TPA, and to C.S.I.R., New Delhi, for financial assistance.

Chemical Laboratories, Mukund B. Mishra.*
Univ. of Allahabad, H. L. Nigam.
Allahabad-2, February 6, 1969.


OCCURRENCE OF A NEW 3-DEHYDRORETINOL CONGENER

Although a true anhydro compound of 3-dehydroretinol is not known to occur in nature, Henbest et al.1 obtained, by subjected anhydroretinol to Wohl-Zeigler reaction, a compound whose absorption spectrum showed bands at 343, 408, 387 mμ indicating a 2-dehydroanhydroretinol structure of the compound. Barua and Nayar2-3 found, during chromatography of liver oils of Bagarius bagarius fish, a fraction exhibiting in its absorption spectrum a number of peaks at 343, 408, 388, 368, 350, 310, 296, 284 mμ. These workers also prepared this compound by treating 3-dehydroretinol with the usual dehydrating agents used in the preparation of anhydro retinol and forwarded evidences to show that the compound was a hydrocarbon. Further work on the nature of this compound was carried out and herein we report the occurrence of a new congeners of dehydroretinol.

Liver of B. bagarius fish was ground, extracted at room temperature with light petroleum (b.p. 40-60°), the solvent was removed by distillation under reduced pressure at 40°. The oil thus obtained was dissolved in light petroleum and chromatographed on a column of water-deactivated (5%, v/v) alumina and developed with the same solvent. The fast moving first fraction showed to be anhydroretinol, the second fraction exhibited absorption peaks at 433, 408, 388, 368, 350, 310, 296, 284 mμ, and the third fraction showed to be β-carotene. The substance from the second zone was also prepared by treatment of dehydroretinol with (i) a saturated solution of hydrogen chloride in light petroleum, or (ii) a saturated solution of p-toluene sulphonic acid in benzene, or (iii) a dry ethanolic solution of hydrogen chloride (N/5). This substance, exhibiting a complex spectrum, was rechromatographed on a column of alumina (active). Development with light petroleum resulted in the separation of three zones which were eluted with light petroleum. The spectral characteristics of the substances from the different zones are described below.

Zone I : λ max 367, 350 (max), 335 mμ (light petroleum); SbCl₅ product λ max 620, ~ 690 mμ.

Zone II : λ max 390, 367 (max.), 350, ~ 335 mμ (light petroleum); SbCl₅ product λ max 610, ~ 670 mμ.

Zone III : λ max 433, 408 (max.), 388 mμ with subsidiary peaks at 310, 296 mμ (light petroleum); SbCl₅ product λ max 595 mμ.

The pattern of the absorption spectrum of the compound from the third zone is similar to that of anhydroretinol. On partition between light petroleum and 95% (v/v) methanol, it was found entirely in the epiphysial layer. All these, along with the observation that it occupied an intermediate position between anhydroretinol and β-carotene in the chromatogram, indicated the compound to be a hydrocarbon which was further supported by its infra-red spectrum. The visible spectrum is indicative of a 2-dehydroanhydroretinol structure of the compound. The extraction of the oil and the isolation of the compound were carried out under very mild conditions described above, and is unlikely that the compound is an artefact. However, the compound was highly sensitive and with time the spectrum was changing with appearance of peaks at 367, 350 mμ and disappearance of peaks at 433, 408 mμ. It soon decomposes making further study difficult.

Grateful thanks are due to Dr. N. N. Siddhanta for encouragement and providing laboratory facilities.
Letters to the Editor

A. B. Barua, M. C. Ghosh

Department of Chemistry, Gauhati University, Gauhati-14, Assam, March 14, 1969.


SOME N-ARYL SUBSTITUTED AMINO-HYDROXY-COUMARINS AND CHROMONES

In earlier communications1–2 the syntheses of some pyranophenoxazine derivatives were reported. It was observed however that if both the ortho-positions of the reactive halogen atom, in the halogeno nitro compound, were not occupied, corresponding uncyclised N-aryl substituted compounds were obtained, on condensation with ortho-amino hydroxy coumarins and chromones instead of the pyranophenoxazines, under the usual experimental conditions.3–4

In the present work these N-aryl substituted 6- and 8-amino-7-hydroxy-4-methylcoumarins and 8-amino-7-hydroxy-2-methylchromones are reported. They were obtained by refluxing equimolecular quantities of amino-hydroxy-coumarins and chromones with the reactive halogeno nitrobenzenes, in ethanolic solution, in presence of sodium acetate. A few compounds were prepared in this way by condensing 6- and 8-amino-7-hydroxy-4-methylcoumarins and 8-amino-7-hydroxy-2-methylchromone with 3-chloro-2, 4-dinitro-, 1, 3-dichloro-4, 6-dinitro and 1-chloro-4, 6-dinitro-3-methylbenzenes (Tables I, II, III).

**Table I**

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