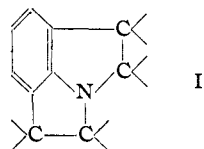
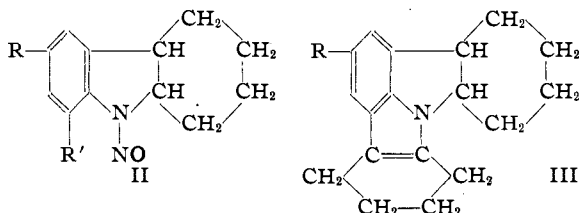


on the spatial configuration of trivalent nitrogen compounds in which three separate groups are attached to the nitrogen atom. They pointed out that "the search for isomerides demanded by a non-planar configuration has been (almost completely) unsuccessful, and it would therefore appear that, in general, the non-planar readily passes into a planar form, from which the original or its enantiomorph may be regenerated; or else the normal configuration is plane [compare Meisenheimer, *Ber.*, **57**, 1747 (1924)].

"Before, however, such conclusions can be accepted, it is desirable that the negative results on which they rest should be supplemented by positive evidence. This would be supplied by the preparation of a compound in the molecule of which a nitrogen atom is common to two ring structures which are at the same time plane and co-planar. Since . . . there is no evidence available which renders doubtful the plane configuration of five-membered ring structures, it would appear that these conditions would be fulfilled by a structure of type I, if Kekulé's formula for benzene and its derivatives be accepted."



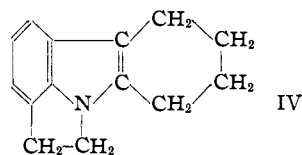
Jackson and Kenner were unable to report the preparation of a compound of this type. However, there had been recorded just previously some experiments by Manjunath [*J. Indian Chem. Soc.*, **4**, 271 (1927)] in which it was shown that treatment of a glacial acetic acid solution of 9-nitroso-hexahydro-carbazole (II, R,R=H) containing cyclohexanone with zinc dust, and then warming, led to formation of a crystalline substance $C_{18}H_{21}N$, which he described as "8,9-(1,2-cyclohexyl)-tetrahydro-carbazole." His structural formula for this substance is obviously incorrect as it represents a substance of formula $C_{19}H_{23}N$. Every analogy suggests that Manjunath's compound should be formulated as III (R = H), that is, as a normal product of a Fischer indole



ring closure, and as a substance fulfilling the requirements of Jackson and Kenner's test.

We have now confirmed Manjunath's result, and his further observation that a similar substance (III, R=CH₃) can be obtained in a similar manner from 9-nitroso-6-methyl-hexahydro-carbazole (II, R=CH₃, R'=H). On the other hand, we have been unable to prepare a substance of similar structure from 9-nitroso-8-methyl-hexahydro-carbazole (II, R=H, R'=CH₃) because the ortho position essential for indole ring closure has been "blocked" by the methyl group.

That the substances III have the structures assigned to them is strongly supported by the fact that addition of zinc dust to an acetic acid solution of 1-nitroso-indoline containing cyclohexanone, followed by warming, leads to formation of a colorless crystalline neutral substance, $C_{14}H_{15}N$, melting at 154°. There can be no doubt that this must be formulated as IV, so that it, also, must be regarded as fulfilling the requirements of Jackson and Kenner's test.



There is thus no doubt that substances can be prepared containing a trivalent nitrogen atom with three separate atoms attached to the nitrogen, in which the three nitrogen valences must be regarded as definitely co-planar.

DEPARTMENT OF ORGANIC CHEMISTRY
THE UNIVERSITY OF SYDNEY
SYDNEY, AUSTRALIA

FRANCIS LIONS
ERNEST RITCHIE

RECEIVED MAY 22, 1939

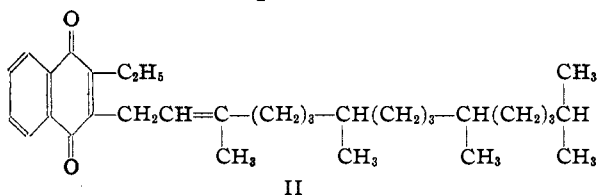
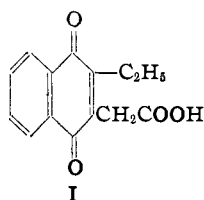
ON THE CONSTITUTION OF VITAMIN K₁

Sir:

In a previous communication [THIS JOURNAL, **61**, 1295 (1939)] we suggested that vitamins K₁ and K₂ contain the quinone structure, and subsequently [*ibid.*, **61**, 1612 (1939)] we confirmed this by preparation of the diacetates by reductive acetylation. The pure yellow color of the vitamins suggests that they belong to the 1,4 series of quinones and this conclusion is supported by the discovery that 1,4-naphthoquinone has vitamin K activity whereas 1,2-naphthoquinone does not. Investigation of a considerable number of quinones has revealed only the derivatives of 1,4-naphthoquinone as having vitamin K activity.

On catalytic hydrogenation vitamin K_1 absorbs four moles of hydrogen with the formation of a hydroquinone. A naphthoquinone nucleus would account for three moles of hydrogen, the fourth mole being used in the saturation of an ethylenic linkage.

Ozonolysis of the diacetate of vitamin K_1 hydroquinone resulted in the formation of a ketone which gave a semicarbazone melting at $66-67^\circ$. *Anal.* Found: C, 70.04; H, 12.13; N, 12.83, 12.88. Calcd. for $C_{19}H_{39}ON_3$: C, 70.10, H, 12.08; N, 12.91. The semicarbazone of 2,6,10-trimethylpentadecanone-14 melts at $66-67^\circ$ [G. F. Fischer and K. Lowenberg, *Ann.*, **464**, 69 (1928)]. The identity of our semicarbazone with that of Fischer and Lowenberg will be tested as soon as a specimen becomes available for determination of the mixed melting point. The formation of this ketone probably indicates the presence of a phytyl side chain in the vitamin molecule.



Vitamin K_1 was oxidized with chromic acid and the oxidation products separated into neutral and acidic fractions. Two crystalline acids were obtained from the latter fractions. One of these acids crystallized from water and had a melting point of 191° in a sealed tube. It was identified as phthalic acid by conversion to the anhydride. This melted at $127-128^\circ$. When mixed with authentic phthalic anhydride (m. p. $128-129^\circ$) the melting point was $128-129^\circ$. *Anal.* Calcd. for $C_8H_4O_3$: C, 64.87; H, 2.72. Found: C, 64.78; H, 3.05.

The second solid acid which was obtained in small amounts crystallized in well-formed yellow needles and melted with decomposition at 210° . If the phytyl radical is directly united to a 1,4-quinone ring, this would presumably be a substituted naphthoquinone acetic acid. This acid, like vitamin K_1 , gives no color reaction with ethyl

cyanoacetate [R. Craven, *J. Chem. Soc.*, 1605 (1931)] and so is presumably substituted in both the 3 and 4 positions. *Anal.* Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 68.69; H, 4.85. The acid is probably 2-ethyl-1,4-naphthoquinone-3-acetic acid (I). The synthesis of this acid is at present in progress for purposes of comparison. On the basis of these degradation products we believe that the structure of the vitamin K_1 molecule is 2-ethyl-3-phytyl-1,4-naphthoquinone (II).

BIOCHEMISTRY DEPARTMENT D. W. MACCORQUODALE
SCHOOL OF MEDICINE S. B. BINKLEY
SAINT LOUIS UNIVERSITY S. A. THAYER
SAINT LOUIS, MISSOURI E. A. DOISY

RECEIVED JUNE 19, 1939

EVIDENCE FOR THE PRESENCE OF VITAMIN A AND CAROTENOIDS IN THE OLFACTORY AREA OF THE STEER

Sir:

In connection with our general project on the chemistry and sources of the fat-soluble vitamins, we became interested in examining the olfactory area of various animals for the presence of these vitamins, especially so for the presence of vitamin A's and their precursors. Since the absence of vitamin A from the diet causes the drying up of the mucous membranes of the body, it was suspected that the epithelia of the olfactory area together with the mucous membranes of the nasal passages in animals having normal diets might be rich in this vitamin. No work has been reported along these lines, and we decided to make a preliminary study of the olfactory area of the steer, but especially that area located at the upper end of the nasal cavity and known as the "yellow patch." This is composed of nerve filaments passing from the brain through the sieve-like cribriform plate into the nasal cavity and terminating at the upper third of this cavity. In the steer the epithelium of the olfactory area is dirty yellowish-brown in color while in the human being it is said to be yellow.

Forty heads of freshly killed steers were split open along the length of the nasal passages and by means of bone-cutters the olfactory area together with the bone and cartilage to which the epithelia were attached were removed. Most of the bone and cartilage were then removed from the yellowish-brown tissue, leaving a sample of about 470 g. This tissue was well ground and autolyzed with ethyl alcohol. Both the alcohol