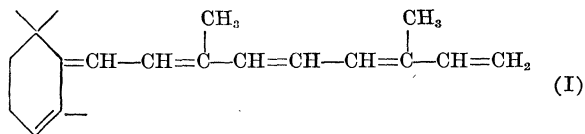
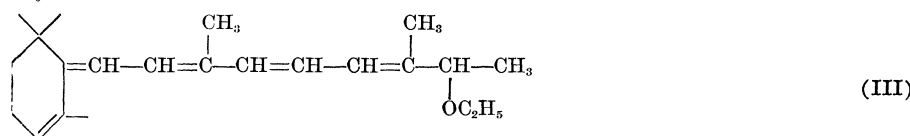
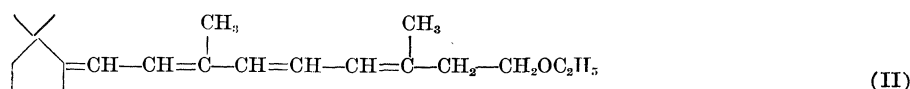


The Structure of "Iso-Anhydrovitamin" A

THE conversion of anhydrovitamin A (I) to "iso-anhydrovitamin A" by the action of dilute ethanolic



hydrogen chloride was discovered more than a decade ago (1) but the structure of the product is still unknown. It has been generally assumed to be a hydrocarbon, as its name implies. Its distribution ratio of 97 : 3 (1) between petroleum ether and 83-percent ethanol has been cited in support of this (2).



The absorption spectrum of "iso-anhydrovitamin A," λ_{max} 332, 348 and 366 m μ (3), strongly suggests a next lower vinyllogue of anhydrovitamin A containing the *retrovitamin* A chromophore (4). On this premise, the simplest explanation for the loss of a double bond by anhydrovitamin A in the above reaction would be solvation of its terminal vinyl group. Either *retrovitamin* A ethyl ether (II) or the secondary ether (III) could possibly result thereby (5). A reinvestigation of this reaction revealed that the

product does indeed consist for the most part, if not wholly, of ethoxylated material, so that "iso-anhydrovitamin A" is not a hydrocarbon but an ethyl ether. This is not inconsistent with the distribution ratio mentioned above.

A distilled reaction product (130–140° at 0.004 mm), still containing considerable unreacted (I) (small band at 390 m μ), analyzed as follows:

Anal. Calcd. for C₂₂H₃₄O: C, 84.02; H, 10.90; ethoxyl, 14.33.

Found: C, 85.28; H, 10.78; ethoxyl, 9.43.

Alumina chromatography yielded a product of much greater purity but not wholly free of (I) (the small band at 390 m μ was considerably decreased but not eliminated).

Found: C, 84.36; H, 10.79; ethoxyl, 11.17.

A second reaction product, also with a substantial

ethoxyl content, was isolated. Its absorption curve, λ_{max} 325 m μ , is strikingly similar to that of vitamin A. This compound is therefore tentatively designated as vitamin A ethyl ether, which is known to result from the addition of ethanol to (I) (5).

Studies are in progress to establish which of the two proposed structures for "iso-anhydrovitamin A," (II) or (III), is correct.

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References and Notes

1. E. M. Shantz, J. D. Cawley and N. D. Embree, *J. Am. Chem. Soc.* **65**, 901 (1943).
2. N. D. Embree and E. M. Shantz, *ibid.* **65**, 906 (1943).
3. These absorption data were obtained in this laboratory. Ref. 1 reported "about 330, 350 and 370 m μ " while O. Isler *et al.* [*Helv. Chim. Acta* **30**, 1911 (1947)] have reported 330, 347 and 367 m μ . Observations in this laboratory indicate that this variation in spectral data can arise from differences in the anhydrovitamin A content of the specimens.
4. W. Oroshnik, G. Karmas, and A. D. Mebane, *J. Am. Chem. Soc.* **74**, 295 (1952).
5. The theory of ionic additions to olefins would predict initiation of reaction by terminal addition of a proton to yield compound (III) rather than (II). However, anhydrovitamin A is known to yield vitamin A ethers or esters by solvation in acidic media [N. D. Embree and E. M. Shantz, U.S. Patent 2,410,575 (1946)] indicating that proton addition to a more highly substituted carbon atom is also possible here. For this reason, the possibility of (II) cannot be ignored.

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