dried melted at 192–193° when carried out under optimum conditions. Reduction of volume to a small volume and addition of ethyl alcohol precipitates the ether. Identification of material was largely by means of infrared analyses in carbon disulfide solution. Diagnostic bands of isolated compounds are listed in Table II.

Preparation of pinacolone. A 2-g. sample of pinacol was dissolved in 40 ml. acetic acid and warmed to 50° on steam cone for 15 min. The acetic acid solution was poured into water, neutralized with sodium carbonate, and extracted with benzene. The benzene extract was dried over sodium sulfate, reduced in volume and diluted with petroleum ether 40–60°. Yield of crude pinacolone m.p. 220° 1.6 g. After recrystallization from benzene–petroleum ether, it melted at 230–232°.

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Chondroitin Sulfate Modifications. II.[1] Peracetylated Sodium Chondroitin Sulfate A

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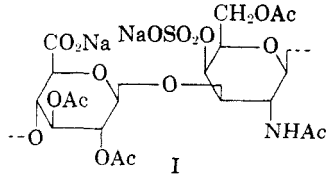
The acetylation of the acidic polysaccharides, pectin[3] and hyaluronic acid,[4] as effected with pyridine and acetic anhydride in formamide, has been reported. We find that this acetylating system can be applied to sodium chondroitin sulfate A under conditions in which the reaction is entirely homogeneous. It is essential that all moisture be excluded. The polysaccharide salt is peracetylated without desulfation and the product (I), after purification by precipitation methods and dialysis, can be isolated as a white, fluffy powder on freeze-drying. This polymeric peracetate is remarkable in being readily soluble in water, formamide and 1:1 water-ethanol. It is insoluble in acetone, chloroform, ethanol, and ether. It may be readily de-*O*-acetylated to yield the original material and can thus be of use in the purification of the polysaccharide.



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EXPERIMENTAL

Peracetylated sodium chondroitin sulfate A (I). An amount of 3.8 g. of sodium chondroitin sulfate A, purified essentially as described previously,[5] was finely pulverized and dried over phosphoric anhydride at 70° and 0.05 mm. for 24 hr. This dry powder was dissolved in 24 ml. of dry, freshly distilled formamide by shaking overnight in a sealed flask. To this solution was added, with agitation, 24 ml. of dry, freshly distilled pyridine followed by 10 ml. of acetic anhydride. The sealed solution was shaken at room temperature for 12 hr. when a further quantity of 13 ml. of acetic anhydride was added, and shaking was continued for a total of 24 hr., during which time the color of the solution became a medium red-brown. The solution was then poured with stirring into 500 ml. of ethanol at 0° and then 400 ml. more ethanol was added to yield a white, flocculent precipitate which was collected by filtration and washed with ethanol. The product was further purified by pouring its solution in 100 ml. of water into 500 ml. of ethanol. Precipitation was effected on the addition of 3–5 ml. of a saturated aqueous sodium chloride solution. This procedure was twice repeated and the final product was dissolved in 100 ml. of water and dialyzed for 2 days against distilled water. Recovery of the product as a fluffy, white, amorphous solid was effected by freeze-drying; yield 3.5 g. (72%), $[\alpha]_D^{30}$ −25° (*c* 1.14, water).

This material was insoluble in acetone, chloroform, ether, ethanol, and methanol but was soluble in water, formamide and 1:1 (by vol.) water-ethanol. It was non-reducing toward Benedict solution and exhibited a positive sulfate test only after hydrolysis with dilute hydrochloric acid. The ninhydrin test for the free amino group was negative; positive tests were obtained for uronic acid and hexosamine. Infrared absorption spectral examination showed the strong acetate ester peak at 1740 cm.$^{-1}$ The prominent bands at 3500 cm.$^{-1}$ and 1670 cm.$^{-1}$ may be attributed to the water of hydration.[6]

Anal. Calcd. for $C_{12}H_{12}NaO_6(NHCOCH_3)(OCOCH_3)_{3.25}(OSO_2ONa\cdot 2H_2O)_{0.75}$: C, 38.38; H, 4.52; N, 2.18; Na, 6.28; CH_3CO, 28.52. Found: C, 37.83; H, 4.53; N, 2.34; Na, 6.14; CH_3CO,[7] 28.05.

De-O-acetylation of peracetylated sodium chondroitin sulfate A. An amount of 600 mg. of the above-described peracetylated sodium chondroitin sulfate A was added at 0° to a filtered solution of 3.0 g. of barium hydroxide octahydrate in 50 ml. of water, and the resultant solution was maintained at 0–5° for 1.5 hr. The solution was then carbonated, filtered, and barium ion was removed exactly with sulfuric acid. The centrifuged, neutral solution was dialyzed against distilled water for 48 hr. and its solid content was recovered as a white powder by freeze-drying; yield 300 mg. (64%), $[\alpha]_D^{32}$ −16° (*c* 1.08, water). The product exhibited a negative ninhydrin reaction for the free amino group.

Anal. Calcd. for $C_{12}H_{16}NaO_6(NHCOCH_3)(OH)_{3.25}(OSO_2ONa\cdot 2H_2O)_{0.75}$: N, 2.77; ash (as sulfate), 24.62; CH_3CO, 8.52. Found: N, 2.50; ash, 24.42; CH_3CO,[7] 8.15.

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