

These compounds yielded on pyrolysis isomeric hydrocarbons of the composition $C_{21}H_{16}$ (m. p. 119 and 270°, respectively), indicating that the method of synthesis is practical and that pyrolysis proceeds without migration of the aroyl group in the naphthalene nucleus. The ketone I was then synthesized as follows: *p*-bromotoluene was converted by the Blanc reaction into a mixture of the two chloromethyl derivatives; this was treated with sodium malonic ester and the product was hydrolyzed and decarboxylated. Ring closure through the acid chloride mixture gave an easily separated mixture of two methylbromohydrindones (m. p. 154 and 95°) which on reduction by the Clemmensen method yielded the same hydrindene (b. p. 265–267°). The Grignard reagent from this hydrindene on reaction with α -naphthoyl chloride gave the ketone I (liquid) and on pyrolysis of I there was obtained a yellow hydrocarbon (*Anal.* Calcd. for $C_{21}H_{16}$: C, 93.98; H, 6.02. Found: C, 94.11, 94.18; H, 6.26, 5.96) which when purified through the picrate formed yellow needles melting at 176.5–177.5°; picrate 180–181°. No depression in the melting points was observed on admixture with samples of methylcholanthrene (m. p. 176–177°) and its picrate (m. p. 178–179°) prepared from desoxycholic acid.

This synthesis of a bile acid degradation product having 21 of the 24 original carbon atoms and all four of the original rings serves to confirm the accepted structures and it opens the way to the preparation of other hydrocarbons of interest in the study of carcinogenic activity. Further work in this direction is in progress. Before reporting the details of the above synthesis we are attempting to establish the structures of the intermediates obtained in the preparation of the ketone I, although this is not essential to a knowledge of the structure of the latter compound.

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THE PREPARATION OF GLUCOSIDODI-HYDROXYACETONE PENTAACETATE

Sir:

It has been pointed out by Evans and Hockett [THIS JOURNAL, 53, 4384 (1931)] that in the alkaline degradation of gentiobiose (6-glucosidoglucose) to lactic acid, 3-glucosido-glyceric aldehyde is a theoretically possible intermediate com-

pound. Under such alkaline conditions it is possible for this derivative of glyceric aldehyde to undergo the well-known Lobry de Bruyn and van Ekenstein rearrangement to give glucosidodihydroxyacetone. It was furthermore pointed out that the alkaline degradation of melibiose (6-galactosidoglucose) should yield 3-galactosido-glyceric aldehyde as an intermediate stage in the reaction.

Through the Koenig and Knorr reaction, with powdered "Drierite" as a desiccant in the chloroform, we have recently synthesized the glucosidodihydroxyacetone pentaacetate in good yields by the use of bromoacetoglucose tetraacetate and dihydroxyacetone monoacetate reported by Fischer, Baer and Feldmann [*Ber.*, 63, 1732 (1930)]. This compound crystallized from ether, having m. p. 103° (corr.); $[\alpha]_D^{18} -25.2^\circ$ ($CHCl_3$); an acetyl number equivalent to 10.81 cc. of 0.1 *N* NaOH per 0.10 g. (calcd., 10.82). Its *p*-nitrophenylhydrazone crystallizes from alcohol as a yellow derivative with m. p. 187° (corr.); $[\alpha]_D^{19} -129.8^\circ$ ($CHCl_3$); an acetyl number equivalent to 8.37 cc. of 0.1 *N* NaOH per 0.10 g. (calcd., 8.37).

The study of the behavior of glucosidodihydroxyacetone pentaacetate toward deacetylation reagents as well as potassium hydroxide after the manner of Evans and Hockett (*loc. cit.*) is now in progress in this Laboratory. The syntheses of the corresponding galactosido compounds as well as the corresponding hexosido-glyceric aldehyde ones are also being studied.

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STRUCTURE OF VITAMIN B

Sir:

On treatment with sulfite the vitamin is quantitatively split into $C_6H_9N_3SO_3$ (I) and C_6H_9NSO (II). (I) on the basis of ultraviolet absorption and chemical evidence is a 6-aminopyrimidine sulfonic acid. We provisionally allocate $-SO_3H$ to position 5 and $-C_2H_5$ to position 4.

The second cleavage product has been submitted to Dr. H. T. Clarke for examination. He has proposed a thiazole ring nucleus, which finding is confirmed by ultraviolet absorption studies. This base contains a free $-OH$ group also present in the vitamin, gives a negative iodo-