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Tannins and Related Compounds. L.¹⁾ Structures of Proanthocyanidin A-1 and Related Compounds

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The structures of proanthocyanidin A-1 (**2**) and two related proanthocyanidins, tentatively named A-4 (**3**) and A-5' (**4**), have been established unambiguously on the basis of spectroscopic evidence and chemical correlations with the structurally known proanthocyanidin A-2 (**1**). Chemical transformation of singly linked proanthocyanidin B-1 (**6**) into **2** also confirmed the stereostructure of **2**.

Keywords—proanthocyanidin A-1; A-type proanthocyanidin; chemical correlation; epimerization; enantiomer; diastereoisomer; polyphenol; flavan-3-ol; catechin

Proanthocyanidins, the oligomers and polymers of which have long been referred to as "condensed tannins or non-hydrolyzable tannins," fall into three distinct classes. One of these consists of flavan-3-ol units linked singly through carbon-carbon linkages at C(4)–C(8) or C(4)–C(6), and is readily convertible by heating with mineral acids into the common anthocyanidins, pelargonidin, cyanidin and delphinidin (the dimers and trimers of this class are designated as proanthocyanidin B-²⁾ and C-types,³⁾ respectively, and are the most commonly present in the vegetable tissues of plants). Another class possesses structures in which two flavan-3-ol units are joined doubly by ether and carbon-carbon linkages, and it is decomposed by acid treatment with the production of a mixture of uncharacterized flavylum salts (the dimers are designated as proanthocyanidin A-type).²⁾ The third class, related to the second in complex anthocyanidin formation, includes a series of compounds containing a substituent, such as a C₆–C₃ or a chalcane moiety, which is attached to the flavan-3-ol framework (*e.g.*, cinchonans,⁴⁾ kandelins⁵⁾ and gambiriins).⁶⁾

The chemistry and structures of the lower-molecular-weight proanthocyanidins of the first class, especially those of the dimers and trimers, have been almost entirely elucidated during the past few years.^{3,5,7–9)} In contrast, much of the chemistry of the second group of proanthocyanidins still remains unclarified, although proanthocyanidins of this type are found as relatively common constituents among plant polyphenolics.

The A-type proanthocyanidins (A-1, A-2 and A-3) were first isolated as methyl ethers by Weinges and his collaborators from *Vaccinium vitis-idaea* and *Aesculus hippocastanum*.²⁾ The structure **1** of proanthocyanidin A-2 was later deduced by Haslam and his co-workers based mainly on spectroscopic evidence,¹⁰⁾ and more recently, the structure was unequivocally established by X-ray crystallography.¹¹⁾ As for proanthocyanidins A-1 and A-3, there is no report on their structures except that the same structure **1** as that of A-2 was formerly proposed for A-1.¹²⁾

In the course of chemical examination of vegetable tannins, we have isolated proanthocyanidin A-1 (**2**) and two related proanthocyanidins (**3** and **4**) (tentatively named A-4

Chart 1

and A-5') from various plant sources, and chemical correlations between A-2 (**1**) and these compounds have now established their structures. Here, we wish to present unequivocal proof of the structures.

Proanthocyanidin A-1 (**2**) was isolated in a crystalline form from *Areca catechu*,⁷⁾ *Vaccinium vitis-idaea*, *Cinnamomum sieboldii* and *C. camphora*. The proton-nuclear magnetic resonance (¹H-NMR) spectrum of **2** resembled that of A-2 (**1**), but differed in flavan C-ring signals. The appearance of a doublet ($J=8$ Hz) at δ 4.73 due to C(2)-H suggested the presence of a flavan-3-ol moiety with 2,3-*trans* (catechin-type) stereochemistry. This was supported by the carbon-13 nuclear magnetic resonance (¹³C-NMR) chemical shift (δ 84.1) of C(2), which is consistent with that (δ 82.3) observed in catechin.³⁾ Methylation of **2** with diazomethane yielded the heptamethyl ether (**2a**). The ¹H-NMR spectrum of **2a** showed, together with six methoxyl signals at δ 3.6—3.9, one upfield methoxyl signal at δ 3.32 assignable to the C(5'')-methoxyl on the basis of nuclear Overhauser effect (NOE) measurements. This unusual upfield shift may be interpreted in terms of a through-space interaction of the lower flavan B-ring, thus suggesting that the two flavan units are linked through the C(4'')- and C(8)-positions. The chemical shift of the above-mentioned C(2)-H signal in **2** also supports the location of the interflavanoid linkage at C(4'')-C(8); a lower field shift of this signal than that of catechin (δ 4.57) implies the presence of steric interaction between C(2)-H and the upper flavan aromatic ring.⁷⁾ On the basis of these observations, A-1 was presumed to be formulated as **2**.

To determine the structure unequivocally, derivation of A-1 from A-2 (**1**) was attempted. Selective oxidation of one of two alcoholic hydroxyl groups in the heptamethyl ether (**1a**) was achieved by the modified Oppenauer method using potassium *tert*-butoxide and 9-fluorenone.¹³⁾ Other oxidation methods using chromium trioxide, dimethyl sulfoxide-acetic

TABLE I. ^{13}C -NMR Chemical Shifts of A, C-Ring Carbons in A-Type Proanthocyanidins

Carbon No.	1 ^{a)}	2 ^{a)}	3 ^{a)}	4 ^{a)}	1a ^{b)}	2a ^{b)}	3a ^{b)}	4a ^{b)}	5 ^{b)}	7 ^{b)}
2	81.1	84.1	83.6	80.6	78.3	80.8	81.4	78.1	83.6	83.1
3	65.7	66.9	67.9	66.6	65.5	67.1	68.7	66.6	205.2	205.9
4	28.5	28.6	— ^{d)}	— ^{d)}	28.7	29.1	28.4	28.1	33.0	34.3
2''	103.6	103.5	103.8	103.9	103.9	103.6	103.4	104.0	103.3	103.5 ^{c)}
3''	67.1	67.3	67.2	67.3	67.5	67.1	67.1	67.2	67.2	67.2
4''	28.7	29.5	— ^{d)}	— ^{d)}	27.7	27.4	27.4	27.6	27.6	27.6
4a	99.5	99.6	100.0	100.1	99.0	99.0	99.0	99.2	99.4	99.3
4a''	102.0	102.8	102.6	101.7	101.7	101.4	102.8	101.3	102.1	103.7 ^{c)}
6,8,6''	96.0 (2C)	96.0 (2C)	96.2	96.2	92.1	91.6	91.8	92.2	92.6	93.0
	97.7	97.6	96.5	96.4	93.2	92.5	92.3	92.7	93.2	93.4
			97.9	97.7	93.5	92.9	92.8	93.1	93.4	94.1
8''	106.3	106.2	106.3	106.5	106.7	105.8	106.0	106.5	107.3	108.2
5,7,9,	151.2 (2C)	150.8	150.5	150.9	151.2	152.4	150.8	151.0	151.2	151.3
5'',7'',9''	153.4	151.3	151.8	151.6	151.6	153.1	151.2	151.3	151.9	152.2
	155.6	153.5	153.9	154.0	152.9	154.9	152.8	153.1	153.3	152.9
	156.0	155.2	155.6	156.1	157.6	157.0	156.8	157.7	156.5	156.4
	157.2	155.8	156.4	156.6	159.0	158.2	158.3	158.7	158.5	158.6
		157.3	157.9	157.9	159.9	159.5	159.5	159.8	160.1	160.1

a) Measured in acetone- d_6 +D $_2$ O. b) Measured in CDCl $_3$. c) Assignments may be interchanged. d) Overlapped with solvent signals.

anhydride, dimethyl sulfoxide-dicyclohexylcarbodiimide and phosphorus pentoxide-dimethyl formamide, yielded a complex mixture of products. The structure of the mono-ketone (**5**) was confirmed by ^1H - and ^{13}C -NMR measurements, which clearly indicate the presence of a

carbonyl (δ 205.2), an isolated methine (δ 5.31, s) and a methylene (δ 3.32 and 3.59, each d, $J=16$ Hz). Subsequent reduction of **5** with sodium borohydride afforded two products in the ratio of *ca.* 1:3, found to be identical with **2a** and **1a**. Thus, the structure of A-1 was established unequivocally to be **2**.

It should be noted that **2** was obtainable from procyanidin B-1 (**6**), a singly linked proanthocyanidin, by oxidation with hydrogen peroxide in a weakly alkaline medium. This fact clearly indicates that the stereostructure including absolute configuration can be represented as **2**.

The new dimeric proanthocyanidin, A-4 (**3**), was obtained as colorless prisms from the seed shells of *Aesculus hippocastanum*. It formed a heptamethyl ether (**3a**) on methylation with diazomethane. The $^1\text{H-NMR}$ spectrum of **3** was almost indistinguishable from that of **2**, but comparison of the $^1\text{H-NMR}$ spectra of their methyl ethers **3a** and **2a** permitted the differentiation of these compounds. The chemical shifts for the methoxys and the lower C-ring protons in **3a** were different from those in **2a**. The unusual upfield shift (δ 3.12) of one methoxyl group, similar to that observed in **2a**, was consistent with the C(4'')-C(8) linkage of two flavan units. From these observations, **3** was assumed to be a diastereoisomer of **2**. The structure of **3** was further confirmed by successful epimerization of C(2) in **1** with weak alkali (potassium carbonate in acetone), providing **3** in a fairly good yield.

Another new proanthocyanidin, A-5' (**4**) was isolated from a commercial *Ephedra* plant (Japanese name: Maō). The $^1\text{H-NMR}$ spectrum was closely correlated with that of **1**, showing a similar broad singlet due to C(2)-H at δ 5.08. A characteristic upfield shift of one methoxyl signal was also observed at δ 3.14 in the $^1\text{H-NMR}$ spectrum of the heptamethyl ether (**4a**). Accordingly, **4** was considered to be an epimer of **1** with respect to the C(2)- and C(3)-

Chart 3

Fig. 1. CD Spectra of **3a**, **3a'**, **4a** and **4a'** (in MeOH)

—, **4a'**; ----, **3a**; - · - ·, **3a'**; - - - -, **4a**.

positions.

Further structural confirmation was obtained by similar synthetic methods. The methyl ether (**3a**) was subjected to the above-mentioned modified Oppenauer oxidation followed by sodium borohydride reduction to yield two products, of which one was identified as the starting material **3a**. Although the ^1H - and ^{13}C -NMR spectra of the other product were found to be identical with those of the heptamethyl ether (**4a**) of A-5', the specific optical rotation and the Cotton effects in the circular dichroism (CD) spectrum (Fig. 1) showed opposite signs, indicating that the synthetic sample is an enantiomer of **4a**. Based on these chemical and spectroscopic findings, the structure of A-5' was established to be **4**.

The enantiomers (**3'** and **1'**) of proanthocyanidins A-4 and A-2, though **1'** is slightly racemic, were also obtained from the *Ephedra* plant. It is interesting from the viewpoint of plant physiology that only the plant belonging to Gymnospermae characteristically produces such enantiomorphous compounds in the secondary metabolism.

Experimental

Melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-4 digital polarimeter (cell length: 0.5 dm). Field-desorption (FD-) and electron-impact (EI-) mass spectra (MS) were recorded with JEOL D-300 and JEOL DX-300 spectrometers. ^1H (100 MHz)- and ^{13}C (25.05 MHz)-NMR spectra were taken with JEOL PS-100 and JEOL FX-100 spectrometers, respectively, with tetramethylsilane as an internal standard; chemical shifts are given on a δ (ppm) scale. CD data were obtained in methanol with a JASCO J-20 spectropolarimeter. Column chromatography was carried out with Sephadex LH-20 (25–100 μ , Pharmacia Fine Chemical Co., Ltd.), Bondapak/C₁₈ Porasil b (37–75 μ , Waters Associates, Inc.) and Kieselgel 60 (70–230 mesh, Merck). Thin-layer chromatography (TLC) was performed on precoated Kieselgel 60 F₂₅₄ plates (0.20 mm, Merck) with benzene–ethyl formate–formic acid (2:7:1) (for phenolics) and benzene–acetone (4:1) (for methyl ethers), and the spots were detected by observing their fluorescence under ultraviolet (UV) light and by the use of 10% sulfuric acid and ferric chloride reagent sprays.

Proanthocyanidin A-1 (2)—This compound was isolated from the seeds of *Areca catechu*,⁷⁾ the leaves of *Vaccinium vitis-idaea*, the root bark of *Cinnamomum sieboldii* and the bark of *Cinnamomum camphora*,¹⁴⁾ and its identity with authentic A-1 was confirmed by comparison of the physical data and the ^1H -NMR spectrum of its heptamethyl diacetyl derivative with those reported in the literature.²⁾ Colorless needles (H₂O), mp > 300 °C, $[\alpha]_D^{26} + 62.9^\circ$ ($c = 1.4$, acetone). ^1H -NMR (acetone- d_6): 2.58 (1H, dd, $J = 8$, 16 Hz, 4-H), 3.04 (1H, dd, $J = 6$, 16 Hz, 4'-H), 4.15 (1H, d, $J = 4$ Hz, 3''-H), 4.22 (1H, d, $J = 4$ Hz, 4''-H), 4.30 (1H, m, 3-H), 4.73 (1H, d, $J = 8$ Hz, 2-H), 5.97 (1H, d, $J = 2$ Hz, 6''-H), 6.09 (1H, d, $J = 2$ Hz, 8''-H), 6.15 (1H, s, 6-H), 6.7–7.3 (6H in total, B, B'-ring H).

Methylation of 2—**2** (100 mg) was methylated overnight with ethereal diazomethane. Work-up was done as usual, and the product was purified by silica gel chromatography with benzene–acetone (17:3) to yield the heptamethyl ether (**2a**) (60 mg). A white amorphous powder, $[\alpha]_D^{21} + 12.5^\circ$ ($c = 1.2$, acetone). ^1H -NMR (CDCl₃): 2.64–2.76 (2H, m, 4-H), 3.32, 3.62, 3.72, 3.74, 3.86, 3.89, 3.90 (OMe), 4.22 (1H, m, 3-H), 4.87 (1H, d, $J = 4$ Hz, 4''-H), 4.98 (1H, d, $J = 6$ Hz, 2-H), 6.03 (1H, d, $J = 2$ Hz, 6''-H), 6.20 (1H, s, 6-H), 6.29 (1H, d, $J = 2$ Hz, 8''-H), 6.7–7.3 (6H in total, B, B'-ring H).

Methylation of 1—Proanthocyanidin A-2 (**1**), colorless needles (H₂O), mp > 300 °C, $[\alpha]_D^{19} + 51.2^\circ$ ($c = 1.1$, acetone), isolated from the seed shells of *Aesculus hippocastanum*, was methylated with ethereal diazomethane. Work-up as described above yielded the heptamethyl ether (**1a**). Colorless needles (*n*-hexane–ethyl acetate), mp 212 °C, $[\alpha]_D^{21} + 31.2^\circ$ ($c = 1.1$, acetone). ^1H -NMR (CDCl₃): 2.70 (1H, dd, $J = 4$, 16 Hz, 4-H), 2.95 (1H, dd, $J = 5$, 16 Hz, 4'-H), 3.45, 3.72 ($\times 2$), 3.80, 3.98 ($\times 2$), 3.99 (OMe), 4.22 (1H, d, $J = 4$ Hz, 3''-H), 4.44 (1H, m, 3-H), 4.92 (1H, d, $J = 4$ Hz, 4''-H), 4.99 (1H, s, 2-H), 6.05 (1H, d, $J = 2$ Hz, 6''-H), 6.20 (1H, s, 6-H), 6.29 (1H, d, $J = 2$ Hz, 8''-H), 6.88–7.36 (6H in total, B, B'-ring H).

Oxidation of 1a—A mixture of **1a** (300 mg), 9-fluorenone (1.0 g) and potassium *tert*-butoxide (160 mg) in dry benzene (40 ml) was heated under reflux for 9 h. The reaction mixture was neutralized with 1 N hydrochloric acid, and the benzene layer was washed with water, dried over sodium sulfate and concentrated under reduced pressure. The residue was chromatographed over silica gel with benzene–acetone (7:1) to give the mono-ketone (**5**) (150 mg). A white amorphous powder, $[\alpha]_D^{21} - 12.5^\circ$ ($c = 1.1$, acetone). *Anal.* Calcd for C₃₇H₃₆O₁₂: C, 66.06; H, 5.39. Found: C, 66.00; H, 5.60. EI-MS m/z : 672 (M^+). ^1H -NMR (CDCl₃): 3.32 (1H, d, $J = 16$ Hz, 4-H), 3.59 (1H, d, $J = 16$ Hz, 4'-H), 3.29, 3.60, 3.73 ($\times 2$), 3.83, 3.88, 3.90 (OMe), 4.25 (1H, t-like, $J = 4$ Hz, 3''-H, on addition of D₂O, this signal changed into a doublet, $J = 4$ Hz), 4.91 (1H, d, $J = 4$ Hz, 4''-H), 5.31 (1H, s, 2-H), 5.96 (1H, d, $J = 2$ Hz, 6''-H), 6.30 (2H, br s, 8''- and 6-H), 6.7–7.4 (6H in total, B, B'-ring H).

Reduction of 5—A solution of **5** (100 mg) in methanol was treated with sodium borohydride (20 mg) at room

temperature for 5 min. The reaction mixture was neutralized with Amberlite IR-120B (H^+ form), and concentrated to dryness under reduced pressure. The residue was subjected to silica gel chromatography with benzene-acetone (17:3) to furnish the A-1 heptamethyl ether (**2a**) (15 mg) and the A-2 methyl ether (**1a**) (48 mg).

Oxidation of 6—A mixture of **6** (200 mg), sodium bicarbonate (50 mg) and hydrogen peroxide (0.5 ml) in ethanol (20 ml) was left at room temperature for 13 h. The reaction mixture was neutralized with Amberlite IR-120B (H^+ form), and the solvent was evaporated off under reduced pressure. The residue was chromatographed over Sephadex LH-20 with 80% aqueous methanol to give A-1 (**1**) (25 mg).

Proanthocyanidin A-4 (3)—This compound was isolated from the seed shells of *Aesculus hippocastanum*.¹⁴⁾ Colorless needles (H_2O), mp $>300^\circ C$, $[\alpha]_D^{21} +63.2^\circ$ ($c=1.1$, acetone). *Anal.* Calcd for $C_{30}H_{24}O_{12} \cdot 5/2H_2O$: C, 57.97; H, 4.70. Found: C, 57.78; H, 4.34. FD-MS m/z : 576 (M^+). 1H -NMR (acetone- $d_6 + D_2O$): 2.58 (1H, dd, $J=8$, 16 Hz, 4-H), 3.01 (1H, dd, $J=6$, 16 Hz, 4-H), 4.10 (1H, m, 3''-H), 4.24 (2H, br s, 3- and 4''-H), 4.77 (1H, d, $J=8$ Hz, 2-H), 5.95 (1H, d, $J=2$ Hz, 6''-H), 6.10 (1H, d, $J=2$ Hz, 8''-H), 6.16 (1H, s, 6-H), 6.76—7.24 (6H in total, B,B'-ring H).

Methylation of 3—**3** (300 mg) was methylated with ethereal diazomethane. Work-up as before yielded the heptamethyl ether (**3a**) (220 mg). Colorless needles (EtOH), mp $173\text{--}174^\circ C$, $[\alpha]_D^{22} +80.2^\circ$ ($c=1.1$, acetone). *Anal.* Calcd for $C_{37}H_{38}O_{12} \cdot 1/2H_2O$: C, 65.00; H, 5.75. Found: C, 65.16; H, 6.04. EI-MS m/z : 674 (M^+). 1H -NMR ($CDCl_3$): 2.53 (1H, dd, $J=9$, 16 Hz, 4-H), 3.12 (1H, dd, $J=6$, 16 Hz, 4-H), 3.12, 3.72, 3.74, 3.91 ($\times 4$) (OMe), 4.28 (1H, t-like, $J=4$ Hz, 3''-H, on addition of D_2O , this signal changed into a doublet, $J=4$ Hz), 4.54 (1H, d, $J=8$ Hz, 2-H), 4.87 (1H, d, $J=4$ Hz, 4''-H), 5.99 (1H, d, $J=2$ Hz, 6''-H), 6.19 (1H, s, 6-H), 6.26 (1H, d, $J=2$ Hz, 8''-H), 6.84—7.40 (6H in total, B,B'-ring H).

Epimerization of 1—A mixture of **1** (600 mg) and potassium carbonate (150 mg) in acetone (30 ml) was heated under reflux for 10 min. After removal of potassium carbonate by filtration, the filtrate was concentrated to dryness under reduced pressure. The residue was subjected to Bondapak/ C_{18} Porasil B chromatography to afford A-4 (**3**) (450 mg).

Proanthocyanidin A-5' (4)—This compound was isolated from a commercial *Ephedra* plant (Maō). Colorless fine needles (H_2O), mp $>300^\circ C$, $[\alpha]_D^{26} -111.0^\circ$ ($c=1.6$, MeOH). *Anal.* Calcd for $C_{30}H_{24}O_{12} \cdot 2H_2O$: C, 58.82; H, 4.61. Found: C, 59.13; H, 4.88. FD-MS m/z : 576 (M^+). 1H -NMR (acetone- $d_6 + D_2O$): 2.88 (2H, br s, $J=3$ Hz, 4-H), 4.24 (1H, d, $J=4$ Hz, 3''-H), 4.28 (1H, br s, 3-H), 4.36 (1H, d, $J=4$ Hz, 4''-H), 5.08 (1H, s, 2-H), 5.90 (1H, d, $J=2$ Hz, 6''-H), 6.07 (1H, d, $J=2$ Hz, 8''-H), 6.14 (1H, s, 6-H), 6.7—7.3 (6H in total, B,B'-ring H).

Methylation of 4—**4** was methylated in the same way as described above to give the heptamethyl ether (**4a**). Colorless needles (MeOH), mp $151\text{--}153^\circ C$, $[\alpha]_D^{26} -12.3^\circ$ ($c=1.3$, acetone). *Anal.* Calcd for $C_{37}H_{38}O_{12} \cdot 1/2H_2O$: C, 65.00; H, 5.75. Found: C, 64.74; H, 5.67. EI-MS m/z : 674 (M^+), 494, 465, 342 (base peak). 1H -NMR ($CDCl_3 + D_2O$): 2.92 (2H, br s, 4-H), 3.14, 3.72 ($\times 2$), 3.92 ($\times 4$) (OMe), 4.24 (1H, m, 3-H), 4.32 (1H, d, $J=4$ Hz, 3''-H), 4.94 (1H, s, 2-H), 4.99 (1H, d, $J=4$ Hz, 4''-H), 5.99 (1H, d, $J=2$ Hz, 6''-H), 6.20 (1H, s, 6-H), 6.27 (1H, d, $J=2$ Hz, 8''-H), 6.8—7.4 (6H in total, B, B'-ring H).

Oxidation of 3a—A mixture of **3a** (200 mg), 9-fluorenone (700 mg) and potassium *tert*-butoxide (400 mg) in dry benzene (30 ml) was heated under reflux for 9 h. The reaction mixture was worked-up as above to yield the mono-ketone (**7**) (105 mg). A white amorphous powder, $[\alpha]_D^{22} +11.2^\circ$ ($c=1.2$, acetone). *Anal.* Calcd for $C_{37}H_{36}O_{12}$: C, 66.06; H, 5.39. Found: C, 66.35; H, 5.00. EI-MS m/z : 672 (M^+). 1H -NMR ($CDCl_3$): 3.34 (1H, d, $J=16$ Hz, 4-H), 3.71 (1H, d, $J=16$ Hz, 4-H), 3.37, 3.75 ($\times 2$), 3.89, 3.92 ($\times 2$), 3.93 (OMe), 4.28 (1H, dd, $J=4$, 6 Hz, 3''-H, on addition of D_2O , this signal changed into a doublet, $J=4$ Hz), 5.00 (1H, d, $J=4$ Hz, 4''-H), 5.12 (1H, s, 2-H), 6.07 (1H, d, $J=2$ Hz, 6''-H), 6.30 (1H, d, $J=2$ Hz, 8''-H), 6.32 (1H, s, 6-H), 6.86—7.40 (6H in total, B,B'-ring H).

Reduction of 7—A solution of **7** (100 mg) in methanol was treated with sodium borohydride (20 mg) at room temperature for 10 min. Work-up as described above yielded the enantiomer (**4a'**) (14 mg) of **4a** and the A-4 heptamethyl ether (**3a**) (24 mg). **4a'**: Colorless needles (EtOH), mp $151\text{--}152^\circ C$, $[\alpha]_D^{21} +10.5^\circ$ ($c=1.1$, acetone). *Anal.* Calcd for $C_{37}H_{38}O_{12} \cdot 1/2H_2O$: C, 65.00; H, 5.75. Found: C, 65.16; H, 5.62. EI-MS m/z : 674 (M^+). The 1H - and ^{13}C -NMR spectra of **4a'** were identical with those of **4a**.

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