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THE STRUCTURE OF MATATABIETHER*

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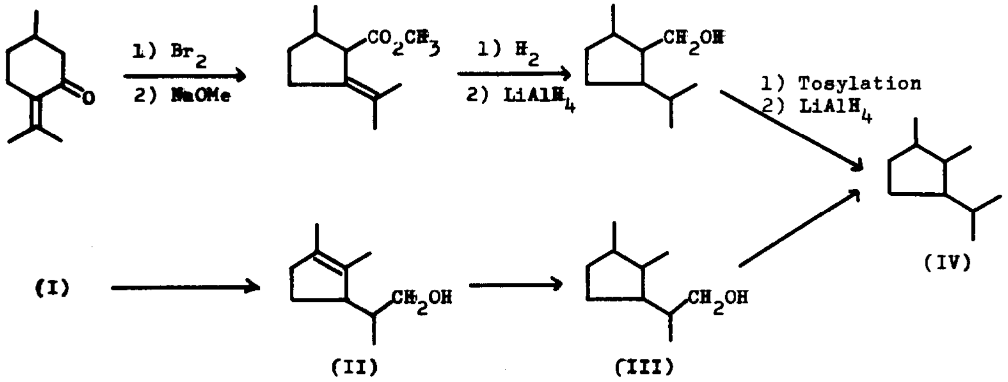
Extraction of the leaves and galls of Actinidia polygama has already afforded a number of new cyclopentanoid monoterpenes (1) including the extremely potent attractants for Chrysopidae and Felidae animals.

The present paper is concerned with the structure elucidation of a new cyclopentanoid monoterpene which we propose the name matatabiether after the Japanese popular name (Matatabi) of the plant.

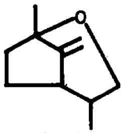
Matatabiether (I), $C_{10}H_{16}O$, (b.p. 67°C/16 mmHg, $n^{16}=1.4771$, $[\alpha]_D^{17}$ -150°) gives positive reactions towards tetranitromethane, bromine solution, Ehrlich reagent (blue→dark violet) and Liebermann reagent (dark violet). The IR spectrum of matatabiether shows bands at 3100 cm^{-1}, 1675 cm^{-1} and 890 cm^{-1} for terminal methylene and at 1045 cm^{-1} and 1085 cm^{-1} for ether linkage. On hydrogenation with 10% Pd/c in methanol, matatabiether absorbs one mole of hydrogen to give an unsaturated alcohol (II), $C_{10}H_{18}O$, (b.p. 121.5°C/27 mmHg) by hydrogenolysis. Unsaturated alcohol (II), on further hydrogenation with Pd/c or Adams catalyst, gives a saturated alcohol (III), $C_{10}H_{20}O$, (b.p. 105°C/12mmHg) which is a mixture of epimers in the approximate ratio 5:1 (G.C.). The IR spectrum of (III) shows a band at 1045 cm^{-1} which indicates primary alcohol. The reaction of the alcohol (III) with p-toluenesulfonyl chloride in pyridine, followed by treatment with $LiAlH_4$, afforded a isomeric mixture of hydrocarbons (IV), $C_{10}H_{20}$. The IR spectrum of (IV) shows a split doublet at 1360 cm^{-1} and 1380 cm^{-1} due to gem-dimethyl, which is not present in original alcohol (III). Therefore the methyl group in alcohol (III) should be vicinal to hydroxyl group.

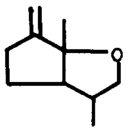
The mass spectrum and IR spectrum of hydrocarbons (IV) is in good agreement with those of 1,2-dimethyl-3-isopropyl-cyclopentane which was derived from pulegone by the following sequence of reactions.



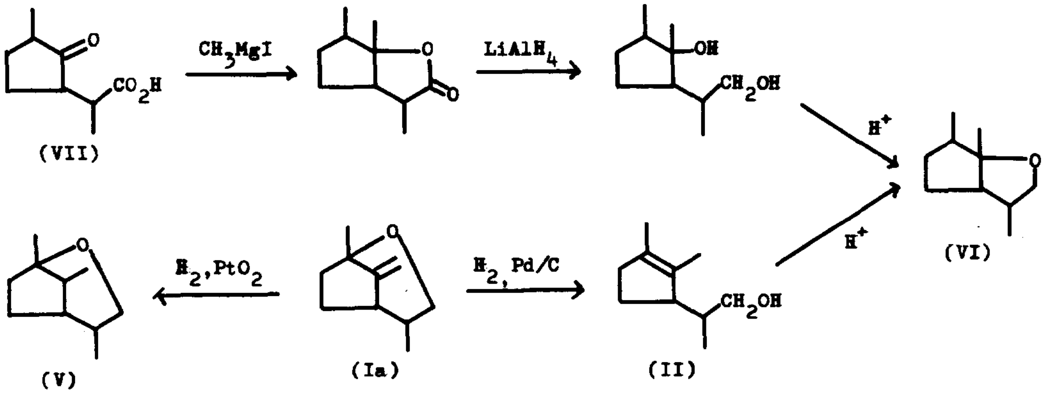
Thus matatabiether was shown to be a cyclopentanoid monoterpene.

The NMR spectrum of matatabiether indicates the presence of terminal methylene at 5.4τ as a sharp singlet and methyl signal of doublet centered at 9.25τ (J=7 cps) and methyl signal attached to the carbon atom adjacent to oxygen function of ether at 8.8τ and methylene protons attached to oxygen at 6.25τ as multiplet. From these findings the structure of matatabiether is represented by formula Ia or Ib.


(Ia)


(Ib)

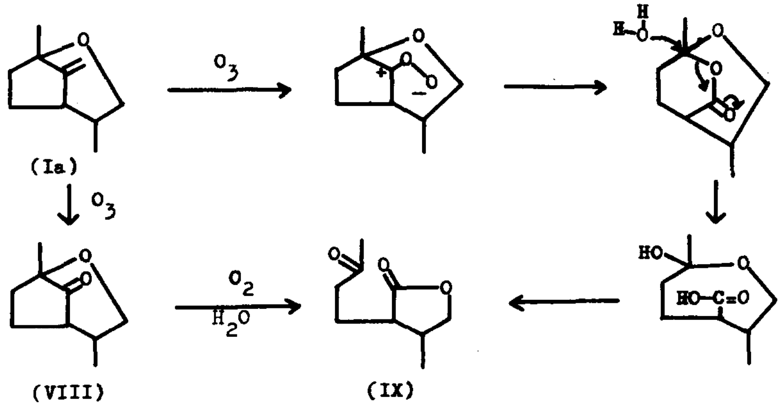
When the hydrogenation was carried out in absolute ether by using Adams catalyst, matatabiether absorbed one mole of hydrogen to afford a dihydromatatabiether (V), $C_{10}H_{18}O$, whose NMR spectrum showed the new signal at 9τ corresponding to three protons instead of the disappearance of the signal due to terminal methylene. The IR spectrum of dihydromatatabiether also indicated the saturation of terminal methylene. Meanwhile, another ether, $C_{10}H_{18}O$, (b.p. 87-88°C/27 mmHg) was obtained from unsaturate alcohol (II) by heating with catalytic amount of p-toluene sulfonic acid in absolute benzene. This second ether was assigned the structure (VI) (dihydro Ib), which was confirmed by its preparation from ketocarboxylic acid (VII) (2) by the sequence reactions illustrated below.



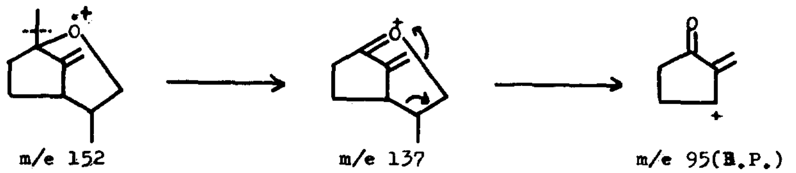
The IR spectrum of (VI) differs in great extent from the complex spectrum of dihydromatatabiether (V), which suggests that dihydromatatabiether be a bridged bicyclic ether (3). Thus matatabiether was assigned the structure Ia.

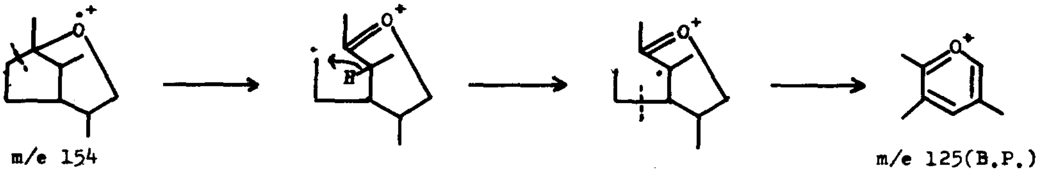
The ozonolysis of matatabiether in chloroform at -35°, followed by treatment with hot water, gave traces of formaldehyde and a mixture of ketones. Chromatography of the mixture of ketones yielded as less polar fraction a ketone, $C_9H_{14}O_2$, which is a keto ether (VIII) as suggested by IR ($\nu_{C=O}$ 1750 cm^{-1}) and NMR spectra. The main product is a ketolactone $C_9H_{14}O_3$, (IX) (NMR; $8.95^{d}\tau$(3H), $7.89^{s}\tau$(3H), $6.00\,\tau$(2H, AB part of ABX pattern) having a γ-lactone ($\nu_{C=O}$ 1760 cm^{-1}) and a methyl ketone ($\nu_{C=O}$ 1750 cm^{-1}, iodoform test positive). The ketolactone (IX) is also formed from ketoether (VIII) by long standing in the air.

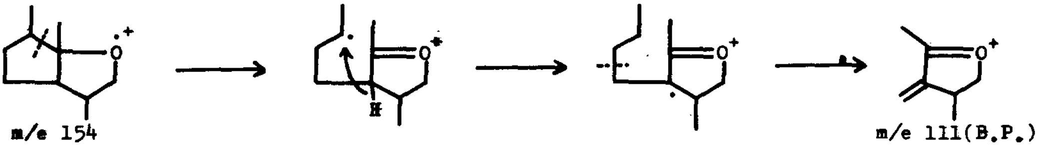
The formation of ketolactone (IX) from matatabiether (Ia) is explained by the following mechanism (4).



The structure of matatabiether (Ia), dihydromatatabiether (V) and ether (VI) are consistent respectively with their mass spectra.

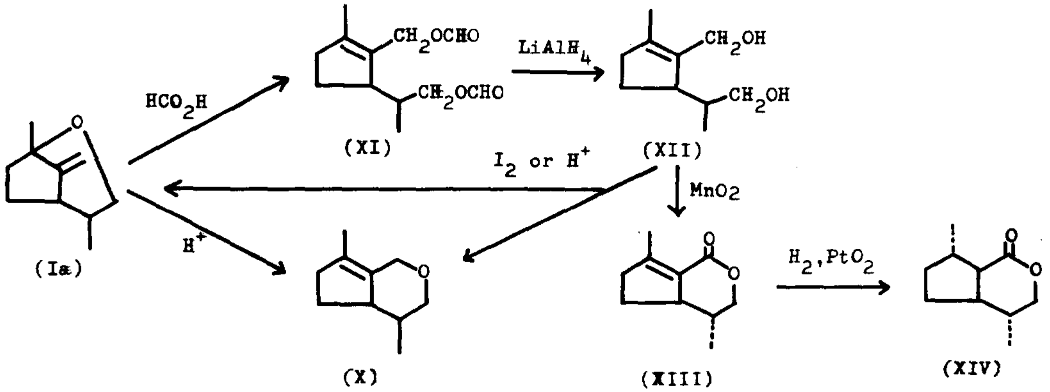






Total synthesis of matatabiether:

The reaction of matatabiether with formic acid in the cold yielded the third ether (X), $C_{10}H_{16}O$, (NMR; $9.12\tau^{d}$(3H), $8.36\tau^{s}$(3H), $5.61\tau^{d}$(1H), $6.45\tau^{m}$(3H).) and formate (XI), $C_{12}H_{18}O_4$, (IR. 1720 cm^{-1}, 1170 cm^{-1}) which was hydrolized to give unsaturated diol (XII), $C_{10}H_{18}O_2$, (NMR; $9.1\tau^{d}$(3H), $8.25\tau^{s}$(3H), $6.4\tau^{m}$(2H), $5.73\tau^{t}$(2H).). The unsaturated diol (XII) has already been synthesized in our laboratory (5) and the identity was provided by the comparison of the IR spectrum and gaschromatogram.



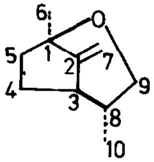
It was originally considered that the reaction of acid on the unsaturated diol (XII) would result in a formation of ether ring to afford a mixture of matatabiether and the ether (X). This possibility was realized when the unsaturated diol (XII) was treated with p-toluene sulfonic acid or iodine in absolute benzene.

By the chromatography of a mixture of ethers on alumina the pure matatabiether and the ether (X) were isolated respectively. Thus the total synthesis of matatabiether was accomplished.

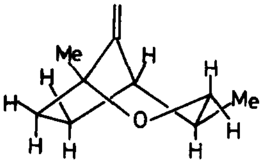
Stereochemistry of matatabiether:

In the NMR spectrum of matatabiether, the signal of protons at C_9 constitutes the AB part of the typical ABX pattern with $J_{AX}=5.5$ cps, $J_{BX}=10.5$ cps and $J_{AB}=12$ cps.

Since the configuration of methyl at C_3 of matatabiether has already been correlated with isodihydronepetalactone (XIV) via neo-nepetalactone (XIII), only the conformation shown in (XV) allows the large coupling constant between vicinal trans diaxial protons (C_8H and C_9H) (6).



(I)



(XV)

Acknowledgements:

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5. Unsaturated diol (XII) has been isolated from Actinidia polygama as one of attractants for the male of Chrysopa. The communications on the chemistry of attractants from Actinidia polygama are forthcoming. We are indebted to Dr. F. Murai for the identification of neonepetalactone (XIII) with synthetic specimen and to Dr. A. Suzui for the synthesis of unsaturated diol (XII).

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