maining syrup crystallized upon trituration with hexane. Recrystallized from ethyl acetate–petroleum ether, compound **10** (1.05 g, 80%) showed mp 161 °C; $[\alpha]_D$ +154° (*c* 1, chloroform), ν_{max} 1740 (OAc), 1560 (NO_2), and 1175 cm^{-1} (OMs); NMR δ 5 region (4 H, ring protons, unresolved), 3.88 (1 H, m, H-5), 3.50 (3 H, s, OCH_3), 3.01 (3 H, s, OMs), 2.10 (3 H, s, OAc), 1.24 (3 H, d, J = 6.5 Hz, C–CH_3).

Anal. Calcd for $C_{10}H_{17}NO_9S$ (327.3): C, 36.69; H, 5.23; S, 9.79. Found: C, 36.82; H, 5.25; S, 9.81.

Methyl 3,6-Dideoxy-2-*O*-methylsulfonyl-3-nitro-α-D-glucopyranoside (11). A solution of the 4-acetate **10** (900 mg) in acetone (1 ml) and 3% methanolic hydrogen chloride (9 ml of a solution that had been made by adding 1 ml of acetyl chloride to 20 ml of dry methanol) was kept at 40–50 °C for a few hours until TLC (solvent B) showed absence of starting material and sole presence of one new spot. The reaction mixture was then evaporated to give a brownish syrup which was passed through a 10-g silica gel column with ether to remove colored impurities. Evaporation of the effluent gave 772 mg of **11** which was recrystallized from ethyl acetate–petroleum ether to give pure **11** (768 mg, 98%): mp 106–107 °C; $[\alpha]_D$ +148° (*c* 1, chloroform); ν_{max} 3500 (OH), 1560 (NO_2), and 1170 cm^{-1} (OMs); NMR δ 3.49 (3 H, s, OMe), 3.03 (3 H, s, OMs), 1.36 (3 H, d, J = 6 Hz, C-Me).

Anal. Calcd for $C_8H_{15}NO_8S$ (285.3): C, 33.68; H, 5.30, S, 11.24. Found: C, 33.80; H, 5.30; S 11.39.

Methyl 2,3,6-Trideoxy-3-nitro-α-D-*erythro*-hex-2-enopyranoside (12). A solution of **11** (700 mg) in benzene (5 ml, dried over CaH_2) and dry sodium bicarbonate (2.5 g) were heated overnight at reflux. The mixture was allowed to cool, then filtered, and the filter residue was washed twice with chloroform. The combined filtrate was evaporated to give a brown syrup that was decolorized by passage through a 15-g silica gel column with ether. Evaporation of the effluent gave crude crystalline **12** which was recrystallized from chloroform–petroleum ether. The yield of pure **12** was 427 mg (92%), mp 124–125 °C (reported[17] for the L enantiomer, 124–125 °C). The NMR data of **12** were identical with those described[17] for its L enantiomer.

Methyl 3,6-Dideoxy-2,4-di-*O*-methylsulfonyl-3-nitro-α-D-glucopyranoside (14). The glucoside[15] **13** (200 mg) in dichloromethane (10 ml) was treated with MsCl (0.08 ml, 1 molar equiv) and triethylamine (0.14 ml) as described for previous experiments. After a reaction time of 5 min there was no change visible in TLC (solvent A). Therefore, five additional 0.08-ml portions of MsCl and equivalent amounts of triethylamine were added in 5-min intervals, without cooling. Eventually progress of reaction resulting in complete consumption of **13** was noted. Ether was then added to the reaction mixture to precipitate salt which was removed. On evaporation the filtrate gave a brownish residue which was repeatedly evaporated with 1-propanol until the smell of MsCl was no longer noticeable. The residue then crystallized copiously upon trituration with ice water. The material was washed with cold water, dissolved in ethyl acetate, dried with Na_2SO_4, and recrystallized by addition of petroleum ether. The yield was 260 mg (74%): mp 132–132.5 °C; $[\alpha]_D$ +110.5° (*c* 0.4, chloroform); ν_{max} 1555 (NO_2), 1170 cm^{-1} (OMs); NMR δ 4.7–5.1 (4 H, ill resolved, H-1, -2, -3, -4), 3.93 (octet, 1 H, H-5, $J_{4,5}$ = 10, $J_{5,6}$ = 6 Hz), 3.51 (s, 3 H, OMe), 3.01 and 3.03 (2 s, 6 H, 2 OMs), 1.44 (d, 3 H, J = 6 Hz, C-Me).

Anal. Calcd for $C_9H_{17}NO_{10}S_2$ (363.4): C, 29.74; H, 4.71; S, 17.64. Found: C, 29.73; H, 4.79; S, 17.66.

Methyl 3,6-Dideoxy-2-*O*-methylsulfonyl-3-nitro-α-L-galactopyranoside (16). The galactoside[16] **15** (300 mg) in dichloromethane (7 ml) was treated with MsCl (0.1 ml) and triethylamine (0.2 ml in 1 ml of dichloromethane). The mixture was stirred for 90 min at 25 °C, after which period TLC (solvent A) indicated reaction to be incomplete. When the TLC pattern remained unchanged after 4 h, a second and a third set of MsCl and TEA were added with a 30-min interval. This caused the reaction to become nearly complete, with only a trace of **15** remaining. Final addition of a fourth set of reagent portions resulted in complete disappearance of **15.** There was one major product spot (**16**) and a quite strong spot that migrated faster (and was seen, by application of another solvent, to be inhomogeneous). The reaction mixture was partially evaporated to a volume of 5 ml, ether (10 ml) was added, and the mixture was kept in a refrigerator for 2 h and then filtered. The filtrate was evaporated with several additions of 1-propanol, and the resulting syrup was chromatographed on silica gel (10 g) using chloroform as eluent. Fractions containing fast-moving material yielded a thick oil (135 mg) which was seen by TLC (with chloroform) to consist of two components moving close together. The NMR spectrum of the oil suggested the presence of two nonmesylated, unsaturated glycosides, one of which appeared to preponderate. There were signals (total intensity 1 H) in the δ 7.0–7.3 region (nitro olefinic protons), unresolved signals (4 H) at δ 3.6–5.3, two 3 H signals close together near δ 3.5 (OCH_3), and two overlapping 3 H doublets centered at δ 1.5 (C–CH_3). Further elution of the column gave syrupy **16** which crystallized on standing for a few hours: large plates (200 mg, 48%); mp 175–176 °C; $[\alpha]_D$ −206.6° (*c* 0.2, chloroform); ν_{max} 3570 (OH), 1555 (NO_2), 1160–1170 cm^{-1} (OMs); NMR δ 5.30 (1 H, q, $J_{1,2}$ = 3.7, $J_{2,3}$ = 11 Hz, H-2), 5.13 (1 H, d, H-1), 4.92 (1 H, q, $J_{3,4}$ = 3 Hz, H-3), 4.4 (1 H, m, H-4), 4.13 (1 H, q, H-5), 3.50 (3 H, s, OCH_3), 3.14 (3 H, s, OMs), 1.32 (3 H, d, J = 7 Hz, C–CH_3).

Anal. Calcd for $C_8H_{15}NO_8S$ (285.3): C, 33.68; H, 5.30; S, 11.24. Found: C, 33.54; H, 5.19; 11.12.

Attempted elimination of the mesyloxy group by refluxing **16** in the presence of sodium bicarbonate in benzene or toluene for 6 h was unsuccessful. The compound remained unchanged.

Methyl 4-*O*-Acetyl-2,3,6-trideoxy-3-nitro-α-D-*erythro*-hex-2-enopyranoside (20). The 4-acetate[15] **19** (100 mg) in anhydrous ether (5 ml) and MsCl (0.02 ml) were stirred for 15 min after which triethylamine (0.5 ml) was added with water cooling. Stirring was continued for 45 min at room temperature. Processing of the mixture as previously described furnished crude **20** as a yellowish syrup which after purification by passage through silica gel (5 g) gave crystalline **20** (60 mg, 65%), mp 81–82 °C (reported[17] for L enantiomer, 81–81.5 °C).

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Solid-State Conformations of Vitamin D_3

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Discoveries within the last 10 years of active metabolites and synthetic analogues of vitamins D_2 (ergocalciferol) and D_3 (cholecalciferol) have stimulated much research in this area

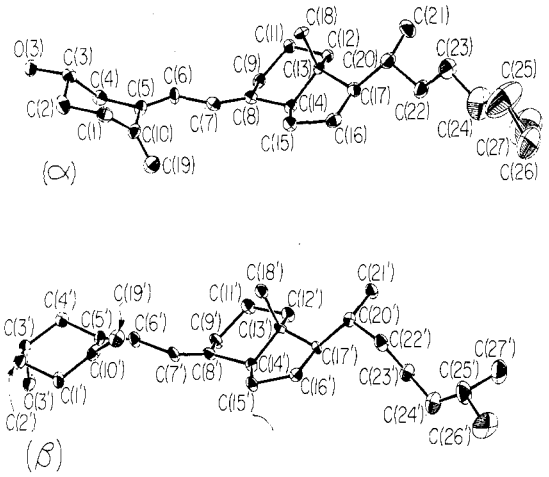

Figure 1. The α and β conformers of vitamin D_3. The thermal ellipsoids of the nonhydrogen atoms in Figures 1 and 3 are scaled at a 15% probability level.

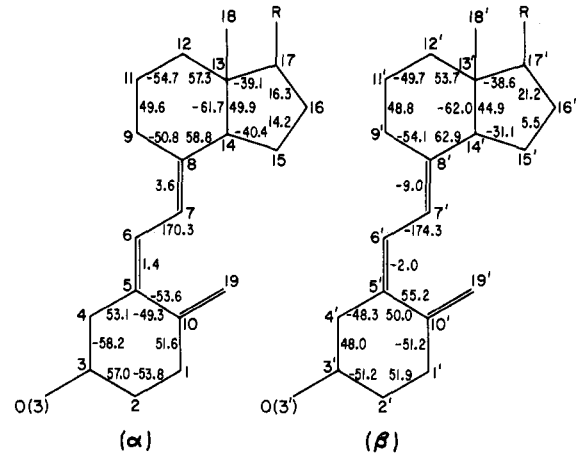

Figure 2. Torsional angles for the two vitamin D_3 conformers. The R substituent at C(17) and C(17') denotes the $-CH(CH_3)-CH_2CH_2CH_2CH(CH_3)_2$ side chain.

which has produced important advances regarding their uses in both medicine and nutrition.[1] Investigations of the modes of vitamin D action at the molecular level necessitate a detailed knowledge of their molecular topologies. Results from several recent ^1H NMR investigations[2-4] on the solution conformations for vitamin D_2[2] and for vitamin D_3 and several metabolites including $1\alpha,25\text{-}(OH)_2\text{-}D_3$,[3,4] with computations based on the crystallographic parameters of two analogues of vitamin D_2, viz., its 4-iodo-5-nitrobenzoate ester (INC)[5] and the 3,20-bis(ethylenedioxy) derivative (ECF),[6] have all been consistent with Havinga's proposal[7] that in solution the ring A of a vitamin D molecule exists in a dynamic equilibrium between the α chair form (in which the CH_2 group is situated below the mean A ring plane) and the β chair form (in which the CH_2 group is situated above the mean A ring plane). As part of a systematic stereochemical investigation in an attempt to correlate the structures of various vitamin D molecules with their properties and biological activities, we report here the outcome of an x-ray diffraction analysis which shows that vitamin D_3 crystallizes in an equimolar ratio of the above two conformers with the 3-OH substituent occupying an equatorial position in the α form and an axial position in the β form.[8] Besides being in accord with the NMR solution conformational analyses, this study also furnishes molecular parameters for both unsubstituted vitamin D_3 conformers and thereby provides clear evidence that the adoption of ring A of a vitamin D molecule to either the α or β chair form does not markedly influence the apparently rigid conformation of the seco-B ring.

Figure 1 shows the two independent molecules of vitamin D_3 displaying different solid-state conformations of the A ring corresponding to those inferred in solution from the ^1H NMR analyses.[2-4] Although the cyclohexane-like A ring in both molecules has a chair conformation, it is apparent that in molecule α (which adopts the α form) the hydroxyl group at C(3) occupies the equatorial position and the $C(19)H_2$ group lies below the mean ring plane, whereas in molecule β (which adopts the β form) the hydroxyl group at C(3') occupies the axial position and the $C(19')H_2$ group lies above the mean ring plane. Corresponding torsional angles (Figure 2) in the A and seco-B rings reflect these two different A ring conformations by having opposite signs in the two molecules. Although corresponding torsional angles in the C–D fused ring system in the two molecules have the same signs, a detailed analysis[9] shows that ring D possesses an essentially half-chair conformation in the α form and a C(13)-envelope conformation in the β form.

The observation that both the mean torsional angles of 53.8 and 50.1° in ring A of molecules α and β, respectively, are smaller than the corresponding experimental value of 55.9° found[10] in cyclohexane can readily be attributed to the flattening effect caused by the two exocyclic double bonds. A further examination of the corresponding torsional angles for both conformations of ring A indicates that the axial 3-OH substituent in the β form induces a significant flattening effect reflected in the two torsional angles C(1')–C(2')–C(3')–C(4') and C(2')–C(3')–C(4')–C(5') being only −51.2 and 48.0°, respectively, in contrast to the equatorial 3-OH substituent in the α form which allows much larger corresponding torsional angles (viz., 57.0 and −58.2°, respectively). The smaller values than 55.9° for these above two torsional angles in the β form and the larger values than 55.9° for the corresponding angles in the α form are deemed to be a consequence not only of intramolecular interactions per se but also, at least in part, to the influence of close-packing interactions of the A rings resulting from the stereochemical requirements of the strong hydrogen-bonding network on the 3-OH substituents (vide infra).[11]

The similarity between the absolute magnitudes of the torsional angle of −53.6° for the C(6)=C(5)–C(10)=C(19) fragment in the α form and the torsional angle of 55.2° for the corresponding fragment in the β form indicates that the result of the steric constraint of the A ring on the large twisting of the above exocyclic cis-diene system from planarity is practically the same in the α and β forms. Torsional angles for the C(5)=C(6)–C(7)=C(8) and C(5')=C(6')–C(7')=C(8') trans-diene system of 170.3 and −174.3°, respectively, show that the seco-B rings in these two conformers possess a nearly planar arrangement such that the trans-diene geometries (which are almost mirror images of each other in the α and β forms) are essentially unaltered upon a change in the A ring conformation. Figures 1 and 3 show that both conformers of vitamin D_3 (including the side chain) exist in an extended fashion with the longest intramolecular distance between nonhydrogen atoms being 17.4 Å for O(3)···C(26) in molecule α and 15.8 Å for C(3')···C(26') in molecule β.

Figure 3 is a view showing the particular hydrogen-bonding network of crystalline vitamin D_3 resulting from the interactions of the 3-hydroxyl substituents of the two types of conformers. The molecules are well separated in the unit cell with all intermolecular nonhydrogen contacts being greater than 3.4 Å except for the relatively short O–H···O distances of 2.71 (1) and 2.73 (1) Å, which indicate reasonably strong O–H···O bonds. It is concluded that the crystal packing of vitamin D_3 including the presence of both conformers is mainly dictated

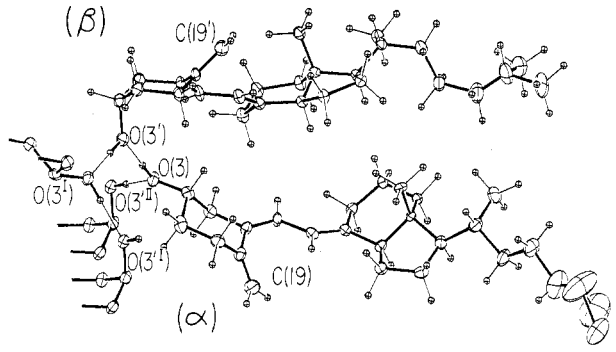

Figure 3. Hydrogen bonding scheme showing the α and β conformers connected in the crystalline state by their single hydroxyl groups to form an infinite spirallike hydrogen-bonded oxygen chain. Each helical chain is constrained about a 2_1 axis in the b direction, with the two conformers occupying alternating positions. O(3^I) and O(3'^{I}) are related to O(3) and O(3'), respectively, by the screw axis, while O(3'^{II}) is related to O(3'^{I}) by a whole lattice translation along the b axis. The unusually large thermal ellipsoids for the isopropyl carbon atoms at the end of the side chain of the α conformer relative to those for the other nonhydrogen atoms are attributed at least in part to these atoms possessing more than one crystal orientation.

by the steric constraints imposed by the infinite helical hydrogen-bonded oxygen chain.

Experimental Section

Vitamin D_3, $C_{27}H_{44}O$, crystallizes with eight molecules in an orthorombic unit cell of dimensions a = 19.730 (4), b = 7.340 (2), and c = 35.716 (6) Å, and of symmetry $P2_12_12_1$ such that the two conformers comprise the crystallographically independent unit.

Intensity data were collected on a Datex-controlled, General Electric diffractometer with an E&A full circle to $2\theta \leq 120°$ with Cu Kα (1.5418 Å) radiation. The data processing included an intensity correction for crystal decay (i.e., ca. 20% over the entire data collection). Of the 4366 measured crystallographically independent reflections, the 2585 reflections for which $I \geq 2\sigma(I)$ were used in the structural analysis.

The structure was solved by the application of MULTAN.[12,13] An E map revealed 34 of the 56 independent nonhydrogen atoms. Subsequent Fourier syntheses yielded unambiguous locations for all nonhydrogen atoms except for the three end carbon atoms [viz., C(25), C(26), and C(27)] on the side chain in one of the two independent molecules. Fourier and difference Fourier maps consistently showed a cluster of small electron-density peaks which from stereochemical considerations was completely compatible with a crystal disorder for this isopropyl carbon fragment. The results reported here are based upon a refinement in which the three strongest peaks in the cluster were taken as whole-weighted occupancies for these carbon atoms. Idealized positions for the hydrogen atoms (except for those attached to the three crystal-disordered carbon atoms) were calculated and then included in the structure factor calculations as fixed-position atom contributors in the final anisotropic full-matrix least-squares refinement which yielded an unweighted $R_1(F)$ index of 8.7% and a weighted $R_2(F)$ index of 10.0%. Bond distances and angles are within their expected ranges[13] except for those corresponding to the three carbon atoms at the end of the side chain of one of the two independent molecules (due to a crystal disorder of this isopropyl carbon fragment).

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Supplementary Material Available. Tables of atomic parameters, bond distances, and bond angles along with their estimated standard deviations (11 pages). Ordering information is given on any current masthead page.

Registry No.—Vitamin D_3, 67-97-0.

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3-*O*-α-L-Rhamnopyranosyl-D-glucose, a New Disaccharide Synthesized by the Koenigs–Knorr Reaction

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The Koenigs–Knorr reaction is probably the most widely applicable and important method for the condensation of two monosaccharide units; by using this reaction, 2-*O*-β-D-glucopyranosyl-D-xylose,[1] rutinose[2] (6-*O*-α-L-rhamnopyranosyl-D-glucose), robinobiose[3] (6-*O*-α-L-rhamnopyranosyl-D-galactose), and other disaccharides have been synthesized. The present work deals with the synthesis of 3-*O*-α-L-rhamnopyranosyl-D-glucose, a new disaccharide prepared by the Koenigs–Knorr reaction. This preparation was carried out as follows (Scheme I): α-acetobromorhamnose (1) was condensed with 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (2) in the presence of mercuric acetate to form the compound **3** which on deacetylation with sodium methoxide and hydrolysis with oxalic acid gave 3-*O*-α-L-rhamnopyranosyl-D-glucose (**4**) in a overall yield of 10%. The structure of this disaccharide was