Like veratrobasine, geralbine has one N-CH$_3$ group: calcd. 4.38%, found 3.96%.

In the infrared spectrum geralbine shows a band typical of ketones at 1715 cm.$^{-1}$.

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STRUCTURE OF HYALURONIC ACID. THE GLUCURONIDIC LINKAGE

Sir:

The isolation of a crystalline disaccharide[1] from the biologically important polysaccharide hyaluronic acid[2] has recently been reported. The glucuronic acid–glucosamine disaccharide, designated hyalobiuronic acid, has now been shown to be D-glucopyruronosido<β-1,3>D-glucosamine. This structure follows from transformation of the disaccharide to D-glucopyranosido<β-1,2>D-arabinose, a new compound whose structure follows in turn from its preparation from laminaribiose (glucopyranosido<β-1,3>glucose[3]) by an application of the Zemplén[4] degradation.

The crystalline glucuronido-glucosamine is produced from umbilical cord hyaluronic acid in yields as high as 61% by the combined enzymatic and acid hydrolysis earlier described,[1] in somewhat lower yield by direct acid hydrolysis. The picture[2] of the polysaccharide as a chain of alternating glucosamine and glucuronic acid residues must therefore be essentially correct. Also, the β-1,3-linkage now found in the disaccharide is apparently the predominating if not sole glucuronidic linkage in the polysaccharide.

In earlier structural investigations, a methylated glucopyruronoside derivative has been isolated in trace quantity on methanolysis of the methylated polysaccharide,[5] and various workers have inferred from the periodic acid consumption of the polysaccharide and its derivatives the presence of 1,3-,[6a] 1,4-[6b] or mixed 1,3- and 1,4-[6c] glucuronidic linkages.

With cold weak methanolic hydrogen chloride the glucuronidoglucosamine (I) gives an amorphous methyl ester hydrochloride (II). Acetylation of this gives heptaacetylglucuronido-glucosamine, methyl ester (III, 65% yield from I), obtained as needles, m.p. 120°, $[\alpha]^{22}\mathrm{D}$ + 25° (chloroform), containing one ethanol of crystallization incompletely lost on drying at 110°. Found (crystals): CH_3O, 8.97; N, 2.08; loss on drying, 5.1. Found (dried substance): CH_3O, 6.05; N, 2.10; C, 48.49; H, 5.77; CH_3CO, 45.9; mol. wt., 668. With ketene the glucuronido-glucosamine (I) gives the amorphous N-acetyl derivative, $[\alpha]^{28}\mathrm{D}$ −32° (water). Found: N, 3.28; uronic acid (CO_2), 48.2; hexosamine, 44.4. Treatment with cold weak methanolic hydrogen chloride, followed by acetylation, gives the heptaacetyl methyl ester (III) described above.

The methyl ester hydrochloride (II), on oxidation with yellow mercuric oxide, followed by sodium borohydride reduction, gives glucosido-glucosaminic acid (20% yield from I), needles, $[\alpha]^{30}\mathrm{D}$ −34° (water; *c*, 0.9). Found: neut. equiv. (formol), 355. Degradation of this amino acid with ninhydrin gives a glucosido-arabinose, isolated as the heptaacetate (IV), needles m.p. 198–199° (micro-block), $[\alpha]^{23}\mathrm{D}$ −47° (chloroform). Found: C, 49.92; H, 6.00. This acetate gives a melting point depression with Zemplén's[4] heptaacetylglucosido<β-1,3>arabinose, $[\alpha]_{\mathrm{D}}$ −17°, and gives no depression with heptaacetylglucosido<β-1,2>-arabinose (IV) from laminaribiose.

Synthetic laminaribiose[3,7] is treated with hydroxylamine. The resulting glass with acetic anhydride and sodium acetate at 110° gives octaacetyllaminaribionitrile, m.p. 140–141°, $[\alpha]^{30}\mathrm{D}$ +3° (chloroform). Found: N, 2.10. Reaction of the nitrile with sodium methoxide and acetylation of the product gives heptaacetyl-glucopyranosido<β-1,2>D-arabinose (IV), m.p. 199.5–200° (micro-block), $[\alpha]^{30}\mathrm{D}$ −46° (chloroform). Found: C, 49.20; H, 5.62; CH_3CO, 47.8.

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[7] We are indebted to Prof. E. L. Hirst for seed material.