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The arabinofuranoside method, a convenient substitute of the fucofuranoside method for determining the absolute configuration of the secondary alcohols

Masaru Kobayashi*

Graduate School of Pharmaceutical Sciences, Hokkaido University, Kita-Ku, Sapporo 060-0812, Japan

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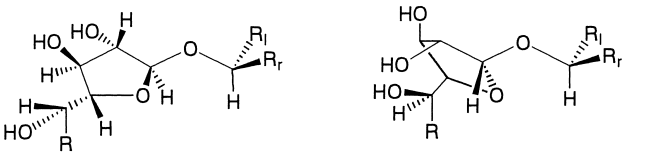
Abstract—As a simple substitute of the fucofuranoside method, a recently devised technique for determining the absolute configuration of secondary alcohols by ^{13}C NMR, the arabinofuranoside method is proposed. Unlike fucose, the derivatizing agent arabinofuranose tetraacetate is available quantitatively by acid treatment of arabinose followed by acetylation. Application to the ten alcohols, previously tested for fucofuranoside method, showed essentially the identical $\Delta\delta_C$ and $\Delta\delta_H$ values, indicating that the arabinofuranoside method is equally useful for determining the absolute configuration of the secondary alcohols.

1. Introduction

In the preceding works the author proposed the fucofuranoside method for determining the absolute configuration of the secondary alcohols, by converting to β-D- and β-L-fucofuranosides.[1–3] The judgment, drawn by the ^{13}C NMR rule, can be substantiated simultaneously by the ^{1}H NMR rule. In the ^{13}C NMR analyses, it utilizes the difference of the glycosidation shifts on the α- and β-carbon of the aglycon, and on the anomeric carbon.[4] For the ^{1}H NMR analyses, it utilizes the uneven paramagnetic effect of the solvent pyridine (pyridine-induced shift),[5] which solvates to the polar and chiral fucofuranosyl moiety. These two effects are influenced by the conformation of the glycosidic linkage, which depends on the steric environment of the hydroxyl group, and cause the difference of the chemical shifts, both in ^{1}H and ^{13}C NMR, between the diastereomeric two fucofuranosides. These explanations have been described in detail in the previous papers.[1–3] The efficacy of the method was proved for nineteen compounds, including monohydroxy secondary alcohols,[1] 1,2-glycols consisting of secondary and tertiary hydroxyl groups,[3] and for the simple tertiary alcohols substituted with methyl and two methylene groups.[2]

Preparation of the derivatizing agent fucofuranose tetraacetate is, however, time-consuming, since the acid treatment (1% methanolic HCl) of fucose gives the pyranose and furanose forms in almost equal amounts.[1] Arabinose, the 6-demethyl analog of fucose, is also commercially available both in D- and L-form. Unlike fucose, it has been known that, by the same acid treatment, it changes into the furanose form predominantly.[6] Owing to the nomenclature rule, however, the β-D-fucofuranose corresponds to α-L-arabinofuranose, and the β-L-fucofuranose corresponds to α-D-arabinofuranose (Fig.1). The present paper shows that the arabinofuranoside method is equally applicable as fucofuranoside method for determining the absolute configuration of secondary alcohols.



α-D-arabinofuranoside: R = H
β-L-fucofuranoside: R = Me

α-L-arabinofuranoside: R = H
β-D-fucofuranoside: R = Me

Figure 1. Side view of the glycosidic linkages of the α-arabinofuranoside and β-fucofuranoside.

2. Results and discussion

In the fucofuranoside method the $\Delta\delta$ values are obtained, both in ^{13}C and ^{1}H NMR, by subtracting the chemical shift of the β-D-isomer from the corresponding chemical shift of the β-L-isomer. For the secondary alcohols, when the glycoside is viewed fixing the α-proton below and the sugar moiety in front, there are following rules.[1,3]

Keywords: alcohol; arabinofuranoside; glycosidation shift; pyridine-induced shift; ^{13}C NMR; ^{1}H NMR; absolute configuration.

* Tel.: +81-011-706-3242; fax: +81-011-706-4989; e-mail: masark@pharm.hokudai.ac.jp

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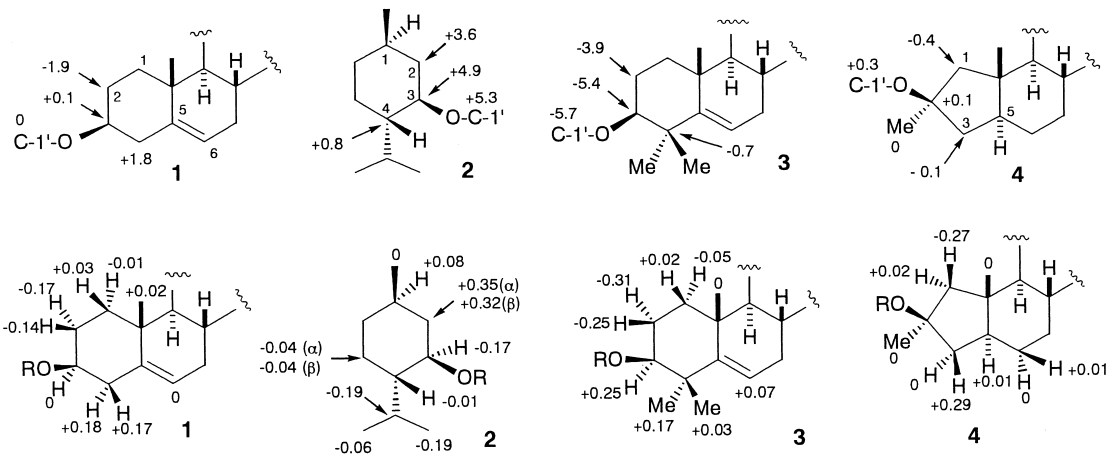

Figure 2. The $\Delta\delta_C$ (upper) and $\Delta\delta_H$ (lower) values of the symmetrical (**1**), *R*-type (**2**) and *S*-type (**3**) secondary alcohols, and the tertiary alcohol **4** reported previously using the fucofuranoside method (in ppm).

^{13}C NMR (Fig. 2, upper part).

(a) When the two β-carbons bear symmetrical steric hindrances, as in cholesterol (**1**), the $\Delta\delta_C$ value of the right β-carbon is positive and that of the left β-carbon is negative while those of the anomeric and α-carbon are negligible.

(b) When the steric hindrances are unsymmetrical, see the order of (a) fucofuranosyl group (b) sterically bulkier β-position (c) less bulky β-position. If it is clockwise (*R*-type) as in *l*-menthol (**2**), the $\Delta\delta_C$ values of the anomeric, α-, and the right β-carbon are positive while that of the left β-carbon is small (mostly positive). In the counterclockwise (*S*-type) case, as in 4,4-dimethylcolesterol (**3**), the $\Delta\delta_C$ values of the anomeric, α-, and the left β-carbon (C-2) are negative while that of the right β-carbon is small (mostly negative).

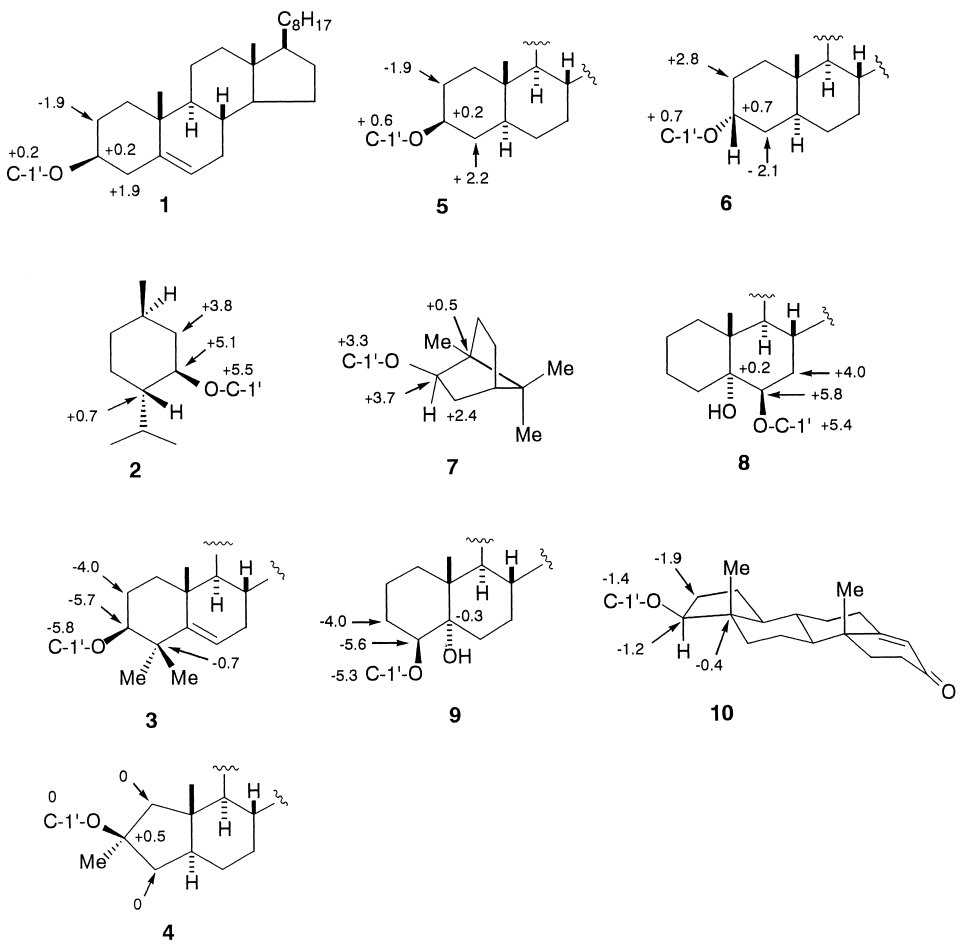

Figure 3. The $\Delta\delta_C$ ($\delta_C^D - \delta_C^L$) values observed for the carbons of the α-D- and α-L-arabinofuranoside derivatives of the symmetrical (**1**, **5**, **6**), *R*-type (**2**, **7**, **8**) and *S*-type (**3**, **9**, **10**) secondary alcohols, and the tertiary alcohol **4** (125 MHz, in ppm).

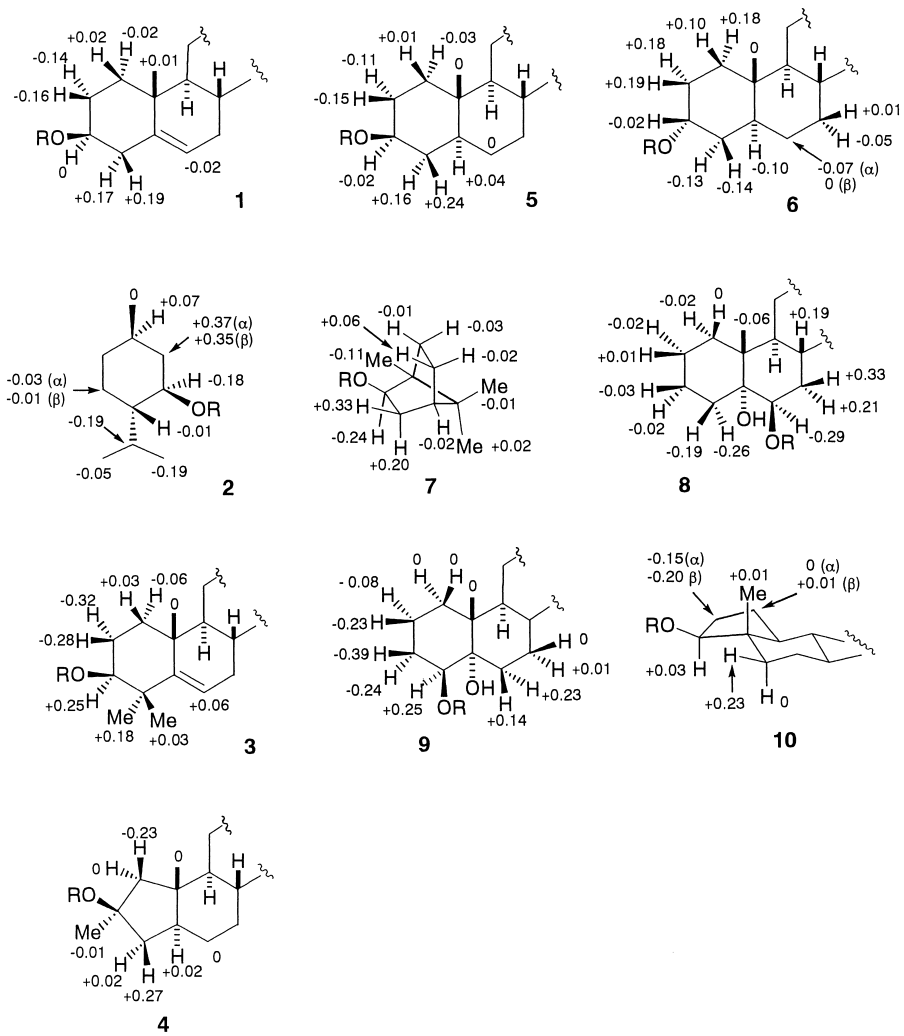

Figure 4. The $\Delta\delta_H$ ($\delta_H^D - \delta_H^L$) values observed for the protons of the α-D- and α-L-arabinofuranoside derivatives of the symmetrical (**1**, **5**, **6**), *R*-type (**2**, **7**, **8**) and *S*-type (**3**, **9**, **10**) secondary alcohols, and the tertiary alcohol **4** (500 MHz, in ppm).

^{1}H NMR (Fig. 2, lower part).

(a) When the two β-carbons bear symmetrical steric hindrances, the $\Delta\delta_H$ values are positive for the right segment protons and negative for the left segment protons while that of the α-proton is negligible (Fig. 2, **1**).
(b) In the unsymmetrical compounds, the $\Delta\delta_H$ values are also positive for the right segment protons and negative for the left segment protons. However, the $\Delta\delta_H$ value of the α-proton is negative in the *R*-type compounds (Fig. 2, **2**), but that is positive in the *S*-type compounds (Fig. 2, **3**).

To confirm that these rules also hold good in arabinofuranoside, three secondary alcohols having methylene group at both β-position (**1**, **5**, **6**), each three unsymmetrically substituted *R*-type (**2**, **7**, **8**) and *S*-type (**3**, **9**, **10**) secondary alcohols, and one tertiary alcohol (**4**), substituted with methyl and two methylene groups, were chosen. The $\Delta\delta_C$ and $\Delta\delta_H$ values of these compounds in the fucofuranoside method have previously been shown.[1–3] These alcohols were converted to arabinofuranosides, using the previously reported procedure, with arabinofuranose tetraacetate, TMSOTf and 4A molecular sieve, followed by hydrolysis.[1,7a] The tertiary alcohol **4** was glycosidated using the 1-bromosugar and silver zeolite.[2,7b,c] Under these conditions, the arabinofuranosides formed are exclusively α-anomers, as confirmed by the characteristic small coupling constant (less than 2.0 Hz) of the anomeric proton. The α-D- and α-L-arabinofuranosides obtained showed the NOE between the anomeric and α-proton, in common with the corresponding β-L- and β-D-fucofuranoside, respectively.

The $\Delta\delta_C$ and $\Delta\delta_H$ values, obtained by subtracting the chemical shift of the α-L-isomer from the corresponding chemical shift of the α-D-isomer, are shown in Figs. 3 and 4. The results are indeed consistent with the rule shown above in the fucofuranoside method. In the symmetrical compounds **1**, **5** and **6**, the $\Delta\delta_C$ value of the right β-carbon is positive and that of the left β-carbon is negative while those of the anomeric and α-carbon are quite small (Fig. 3). In the *R*-type compounds **2**, **7** and **8**, the $\Delta\delta_C$ values of the anomeric, α-, and the right β-carbon are positive while that of the left β-carbon is small. In contrast, in the *S*-type compounds **3**, **9** and **10**, the $\Delta\delta_C$ values of the anomeric, α-,

and the left β-carbon are negative while that of the right β-carbon is small.

The ^{1}H NMR showed also the results, consistent with the rule (Fig. 4). The significant $\Delta\delta_H$ values, caused by the pyridine-induced shift, are positive for the right segment protons and negative for the left segment protons. The $\Delta\delta_H$ values of the α-proton in the symmetrical compounds **1**, **5** and **6** are negligible. In contrast, they are significant and negative in the *R*-type compounds **2**, **7** and **8**, but are positive in the *S*-type compounds **3**, **9** and **10**. The diastereomeric glycosides generally show small difference of the chemical shifts, unrelated to the pyridine-induced anisotropy, so that the $\Delta\delta_H$ values up to a magnitude of 0.02 ppm should be regarded as meaningless.

The fucofuranoside method has been shown to be effective for the six-membered cyclic tertiary alcohols substituted with methyl and two methylene groups.[2] However, it was not in the ^{13}C NMR of the five-membered 4-norcholestane type alcohol **4** (Fig. 2). The 4′-oxygen atom of the furanose unit influences on one of the β-carbons of the six-membered compounds causing small difference between the diastereomeric two glycosides. Probably, this effect is lost in the five-membered compound due to the increased distance between the two positions. It was also the case in the present study as shown in Fig. 3 but, in contrast, in the ^{1}H NMR (Fig. 4) it showed substantial $\Delta\delta_H$ values due to the 3β-H (right, +0.27 ppm) and the 1β-H (left, −0.23 ppm).

The magnitude of the $\Delta\delta_C$ and $\Delta\delta_H$ values, observed in the present study, are virtually identical with the corresponding values found in the fucofuranosides (Fig. 2). This indicates that the conformation of the each glycosidic linkage in compounds **1** to **10** is also virtually identical with that of the corresponding fucofuranoside. In summary, the arabinofuranoside method is shown to be equal to the fucofuranoside method and more convenient because of the easier preparation of the derivatizing agent arabinofuranose tetraacetate.[6]

3. Experimental

3.1. 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 ALPHA 500 spectrometer at 500 MHz (^{1}H) and at 125 MHz (^{13}C) and were referenced to the residual proton of the solvent (7.20 ppm) or the solvent carbon (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 chromatography was performed on silica gel (Wako gel C-300, 200–300 mesh, Wako Pure Chemical Industries).

3.2. D- and L-arabinofuranose tetraacetates

D-Arabinose or L-arabinose (5 g) was dissolved in a mixture of H_2SO_4 (0.9 ml) in 130 ml of dry MeOH and stirred at 3°C for 1 d. Pyridine (40 ml) was added and the solvent was evaporated off. The residue was dissolved, with cooling, in 40 ml of pyridine and 15 ml of Ac_2O and kept at room temperature overnight. The mixture was added into ice-water and stirred for 1 h. The mixture was extracted with $CHCl_3$ and the extract was thoroughly washed with saturated $NaHCO_3$ solution, H_2O and saturated NaCl solution, and then the solvent was evaporated off. It was dissolved in a mixture of AcOH (50 ml) and Ac_2O (12.5 ml) and treated, with cooling, with conc. H_2SO_4 (2.5 ml), and kept at room temperature overnight. The mixture was added with ice-water (75 ml), stirred for 50 min, and extracted with $CHCl_3$. The extract was washed with H_2O, saturated $NaHCO_3$ solution, H_2O and saturated NaCl solution, and the solvent was evaporated giving crude arabinofuranoside (6.9 g). A portion (2.5 g) of the product was purified by flash chromatography over a column of silica gel with ethyl-acetate–hexane (1.3:2) to remove the trace amount of the more polar by-product. The arabinofuranoside tetraacetate obtained is a ca. 10:1 mixture of α-anomer and β-anomer but gives the α-furanoside exclusively in the following glycosidation condition.

3.3. Preparation of α-D- and α-L-arabinofuranosides

TMSOTf (10 μl) was added to the mixture of the arabinofuranose tetraacetate (75 mg, 0.24 mmol) and powdered and freshly dried 4A molecular sieve (250 mg) in dry CH_2Cl_2 (1.5 ml) and stirred for 3 min. The starting alcohol (0.1 mmol) was added and the mixture was stirred at room temperature for 30–60 min. Excess TMSOTf was quenched with one drop of triethylamine and the mixture was filtered. The filtrate was evaporated to dryness and dissolved in 1 ml of MeOH and one drop of 28% NaOMe in MeOH and kept at 60°C 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 α-arabinofuranoside (20–50% yield).

3.3.1. Cholest-5-en-3β-ol 3-*O*-α-D-arabinofuranoside (1a). Mp 240–242°C (from acetone); $[\alpha]_D^{23}$=+44.2° (*c* 2.34, pyridine); δ_H 0.66 (3H, s, 18-H$_3$), 0.98 (3H, s, 19-H$_3$), 1.77 (1H, dt, *J*=13.5, 3.5 Hz, 1β-H), 1.91 (1H, dddd, *J*=17.5, 5.5, 5.5, 2.5 Hz, 7β-H), 1.98 (2H, m, 2α, 12β-H), 2.57 (1H, br t, *J*=13.5 Hz, 4β-H), 2.74 (1H, ddd, *J*=13.5, 5.0, 2.0 Hz, 4α-H), 3.80 (1H, m, 3α-H), 5.32 (1H, m, 6-H), 5.70 (1H, d, *J*=2.0 Hz, 1′-H) [0.95 (9α-H), 1.00 (1α-H), 1.39 (8β-H), 1.39 (11β-H), 1.46 (11α-H), 1.53 (7α-H) and 1.60 (2β-H) detected by HSQC spectrum]; δ_C 12.0 (C-18), 19.5 (C-19), 21.3 (C-11), 24.5 (C-15), 28.5 (C-16), 28.6 (C-2), 32.1 (C-8), 32.2 (C-7), 36.9 (C-10), 37.5 (C-1), 40.0 (C-12), 41.1 (C-4), 42.5 (C-13), 50.4 (C-9), 56.4 (C-17), 56.9 (C-14), 77.3 (C-3), 62.9 (C-5′), 78.8 (C-3′), 84.2 (C-2′), 85.4 (C-4′), 107.8 (C-1′), 121.8 (C-6), 141.2 (C-5). [Found: MNa^+, *m/z* 541.3884. $C_{32}H_{54}O_5Na$ requires 541.3869].

3.3.2. Cholest-5-en-3β-ol 3-*O*-α-L-arabinofuranoside (1b). Mp 201–203°C (from acetone); $[\alpha]_D^{23}$=−99.1° (*c* 2.32, pyridine); δ_H 0.66 (3H, s, 18-H$_3$), 0.97 (3H, s, 19-H$_3$), 1.76 (1H, m, 2β-H), 1.92 (1H, br d, *J*=17.5 Hz, 7β-H), 2.16 (1H, m, 2α-H), 2.39 (1H, br t, *J*=13.0 Hz, 4β-H), 2.57 (1H, ddd, *J*=13.0, 5.0, 2.0 Hz, 4α-H), 3.80 (1H, m, 3α-H), 5.34 (1H, m, 6-H), 5.71 (1H, d, *J*=2.0 Hz, 1′-H) [0.95 (9α-H), 1.02 (1α-H), 1.38 (8β-H), 1.54 (7α-H), 1.39 (11β-H), 1.46

(11α-H), and 1.75 (1β-H) detected by HSQC spectrum]; δ_C 12.0 (C-18), 19.5 (C-19), 21.3 (C-11), 24.5 (C-15), 28.5 (C-16), 30.5 (C-2), 32.1 (C-8), 32.2 (C-7), 37.0 (C-10), 37.6 (C-1), 39.3 (C-4), 40.0 (C-12), 42.5 (C-13), 50.4 (C-9), 56.4 (C-17), 56.8 (C-14), 62.9 (C-5′), 77.0 (C-3), 78.7 (C-3′), 84.2 (C-2′), 85.3 (C-4′), 107.7 (C-1′), 121.9 (C-6), 141.0 (C-5). [Found: MNa^+, *m/z* 541.3870. $C_{32}H_{54}O_5Na$ requires 541.3869].

3.3.3. (−)-Menthol 3-*O*-α-D-arabinofuranoside (2a). Mp 113–114°C (from acetone); $[\alpha]_D^{23}=+43.7°$ (*c* 1.58, pyridine); δ_H 0.74 (1H, m, 6β-H), 0.76 (3H, d, *J*=7.0 Hz, 9-H_3), 0.79 (3H, d, *J*=7.0 Hz, 7-H_3), 0.81 (3H, d, *J*=7.0 Hz, 10-H_3), 0.88 (1H, dq, *J*=3.5, 12.5 Hz, 5α-H), 1.19 (1H, br q, *J*=11.5 Hz, 2β-H), 1.24 (1H, m, 1α-H), 1.32 (1H, ddt, *J*=12.0, 10.5, 3.0 Hz, 4β-H), 1.50 (1H, m, 5β-H), 1.50 (1H, m, 6α-H), 2.40 (1H, d sept, *J*=2.0, 7.0 Hz, 8-H), 2.50 (1H, m, 2α-H), 3.50 (1H, dt, *J*=4.5, 10.5 Hz, 3α-H), 5.58 (1H, d, *J*=2.0 Hz, 1′-H); δ_C 16.4 (C-9), 21.2 (C-10), 22.4 (C-7), 23.6 (C-5), 25.7 (C-8), 31.8 (C-1), 34.6 (C-6), 44.0 (C-2), 49.1 (C-4), 62.8 (C-5′), 78.5 (C-3′), 79.6 (C-3), 83.9 (C-2′), 85.4 (C-4′), 111.0 (C-1′). [Found: MH^+, *m/z* 289.1995. $C_{15}H_{29}O_5$ requires 289.2015].

3.3.4. (−)-Menthol 3-*O*-α-L-arabinofuranoside (2b). Mp 135–137°C (from acetone); $[\alpha]_D^{23}=-162°$ (*c* 1.58, pyridine); δ_H 0.74 (1H, m, 6β-H), 0.79 (3H, d, *J*=7.0 Hz, 7-H_3), 0.84 (1H, br q, *J*=11.5 Hz, 2β-H), 0.86 (3H, d, *J*=7.0 Hz, 10-H_3), 0.91 (1H, m, 5α-H), 0.95 (3H, d, *J*=7.0 Hz, 9-H_3), 1.17 (1H, m, 1α-H), 1.32 (1H, ddt, *J*=12.5, 10.5, 2.5 Hz, 4β-H), 1.51 (2H, br d, *J*=11.0 Hz, 5β, 6α-H), 2.14 (1H, m, br d, *J*=12.0 Hz, 2α-H), 2.59 (1H, d sept, *J*=2.0, 7.0 Hz, 8-H), 3.69 (1H, dt, *J*=2.0, 7.0 Hz, 3α-H), 5.65 (1H, d, *J*=2.0 Hz, 1′-H); δ_C 15.9 (C-9), 21.2 (C-10), 22.4 (C-7), 23.4 (C-5), 25.6 (C-8), 31.5 (C-1), 34.8 (C-6), 40.2 (C-2), 48.4 (C-4), 62.7 (C-5′), 74.5 (C-3), 79.0 (C-3′), 84.5 (C-2′), 85.4 (C-4′), 105.5 (C-1′). [Found: MH^+, *m/z* 289.2018. $C_{15}H_{29}O_5$ requires 289.2015].

3.3.5. 4,4-Dimethylcholest-5-en-3β-ol 3-*O*-α-D-arabinofuranoside (3a). Mp 183–188°C (from acetone); $[\alpha]_D^{23}=+5.6°$ (*c* 2.28, pyridine); δ_H 0.67 (3H, s, 18-H_3), 1.12 (3H, s, 19-H_3), 1.30 (3H, s, 4β-Me), 1.45 (3H, s, 4α-Me), 1.95 (1H, dq, *J*=13.5, 3.5 Hz, 2α-H), 2.08 (1H, dt, *J*=18.5, 5.0 Hz, 7β-H), 3.59 (1H, dd, *J*=12.0, 5.5 Hz, 3α-H), 5.67 (1H, d, *J*=1.0 Hz, 1′-H), 5.64 (1H, br dd, *J*=4.0, 3.0 Hz, 6-H) [0.90 (9α-H), 0.96 (1α-H), 1.48 (8β-H), 1.67 (1β-H), 1.66 (7α-H) and 1.73 (2β-H) detected by HSQC spectrum]; δ_C 12.1 (C-18), 20.9 (C-11), 21.6 (C-19), 22.7 (C-2), 24.4 (C-15), 25.3 (4β-Me), 27.8 (4α-Me), 28.6 (C-16), 31.2 (C-8), 32.9 (C-7), 36.8 (C-1), 37.0 (C-10), 40.1 (C-12), 41.4 (C-4), 42.5 (C-13), 51.2 (C-9), 56.3 (C-17), 57.5 (C-14), 63.0 (C-5′), 79.0 (C-3′), 80.3 (C-3), 84.2 (C-2′), 85.6 (C-4′), 106.1 (C-1′), 120.2 (C-6), 150.4 (C-5). [Found: MNa^+, *m/z* 569.4182. $C_{34}H_{58}O_5Na$ requires 569.4182].

3.3.6. 4,4-Dimethylcholest-5-en-3β-ol 3-*O*-α-L-arabinofuranoside (3b). Mp 225–230°C (from acetone); $[\alpha]_D^{23}=-97.1°$ (*c* 1.92, pyridine); δ_H 0.67 (3H, s, 18-H_3), 1.11 (3H, s, 19-H_3), 1.26 (3H, s, 4β-Me), 1.27 (3H, s, 4α-Me), 2.01 (1H, m, 2β-H), 2.06 (1H, dt, *J*=18.5, 5.5 Hz, 7β-H), 2.27 (1H, dq, *J*=13.5, 4.0 Hz, 2α-H), 3.34 (1H, dd, *J*=12.0, 4.0 Hz, 3α-H), 5.58 (1H, d, *J*=2.0 Hz, 1′-H), 5.58 (1H, dd, *J*=4.0, 3.0 Hz, 6-H) [0.90 (9α-H), 1.02 (1α-H), 1.48 (8β-H), 1.64 (1β-H) and 1.66 (7α-H) detected by HSQC spectrum]; δ_C 12.0 (C-18), 20.9 (C-11), 21.6 (C-19), 24.4 (C-15), 25.2 (4β-Me), 26.7 (C-2), 27.4 (4α-Me), 28.6 (C-16), 31.2 (C-8), 32.9 (C-7), 36.8 (C-10), 37.0 (C-1), 40.0 (C-12), 42.1 (C-4), 42.5 (C-13), 51.2 (C-9), 56.3 (C-17), 57.5 (C-14), 62.9 (C-5′), 78.7 (C-3′), 84.1 (C-2′), 86.0 (C-3), 85.2 (C-4′), 111.9 (C-1′), 120.2 (C-6), 150.4 (C-5). [Found: MNa^+, *m/z* 569.4160. $C_{34}H_{58}O_5Na$ requires 569.4182].

3.3.7. 2α-Methyl-4-nor-5α-cholestan-2β-ol 2-*O*-α-D-arabinofuranoside (4a). Colorless oil; $[\alpha]_D^{23}=+34.7°$ (*c* 1.85, pyridine); δ_H 0.64 (3H, s, 18-H_3), 0.69 (1H, dt, *J*=3.5, 11.2 Hz, 9α-H), 1.07 (3H, s, 19-H_3), 1.51 (3H, s, 2α-Me), 1.74 (1H, dd, *J*=13.0, 6.0 Hz, 3α-H), 2.10 (1H, d, *J*=13.0 Hz, 1β-H), 2.33 (1H, dd, *J*=12.5, 13.0 Hz, 3β-H), 5.69 (1H, d, *J*=2.4 Hz, 1′-H) [0.84 (7α-H), 1.16 (1α-H), 1.25 (11α-H), 1.28 (6β-H), 1.29 (5α-H), 1.28 (8β-H), 1.40 (11β-H), 1.47 (6α-H), 1.63 (7β-H) detected by HSQC spectrum]; δ_C 12.4 (C-18), 14.0 (C-19), 23.6 (C-11), 24.6 (C-15), 25.1 (C-6), 28.5 (C-16), 29.7 (2α-Me), 32.4 (C-7), 35.4 (C-8), 40.2 (C-12), 43.2 (C-13), 44.3 (C-10), 44.8 (C-3), 49.5 (C-5), 54.3 (C-1), 55.4 (C-9), 56.3 (C-14), 56.5 (C-17), 62.8 (C-5′), 78.0 (C-3′), 84.2 (C-2′), 84.6 (C-2), 84.8 (C-4′), 105.1 (C-1′). [Found: MNa^+, *m/z* 543.4036. $C_{32}H_{56}O_5Na$ requires 543.4025].

3.3.8. 2α-Methyl-4-nor-5α-cholestan-2β-ol 2-*O*-α-L-arabinofuranoside (4b). Colorless oil; $[\alpha]_D^{23}=-29.1°$ (*c* 1.46, pyridine); δ_H 0.64 (3H, s, 18-H_3), 0.68 (1H, dt, *J*=3.5, 11.2 Hz, 9α-H), 1.05 (3H, s, 19-H_3), 1.52 (3H, s, 2α-Me), 1.72 (1H, dd, *J*=12.5, 6.0 Hz, 3α-H), 2.06 (1H, dd, *J*=12.0, 12.5 Hz, 3β-H), 2.33 (1H, d, *J*=13.0 Hz, 1β-H), 5.68 (1H, d, *J*=2.4 Hz, 1′-H) [0.84 (7α-H), 1.16 (1α-H), 1.28 (6β-H), 1.27 (5α-H), 1.25 (11α-H), 1.28 (8β-H), 1.41 (11β-H), 1.47 (6α-H), 1.63 (7β-H) detected by HSQC spectrum]; δ_C 12.4 (C-18), 14.0 (C-19), 23.6 (C-11), 24.6 (C-15), 25.1 (C-6), 28.5 (C-16), 29.7 (2α-Me), 32.4 (C-7), 35.4 (C-8), 40.2 (C-12), 43.2 (C-13), 44.3 (C-10), 44.8 (C-3), 49.5 (C-5), 54.3 (C-1), 55.4 (C-9), 56.3 (C-14), 56.5 (C-17), 84.1 (C-2), 62.8 (C-5′), 78.0 (C-3′), 84.6 (C-2′), 84.8 (C-4′), 105.1 (C-1′). [Found: MNa^+, *m/z* 543.4025. $C_{32}H_{56}O_5Na$ requires 543.4025].

3.3.9. 5α-Cholestan-3β-ol 3-*O*-α-D-arabinofuranoside (5a). Mp 168–173°C (from acetone); $[\alpha]_D^{23}=+46.6°$ (*c* 2.37, pyridine); δ_H 0.54 (1H, dt, *J*=3.5, 11.2 Hz, 9α-H), 0.64 (3H, s, 18-H_3), 0.73 (3H, s, 19-H_3), 3.80 (1H, m, 3α-H), 5.51 (1H, d, *J*=2.0 Hz, 1′-H) [0.83 (1α-H), 0.85 (7α-H), 0.96 (5α-H), 1.14 (6-H_2), 1.20 (11β-H), 1.24 (8β-H), 1.43 (11α-H), 1.50 (2β-H), 1.54 (4β-H), 1.58 (7β-H), 1.61 (1β-H), 1.86 (4α-H), 1.97 (1H, br d, *J*=14.0 Hz, 2α-H) detected by HSQC spectrum]; δ_C 12.2 (C-18/19), 12.3 (C-19/18), 21.5 (C-11), 24.4 (C-15), 28.3 (C-2), 28.5 (C-16), 29.0 (C-6), 32.3 (C-7), 35.6 (C-8), 35.7 (C-10), 36.9 (C-4), 37.2 (C-1), 40.2 (C-12), 42.8 (C-13), 45.0 (C-5), 54.4 (C-9), 56.5 (C-14, C-17), 76.3 (C-3), 62.9 (C-5′), 78.7 (C-3′), 84.1 (C-2′), 85.4 (C-4′), 107.8 (C-1′). [Found: MNa^+, *m/z* 543.4006. $C_{32}H_{56}O_5Na$ requires 543.4025].

3.3.10. 5α-Cholestan-3β-ol 3-*O*-α-L-arabinofuranoside (5b). Mp 188–194°C (from acetone); $[\alpha]_D^{23}=-40.7°$ (*c* 2.42, 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), 2.08 (1H, br d, J=14.0 Hz, 2α-H), 3.82 (1H, m, 3α-H), 5.71 (1H, br s, 1′-H) [0.85 (7α-H), 0.86 (1α-H), 1.14 (6-H_2), 0.92 (5α-H), 1.20 (11β-H), 1.24 (8β-H), 1.30 (4β-H), 1.43 (11α-H), 1.59 (7β-H), 1.60 (1β-H), 1.65 (2β-H), 1.70 (4α-H), detected by HSQC spectrum]; δ_C 12.2 (C-18/19), 12.3 (C-19/18), 21.4 (C-11), 24.4 (C-15), 28.5 (C-16), 30.2 (C-2), 29.1 (C-6), 32.3 (C-7), 35.6 (C-8), 35.8 (C-10), 34.7 (C-4), 37.3 (C-1), 40.2 (C-12), 42.8 (C-13), 44.8 (C-5), 54.5 (C-9), 56.5 (C-14, 17), 76.1 (C-3), 62.9 (C-5′), 78.7 (C-3′), 84.2 (C-2′), 85.2 (C-4′), 107.2 (C-1′). [Found: MNa^+, m/z 543.4050. $C_{32}H_{56}O_5Na$ requires 5543.4025].

3.3.11. 5α-Cholestan-3α-ol 3-*O*-α-D-arabinofuranoside (6a). Mp 168–169°C (from acetone); $[\alpha]_D^{23}$=+58.8° (*c* 2.17, pyridine); δ_H 0.65 (3H, s, 18-H_3), 0.76 (3H, s, 19-H_3), 1.70 (1H, m, 5α-H), 2.07 (1H, br d, J=13.0 Hz, 2α-H), 4.13 (1H, br s, 3β-H), 5.62 (1H, d, J=2.0 Hz, 1′-H) [0.63 (9α-H), 0.79 (7α-H), 1.07 (12α-H), 1.14 (6-H_2), 1.21 (11β-H), 1.27 (8β-H), 1.34 (4β-H), 1.45 (1β-H), 1.48 (11α-H), 1.53 (1α-H), 1.57 (7β-H), 1.62 (2β-H) and 1.65 (4α-H) detected by HSQC spectrum]; δ_C 11.6 (C-19), 12.3 (C-18), 21.1 (C-11), 24.4 (C-15), 28.2 (C-2), 28.6 (C-16), 28.9 (C-6), 32.3 (C-7), 33.0 (C-4), 33.3 (C-1), 35.6 (C-8), 36.2 (C-10), 39.8 (C-5), 40.3 (C-12), 42.8 (C-13), 54.4 (C-9), 56.7 (C-14, 17), 62.9 (C-5′), 72.4 (C-3), 78.7 (C-3′), 84.2 (C-2′), 85.3 (C-4′), 108.1 (C-1′). [Found: MNa^+, m/z 543.4025. $C_{32}H_{56}O_5Na$ requires 573.4025].

3.3.12. 5α-Cholestan-3α-ol 3-*O*-α-L-arabinofuranoside (6b). Mp 179–181°C (from acetone); $[\alpha]_D^{23}$=−6.8° (*c* 2.28, pyridine); δ_H 0.65 (3H, s, 18-H_3), 0.76 (3H, s, 19-H_3), 1.89 (1H, br d, J=14.0 Hz, 2α-H), 4.15 (1H, br s, 3β-H), 5.61 (1H, d, J=2.0 Hz, 1′-H) [0.61 (9α-H), 0.84 (7α-H), 1.14 (6β-H), 1.19 (11β-H), 1.21 (6α-H), 1.26 (8β-H), 1.35 (1-H_2), 1.42 (11α-H), 1.43 (2β-H), 1.48 (4β-H), 1.56 (7β-H), 1.78 (4α-H) and 1.80 (5α-H) detected by HSQC spectrum]; δ_C 11.6 (C-19), 12.3 (C-18), 21.0 (C-11), 24.4 (C-15), 25.4 (C-2), 28.6 (C-16), 28.9 (C-6), 32.3 (C-7), 32.9 (C-1), 35.1 (C-4), 35.6 (C-8), 36.1 (C-10), 40.0 (C-5), 40.3 (C-12), 42.8 (C-13), 54.3 (C-9), 56.6 (C-14, 17), 62.8 (C-5′), 71.7 (C-3), 78.7 (C-3′), 84.3 (C-2′), 85.2 (C-4′), 107.4 (C-1′). [Found: MNa^+, m/z 543.4008. $C_{32}H_{56}O_5Na$ requires 543.4025].

3.3.13. (1*S*)-*endo*]-(−)-Borneol 2-*O*-α-D-arabinofuranoside (7a). Mp 150–152°C (from acetone); $[\alpha]_D^{23}$=+75° (*c* 1.68, pyridine); δ_H 0.76 (3H, s, 9-H_3), 0.77 (3H, s, 8-H_3), 0.87 (10-H_3), 1.19 (1H, m, 6-*exo*), 1.25 (1H, m, 5-*endo*), 1.45 (1H, dd, J=13.5, 3.5 Hz, 3-*endo*), 1.53 (1H, br t, J=4.5 Hz, 4-H), 1.63 (1H, m, 5-*exo*), 2.25 (1H, m, 6-*endo*), 2.32 (1H, m, 3-*exo*), 4.02 (1H, ddd, J=10.0, 3.0, 2.0 Hz, 2-*exo*), 5.53 (1H, d, J=2.0 Hz, 1′-H); δ_C 14.0 (C-10), 18.8 (C-8), 19.8 (C-9), 27.1 (C-6), 28.6 (C-5), 38.3 (C-3), 45.3 (C-4), 47.5 (C-7), 49.6 (C-1), 62.7 (C-5′), 78.7 (C-3′), 83.9 (C-2′), 84.2 (C-2), 85.1 (C-4′), 111.0 (C-1′). [Found: MH^+, m/z 287.1849. $C_{15}H_{27}O_5$ requires 287.1858].

3.3.14. (1*S*)-*endo*]-(−)-Borneol 2-*O*-α-L-arabinofuranoside (7b). Mp 188–194°C (from acetone); $[\alpha]_D^{23}$=−140° (*c* 1.62, pyridine); δ_H 0.75 (3H, s, 8-H_3), 0.78 (9-H_3), 0.98 (10-H_3), 1.12 (1H, dd, J=13.0, 3.5 Hz, 3-*endo*), 1.19 (1H, m, 5-*endo*), 1.22 (1H, m, 6-*exo*), 1.55 (1H, t, J=4.5 Hz, 4-H), 1.65 (1H, m, 5-*exo*), 2.12 (1H, m, 3-*exo*), 2.26 (1H, m, 6-*endo*), 4.26 (1H, dt, J=8.5, 2.5 Hz, 2-*exo*), 5.51 (1H, s, 1′-H); δ_C 13.9 (C-10), 18.9 (C-8), 19.8 (C-9), 27.1 (C-6), 28.5 (C-5), 35.9 (C-3), 45.3 (C-4), 47.8 (C-7), 49.1 (C-1), 62.7 (C-5′), 78.7 (C-3′), 80.5 (C-2), 84.1 (C-2′), 85.2 (C-4′), 107.7 (C-1′). [Found: MH^+, m/z 287.1884. $C_{15}H_{27}O_5$ requires 287.1858].

3.3.15. Cholestan-5α,6β-diol 6-*O*-α-D-arabinofuranoside (8a). Mp 169–172°C; $[\alpha]_D^{23}$=+37.6° (*c* 1.32, pyridine); δ_H 0.69 (3H, s, 18-H_3), 1.34 (3H, s, 19-H_3), 2.16 (1H, td, J=12.5, 3.0 Hz, 7α-H), 2.28 (1H, dt, J=12.5, 2.5 Hz, 7β-H), 2.44 (1H, td, J=12.5, 4.0 Hz, 4β-H), 3.87 (1H, br t, J=2.5 Hz, 6α-H), 5.56 (1H, br s, 1′-H) [1.98 (1α-H), 1.40 (1β-H), 1.48 (2α-H), 1.37 (2β-H), 2.12 (3α-H), 1.52 (3β-H), 1.42 (4α-H), 2.05 (8β-H), 1.87 (9α-H), 1.56 (11-H_2) detected by HSQC spectrum]; δ_C 12.3 (C-18), 16.8 (C-19), 21.1 (C-2/3), 21.2 (C-3/2), 21.7 (C-11), 24.6 (C-15), 28.6 (C-16), 31.5 (C-8), 32.2 (C-4), 33.6 (C-1), 34.0 (C-7), 39.5 (C-10), 40.6 (C-12), 42.9 (C-13), 45.9 (C-9), 56.5 (C-14/17), 56.6 (C-17/14), 73.5 (C-5), 85.0 (C-6), 62.6 (C-5′), 78.9 (C-3′), 84.3 (C-2′), 85.3 (C-4′), 111.7 (C-1′). [Found: MNa^+, m/z 559.3947. $C_{32}H_{56}O_6Na$ requires 559.3975].

3.3.16. Cholestan-5α,6β-diol 6-*O*-α-L-arabinofuranoside (8b). Colorless oil; $[\alpha]_D^{23}$=−74° (*c* 0.80, pyridine); δ_H 0.63 (3H, s, 18-H_3), 1.34 (3H, s, 19-H_3), 2.14 (1H, m, 3α-H), 2.63 (1H, td, J=13.5, 4.0 Hz, 4β-H), 4.16 (1H, br s, 6α-H), 5.61 (1H, br s, 1′-H) [2.00 (1α-H), 1.40 (1β-H), 1.50 (2α-H), 1.36 (2β-H), 1.55 (3β-H), 1.68 (4α-H), 1.95 (7-H_2), 1.86 (8β-H), 1.91 (9α-H), 1.58 (11-H_2) detected by HSQC spectrum]; δ_C 12.4 (C-18), 16.5 (C-19), 21.1 (C-2/3), 21.2 (C-3/2), 21.7 (C-11), 24.4 (C-15), 28.5 (C-16), 31.2 (C-8), 32.3 (C-4), 33.6 (C-1), 30.0 (C-7), 39.4 (C-10), 40.6 (C-12), 42.9 (C-13), 46.0 (C-9), 56.5 (C-14, C-17), 73.3 (C-5), 79.2 (C-6), 63.0 (C-5′), 79.5 (C-3′), 84.3 (C-2′), 85.7 (C-4′), 106.3 (C-1′). [Found: MNa^+, m/z 559.3989. $C_{32}H_{56}O_6Na$ requires 559.3975].

3.3.17. Cholestan-4β,5α-diol 4-*O*-α-D-arabinofuranoside (9a). Mp 215–216°C; $[\alpha]_D^{23}$=+124° (*c* 1.89, pyridine); δ_H 2.28 (1H, br tt, J=12.0, 4.0 Hz, 3α-H), 4.15 (1H, br s, 4α-H), 2.51 (1H, td, J=13.5, 4.5 Hz, 6β-H), 0.71 (3H, s, 18-H_3), 1.33 (3H, s, 19-H_3), 5.54 (1H, br s, 1′-H) [1.90 (1α-H), 1.38 (1β-H), 1.47 (2α-H), 1.88 (2β-H), 1.81 (3β-H), 1.67 (6α-H), 1.74 (7α-H), 1.46 (7β-H), 1.45 (8β-H), 1.93 (9α-H) detected by HSQC spectrum]; δ_C 12.4 (C-18), 15.8 (C-19), 17.8 (C-2), 20.7 (C-11), 24.1 (C-3), 24.4 (C-15), 26.5 (C-7), 28.6 (C-16), 32.0 (C-6), 32.3 (C-1), 35.2 (C-8), 39.4 (C-10), 40.6 (C-12), 43.0 (C-13), 46.8 (C-9), 56.6 (C-14/17), 56.7 (C-17/14), 73.3 (C-5), 79.4 (C-4), 63.0 (C-5′), 79.6 (C-3′), 84.6 (C-2′), 85.6 (C-4′), 106.5 (C-1′). [Found: MNa^+, m/z 559.3988. $C_{32}H_{56}O_6Na$ requires 559.3975].

3.3.18. Cholestan-4β,5α-diol 4-*O*-α-L-arabinofuranoside (9b). Mp 240–242°C (from acetone); $[\alpha]_D^{23}$=+3.2° (*c* 0.89, pyridine); δ_H 2.11 (1H, qt, J=12.5, 3.5 Hz, 2β-H), 2.52 (1H, tt, J=13.0, 4.0 Hz, 3α-H), 2.20 (1H, br d, J=13.0 Hz, 3β-H), 3.90 (1H, H, br s, 4α-H), 2.37 (1H, td, J=13.0, 4.5 Hz, 6β-H), 1.73 (1H, qd, J=12.5, 4.0 Hz, 7α-H), 0.69 (3H, s, 18-H_3), 1.32 (3H, s, 19-H_3), 5.57 (1H, d, J=2.0 Hz, 1′-H) [1.90 (1α-H), 1.38 (1β-H), 1.55 (2α-H), 1.43 (6α-H), 1.46

(7β-H), 1.42 (8β-H), 1.90 (9α-H), detected by HSQC spectrum]; δ_C 12.3 (C-18), 15.7 (C-19), 18.2 (C-2), 20.7 (C-11), 28.1 (C-3), 24.5 (C-15), 26.6 (C-7), 28.6 (C-16), 31.9 (C-6), 32.1 (C-1), 35.1 (C-8), 39.5 (C-10), 40.5 (C-12), 42.9 (C-13), 46.7 (C-9), 56.5 (C-14/17), 56.6 (C-17/14), 73.6 (C-5), 85.0 (C-4), 62.8 (C-5′), 78.8 (C-3′), 84.3 (C-2′), 85.3 (C-4′), 111.8 (C-1′). [Found: MNa^+, *m/z* 559.3960. $C_{32}H_{56}O_6Na$ requires 559.3975].

3.3.19. Androst-4-en-17β-ol-3-one 17-*O*-α-D-arabinofuranoside (10a). Mp 154–156°C (from acetone); $[\alpha]_D^{23}=+160°$ (*c* 2.31, pyridine); δ_H 0.88 (3H, s, 18-H_3), 0.98 (3H, s, 19-H_3), 1.06 (1H, dt, *J*=4.5, 13.0 Hz, 12α-H), 1.18 (1H, dq, *J*=6.0, 12.0 Hz, 15β-H), 2.00 (1H, m, 16α-H), 2.13 (1H, dt, *J*=13.0, 3.0 Hz, 12β-H), 3.80 (1H, t, *J*=8.5 Hz, 17α-H), 5.49 (1H, br s, 1′-H), 5.84 (1H, br s, 4-H) [0.69 (9α-H), 0.80 (14α-H), 0.80 (7α-H), 1.24 (11β-H), 1.34 (11α-H), 1.36 (8β-H), 1.45 (15α-H), 1.60 (7β-H) and 1.62 (16β-H) detected by HSQC spectrum]; δ_C 12.1 (C-18), 17.1 (C-19), 20.8 (C-11), 23.4 (C-15), 27.7 (C-16), 31.7 (C-7), 32.7 (C-6), 34.3 (C-2), 35.4 (C-8), 35.8 (C-1), 36.9 (C-12), 38.7 (C-10), 42.6 (C-13), 50.7 (C-14), 54.1 (C-9), 62.8 (C-5′), 78.8 (C-3′), 84.2 (C-2′), 85.9 (C-17), 85.3 (C-4′), 108.5 (C-1″), 123.7 (C-4), 170.6 (C-5), 198.3 (C-3). [Found: MH^+, *m/z* 421.2616. $C_{24}H_{37}O_6$ requires 421.2590].

3.3.20. Androst-4-en-17β-ol-3-one 17-*O*-α-L-arabinofuranoside (10b). Mp 164–166°C (from acetone); $[\alpha]_D^{23}=+15°$ (*c* 2.34, pyridine); δ_H 0.69 (1H, dt, *J*=4.5, 11.5 Hz, 9α-H), 0.87 (3H, s, 18-H_3), 0.97 (3H, s, 19-H_3), 1.06 (1H, dt, *J*=4.5, 12.5 Hz, 12α-H), 1.17 (1H, dq, *J*=6.0, 12.0 Hz, 15β-H), 1.24 (1H, dq, *J*=3.5, 12.5 Hz, 11β-H), 1.45 (1H, m, 15α-H), 1.82 (1H, m, 16β-H), 1.90 (1H, dt, *J*=12.5, 3.0 Hz, 12β-H), 2.15 (1H, m, 16α-H), 3.77 (1H, t, *J*=8.5 Hz, 17α-H), 5.59 (1H, d, *J*=2.0 Hz, 1′-H), 5.84 (1H, br s, 4-H) [0.80 (14α-H), 0.80 (7α-H), 1.34 (11α-H), 1.34 (8β-H), 1.59 (7β-H) detected by HSQC spectrum]; δ_C 12.0 (C-18), 17.1 (C-19), 20.8 (C-11), 23.5 (C-15), 29.6 (C-16), 31.7 (C-7), 32.6 (C-6), 34.2 (C-2), 35.3 (C-8), 35.8 (C-1), 37.5 (C-12), 38.6 (C-10), 43.0 (C-13), 50.5 (C-14), 54.0 (C-9), 62.8 (C-5′), 78.8 (C-3′), 84.1 (C-2′), 87.1 (C-17), 85.3 (C-4′), 109.9 (C-1′), 123.8 (C-4), 170.5 (C-5), 198.3 (C-3). [Found: MH^+, *m/z* 421.2600. $C_{24}H_{37}O_6$ requires 421.2590].

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