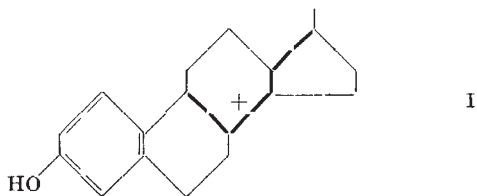


If this is accompanied by protonation and rearrangement of the double bond and angular methyl group at C13, as has frequently been observed with steroids reacting in acidic conditions⁸, a carbonium ion is produced which is capable of undergoing resonance by a hyperconjugation which involves several adjacent tertiary carbon sites and is represented by structure I.



An oxygen function (hydroxyl or methoxyl) must be present in ring A.

The steroid must possess an aromatic ring A. Androstane derivatives with a saturated ring A are Kober negative. Provided there is a C17 oxygen function in the molecule, 19-norandrogens with 4-en-3-one groups are feebly Kober positive, while androsta-1,4-dien-3-ones are strongly positive. It is suggested that the latter compounds undergo the dienone phenol rearrangement, the 19-norandrogens dehydrogenation at C1-C2 and then rearrangement to the phenol structure. Experimental support for this theory has been obtained by measurements in the ultra-violet region.

Absence of the angular methyl group at C13 does not block the first stage of reaction—formation of the yellow chromogen χ_3 , which absorbs maximally at 450–500 m μ —but the conversion of χ_3 to χ_4 in the second stage is inhibited in the absence of the methyl group.

A yellow chromogen (χ_2) absorbing in the region 400–440 m μ is frequently formed as a product of the Kober reaction and appears to be derived from χ_3 as an alternative to its conversion into χ_4 . χ_1 is a chromogen absorbing at 350–370 m μ formed at either stage of either procedure from some of the oestrane derivatives examined.

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Artefact of Hydrolysis of Glucosamine Derivatives

An unusual amino sugar derivative has been reported in acid hydrolysates of the cell wall of *Penicillium notatum*^{1,2}, and we report here the isolation of an apparently identical compound in acid hydrolysates of pure *N*-acetyl glucosamine.

N-acetyl glucosamine (100 mg) was heated in 10 ml. of 4 normal hydrochloric acid at 100° C for 20 h in a silicone greased, evacuated hydrolysis tube. The material

remaining after hydrolysis was recovered by evaporation of the centrifuged solution over phosphorus pentoxide and potassium hydroxide in a vacuum desiccator previously purged with nitrogen. This procedure is identical to that described for hydrolysis of the cell walls of *P. notatum*².

Chromatography of the product on Whatman 3 MM paper using *n*-butanol, acetic acid and water (4:1:5) showed traces of a compound at an *R* glucose value of 1.65. After chromatography the area corresponding to this spot was eluted and just less than 1 mg of material was isolated. The compound gave a positive reaction to the silver nitrate³, aniline phosphate⁴, ninhydrin and Elson-Morgan sprays⁴, had the same *R* glucose values in *n*-butanol, pyridine and water (6:4:3) as the previously reported compound, and co-chromatographed with it in *n*-butanol, acetic acid and water (4:1:5) and *n*-butanol, ethanol and water (4:1:1).

Acid hydrolysis of the compound in 2 normal hydrochloric acid at 100° C gave glucosamine, identified as described before^{1,2}. *N*-acetylation of the compound gave an *N*-acetyl derivative which co-chromatographed with the previously reported *N*-acetylated derivative in *n*-butanol, acetic acid and water (4:1:5) and *n*-butanol, ethanol and water (4:1:1).

An apparently similar compound can be detected in acid hydrolysates of lobster chitin and of the chitinous cell walls of *Penicillium roquefortii* and *Penicillium patulum*, but whereas it is produced in easily detectable amounts from the cell walls of the *Penicillium* species only traces can be produced from the other sources, including *N*-acetyl glucosamine.

The amino sugar derivative previously reported is therefore probably an artefact of acid hydrolysis of *N*-acetyl glucosamine or its derivatives. The extreme acid lability of the compound may mean that the aniline phosphate and Elson-Morgan reactions are spurious and caused by acid hydrolysis to glucosamine. No structural data are available on the small amounts of materials isolated. The compound is being described because other workers may detect it in hydrolysates of glucosamine containing polysaccharides.

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Role of Cyclic 3',5'-Adenosine Monophosphate in the Release of Growth Hormone *in vitro*

Cyclic 3',5'-adenosine monophosphate (3',5'-AMP) may be involved in the synthesis or release of several hormones. Corticotropin increases the concentration of cyclic 3',5'-AMP in adrenal cortex¹, and cyclic 3',5'-AMP stimulates the synthesis of adrenal corticosteroids². Luteinizing hormone increases the concentration of cyclic 3',5'-AMP in beef corpus luteum³, and cyclic 3',5'-AMP stimulates the synthesis of progesterone⁴. Theophylline (1,3-dimethyl-xanthine), which increases the intracellular concentration of cyclic 3',5'-AMP by inhibition of cyclic nucleotide diesterase⁵, increases the secretion of insulin *in vivo*⁶. Glucagon and epinephrine, which may affect the rate of synthesis of cyclic 3',5'-AMP⁷, also influence the release of insulin⁸. The suggestion that cyclic 3',5'-