Using the techniques suggested by Yundt, with slight modifications, and starting with a slash pine holocellulose, a crystalline glucomannan was isolated, which, on hydrolysis, gave 77% mannose and 23% glucose. Small amounts of ash, but no other sugar units were present.

The sugars were identified chromatographically and by the preparation of crystalline derivatives. The rod-shaped crystals were about 2.5 μ long and showed strong birefringence under polarized light. X-ray powder diagrams and chromatographic data were obtained at various stages of the purification, in the course of which other sugar units (xylose and galactose) were gradually removed. The final X-ray diffraction of the dry material showed relatively sharp peaks.

In future work, the degree of polymerization of the glucomannan fragment, its physicochemical properties, and the oligosaccharides obtained on graded hydrolysis will be studied.

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Preparation of 1,2,3,4,5-Pentamethylcyclopentadiene, 1,2,3,4,5,5-Hexamethylcyclopentadiene, and 1,2,3,4,5-Pentamethylcyclopentadienylcarbinol

Sir:

The author wishes to report the synthesis of the novel compounds: 1,2,3,4,5-pentamethylcyclopentadiene (I), 1,2,3,4,5-bexamethylcyclopentadiene (II), and 1,2,3,4,5-pentamethylcyclopentadienylcarbinol (III). These compounds have been unavailable thus far due to inherent difficulties in the exhaustive methylation of cyclopentadiene. They are of obvious interest as nondimerizing cyclopentadiene derivatives, for instance, in photo-isomerization reactions.¹ Of special interest are the derived nonclassical cations, one of which is intensely colored.²

Preparation of I: Treatment of tiglaldehyde with 2-butenyl-2-lithium³ gave di(*sec*)-2-butenylcarbinol (IV), b.p. 56.3° (1.5 mm.) n_D^{20} 1.4719 ν (C==C) 1632 cm.⁻¹ (m). Oxidation of IV with active manganese dioxide⁴ in pentane gave di(*sec*)-2butenyl ketone (V) in good yield, b.p. 58.0° (4.2 mm.) n_D^{20} 1.4731. $\lambda_{\text{max}}^{C_2H_0OH}$ 239.6, 328 m μ , ϵ_{max} 1.22 × 10⁴, 47. ν (C=C-C=O), 1642 cm.⁻¹ (vs). Cyclization of V in formic acid-phosphoric acid in accordance with the Nazarov ring closure⁵ gave in good yield 2,3,4,5-tetramethylcyclopent-2-en-1-one (VI) b.p. 59.8° (3.3 mm.) n_D^{20} 1.4772. $\lambda_{max}^{C_{\rm 2HeOH}}$ 236, 302 m μ ; ϵ_{max} , 1.39 × 10⁴, 97.6. ν (C=O), 1700 cm.⁻¹ (vs); ν (C=C), 1650 cm.⁻¹ (s). Treatment of VI with methyllithium gave the expected tertiary alcohol as the initial product. Water was lost spontaneously upon addition of a trace of iodine; distillation of the product yielded I (75%), b.p. 58.3° (13.5 mm.) n_D^{20} 1.4748. Mass spec. mol. wt. 136. $\lambda_{max}^{\rm isoôctane}$ 232 (sh), 248, 265 (sh) m $\mu \epsilon_{max}$ 2780, 3180, 2730. ν (C=C-C=C), 1653 cm.⁻¹ (m), 1620 cm.⁻¹ (w).

Preparation of II: Addition of I to one equivalent of sodamide⁶ in liquid ammonia gave smoothly pentamethylcyclopentadienyl sodium (VII); addition of one equivalent of methyl iodide to VII gave II (67% yield), b.p. 52.8° (6.4 mm.) $n_{\rm D}^{20}$ 1.4719; mass spec. mol. wt. 150. $\lambda_{\rm max}^{\rm isoŏctane}$ 252.4 m $\mu \epsilon_{\rm max}$ 4140. ν (C=C-C=C) 1654 cm.⁻¹ (m), 1620 cm.⁻¹ (w). A characteristic strong band occurred at 1080 cm.⁻¹ nmr spectrum (40 M.c.) in c.p.s. rel. to internal Si(CH₃)₄ capillary: -36.4, rel. area 6 (gem-dimethyl); -67.8, rel. area 12 (four vinyl methyl groups).

Preparation of III: VII was prepared as above. The ammonia was removed, finally *in vacuo*. The residue was dispersed in tetrahydrofuran (distilled from lithium aluminum hydride); 1 equivalent of ethyl chloroformate (VIII) was now added. After 1-hr. reflux, sodium chloride was removed by filtration. Tetrahydrofuran and excess VIII were removed by distillation. The ester residue was reduced with lithium aluminum hydride in ether. The product was III in 52% yield, b.p. 65.5° (1.1 mm.) n_D^{20} 1.4955. The distillate crystallized, m.p. 30.5°: λ isoöctane 262.4 m μ (ϵ , 3230); ν (O—H), 3580 cm.⁻¹ (vs); ν (C—C—C—C) 1656 cm.⁻¹ (m); ν (C—O) 1040 cm.⁻¹ (vs).

Anal. Calcd. for I ($C_{10}H_{16}$): C, 88.14; H, 11.86. Found: C, 87.89; H, 12.02. Calcd. for II ($C_{11}H_{18}$): C, 87.90; H, 12.10. Found: C, 87.74; H, 11.91. Calcd. for III ($C_{11}H_{18}$ O): C, 79.44; H, 10.93. Found: C, 79.71; H, 10.99. I, II, and III were homogeneous in vapor phase chromatography. Absorption above 3000 cm.⁻¹ or at 870–900 cm.⁻¹ characteristic of exocyclic methylene is absent in the infrared spectra of all three compounds. IV, V, and VI gave satisfactory C—H analyses.

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