The Structure of Kitol

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KITOL occurs in whale liver oil,[1] and yields vitamin A,[2] and pseudo-kitol[3] on pyrolysis. Japanese authors have proposed structures (I)[3,4] and (II)[3] for kitol and pseudo-kitol respectively. However, comparison of the u.v. light absorption properties* of kitol[5] with those of the alcohols (III)[6] and (IV)[7] favours a structure of the type (II) or (V).

The n.m.r. spectrum of kitol[8] (see Table) is also compatible with (II) or (V), but not (I). When the signals associated with the methyl groups of the β-ionone rings have been assigned, a signal corresponding to *one* methyl group in a saturated environment remains (τ 8·87). Moreover, the distinction evident in each case between the C–9 and C–9′ methyl group (τ 8·22, 8·13), the 7,8 and 7′,8′ olefinic protons (τ 4·06, 4·02), and the hydroxymethylene groups (multiplet at $\sim\tau$ 6·28),

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* Unless stated otherwise, u.v., i.r., and n.m.r. spectra were determined in alcohol, chloroform, and deuterochloroform solutions respectively.

[1] H. Pritchard, H. Wilkinson, J. R. Edisbury, and R. A. Morton, *Biochem. J.*, 1937, **31**, 258.

[2] N. D. Embree and E. M. Shantz, *J. Amer. Chem. Soc.*, 1943, **65**, 910.

[3] Y. Omote, *J. Chem. Soc. Japan*, 1959, **80**, 191; *Chem. Abs.*, 1961, **55**, 3093; *Bitamin*, 1963, **28**(4), 267; *Chem. Abs.*, 1964, **60**, 5803.

[4] R. Kaneko, *Rep. Govt. Chem. Ind. Res. Inst. Tokyo*, 1962, **57**, 194 (English summary in appendix, p. 22).

[5] H. Chatain and M. Debodard, *Compt. rend.*, 1951, **233**, 105.

[6] H. O. Huisman, A. Smit, P. H. van Leeuwen, and J. H. van Rij, *Rec. Trav. chim.*, 1956, **75**, 977.

[7] λ_{max} 295 mμ, ϵ = 32,000.

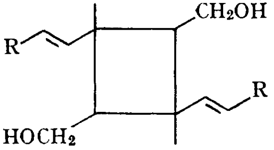
[8] The sample used in the present studies was crystallised from methyl formate, and had m.p. 138—139°, λ_{max} 295 mμ, ϵ = 48,900. No optical rotation was detected on a 0·5% solution in methanol at wavelengths down to 320 mμ. Pyrolysis yielded vitamin A.

TABLE

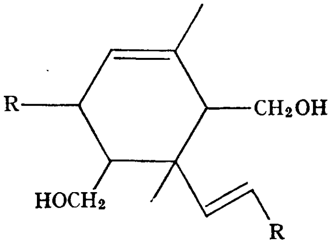
Nuclear magnetic resonance spectra: chemical shifts (τ) at 60 Mc./sec., and assignment of methyl signals

R.CH$_2$OH (III)—	8·18 (C–9)		8·33 (C–5)			8·99 (2C–1)
R.CH=CHCH$_2$OH (IV)—	8·11 (C–9)		8·33 (C–5)			8·99 (2C–1)
Kitol*—	8·13 (C–9′)	8·22 (C–9 + C–13)	8·34 (C–5 + C–5′)		8·87 (C–13′)	8·99 (2C–1 + 2C–1′)
(VI)‡—	8·16 (C–9)			8·29 (C–5 + C–13)	8·70 (C–13′)	8·98 (2C–1)
(VII)†‡—	8·13 (C–9)			8·30 (C–5 + C–13)	8·83 (C–13′)	8·96 (2C–1)

* In 25% CDCl$_3$ in CCl$_4$.
† In acetone.
‡ For convenience the numbering used here for these compounds corresponds to that shown in structure (V).



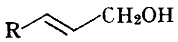
(I)



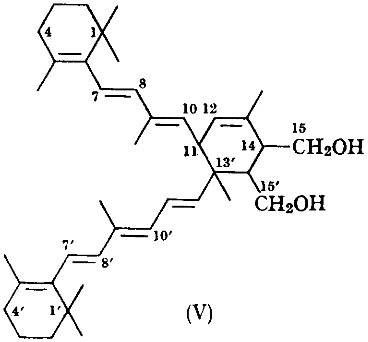
(II)

R – CH$_2$OH

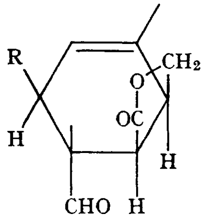
(III)



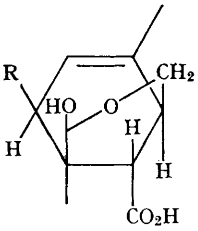
(IV)



(V)



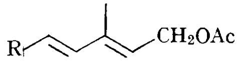
(VI)



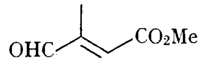
(VII)

suggests that the molecule is unsymmetrical. Two doublets (τ 4·58, J = 6 c./sec., and τ 4·86, J = 10·5 c./sec.) are attributed to the protons at C–10 and C–12 respectively. Similar doublets (τ 4·53, J = 4 c./sec., and τ 4·83, J = 10·3 c./sec.) are observed with the lactone (VI). The latter, ν_{max} 1720 and 1760 cm.$^{-1}$, λ_{max} 260 mμ (ϵ = 16,200), was obtained, together with the acid (VII), m.p. 172—174°, ν_{max} 1702 cm.$^{-1}$, λ_{max} 262 mμ (ϵ = 19,500), and other products, by a Diels–Alder reaction between vitamin A acetate (VIII) and methyl *trans*-β-formylcrotonate (IX), followed by hydrolysis.

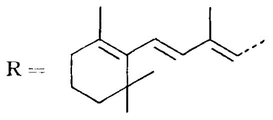
Catalytic hydrogenation of kitol, and subsequent chromic acid oxidation gave a product regarded as a γ-lactone, ν_{max} 1753 cm.$^{-1}$ [*cf.* δ-lactone-ester, ν_{max} 1725 cm.$^{-1}$, formed from (VII) by reduction, esterification, and chromic acid oxidation; γ-lactone-alcohol, ν_{max} 1755 cm.$^{-1}$, formed from (VI) by hydrogenation]. Structure (V) is therefore proposed for kitol.



(VIII)



(IX)



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