derived from muristerone A by simple dehydration of the 11-hydroxyl group. It can be expected that a suitable derivative of muristerone A (II) would yield a derivative of kaladasterone. Such a chemical correlation was achieved by preparation of 2,3; 20,22-diacetonide-11-tosylate (III) of muristerone and elimination of the tosyl group on heating III with Al_2O_3 in $CHCl_3$. In this way kaladasterone 2,3; 20,22-diacetonide was obtained in almost quantitative yield.

Kaladasterone is also formed when muristerone A is treated with 5% methanolic NaOH. We do not think, however, that it was formed during isolation, as we found by TLC experiments that various isolation procedures give a stable ratio muristerone A: kaladasterone.

Zusammenfassung. Isolierung und Strukturaufklärung von Kaladasteron ($C_{27}H_{42}O_7$), eines neuen Phytoecdysons, werden beschrieben.

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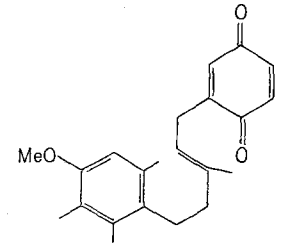
[6] On leave of absence from the Department of Chemistry, University of Sofia, Sofia 26, Bulgaria.

[7] Acknowledgement: We would like to express our gratitude to Dr. P. Beynon and Dr. S. Murakami (Jeol Co., London and Milan) for running the CMR-spectra on the PS 100 PFT Spectrometer. We are also greatly indebted to Dr. S. Maroni for letting us have the high resolution mass spectrum on the Varian Mat 311 instrument.

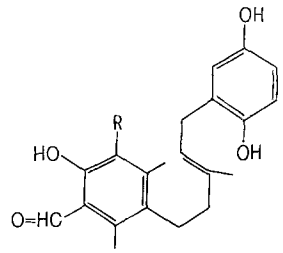
Methyl *Trans*-Monocyclofarnesate from the Sponge *Halichondria panicea*

Recently we isolated[1] from the sponge *Halichondria panicea* a group of 'triprenyl phenols', the paniceins (**1–3**, panicein-B_1 and B_2 are the corresponding quinone and chromenol of panicein-B_3, respectively), which contain an aromatic sesquiterpenoid moiety linked to a quinol or a quinone system. These compounds represent another example of mixed biogenesis and may be formally considered to derive by a combination of a sesquiterpene and a quinol residue. Paniceins have the uncommon feature of an aromatic ring in the sesquiterpenoid moiety which, very likely, originates from a farnesyl precursor by an electrophile-catalyzed cyclization initiated at the isopropylidene group to a monocyclofarnesyl derivative (e.g. **4**), followed by 1,2 methyl migration and subsequent oxidation.

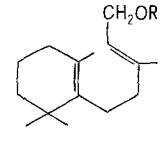
Examination of the less polar fractions eluted with benzene from the SiO_2 column of the solvent extracts from *Halichondria panicea*[1,2] has now led to the isolation (preparative TLC on Merck precoated SiO_2 F_{254} plates; eluent: 40–70° light petroleum-benzene, 6:4) of the methyl *trans*-monocyclofarnesate (**5**; oil; Rf = 0.4; ca. 0.1% of dry sponge). The cooccurrence of **5** and paniceins supports the intermediacy of a monocyclofarnesyl precursor for these latter.



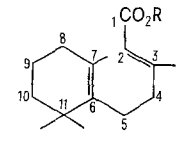
1; panicein A



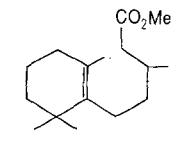
2; R=H; panicein-B_3
3; R=OH; panicein-C



4



5; R=Me
6; R=H



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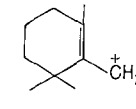

a

[1] G. Cimino, S. De Stefano and L. Minale, Tetrahedron, in press.

[2] The sponges, collected in the Bay of Naples, were obtained from the supply department of the Zoological Station (Naples).