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The Absolute Configuration of Terrestrol

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The main component of the marking perfume of male bumble bees of the species *Bombus terrestris* L. has been shown [1] to be one of the optical isomers of 3,7,11-trimethyldodeca-6*trans*,10-dien-1-ol (I). In order to have a less cumbersome name, particularly in connexion with biological work, the name terrestrol is now proposed for this compound. Both enantiomers of (I) have recently been synthesized in this laboratory.[2] Owing to the comparatively low optical rotation of the molecule and the small amount of the natural product available the observed rotation was only α_{5463}^{23} $-0.018°$, which was too small to allow safe conclusions regarding the absolute configuration. An attempt was therefore made to determine the configuration by comparing the gas chromatographic retention times of stereoisomeric esters obtained through esterification of terrestrol with the enantiomers of 2-methylbutanoic acid, and through preparation of the bornyl ethers, respectively. No gas chromatographic separation of these stereoisomers could be achieved, however. Next, the alcohols were converted into the corresponding aldehydes (II), which were further converted into cyclic

acetals (III) with D(−)-butane-2,3-diol.[3] * In this case mixing (III) from terrestrol with (III) from dextrorotatory synthetic alcohol (I) gave a slight broadening of the peak in the gas chromatogram, indicating that these two acetals are stereochemically different. Although this tallies with the observed levo-rotation of terrestrol more clear-cut evidence was desirable.

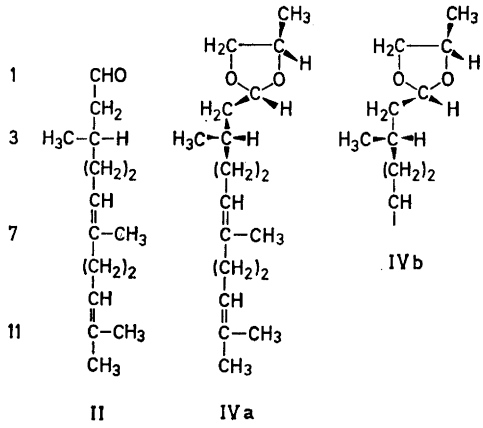

Fig. 1. II: L(−); IVa=2*R*(2*S*,6,10-trimethylhendeca-5*trans*, 9-dienyl)-4*R*-methyl-1,3-dioxalane; IVb.

A definite proof of the absolute configuration was finally obtained through a study of the cyclic acetals (IV) prepared from (II) and D(−)-propane-1,2-diol.[4] * The formation of these acetals involves the creation of a new asymmetric centre at the carbon atom of the initial aldehyde group. The ring closure to cyclic acetal leads preferentially (~3:1) to the *trans*-form (IVa), which is readily separated from the *cis*-form (IVb) by gas chromatography. The retention time of the *trans*-form is not influenced to an appreciable extent by the configuration of carbon atom 3 in the original alcohol (I). By contrast, the effect of the configuration of this carbon atom is easily observed for the *cis*-form of the acetal. The retention time data given in Table 1 show conclusively that terrestrol is (−)-3L,7,11-trimethyldodeca-6*trans*,10-dien-1-ol.

Inspection of models shows that *cis*-configuration of the substituents of the dioxalane ring leads to a closer contact between the methyl group in the ring and that attached to carbon atom 2 of the side chain for *R* (D) than for *S* (L) configuration of this carbon atom, whereas no interference is possible when the substituents of the ring are *trans*-oriented. This seems to explain why GLC retention time data are almost identical for compounds with *trans* but significantly different for compounds with *cis*-oriented ring substituents.

Experimental. The preparation of acetals (IV) via aldehyde (II).[6] 0.5 to 2 mg of alcohol [2] was placed under nitrogen in a Reacti-vial **

* The author is indebted to Dr. Karl Smiley, Fermentation Laboratory, U.S. Department of Agriculture, Peoria, Ill., for a specimen of this compound.

* Obtained from Research Organic/Inorganic Chemical Co., Sun Valley, California 91352.

**Obtained from Pierce Chemical Company, Box 117, Rockford, Ill.

Table 1.

Compound	Gas chromatographic retention time, minutes [a]			
	Alcohol	Acetals		Measured difference
	I	IVa	IVb	(IVb−IVa)
(I), (+)-synthetic	64.4	84.7	89.2	4.46
terrestrol	64.4	84.5	88.4	3.86
(I), (−)-synthetic	64.8	85.4	89.3	3.88
(I), (+)-synthetic	65.0	85.5	90.0	4.50

[a] Glass capillary column, length 39 m, internal diameter 0.37 mm. Nitrogen at 0.5 kg/cm². The column was carbonized as described by Grob [5] and coated with 8 % UCON 50LS 1200X. The efficiency measured on (IVb) was 87 000 theoretical plates.

and 30 μl of a 10 % solution of phosgene in ether added. Mixing was performed by vibrating the vial. After 2 h at room temperature excess phosgene and the solvent were removed by suction through a syringe needle. The pressure in the vial was restored with nitrogen and 20 μl of dimethylsulfoxide added. After 15 min at room temperature 1.5 μl of triethylamine was added. The reaction mixture was vibrated and the formation of aldehyde (II) was followed by GLC. After about 20 min, 2 μl of D(−)-propane-1,2-diol was injected into the vial, immediately followed by 20 μl of a 10 % solution of *p*-toluenesulfonic acid in dimethylsulfoxide. The formation of acetal (IV) was followed by GLC. The reaction was complete after about 3 h, and 40 μl of heptane was then added. The heptane solution was used to obtain GLC retention data and to identify the compounds by their mass spectra.

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Solvent Effects in the Hydrolysis of Orthoesters and Their Value as Criteria of Reaction Mechanism

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In recent papers [1–3] we concluded that the hydrolysis of an alkyl orthoformate is either an A-1 reaction or a rate-determining proton transfer reaction depending on the structure of the ester. The structural effects, the lack of general acid catalysis and the magnitude of solvent deuterium isotope effect, $k_{D_3O^+}/k_{H_3O^+}$ about three, suggest that the hydrolysis of isopropyl and ethyl orthoformates proceeds by way of a protonation pre-equilibrium. In the hydrolysis of 2-methoxyethyl and 2-chloroethyl orthoformates general acid catalysis was detected and the solvent deuterium isotope effect is close to two. These results were best interpreted in terms of a ratedetermining proton transfer reaction. This kind of mechanistic change is likely as the free energy of activation of the proton transfer step increases with the electronegativity of the alkyl groups attached to the oxygen atoms. Although the A-S_E2 mechanism is evident in the hydrolysis of these esters, the A-2 mechanism cannot be excluded on the basis of the abovementioned kinetic data, as solvent deuterium isotope effects are almost equal for these mechanisms and, in addition, general acid catalysis should be detected in both of the reactions. It is noteworthy that Kresge and Preto [4] ruled out the A-2 mechanism of hydrolysis of orthocarbonates on the basis of the absence of nucleophilic catalysis.

This paper presents kinetic data for the hydrolysis of various orthoformates in water-dioxane mixtures and the mechanistic conclusions that can be drawn on the basis of the results, particularly in cases where a decision is to be made between an A-S_E2 and an A-2 mechanism.

Experimental. Ethyl, methyl, 2-methoxyethyl, and 2-chloroethyl orthoformates were the preparations used in the previous studies.[5] The dioxane used as the solvent in the kinetic measurements was purified by the standard method.[6]