the reversible formation of the symmetrical carbonium ion intermediate **5**. This is further support for the previously proposed intermediacy of a free carbonium ion in the photoaddition of hydroxylic media to cyclohexenes and -heptenes.[2,3]

Experimental Section[6]

Irradiation of (+)-Limonene. A. Under Aqueous Conditions.—A solution containing 3.0 g of limonene, $[\alpha]^{22}D$ +112°, and 3.0 g of *m*-xylene in 150 ml of 50% aqueous *t*-butyl alcohol containing 1% sulfuric acid was irradiated for 2 hr. Gas chromatographic analysis revealed the continued presence of limonene (17%) and the formation of the diene 6 (2%), a 1.2:1 mixture of *cis*- and *trans*-β-terpineol (**3**, 74%), and several unidentified minor products.

The reaction mixture was neutralized with sodium hydroxide solution and the organic materials were isolated by extraction with ether in the usual fashion. Isolation by preparative gas chromatography of the first component afforded a colorless liquid, *m/e* 138, which was not further characterized but is assumed to be *p*-menth-8-ene.[7]

Isolation of the second component afforded a colorless liquid [*m/e* 136 (34), 93 (100), and 79 (57)] which exhibited an infrared spectrum identical with that of *p*-mentha-1(7),8-diene (**6**).[8] Isolation of the third component afforded recovered limonene, $[\alpha]^{30}D$ +18° (*c* 0.20, ethanol).

Isolation of the fourth component afforded ***trans*-β-terpineol** as colorless needles: mp 28–28.5° (sealed capillary); nmr spectrum τ 5.37 (s, 2, CH_2-9), 8.30 (s, CH_3-10), and 8.81 (s, CH_3-7); *m/e* 136 (52), 121 (32), 107 (32), 99 (32), 93 (60), 71 (100), 69 (41), 68 (34), and 43 (64). The infrared spectrum was identical with that reported by Mitzner, *et al.*, for "*cis*-β-terpineol"[9] and with that reported by Henbest and McElhinney for the "*trans*" isomer.[10]

Isolation of the final component afforded ***cis*-β-terpineol** as colorless needles: mp 33–34° (sealed capillary); nmr spectrum τ 5.36 (s, 2, CH_2-9), 8.31 (s, CH_3-10), and 8.79 (s, CH_3-7); *m/e* 154 (tr), 136 (84), 121 (42), 108 (28), 107 (48), 94 (19), 52 (93), 84 (20), 79 (24), 71 (100), 69 (42), 68 (29), 67 (20), 58 (20), 55 (23), and 43 (64). The infrared spectrum was identical with that reported for "*trans*-β-terpineol" by Mitzner, *et al.*,[9] and for the "*cis*" isomer by Henbest and McElhinney,[10] lit.[10] mp 36°.

B. In Methanol.—A 150-ml methanolic solution containing 3.0 g of (+)-limonene and 3.0 g of *m*-xylene was irradiated for 10 hr. Gas chromatographic analysis revealed the continued presence of limonene (6%) and the formation of *p*-mentha-1(7),8-diene (6) and the ethers *cis*- and *trans*-**3b** in yields of 39, 28, and 18%, respectively.

Isolation of the principal ether product afforded ***cis*-*p*-menth-8-en-1-yl methyl ether** as a colorless liquid: λ_{max} 6.02 and 11.22 μ; nmr spectrum τ 5.31 (s, 2, CH_2-9), 6.78 (s, 3, CH_3O–), 8.29 (s, CH_3-10), and 8.83 (s, 3, CH_3-7); *m/e* 168.1531 (calcd for $C_{11}H_{20}O$: 168.1514), 85 (100), 72 (36), 55 (64), 43 (34), and 39 (50).

Isolation of the minor ether component afforded ***trans*-*p*-menth-8-en-1-yl methyl ether** as a colorless liquid: λ_{max} 5.98 and 11.16 μ; nmr spectrum τ 5.33 (s, 2, CH_2-9), 6.85 (s, 3, CH_3O–), 8.29 (s, CH_3-10), and 8.91 (s, 3, CH_3-7); *m/e* 168.1524 (calcd for $C_{11}H_{20}O$: 168.1514), 136 (41), 93 (44), 72 (49), 69 (45), 55 (60), 43 (100), 42 (79), 41 (66), 40 (44), and 39 (52).

(6) Infrared spectra were obtained on neat samples with a Perkin-Elmer Infracord spectrophotometer. Nuclear magnetic resonance spectra were determined in chloroform-*d*$_1$ solution with a Varian HA-100 spectrometer, using tetramethylsilane as an internal standard. Gas chromatographic analyses were performed on an Aerograph 90-P instrument using 10 ft × 0.25 in. columns packed with 20% SE-30 or Carbowax 20M on 60–80 mesh Chromosorb W. Mass spectra were obtained using an Atlas Model CH-4 or SM-1 spectrometer. Irradiations were conducted using a Hanovia 450-W, medium-pressure mercury arc and a water-cooled Vycor immersion well. Vigorous stirring of the reaction mixture was effected by the introduction of a stream of nitrogen through a jet opening in the bottom of the outer jacket.

(7) Some reduction normally accompanies the photoprotonation of cyclohexenes; see J. A. Marshall and A. R. Hochstetler, *Chem. Commun.*, 296 (1968).

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Registry No.—(+)-**1**, 5989-27-5; *cis*-**3a**, 20288-25-9; *trans*-**3a**, 20288-26-0; *cis*-**3b**, 24655-71-8; *trans*-**3b**, 24655-72-9.

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Studies in the Ganglioside Series. V. Synthesis of 2-Acetamido-2-deoxy-*O*-β-D-glucopyranosyl-(1→3)-*O*-β-D-galactopyranosyl-(1→4)-D-glucose[1]

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In recent communications[2-4] we described a new, highly stable and reactive hexosaminyl bromide of type III which facilitates the synthesis of aminosaccharides. We now report the synthesis of the title compound (VI, Chart I). This trisaccharide has been isolated from hydrolysates of the polysaccharides found in human milk.[5,6] It is structurally related to the so-called "ganglio-*N*-triose-II"[7] which is inherent in the molecule of the abnormal ganglioside accumulating in brain tissue with Tay–Sachs disease.[8,9]

In an earlier report[10] we have shown that selective substitution of lactose can be achieved *via* its isopropylidene derivative I and that bromo sugars react preferentially with the equatorial C-3 hydroxyl group of the benzyl lactoside II under Koenigs–Knorr conditions.

The benzyl lactoside II, previously isolated as a viscous mass, could now be obtained in pure crystalline form. It was observed that hydrolysis of I with hot aqueous acetic acid, a method commonly employed for the removal of an isopropylidene group, was invariably accompanied by partial deacetylation. Trifluoroacetic acid was found to be more suitable. The hydrolysis is carried out in chloroform containing 10% of the reagent and is complete after 20–30 min, whereby only traces of by-products are formed. While this method was being practiced in our laboratory, Goodman[11] reported the use of 90% aqueous trifluoroacetic acid for the hydrolysis of ketals in various sugar derivatives which were, however, devoid of acetoxyl groups.

The Koenigs–Knorr reaction of II with the bromide III afforded, after column chromatography, the pure substituted trisaccharide IV. Catalytic de-*O*-acylation

(1) This work was supported by U. S. National Institutes of Health, PL 480, Agreement No. 425115.

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(5) R. Kuhn and H. H. Baer, *Chem. Ber.*, **89**, 504 (1956).

(6) R. Kuhn, A. Gauhe, and H. H. Baer, *ibid.*, **89**, 1027 (1956).

(7) R. Kuhn and H. Wiegandt, *ibid.*, **96**, 866 (1963).

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(9) L. Svennerholm, *J. Neurochem.*, **10**, 613 (1963).

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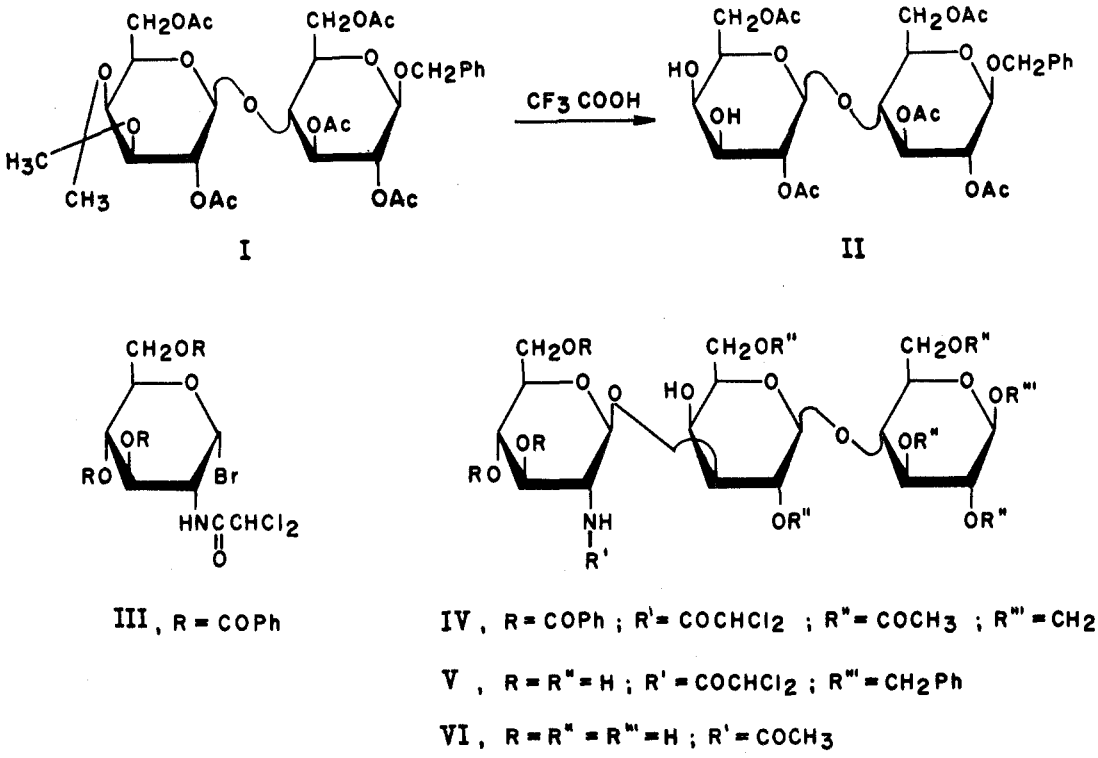
CHART I



under very mild conditions gave the dichloroacetyl derivative V, whose structure was confirmed by periodate oxidation. Hydrogenation of the latter compound resulted both in debenzylation and conversion of the dichloroacetyl into the acetyl group. In view of the lability of the 1→3 bond to alkali, the latter reaction is preferable to hydrolysis by dilute barium hydroxide previously reported.[2] The final trisaccharide (VI) thus obtained showed identity with the natural product in melting point and optical rotation.

Experimental Section

Benzyl 4-*O*-(2,6-Di-*O*-acetyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (I).—The compound was prepared following the procedure described previously.[10] The syrupy product eluted from the silica gel column could be crystallized from 2-propanol, $[\alpha]^{23}D$ −10.2° (*c* 2, chloroform), mp 85–86°.

Anal. Calcd for $C_{32}H_{42}O_{16}$: C, 56.30; H, 6.20. Found: C, 56.58; H, 6.16.

Benzyl 4-*O*-(2,6-Di-*O*-acetyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (II).—A solution of I (5.0 g) in chloroform (45 ml) was treated at room temperature for 20–30 min with trifluoroacetic acid containing 1% of water (5 ml). The optimal reaction time was determined by tlc. The solution was concentrated *in vacuo* at room temperature, and the reagent was completely removed by coevaporation with toluene. Tlc (ethyl acetate–benzene 3:1) showed one reaction product and only traces of deacetylation. Dichloromethane–ethyl acetate (4:1) eluted from a silica gel column pure starting material (1.1 g, 22%). A 1:1 mixture of the same solvents yielded II (3.18 g, 67%), which was crystallized from ether: $[\alpha]^{23}D$ −28° (*c* 2, chloroform), mp 158–159°; reported[10] as a syrup, $[\alpha]D$ −23.2° (chloroform).

Anal. Calcd for $C_{29}H_{38}O_{16}$: C, 54.20; H, 5.96. Found: C, 54.18; H, 5.83.

Benzyl (2-Deoxy-2-dichloroacetamido-3,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,6-di-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (IV).—To a solution of II (1.0 g) in dry dichloroethane (30 ml) were added mercuric cyanide (0.75 g) and 3,4,6-tri-*O*-benzoyl-2-deoxy-2-dichloroacetamido-α-D-glucopyranosyl bromide (III, 3.5 g), and the reaction was allowed to proceed with stirring at 40° for 7 days. The cooled solution was poured into a mixture of ice–water (100 ml) and chloroform (150 ml). The chloroform layer was washed several times with cold water, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel Davison, grade 950, 60–200 mesh (200 g), from which IV was eluted with methylene chloride–ethyl acetate (84:16). Crystallization from alcohol and a few drops of hexane gave 0.4 g (19%) of pure IV: tlc (ethyl acetate) R_{III} 1.4; mp 125–127°; $[\alpha]^{18}D$ −50° (*c* 1, chloroform); ir (KBr) 5.9, 6.4 (amide), 11, 2 (β-glycoside), and 12.3 μ (CCl). The nmr spectrum showed signals at τ 2–2.8 (20 aromatic protons), 7.84–7.97 (15 acetyl protons), and 4.15 (1 dichloroacetyl proton).

Anal. Calcd for $C_{58}H_{61}Cl_2NO_{24}$: C, 56.77; H, 5.01; Cl, 5.78. Found: C, 56.82; H, 4.91; Cl, 5.55.

Benzyl (2-Deoxy-2-dichloroacetamido-*O*-β-D-glucopyranosyl)-(1→3)-*O*-(β-D-galactopyranosyl)-(1→4)-β-D-glucopyranoside (V).—For de-*O*-acylation, compound IV (350 mg) was dissolved in chloroform (3 ml) and absolute methanol (20 ml). The solution was cooled to −10° and a solution of 1 *N* barium methoxide (0.3 ml) was added. After standing at 2–5° overnight, the solution was neutralized with Dowex 50 X 8, 50–100 mesh, H^+ form. The filtrate was evaporated *in vacuo*, and the residue was crystallized from absolute alcohol and a few drops of ether: tlc (benzene–methanol, 1:1) R_{IV} 0.54, $R_{lactose}$ 2.5; yield 180 mg (90%); mp 194–195°; $[\alpha]^{18}D$ −22.6° (*c* 0.8, methanol). It consumed 2.08 mol of sodium metaperiodate during 72 hr at 40°.

Anal. Calcd for $C_{27}H_{39}Cl_2NO$: Cl, 10.07. Found: Cl, 10.22.

2-Acetamido-2-deoxy-*O*-β-D-glucopyranosyl-(1→3)-*O*-β-D-galactopyranosyl-(1→4)-D-glucose (VI).—The preceding compound (V, 150 mg) was hydrogenated in methanol (50 ml) with 10% palladium-on-charcoal (2 g) at 40° and 55 psi. After 48 hr, the suspension was allowed to cool and filtered through a Celite bed. The residue resulting from the evaporation of the solvent crystallized from a mixture of ethanol (4 ml), ether (1 ml), and a few drops of water: yield 75 mg (64.6%); mp 205–209°; $[\alpha]^{20}D$ +39.5° (*c* 0.8, water) (reported[6] mp 201–202°; $[\alpha]D$ +40.7°); tlc (1-butanol–acetone–water, 4:5:1) R_{VIII} 0.8, $R_{lactose}$ 0.7.

Anal. Calcd for $C_{20}H_{35}NO_{16}$: C, 44.03; H, 6.47. Found: C, 43.68; H, 6.63.

Registry No.—I, 18404-74-5; II, 18404-75-6; IV, 24741-58-0; V, 24741-59-1; VI, 24741-60-4.