COMMUNICATION

The Structure of Iso-anhydro Vitamin A

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Iso-anhydro vitamin A, provisionally called, is one of the major degradation products of vitamin A (I). Because of its positive behavior toward Carr-Price reaction and ultraviolet (UV) spectroscopic properties, this compound can not be ignored on the quantitative evaluation of vitamin A. Iso-anhydro vitamin A was first obtained by prolonged treatment of vitamin A or anhydro vitamin A (II) with an ethanolic hydrogen chloride (1) and its conversion to chloro-containing "Substance X" was later described (2). The alternative chemical structure (III) or (IV) deduced from UV spectral data was proposed tentatively for iso-anhydro vitamin A (3). No further criteria on the chemical structure of this compound have been available. We now report that the title compound prepared from anhydro vitamin A (M^+ , m/e 268; $\lambda_{\max}^{\text{hexane}}$, 390, 368.5, and 350.5 $m\mu$) and 1/30 N-HCl in methanol is shown to be a structure (IV').

- (II) : $R = -CH=CH_2$
 (III) : $R = -CH_2CH_2OC_2H_5$
 (III') : $R = -CH_2CH_2OCH_3$
 (IV) : $R = -CH(CH_3)OC_2H_5$
 (IV') : $R = -CH(CH_3)OCH_3$

Iso-anhydro vitamin A, an unstable yellowish viscous oil, can be distilled at 150-5° (bath temp.) under 0.002 mmHg and its initial blue coloration ($\lambda_{\max}^{\text{CH}_2\text{Cl}_2}$ 620 $m\mu$) produced from the compound and $SbCl_3$ in CH_2Cl_2 turns into violet (620 and 556 $m\mu$) or red violet (555 $m\mu$) after standing at room temperature for 2 or 4 minutes, respectively. The compound exhibits UV absorptions in hexane at 365.5, 347, 331.5, and 248 $m\mu$. Considering a shape of the spectral curve keeping a characteristic fine structure and the positions of $\lambda_{\max}$, this compound is strongly suggested to be a next lower vinylogue of anhydro vitamin A (3, 4). The molecular ion peak appears as a base peak at m/e 300 which is 32 mass units higher than that of the starting material. The presence of a methoxyl group is verified from a nuclear magnetic resonance (NMR) signal at 6.80 τ (3H) along with mass spectrum peaks at m/e 269 [$M-31$ (OMe)] and 268 [$M-32$ (MeOH)]. Furthermore, appearance of signals at 6.29 τ (quartet, 1H, $J=6.5$ cps) and 8.76 τ (doublet, 3H, $J=6.5$ cps) as well as significant paramagnetic shifts of the three signals (8.76, 6.80, and 6.29 τ) caused by tris (dipivalomethanato) europium (5) clearly indicate that this methoxyl group should locate on C-14 and a structure (III') has to be abandoned. Besides UV and NMR spectral information described above, the presence of a signal at *ca.* 4.3 τ (multiplet, 1H) which can be attributed to a C-4 proton can exclude a 4-methoxy-axerophthene-like

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structure. Our conclusion is further supported by $\nu_{\max}^{\text{CS}_2}$ at 1625 (conj. C = C), 1364 and 1352 (gem. CH₃), 2830 and 1100 (OMe), 952 (*trans* -CH=CH-), and 870 cm⁻¹ (-CH=C<), and all spectral data are consistent decisively with the structure (IV').

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