The Structure of Kitol

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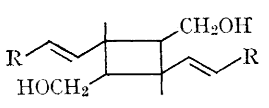
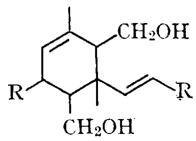
THE recent communication of Burger *et al.*[1] proposing the structure (III) for kitol, based mainly on n.m.r. spectral data, prompts us to report our results leading, principally by mass spectrometry,[2] to the same structure (III) for this natural "vitamin A dimer".

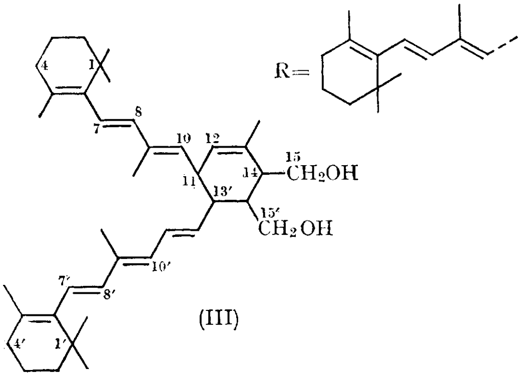
Mass-spectrometric determination of the molecular weight of kitol (m.w. 572; $C_{40}H_{60}O_2$) confirms the formula corresponding to a dimer of vitamin A. The base peak in the mass spectrum of kitol was found at *m/e* 286[3] corresponding to the mass number of vitamin A ($C_{20}H_{30}O$). Formation of this ion fragment corresponding to the monomeric structure upon electron impact (or by thermal effect) is compatible with any of the structures (I, II, or III) considered for kitol (see reference 1).



(I)



(II)



(III)

Catalytic hydrogenation of kitol diacetate (m.w. 656; $C_{44}H_{64}O_4$) produced a fully saturated compound, *viz.*, perhydrokitol diacetate (IV). The mass number of the latter is 672, consistent with a molecular formula $C_{44}H_{80}O_4$. This clearly indicates that kitol has eight double bonds and thus must have three rings.

A peak observed at *m/e* 458 (corresponding to $C_{33}H_{62}$ as shown by high-resolution mass-measurement) in the mass spectrum of perhydrokitol diacetate (IV) is very significant. The formation of this ion (by disruption of the central ring as shown in Scheme I) can be explained only on the basis of the structure (IV) (no stereochemistry implied), but not in terms of the structures which would be obtained by the hydrogenation of the diacetates of (I) and (II).

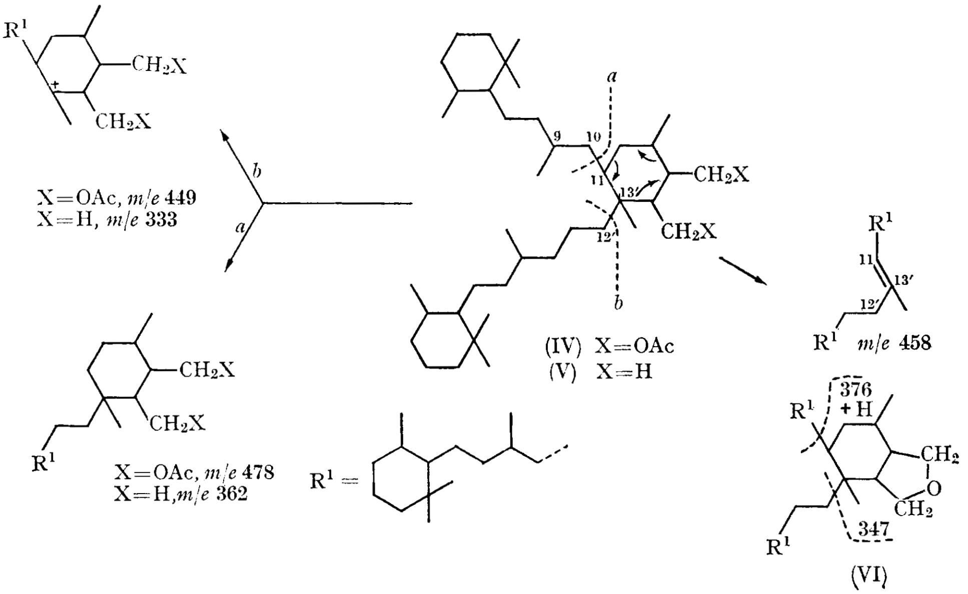
Other principal mass-spectral fragments are also compatible with structure (IV). Cleavage (*b*) of the bond between C-12′ and C-13′ with retention of the positive charge on the tertiary carbon-13′ leads to an ion peak at *m/e* 449 ($M-223$). Subsequent loss of one or two molecules of acetic acid results in peaks appearing at *m/e* 389 and 329. The occurrence of a small peak at *m/e* 478 ($M-194$) is probably caused by the C-10–C-11 bond fission (*a*) with simultaneous migration of a hydrogen atom from C-9 to C-11. Peaks at *m/e* 418 and 358 correspond to the ions obtained by loss of one and two molecules of acetic acid respectively from *m/e* 478.

The n.m.r. spectrum of perhydrokitol diacetate exhibits the presence of the two acetyl methyl groups (τ8·30 and 8·23) and the acetoxymethylenes (4 H; multiplet at $\sim\tau$ 5·85) confirming the primary nature of the alcohol groups in kitol.

The peak at *m/e* 458 (mentioned above) is also observed in the mass spectrum of the hydrocarbon (V) (m.w. 556; $C_{40}H_{76}$) obtained on treating perhydrokitol ditosylate[5] with boiling pyridine followed by catalytic hydrogenation. This supports the mechanism suggested for the formation of the same ion fragment from perhydrokitol diacetate by disruption of the central ring (see Scheme I). The mass spectrum of (V) also exhibits peaks corresponding to $M-223$ and $M-194$ at *m/e* 333 and 362. The n.m.r. spectrum of the hydrocarbon (V) shows the presence of twelve methyl groups in agreement with the structure proposed.

Perhydrokitol ditosylate, on reduction with $LiAlH_4$ in ether, gave a product which showed a molecular ion peak at *m/e* 570 corresponding to the formula $C_{40}H_{74}O$. Absence of hydroxyl absorption in the infrared spectrum of this compound and strong bands at ν_{max} 1065 and 895 cm.$^{-1}$ suggest that the product is the tetrahydrofuran derivative (VI). The methylenes adjacent to the ether oxygen appear as a multiplet (4H; ~τ6·2) in its n.m.r. spectrum. The base peak in the mass spectrum is observed at *m/e* 347 which corresponds to the $M-223$ peak discussed above. The $M-194$ peak is found at *m/e* 376.

SCHEME I



All these results are in agreement with formula (III) for kitol, as proposed by Burger *et al.*[1]

Formula (III) has four asymmetric carbon atoms and thus kitol would be expected to be optically active. Embree and Shantz[4] report $[\alpha]_D-1\cdot35°$ ($CHCl_3$), Büchi and Albrecht have found $-1\cdot95°$ ($CHCl_3$), whereas Burger *et al.*[1] state that "no optical rotation was detected on a 0·5% solution in methanol at wavelengths down to 320 mμ".

Our purest kitol preparation gave $[\alpha]_D = -2\cdot6°$ ($CHCl_3$; *c*, 1·1). The diacetate gave $-4°$ ($CHCl_3$; *c*, 2·4).

The optical activity of kitol is of importance because it is a strong indication in favour of an enzymatic origin for kitol.

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[1] B. V. Burger, C. F. Garbers, K. Pachler, R. Bonnett, and B. C. L. Weedon, *Chem. Comm.*, 1965, 588.
[2] All mass spectra were measured with an A.E.I. MS9 mass spectrometer.
[3] Appropriately shifted to *m/e* 328 in the mass spectrum of kitol diacetate.
[4] N. D. Embree and E. M. Shantz, *J. Amer. Chem. Soc.*, 1953, **65**, 910.
[5] G. Büchi and R. Albrecht, personal communication.