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The fucofuranoside method for determining the absolute configuration of the tertiary alcohols substituted with methyl and two methylene groups

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Abstract

The fucofuranoside method, a recently devised new method for determining the aboslute configuration of secondary alcohols, by derivatizing to β-D- and β-L-fucofuranosides, is applied to six chiral tertiary alcohols (**1** to **6**) substituted with methyl and two methylene groups. The Δδ values ($\delta^L - \delta^D$) of the protons and carbons are derived from the ^{1}H and ^{13}C NMR spectra in pyridine-d_5. When the compounds are viewed placing the furanosyl group in front and the methyl group below (Fig. 1B), the following generalizations are derived. (**a**) In the ^{1}H NMR, the $\Delta\delta_H$ values are positive for the proximate protons in the right segment (R_r) and negative for the proximate protons in the left segment (R_l) (Fig. 2). (**b**) In the ^{13}C NMR, the $\Delta\delta_C$ values are positive for the right β-carbon and negative for the left β-carbon, except for the five-membered compound **5**, which gave an ambiguous result (Fig. 3).

Keywords: Alcohols; Configuration; Glycosidation; NMR

Introduction

For determining the absolute configuration of secondary hydroxyl groups, many efficient methods, e. g., MTPA (2-methoxy-2-trifluoromethylphenyl acetic acid) (Mosher) ester [1-8], *O*-methylmandelate ester [9-11], and other ^{1}H NMR methods [12-15], and also the Horeau method [16], have been available and are frequently utilized. In contrast, for the tertiary hydroxyl groups, no such procedures are available and the development of pertinent methodology has been a long-pending subject in natural product chemistry. One possible way is the introduction of a chiral and enantiomeric substituent to the hydroxyl group, to utilize its certain uneven influences on the alcohol moiety. The uneven shielding effect from the diamagnetic phenyl substituent of the MTPA esters in the Mosher determination corresponds to this [1]. However, introduction of the ester substituent to the tertiary hydroxyl group is generally difficult. Also, to correctly interpret the difference in the chemical shifts (Δδ), the conformation of the two enantiomeric substituents in solution should be recognized, but this is also quite difficult in the case of ester substituents.

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The fucofuranoside method is a new NMR method recently proposed by us for determining the absolute configuration of secondary alcohols, by derivatizing them to β-D- and β-L-fucofuranosides [17]. Both the ^{1}H and ^{13}C NMR spectra afford information, though, of course, one of the two is sufficient for the judgment. A characteristic of the fucofuranoside method is that, unlike the MTPA method, for the ^{1}H NMR analyses it utilizes the strong and uneven paramagnetic (deshielding) effect of pyridine [18], the solvent which solvates to the polar and chiral fucofuranosyl substituents. For the ^{13}C NMR analyses it utilizes the specific glycosidation shifts on the α- and β-carbons of the aglycon, and anomeric carbon, which cause carbon chemical shifts remarkably different between the two diastereomeric furanosides. The prominent advantages of the glycosidic linkages are that they are subjected to the orientation (exo-anomeric) effect of the sugar moiety [19], and that their major conformations could be recognized by the NOEs between the anomeric proton and the aglycon protons. Glycosidation of tertiary hydroxyl groups is possible, though there are no pertinent methods and the yields are low compared with those for secondary alcohols. In the present paper we applied the principles of the fucofuranoside method to the most simple tertiary alcohols **1** to **6**, in which the asymmetric carbon bearing a hydroxyl group is substituted with methyl and two methylene groups.

Results and Discussion

Influences of the conformation of the glycosidic linkage to ^{1}H and ^{13}C chemical shifts

In the typical β-glucopyranosidic linkage, due to the exo-anomeric effect from the sugar moiety, the torsion angle φ between H-1'- C-1' and O-1'-C(α) becomes nearly gauche [19,20]. It was assumed that a similar orientating effect exists in the β-fucofuranosidic linkage. This means that the carbinyl (α-) carbon and the C-2' in the sugar moiety are nearly anti-periplanar to each other, as shown in Fig. 1A. In contrast, the torsion angle ψ between C-1'-O-1' and C(α)-Me (the smallest substituent) would vary according to the individual compounds. However, if the steric hindrances of the left (R_l) and the right (R_r) substituents were equivalent, the conformations of the fucofuranosyl substituent of the β-D- and β-L-diastereomers would become symmetrical with each other, with respect to the O-1'-C(α)-Me plane. Consequently, the anomeric proton of the both diastereomers would show common NOE with the methyl group.

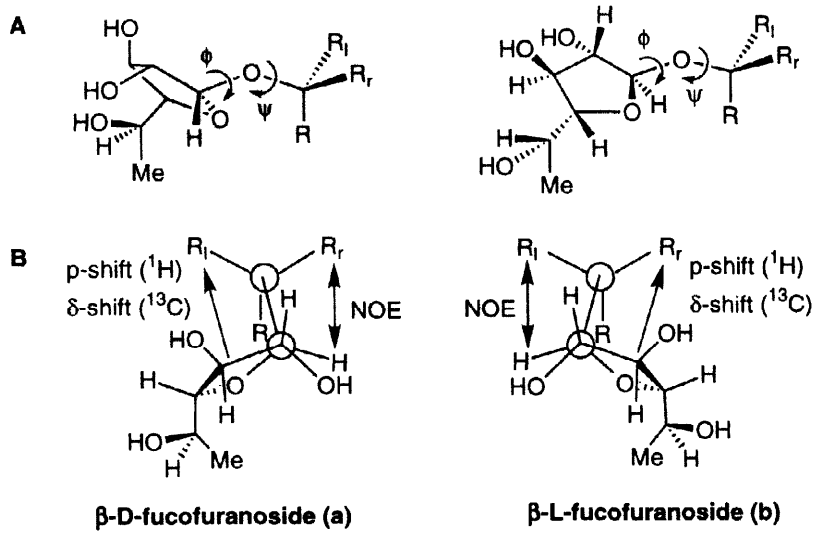


Fig. 1 Side (**A**) and front view (**B**) of the β-D-fucofuranoside and β-L-fucofuranoside of the secondary (R = H) and tertiary (R = Me) alcohols.

In the ^{1}H NMR of the β-fucofuranosides, the pyridine-induced shift (p-shift) arising from the solvent pyridine molecules, solvated to the polar site involving the 4'-O atom (oxa-side), is substantially larger than that due to the remote 2'-OH (oxy-side) [17]. Consequently, in the conformation such as shown in Fig. 1B (the O-1' and carbinyl carbon, and the C-1' and C-2' shown in Newman projection), the left-side (R_l) protons of the β-D-isomer (**a**), and the right-side (R_r) protons of the β-L-isomer (**b**), are more deshielded. In this case the anomeric proton shows NOEs with the proximate right-side (R_r) protons in the β-D-isomer (**a**), and with the left-side (R_l) protons in the β-L-isomer (**b**). In the ^{13}C NMR, glycosidation causes specific glycosidation shifts on the aglycon carbons [21-23]. It is deshielding for the α-carbon but is uneven shielding for the β-carbons, relative to the corresponding carbons of the starting alcohol. This is due to the partial deshielding of the one β-carbon which is influenced by the δ-effect of the nearby 4'-O atom (Fig. 1B) [24,25]. Accordingly, in the conformation shown in Fig. 1B the left-side β-carbon in the β-D-isomer (**a**), and the right-side β-carbon in the β-L-isomer (**b**), are more deshielded.

General procedure

The general procedure is essentially identical to that in the case of secondary alcohols in the preceding report [17]: The D- and L-fucofuranose tetraacetate was brominated by trimethylsilylbromide in CH_2Cl_2 [26,27]. Tertiary alcohols were glycosidated with the bromide in the presence of silver zeolite in CH_2Cl_2 [28,29]. Alkaline hydrolysis followed by column chromatography gave β-fucofuranoside as confirmed by the small coupling constant of 1'-H (J = 2.0 to 2.5 Hz) [30], though in poor yields (Experimental). The NMR (^{1}H and ^{13}C) spectra of the two diastereomeric furanosides were measured in pyridine-d_5 at identical concentration and temperature, and the chemical shifts were assigned by using HSQC and HMBC spectra and NOE differential spectra. The preferential conformation was estimated from the NOEs between the anomeric proton and the aglycon protons (see below). The $\Delta\delta_H$ ($\delta_H^L - \delta_H^D$) and $\Delta\delta_C$ ($\delta_C^L - \delta_C^D$) values were obtained by subtracting the chemical shifts of the β-D-isomer from the corresponding chemical shifts of the β-L-isomer. When the glycosides are viewed as illustrated in Fig. 1B, placing the furanosyl group in front and the methyl group below, the $\Delta\delta_H$ values should be positive for the protons in the right segment (R_r) and negative for the protons in the left segment (R_l). Also, the $\Delta\delta_C$ values should be positive for the right β-carbon and negative for the left β-carbon, while they are small for the anomeric, α- and the methyl carbons.

^{1}H NMR spectra

Six most simple compounds, six-membered (**1** - **4**), and five-memmbered (**5**) cyclic alcohols, and (3S)-3,7-dimethyl-3-octanol (**6**) prepared from (-)-linalool, all of them substituted with methyl and two methylene groups, were chosen. The hydroxyl group of **1** and **4** is equatorially, and that of **2** and **3** is axially oriented. Application of the Mosher method for the axial secondary hydroxyl groups is often difficult .

The results obtained from the ^{1}H NMR spectra of these compounds are shown in Fig. 2. It should be emphasized here that the minute $\Delta\delta_H$ values observed in the remote protons are meaningless. This is because the β-D-fucofuranoside and β-L-fucofuranoside are different compounds. Even a slight difference in the aglycon framework can cause small changes in the chemical shifts which are unrelated to p-shifts. For this reason, except for **6a,b**, such $\Delta\delta_H$ values from +0.02 ppm to -0.02 ppm are omitted.

The anomeric proton of these β-fucofuranosides, except for that of **6a,b**, shows NOEs with the methyl group and R_r protons in the β-D-isomer, and with the methyl group and R_l protons in the β-L-isomer. For example, the anomeric proton of 3α-methyl-5α-cholestan-3β-ol β-fucofuranosides (**1a,b**) shows NOEs with the 3α-methyl and 4-H_2 in the β-D-isomer, and with the 3α-methyl and 2-H_2 in the β-L-isomer. Similarly, the

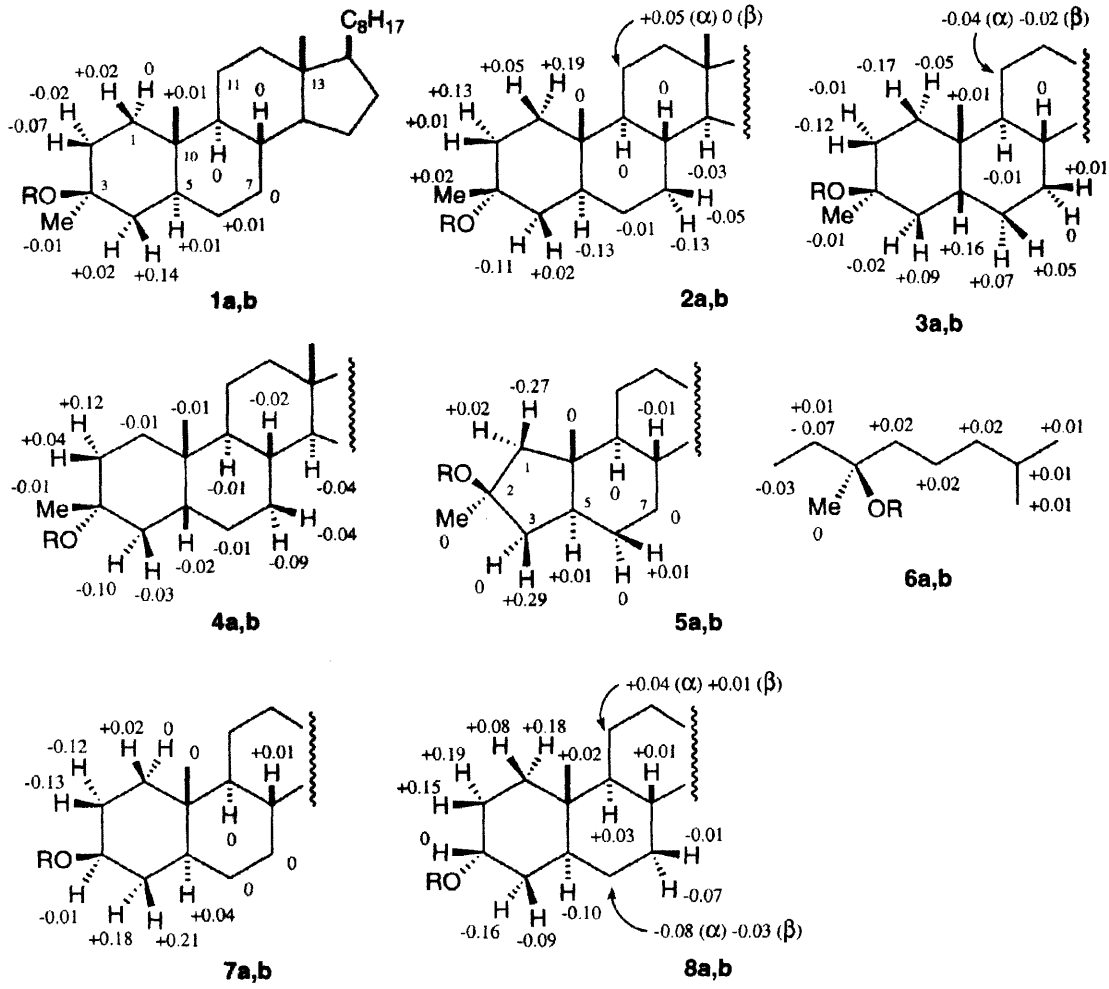


Fig. 2 The $\Delta\delta_H$ (δ_H^L - δ_H^D) values observed for the protons of the β-D- and β-L-fucofuranoside derivatives of the chiral tertiary alcohols **1** to **6**, and the secondary alcohols **7** and **8** (400 MHz, in ppm).

anomeric proton of 3β-methyl-5α-cholestan-3α-ol β-fucofuranosides (**2a,b**) shows NOEs with the 3β-methyl and 2α-H in the β-D-isomer, and with the 3β-methyl and 4α-H in the β-L-isomer. These results indicate that in compounds **1** to **5**, the conformations of the fucofuranosyl substutient of β-D- and β-L-isomers are symmetrical with regard to the plane involving O-1'-C(α)-Me as shown in Fig. 1B.

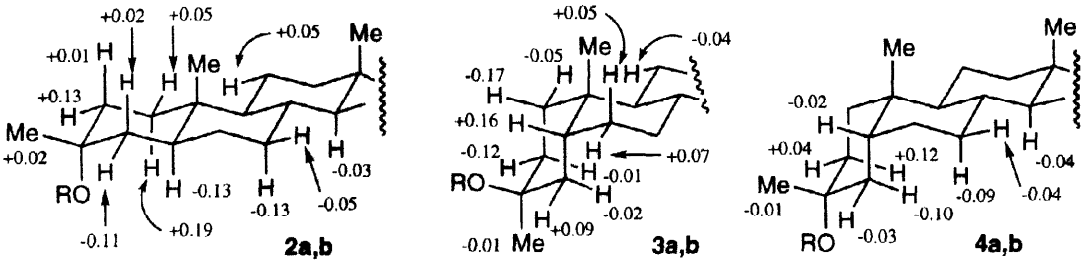
In the β-fucofuranosides of 3α-methyl-5α-cholestan-3β-ol (**1a,b**), the positive (+0.02 and +0.14 ppm) and negative (-0.02 and -0.07 ppm) $\Delta\delta_H$ values were derived for the 4-H_2 (right) and 2-H_2 (left), respectively, whilst that of the 3α-methyl is small (-0.01 ppm). In 3β-methyl-5α-cholestan-3α-ol β-fucofuranosides **2a,b**, the absolute configuration is inverted; the $\Delta\delta_H$ values of the right-side protons (1-H_2, 2-H_2) are positive but those of the left-side protons (4α-, 5α-H and 7-H_2), except for the 4β-H (+0.02 ppm), are negative. In spite of the axial orientation of the substituent, the distribution of the Δδ values are clear-cut and their magnitudes are substantial. The results obtained for **1a,b** and **2a,b** are virtually the same as those of the corresponding secondary alcohols, 5α-cholestan-3β-ol (**7**) (Experimental) and 5α-cholestan-3α-ol (**8**) [17], respectively, as shown in Fig. 2. The 1β-H signal of **1a,b** shows small opposite $\Delta\delta_H$ value (+0.02 ppm). Interestingly, the same opposite value for the 1β-H signal was observed in **7a,b** (+0.02 ppm), and also in the β-fucofuranosides of the related 3β-hydroxycholestane derivatives, cholesterol (+0.03 ppm) and 4,4-dimethylcholesterol (+0.02

ppm) previously reported [17].

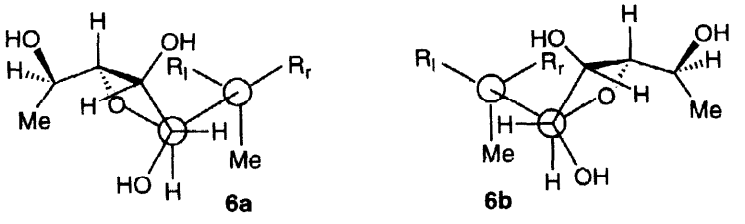
For the β-fucofuranosides of the two A/B-cis-steroids 3α-methyl-5β-cholestan-3β-ol (**3a,b**) and 3β-methyl-5β-cholestan-3α-ol (**4a,b**), both derived from coprostanone, the unequivocal distribution of the positive $\Delta\delta_H$ values in the right segment, and the negative $\Delta\delta_H$ values in the left segment, was confirmed. It has been known that the protons having gauche or 1,3-synperiplanar relation with respect to the polar hydroxyl function are strongly deshielded by p-shifts but those having 1,2-antiperiplanar relation are less affected. [18] A similar phenomenon was observed for the fucofuranosyl substituents of **2a,b** and **3a,b** and for this reason such axial protons show negligible or small opposite $\Delta\delta_H$ values (4β-H of **2a,b** and 4α-H of **3a,b**).

The magnitudes of the $\Delta\delta_H$ values of 3β-H (right, +0.29 ppm) and 1β-H (left, -0.27 ppm) of the five-membered alcohol, 2α-methyl-4-nor-5α-cholestan-2β-ol fucofuranosides (**5a,b**), are the largest observed in compounds **1** to **6**. In contrast, the chemical shifts of the 1α- and 3α-protons show, probably due to the nearly anti-relation with the substituent, little difference between the two diastereomers, and the $\Delta\delta_H$ values observed are zero (3α-H) and small opposite value, +0.02 ppm (1α-H).

The meaningful $\Delta\delta_H$ values caused by the equatorialy-oriented fucofuranosyl group of the A/B-trans steroid **1a,b** are limited within the neighboring β-methylene protons. In contrast, significant $\Delta\delta_H$ values are observed also in the remote protons in compounds **2**, **3** and **4**. This demonstrates that the p-shifts of the polar furanosyl substituent spread to the fairly remote protons. A similar long-range deshielding has previously been observed in the β-fucofuranosides of the linear furanoterpene secondary alcohol [17].



In the β-fucofuranosides of the linear compound (3S)-3,7-dimethyl-3-octanol (**6a,b**), the 2-H_2 signal appears as a single quartet at δ_H 1.67 in the β-D-isomer (**6a**) but as two double quartets at δ_H 1.60 and 1.68 in the β-L-isomer (**6b**). It showed normal distribution of the $\Delta\delta_H$ values, except for one of the 2-H_2 protons having a small opposite value (+0.01 ppm). Their magnitudes are, however, markedly smaller when compared with those found in **1a,b** to **5a,b**. This indicates the substantially high degree of free rotation about the glycosidic linkage of **6a,b**, thereby limiting the ratio of the ideal conformer. In contrast to that of **1a,b** to **5a,b**, the anomeric proton shows NOEs with the 3-methyl and R_l proton (2-H_2) in the β-D-isomer, and with the 3-methyl and R_r proton (4-H_2) in the β-L-isomer. This suggests that although the two fucofuranosyl substituetns are symmetrical with each other, their ψ angles are substiantially different from those of **1a,b** to **5a,b**. If **6a,b** takes such conformation as shown below, it would satisfy these NOEs and the normal influences of the p-shifts and δ-shifts (see below) observed .



^{13}C NMR spectra

Fucofuranoside of tertiary alcohols lacks the HC interaction [31-34], the interaction between the anomeric and carbinyl protons which is useful in the case of secondary alcohols [17]. The only available clue which reflects the absolute configuration is the δ-shift of the β-carbon caused by the ring-oxygen atom (4'-O) of the sugar moiety. By glycosidating the hydroxyl groups, the β-carbons become upfield-shifted [21-23]. However, the 4'-O atom of the furanosyl group effects a small deshielding δ-effect [24,25] on the proximate β-carbon (Fig. 1B), thereby partially cancelling the shielding β-shift. In the conformations shown in Fig. 1B, and also in that for **6a,b** shown above, the 4'-O atom deshields the left-side β-carbon in the β-D-isomer, and the right-side β-carbon in the β-L-isomer.

The $\Delta\delta_C$ values (in ppm) obtained from the ^{13}C NMR spectra of the compounds **1a,b** to **6a,b** are shown in Fig. 3. All the six-membered tertiary alcohols (**1a,b** - **4a,b**) show definite $\Delta\delta_C$ values, positive in the right β-carbon, and negative in the left β-carbon, as expected. The results obtained for **1a,b** and **2a,b** are virtually

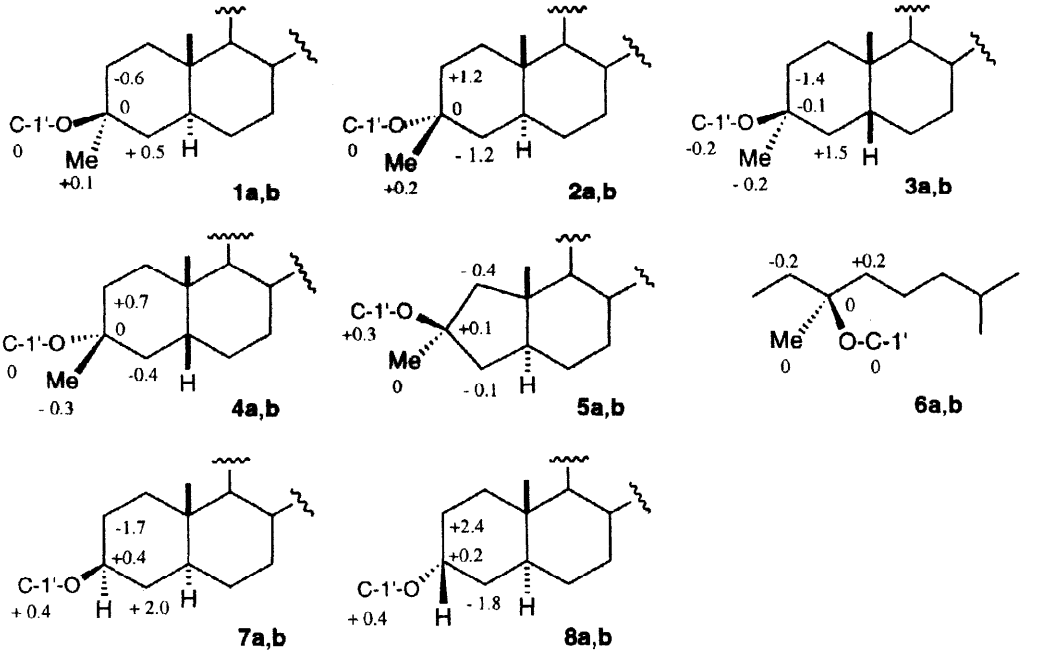


Fig. 3 The $\Delta\delta_C$ ($\delta_C{}^L$ - $\delta_C{}^D$) values observed for the α-, β-, and anomeric carbons of the β-D- and β-L-fucofuranoside derivatives of the chiral tertiary alcohols **1** to **6**, and the secondary **7** and **8** (100 MHz, in ppm).

the same as those already found in the corresponding secondary alcohols, 5α-cholestan-3β-ol (**7**) and 5α-cholestan-3α-ol (**8**), respectively. The smaller $\Delta\delta_C$ values found in **1a,b** and **2a,b** implies that, due to the enhanced steric hindrance, the contribution of δ-effect becomes smaller in the tertiary alcohols, compared with the corresponding secondary alcohols.

In the five-membered alcohol **5**, the $\Delta\delta_C$ value of the left β-carbon is indeed negative, but that of the right β-carbon is also a small negative value. This deviation suggests that the conformations of the two furanosyl substituents may not be sufficiently symmetrical. Also, due to the five-membered ring, the two β-carbons should become remoter from the 4'-O atom. The ^{13}C NMR rule mentioned above is not applicable to this compound as it is, but the meaning of such $\Delta\delta_C$ values could be clarified by further study.

As was deduced in the ^{1}H NMR of **6a,b**, due to the high degree of free rotation about the glycosidic linkage, the $\Delta\delta_C$ values of the two β-carbons are small (+0.2 ppm and -0.2 ppm). However, they are symmetrical and the $\Delta\delta_C$s of the anomeric, α- and methyl carbons are zero so that the arrangement of the ethyl group at the left, and the isohexyl group at the right side is evidently recognizable.

Application to other compounds having a different substitution pattern

For the tertiary alcohols having a more complex substitution pattern than **1** to **6**, several factors remain undetermined and such simple results as above are not available. In many examples, the glycosidation is unsuccessful, or results in the formation of dehydration products. Moreover, the glycosidated compounds show a rather random distribution of the $\Delta\delta$ values, especially in the ^{13}C NMR spectra (data not shown). In the compounds bearing a bulky substituent at the β-position, the aglycon framework itself seems to be distorted by glycosidation, resulting in the presently inexplicable $\Delta\delta_C$ values. However, in the ^{1}H NMR, the difference of the NOEs from the anomeric protons between the β-D- and β-L-isomers should necessarily reflect the absolute configuration of the asymmetric carbon. Further investigation is currently in progress, to discover a general rule in view of these findings.

Conclusions

The fucofuranoside method is applicable for determining the absolute configuration of tertiary alcohols substituted with methyl and two methylene groups, as exemplified by six chiral alcohols **1** to **6**. The $\Delta\delta_H$ and $\Delta\delta_C$ values are derived by subtracting the chemical shifts, in pyridine-d_5, of the β-D-fucofuranoside from the corresponding chemical shifts of the β-L-fucofuranoside. When the compounds are viewed placing the furanosyl group in front and the methyl group below (Fig. 1B), the following generalizations are derived.

(**a**) In the ^{1}H NMR, the $\Delta\delta_H$ values are positive for the proximate protons in the right segment (R_r) and negative for the proximate protons in the left segment (R_l) (Fig. 2).

(**b**) In the ^{13}C NMR, the $\Delta\delta_C$ values are positive for the right β-carbon and negative for the left β-carbon (Fig. 3), except for the five-membered compound **5**, which gave an ambiguous result.

The principle of the ^{13}C NMR rule is irrelevant to the solvent, so that it is applicable to the spectra taken in the solvents other than pyridine-d_5. Efficient glycosidation of tertiary alcohols is one of the unsolved subjects in the synthetic chemistry. At present, due to the low yield, the present method is applicable only when the sufficient starting materials are available.

Experimental

General

Mps were determined on a Kofler hot stage and are uncorrected. The optical rotations were determined on a JASCO DIP-370 digital polarimeter. NMR spectra were determined in pyridine-d_5 on a JEOL JNM GX 400 spectrometer at 400 MHz (^{1}H) and at 100 MHz (^{13}C) and were referenced to the residual protons in the solvents (^{1}H: CHCl3, 7.26 ppm; pyridine, 7.20 ppm) or the solvent carbons ($CDCl_3$, 77.03 ppm; pyridine-d_5 123.50 ppm) as internal standards. *J* values are given in Hz. Mass spectra were determined on a JEOL JMS DX 303 (EI) and JEOL JMS HX 110 (FAB) mass spectrometer. Flash column chromatographyn was performed on silica gel (Wako gel C-300, 200-300 mesh, Wako Pure Chemical Industries).

Preparation of β-D- and β-L-fucofuranosides

D- and L-fucofuranose tetraacetate (0.073 mmol) in 1.5ml of dry CH_2Cl_2 was brominated with 54 mg (0.35 mmol) of trimethylbromosilane at room temperature overnight. The solvent was evaported to dryness, and the bromide was stirred, monitoring by thin-layer chromatography, with a mixture of the alcohol (0.05 mmol) and powdered dry silver zeolite (200 mg) in dry CH_2Cl_2 (1 ml) for several hours. The mixture was filtered and the filtrate was evaporated to dryness and dissolved in 1ml of MeOH and one drop of 28 % NaOMe in MeOH and kept for 30 min. After usual work-up, the mixture was subjected to flash chromatography over a column of silica gel with 2-4 % MeOH in $CHCl_3$ giving the β-glycoside. The yields are specified for each compounds.

3α-Methyl-5α-cholestan-3β-ol 3-*O*-β-D-fucofuranoside 1a. (21 % yield); Colorless oil; $[\alpha]^{23}_D$ -21.4° (*c* 2.90, pyridine); δ_H 0.62 (1H, dt, *J* 3.5, 11.2 Hz, 9α-H), 0.67 (3H, s, 18-H_3), 0.75 (3H, s, 19-H_3), 0.98 (3H, d, *J* 6.5 Hz, 21-H_3), 1.48 (3H, s, 3α-Me), 1.61 (3H, d, *J* 6.5 Hz, 6'-H_3), 1.75 (1H, br t, *J* 12.0 Hz, 4β-H), 1.76 (1H, dq, *J* 12.0, 2.0 Hz, 2α-H), 5.82 (1H, d, *J* 2.4 Hz, 1'-H) [1.19 (5α-H), 1.19 (6-H_2), 1.24 (11β-H), 1.29 (8β-H), 1.47 (11α-H), 1.54 (1β-H), 1.55 (4α-H), 1.63 (7β-H), 2.00 (1H, m, 2β-H) detected by HSQC spectrum]; δ_C 36.2 (C-1), 34.8 (C-2), 77.3 (C-3), 24.3 (3α-Me), 41.0 (C-4), 43.9 (C-5), 29.2 (C-6), 32.4 (C-7), 35.8 (C-8), 54.6 (C-9), 36.3 (C-10), 21.5 (C-11), 40.3 (C-12), 42.9 (C-13), 56.7 (C-14), 24.5 (C-15), 28.6 (C-16), 56.7 (C-17), 12.3 (C-18), 12.1 (C-19), 36.1 (C-20), 19.0 (C-21), 36.5 (C-22), 24.2 (C-23), 39.8 (C-24), 28.3 (C-25), 22.7 (C-26), 22.9 (C-27), 103.4 (C-1'), 84.7 (C-2'), 78.6 (C-3'), 87.5 (C-4'), 67.6 (C-5'), 20.5 (C-6'); [Found (HRFABMS, negative ion): M-H^+, m/z 547.4367. $C_{34}H_{59}O_5$ requires 547.4363].

3α-Methyl-5α-cholestan-3β-ol 3-*O*-β-L-fucofuranoside 1b. (12 % yield); Mp 166.5-167.5 °C (from acetone); $[\alpha]^{23}_D$ +67.1° (*c* 1.58, pyridine); δ_H 0.62 (1H, dt, *J* 3.5, 11.2 Hz, 9α-H), 0.67 (3H, s, 18-H_3), 0.76 (3H, s, 19-H_3), 0.98 (3H, d, *J* 6.5 Hz, 21-H_3), 1.61 (3H, d, *J* 6.5 Hz, 6'-H_3), 1.47 (3H, s, 3α-Me), 1.74 (1H, dq, *J* 12.0, 2.0 Hz, 2α-H), 1.89 (1H, br t, *J* 12.0 Hz, 4β-H), 5.83 (1H, d, *J* 2.4 Hz, 1'-H) [1.02 (1α-H), 1.20 (5α-H), 1.20 (6-H_2), 1.24 (11β-H), 1.29 (8β-H), 1.46 (11α-H), 1.56 (1β-H), 1.57 (4α-H), 1.63 (7β-H), 1.93 (2β-H), detected by HSQC spectrum]; δ_C 36.4 (C-1), 34.2 (C-2), 77.3 (C-3), 24.4 (3α-Me), 41.5 (C-4), 43.8 (C-5), 29.2 (C-6), 32.4 (C-7), 35.8 (C-8), 54.6 (C-9), 36.3 (C-10), 21.5 (C-11), 40.4 (C-12), 42.9 (C-13), 56.7 (C-14), 24.5 (C-15), 28.6 (C-16), 56.7 (C-17), 12.3 (C-18), 12.1 (C-19), 36.1 (C-20), 19.0 (C-21), 36.5 (C-22), 24.2 (C-23), 39.8 (C-24), 28.3 (C-25), 22.7 (C-26), 23.0 (C-27), 103.4 (C-1'), 84.7 (C-2'), 78.6 (C-3'), 87.5 (C-4'), 67.6 (C-5'), 20.6 (C-6'); [Found (HRFABMS, negative ion): M-H^+, m/z 547.4347. $C_{34}H_{59}O_5$ requires 547.4363].

3β-Methyl-5α-cholestan-3α-ol 3-*O*-β-D-fucofuranoside 2a. (18 % yield); Mp 181-183 °C (from acetone); $[\alpha]^{23}_D$ -23.2° (*c* 2.42, pyridine); δ_H 0.68 (3H, s, 18-H_3), 0.71 (1H, dt, *J* 3.5, 11.2 Hz, 9α-H), 0.78 (3H, s, 19-H_3), 0.98 (3H, d, *J* 6.5 Hz, 21-H_3), 1.33 (3H, s, 3β-Me), 1.62 (3H, d, *J* 6.5 Hz, 6'-H_3), 1.72 (1H, ddd, *J* 13.0, 3.0, 3.0 Hz, 4α-H), 1.87 (1H, dq, *J* 14.0, 2.5 Hz, 2α-H), 5.65 (1H, d, *J* 2.4 Hz, 1'-H) [0.90 (14α-H), 0.95 (7α-H), 1.21 (6-H_2), 1.26 (4β-H), 1.25 (11β-H), 1.32 (8β-H), 1.43 (1β-H), 1.43 (2β-H), 1.46 (11α-H), 1.52 (1α-H), 1.65 (7β-H), 1.91 (5α-H),) detected by HSQC spectrum]; δ_C 34.3 (C-1), 33.1 (C-2), 75.3 (C-3), 27.8 (3β-Me), 41.2 (C-4), 40.9 (C-5), 28.7 (C-6), 32.4 (C-7), 35.8 (C-8), 54.6 (C-9), 35.6 (C-10), 21.3 (C-11), 40.3 (C-12), 42.9 (C-13), 56.7 (C-14), 24.5 (C-15), 28.6 (C-16), 56.7 (C-17), 12.3 (C-18), 11.9 (C-19), 36.1 (C-20), 19.0 (C-21), 36.5 (C-22), 24.2 (C-23), 39.8 (C-24), 28.3 (C-25), 22.7 (C-26), 22.9 (C-27), 103.7 (C-1'), 84.8 (C-2'), 78.6 (C-3'), 87.7 (C-4'), 67.3 (C-5'), 20.7 (C-6');

[Found (HRFABMS, negative ion): M-H$^+$, m/z 547.4384. $C_{34}H_{59}O_5$ requires 547.4363].

3β-Methyl-5α-cholestan-3α-ol 3-*O*-β-L-fucofuranoside 2b. (13 % yield); Mp 125-127 °C (from acetone); $[\alpha]^{23}_D$ +77.9° (*c* 1.68, pyridine); δ_H 0.67 (3H, s, 18-H_3), 0.71 (1H, dt, *J* 3.5, 11.2 Hz, 9α-H), 0.78 (3H, s, 19-H_3), 0.98 (3H, d, *J* 6.5 Hz, 21-H_3), 1.35 (3H, s, 3β-Me), 1.61 (3H, d, *J* 6.5 Hz, 6'-H_3), 1.71 (1H, td, *J* 13.0, 3.5 Hz, 1α-H), 2.00 (1H, dq, *J* 14.0, 2.5 Hz, 2α-H) 5.66 (1H, d, *J* 2.4 Hz, 1'-H) [0.82 (7α-H), 0.87 (14α-H), 1.20 (2H, 6-H_2), 1.25 (11β-H), 1.28 (4β-H), 1.32 (8β-H), 1.44 (2β-H), 1.48 (1β-H), 1.51 (11α-H), 1.60 (7β-H), 1.61 (4α-H), 1.78 (5α-H), detected by HSQC spectrum]; δ_C 34.6 (C-1), 34.3 (C-2), 75.3 (C-3), 28.0 (3β-Me), 40.0 (C-4), 40.8 (C-5), 28.8 (C-6), 32.3 (C-7), 35.7 (C-8), 54.6 (C-9), 35.6 (C-10), 21.4 (C-11), 40.3 (C-12), 42.9 (C-13), 56.6/56.7 (C-14), 24.4 (C-15), 28.5 (C-16), 56.7/56.6 (C-17), 12.3 (C-18), 11.9 (C-19), 36.1 (C-20), 19.0 (C-21), 36.5 (C-22), 24.2 (C-23), 39.8 (C-24), 28.2 (C-25), 22.7 (C-26), 22.9 (C-27), 103.7 (C-1'), 84.8 (C-2'), 78.7 (C-3'), 87.7 (C-4'), 67.4 (C-5'), 20.6 (C-6'); [Found (HRFABMS, negative ion): M-H$^+$, m/z 547.4350. $C_{34}H_{59}O_5$ requires 547.4363].

3α-Methyl-5β-cholestan-3β-ol 3-*O*-β-D-fucofuranoside 3a. (21 % yield); Mp 150-151 °C (from acetone); $[\alpha]^{23}_D$ -23.8° (*c* 2.98, pyridine); δ_H 0.67 (3H, s, 18-H_3), 0.95 (3H, s, 19-H_3), 0.99 (3H, d, *J* 6.5 Hz, 21-H_3), 1.43 (3H, s, 3α-Me), 1.61 (3H, d, *J* 6.5 Hz, 6'-H_3), 5.67 (1H, d, *J* 2.4 Hz, 1'-H) [1.05 (7α-H), 1.17 (6α-H), 1.24 (11β-H), 1.36 (9α-H), 1.37 (7β-H), 1.42 (11α-H), 1.35 (8β-H), 1.45 (2α-H), 1.59 (1α-H), 1.60 (4β-H), 1.83 (6β-H), 1.84 (1β-H), 1.85 (4α-H), 1.87 (2β-H), 1.94 (5β-H) detected by HSQC spectrum]; δ_C 32.3 (C-1), 33.4 (C-2), 75.9 (C-3), 28.1 (3α-Me), 37.7 (C-4), 38.3 (C-5), 27.2 (C-6), 26.7 (C-7), 36.0 (C-8), 40.4 (C-9), 34.7 (C-10), 21.5 (C-11), 40.5 (C-12), 43.0 (C-13), 56.7 (C-14), 24.5 (C-15), 28.6 (C-16), 56.7 (C-17), 12.3 (C-18), 24.1 (C-19), 36.1 (C-20), 19.0 (C-21), 36.6 (C-22), 24.2 (C-23), 39.8 (C-24), 28.3 (C-25), 22.6 (C-26), 23.0 (C-27), 103.9 (C-1'), 84.9 (C-2'), 78.8 (C-3'), 87.8 (C-4'), 67.4 (C-5'), 20.6 (C-6'); [Found (HRFABMS, negative ion): M-H$^+$, m/z 547.4355. $C_{34}H_{59}O_5$ requires 547.4363].

3α-Methyl-5β-cholestan-3β-ol 3-*O*-β-L-fucofuranoside 3b. (18 % yield); Mp 164-166 °C (from acetone); $[\alpha]^{23}_D$ +55.1° (*c* 2.42, pyridine); δ_H 0.67 (3H, s, 18-H_3), 0.96 (3H, s, 19-H_3), 0.99 (3H, d, *J* 6.5 Hz, 21-H_3), 1.42 (3H, s, 3α-Me), 1.60 (3H, d, *J* 6.5 Hz, 6'-H_3), 1.83 (1H, t, *J* 13.5 Hz, 4α-H), 2.10 (1H, m, 5β-H), 5.66 (1H, d, *J* 2.4 Hz, 1'-H) [1.05 (7α-H), 1.22 (11β-H), 1.24 (6α-H), 1.35 (9α-H), 1.35 (8β-H), 1.38 (7β-H), 1.38 (11α-H), 1.44 (2α-H), 1.54 (1α-H), 1.67 (1β-H), 1.69 (4β-H), 1.75 (2β-H), 1.88 (6β-H) detected by HSQC spectrum]; δ_C 32.1 (C-1), 32.0 (C-2), 75.8 (C-3), 28.0 (3α-Me), 39.2 (C-4), 38.4 (C-5), 27.1 (C-6), 26.7 (C-7), 36.0 (C-8), 40.4 (C-9), 34.6 (C-10), 21.4 (C-11), 40.5 (C-12), 43.0 (C-13), 56.7 (C-14), 24.5 (C-15), 28.6 (C-16), 56.7 (C-17), 12.3 (C-18), 24.1 (C-19), 36.1 (C-20), 19.0 (C-21), 36.5 (C-22), 24.2 (C-23), 39.8 (C-24), 28.3 (C-25), 22.7 (C-26), 22.9 (C-27), 103.7 (C-1'), 84.9 (C-2'), 78.7 (C-3'), 87.6 (C-4'), 67.2 (C-5'), 20.7 (C-6'); [Found (HRFABMS, negative ion): M-H$^+$, m/z 547.4391. $C_{34}H_{59}O_5$ requires 547.4363].

3β-Methyl-5β-cholestan-3α-ol 3-*O*-β-D-fucofuranoside 4a. (6.0 % yield); Mp 130-132 °C (from acetone); $[\alpha]^{23}_D$ -20.3° (*c* 0.76, pyridine); δ_H 0.63 (3H, s, 18-H_3), 0.78 (1H, m, 14α-H), 0.92 (3H, s, 19-H_3), 0.98 (3H, d, *J* 6.5 Hz, 21-H_3), 1.48 (3H, s, 3β-Me), 1.61 (3H, d, *J* 6.5 Hz, 6'-H_3), 2.39 (1H, t, *J* 13.5 Hz, 4α-H), 5.86 (1H, d, *J* 2.4 Hz, 1'-H) [1.06 (1β-H), 1.08 (7α-H), 1.15 (11β-H), 1.17 (6α-H), 1.28 (8β-H), 1.30 (11α-H), 1.32 (7β-H), 1.38 (9α-H), 1.42 (5β-H), 1.51 (4β-H), 1.67 (2β-H), 1.71 (1α-H), 1.81

(6β-H), 1.87 (2α-H) detected by HSQC spectrum]; δ_C 34.5 (C-1), 33.1 (C-2), 78.0 (C-3), 23.9 (3β-Me), 39.6 (C-4), 40.9 (C-5), 27.5 (C-6), 26.6 (C-7), 35.9 (C-8), 40.2 (C-9), 35.3 (C-10), 21.2 (C-11), 40.3 (C-12), 42.8 (C-13), 56.4 (C-14), 24.4 (C-15), 28.5 (C-16), 56.4 (C-17), 12.3 (C-18), 23.7 (C-19), 36.0 (C-20), 19.0 (C-21), 36.6 (C-22), 24.1 (C-23), 39.8 (C-24), 28.3 (C-25), 22.7 (C-26), 22.9 (C-27), 103.4 (C-1'), 84.7 (C-2'), 78.5 (C-3'), 87.4 (C-4'), 67.5 (C-5'), 20.6 (C-6'); [Found (HRFABMS, negative ion): M-H$^+$, m/z 547.4366. $C_{34}H_{59}O_5$ requires 547.4363].

3β-Methyl-5β-cholestan-3α-ol 3-*O*-β-L-fucofuranoside 4b. (7.3 % yield); Colorless oil; $[\alpha]^{23}_D$ +56.5° (*c* 0.96, pyridine); δ_H 0.63 (3H, s, 18-H_3), 0.91 (3H, s, 19-H_3), 0.98 (3H, d, *J* 6.5 Hz, 21-H_3), 1.47 (3H, s, 3β-Me), 1.61 (3H, d, *J* 6.5 Hz, 6'-H_3), 1.99 (1H, td, J 13.5, 3.5 Hz, 2α-H), 2.29 (1H, t, *J* 13.5 Hz, 4α-H), 5.86 (1H, d, *J* 2.4 Hz, 1'-H) [0.99 (7α-H), 1.05 (1β-H), 1.14 (11β-H), 1.16 (6α-H), 1.26 (8β-H), 1.28 (7β-H), 1.29 (11α-H), 1.37 (9α-H), 1.40 (5β-H), 1.48 (4β-H), 1.70 (1α-H), 1.71 (2β-H), 1.80 (6β-H) detected by HSQC spectrum]; δ_C 34.4 (C-1), 33.8 (C-2), 78.0 (C-3), 23.6 (3β-Me), 39.2 (C-4), 41.1 (C-5), 27.5 (C-6), 26.6 (C-7), 35.9 (C-8), 40.2 (C-9), 35.3 (C-10), 21.2 (C-11), 40.3 (C-12), 42.8 (C-13), 56.3 (C-14), 24.4 (C-15), 28.5 (C-16), 56.4 (C-17), 12.3 (C-18), 23.7 (C-19), 36.0 (C-20), 19.0 (C-21), 36.6 (C-22), 24.1 (C-23), 39.8 (C-24), 28.3 (C-25), 22.7 (C-26), 22.9 (C-27), 103.4 (C-1'), 84.6 (C-2'), 78.4 (C-3'), 87.5 (C-4'), 67.7 (C-5'), 20.6 (C-6'); [Found (HRFABMS, negative ion): M-H$^+$, m/z 547.4382. $C_{34}H_{59}O_5$ requires 547.4363].

2α-Methyl-4-nor-5α-cholestan-2β-ol 2-*O*-β-D-fucofuranoside 5a. (9.6% yield); Mp 139-140 °C (from acetone); $[\alpha]^{23}_D$ -31.2° (*c* 1.84, pyridine); δ_H 0.64 (3H, s, 18-H_3), 0.69 (1H, dt, *J* 3.5, 11.2 Hz, 9α-H), 0.97 (3H, d, *J* 6.5 Hz, 21-H_3), 1.05 (3H, s, 19-H_3), 1.49 (3H, s, 2α-Me), 1.64 (3H, d, *J* 6.5 Hz, 6'-H_3), 1.71 (1H, dd, *J* 12.5, 6.0 Hz, 3α-H), 2.04 (1H, dd, *J* 12.0, 12.5 Hz, 3β-H), 2.36 (1H, d, *J* 13.0 Hz, 1β-H), 5.66 (1H, d, *J* 2.4 Hz, 1'-H) [0.87 (7α-H), 1.15 (1α-H), 1.28 (6β-H), 1.28 (5α-H), 1.30 (11α-H), 1.31 (8β-H), 1.43 (11β-H), 1.49 (6α-H), 1.66 (7β-H) detected by HSQC spectrum]; δ_C 54.2 (C-1), 84.1 (C-2), 29.6 (2α-Me), 44.9 (C-3), 49.6 (C-5), 25.2 (C-6), 32.5 (C-7), 35.5 (C-8), 55.5 (C-9), 44.4 (C-10), 23.7 (C-11), 40.3 (C-12), 43.3 (C-13), 56.5 (C-14), 24.7 (C-15), 28.5 (C-16), 56.6 (C-17), 12.4 (C-18), 14.0 (C-19), 36.1 (C-20), 19.0 (C-21), 36.6 (C-22), 24.2 (C-23), 39.8 (C-24), 28.3 (C-25), 22.7 (C-26), 22.9 (C-27), 104.9 (C-1'), 84.9 (C-2'), 78.5 (C-3'), 87.3 (C-4'), 67.3 (C-5'), 20.6 (C-6'); [Found (HRFABMS, negative ion): M-H$^+$, m/z 533.4213. $C_{33}H_{57}O_5$ requires 533.4206].

2α-Methyl-4-nor-5α-cholestan-2β-ol 2-*O*-β-L-fucofuranoside 5b. (11.6% yield); Mp 144-145 °C (from acetone); $[\alpha]^{23}_D$ +33.4° (*c* 2.24, pyridine); δ_H 0.65 (3H, s, 18-H_3), 0.69 (1H, dt, *J* 3.5, 11.2 Hz, 9α-H), 0.97 (3H, d, *J* 6.5 Hz, 21-H_3), 1.05 (3H, s, 19-H_3), 1.49 (3H, s, 2α-Me), 1.62 (3H, d, *J* 6.5 Hz, 6'-H_3), 1.71 (1H, dd, *J* 13.0, 6.0 Hz, 3α-H), 2.09 (1H, d, *J* 13.0 Hz, 1β-H), 2.33 (1H, dd, *J* 12.5, 13.0 Hz, 3β-H), 5.66 (1H, d, *J* 2.4 Hz, 1'-H) [0.87 (7α-H), 1.17 (1α-H), 1.27 (11α-H), 1.29 (6β-H), 1.29 (5α-H), 1.30 (8β-H), 1.41 (11β-H), 1.49 (6α-H), 1.66 (7β-H) detected by HSQC spectrum]; δ_C 53.8 (C-1), 84.2 (C-2), 29.6 (2α-Me), 44.8 (C-3), 49.9 (C-5), 25.2 (C-6), 32.4 (C-7), 35.5 (C-8), 55.4 (C-9), 44.4 (C-10), 23.7 (C-11), 40.3 (C-12), 43.3 (C-13), 56.4 (C-14), 24.7 (C-15), 28.5 (C-16), 56.6 (C-17), 12.4 (C-18), 14.0 (C-19), 36.1 (C-20), 19.0 (C-21), 36.6 (C-22), 24.2 (C-23), 39.8 (C-24), 28.3 (C-25), 22.7 (C-26), 22.9 (C-27), 105.2 (C-1'), 84.6 (C-2'), 78.6 (C-3'), 87.6 (C-4'), 67.4 (C-5'), 20.6 (C-6'); [Found (HRFABMS, negative ion): M-H$^+$, m/z 533.4211. $C_{33}H_{57}O_5$ requires 533.4206].

(3S)-3,7-Dimethyl-3-octanol 3-*O*-β-D-fucofuranoside 6a. (2 % yield); Colorless oil; $[\alpha]^{23}_D$ -71° (*c* 0.18, pyridine); δ_H 0.85, 0.85 (each 3H, d, *J* 7.0 Hz, 7-Me and 8-H_3), 0.97 (3H, t, *J* 7.0 Hz, 1-H_3), 1.14 (2H, m, 6-H_2), 1.29 (3H, s, 3-Me), 1.45 (2H, m, 5-H_2), 1.49 (1H, m, 7-H), 1.58 (3H, d, *J* 6.5 Hz, 6'-H_3), 1.60 (2H, m, 4-H_2), 1.67 (2H, q, *J* 7.0 Hz, 2-H_2), 5.63 (1H, d, *J* 2.4 Hz, 1'-H); δ_C 8.41 (C-1), 32.33 (C-2), 78.66 (C-3), 23.90 (3-Me), 39.52 (C-4), 21.71 (C-5), 39.83 (C-6), 28.13 (C-7), 22.75 (C-8), 22.79 (7-Me); [Found (HRFABMS, negative ion): M-H^+, m/z 303.2181. $C_{16}H_{31}O_5$ requires 303.2171].

(3S)-3,7-Dimethyl-3-octanol 3-*O*-β-L-fucofuranoside 6b. (4.4 % yield); Colorless oil; $[\alpha]^{23}_D$ +60° (*c* 0.40, pyridine); δ_H 0.86, 0.86 (each 3H, d, *J* 7.0 Hz, 7-Me and 8-H_3), 0.94 (3H, t, *J* 7.0 Hz, 1-H_3), 1.16 (2H, m, 6-H_2), 1.29 (3H, s, 3-Me), 1.47 (2H, m, 5-H_2), 1.50 (1H, m, 7-H), 1.58 (3H, d, *J* 6.5 Hz, 6'-H_3), 1.60 (1H, dq, *J* 14.5, 7.0 Hz, 2-H), 1.62 (2H, m, 4-H_2), 1.68 (1H, dq, *J* 14.5, 7.0 Hz, 2-H), 5.63 (1H, d, *J* 2.4 Hz, 1'-H); δ_C 8.43 (C-1), 32.13 (C-2), 78.66 (C-3), 23.89 (3-Me), 39.74 (C-4), 21.71 (C-5), 39.87 (C-6), 28.17 (C-7), 22.77 (C-8), 22.81 (7-Me); [Found (HRFABMS, negative ion): M-H^+, m/z 303.2163. $C_{16}H_{31}O_5$ requires 303.2171].

5α-Cholestan-3β-ol 3-*O*-β-D-fucofuranoside 7a. Prepared by the condition shown in lit. 17 (20 % yield); Mp 199-202 °C (from acetone); $[\alpha]^{23}_D$ -31.2° (*c* 2.78, pyridine); δ_H 0.53 (dt, *J* 3.5, 11.2 Hz, 9α-H), 0.64 (3H, s, 18-H_3), 0.73 (3H, s, 19-H_3), 0.96 (3H, d, *J* 6.5 Hz, 21-H_3), 1.66 (3H, d, *J* 6.5 Hz, 6'-H_3), 2.09 (1H, br d, *J* 14.0 Hz, 2α-H), 3.80 (1H, m, 3α-H), 5.68 (1H, br s, 1'-H) [0.85 (1α-H), 0.86 (7α-H), 1.17 (6-H_2), 0.94 (5α-H), 1.22 (11β-H), 1.26 (8β-H), 1.31 (4β-H), 1.43 (11α-H), 1.60 (7β-H), 1.61 (1β-H), 1.63 (2β-H), 1.69 (4α-H), detected by HSQC spectrum]; δ_C 37.3 (C-1), 30.2 (C-2), 76.3 (C-3), 34.9 (C-4), 44.9 (C-5), 29.1 (C-6), 32.4 (C-7), 35.7 (C-8), 54.6 (C-9), 35.8 (C-10), 21.5 (C-11), 40.3 (C-12), 42.9 (C-13), 56.6 (C-14), 24.5 (C-15), 28.5 (C-16), 56.6 (C-17), 12.3 (C-18), 12.4 (C-19), 36.1 (C-20), 19.0 (C-21), 36.5 (C-22), 24.2 (C-23), 39.8 (C-24), 28.3 (C-25), 22.7 (C-26), 22.9 (C-27), 107.3 (C-1'), 84.2 (C-2'), 79.3 (C-3'), 88.2 (C-4'), 67.9 (C-5'), 20.5 (C-6'); [Found (HRFABMS, positive ion): MH^+, m/z 535.4351. $C_{33}H_{59}O_5$ requires 535.4362].

5α-Cholestan-3β-ol 3-*O*-β-L-fucofuranoside 7b. Prepared by the condition shown in lit. 17 (23 % yield); Mp 204-206 °C (from acetone); $[\alpha]^{23}_D$ +48.2° (*c* 3.16, pyridine); δ_H 0.53 (dt, *J* 3.5, 11.2 Hz, 9α-H), 0.64 (3H, s, 18-H_3), 0.73 (3H, s, 19-H_3), 0.85 (1α-H), 0.96 (3H, d, *J* 6.5 Hz, 21-H_3), 1.66 (3H, d, *J* 6.5 Hz, 6'-H_3), 3.79 (1H, m, 3α-H), 5.68 (1H, d, *J* 2.0 Hz, 1'-H) [0.86 (7α-H), 0.98 (5α-H), 1.17 (6-H_2), 1.22 (11β-H), 1.27 (8β-H), 1.45 (11α-H), 1.50 (2β-H), 1.52 (4β-H), 1.60 (7β-H), 1.63 (1β-H), 1.87 (4α-H), 1.97 (1H, br d, *J* 14.0 Hz, 2α-H) detected by HSQC spectrum];δ_C 37.2 (C-1), 28.5 (C-2), 76.7 (C-3), 36.9 (C-4), 45.1 (C-5), 29.1 (C-6), 32.3 (C-7), 35.7 (C-8), 54.6 (C-9), 35.8 (C-10), 21.5 (C-11), 40.3 (C-12), 42.9 (C-13), 56.6/56.7 (C-14), 24.5 (C-15), 28.5 (C-16), 56.7/56.6 (C-17), 12.3 (C-18), 12.4 (C-19), 36.1 (C-20), 19.0 (C-21), 36.5 (C-22), 24.2 (C-23), 39.8 (C-24), 28.3 (C-25), 22.7 (C-26), 23.0 (C-27), 107.7 (C-1'), 84.2 (C-2'), 79.4 (C-3'), 88.4 (C-4'), 67.9 (C-5'), 20.5 (C-6'); [Found (HRFABMS, positive ion): MH^+, *m/z* 535.4351. $C_{33}H_{59}O_5$ requires 535.4362].

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