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Note

Non-conventional epimerisation and functionalisation of quinic acid and shikimic acid methyl esters†

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Abstract

In a convenient one-pot acetalation procedure using chloral/DCC, methyl (-)-quinate and methyl (-)-shikimate were converted into their 4-*epi*-derivatives containing a carbamoyl function in 3-position and the trichloroethylidene acetal group in 4,5-position. Additionally, an spiro-byproduct, *1*R, *3*R, *4*R, *5*R)-*3′*-N-*cyclohexyl-3*-O-(*cyclohexylcarbomyl*)-*4,5*-O-(*2,2,2-trichloroethylidene) spiro[[cyclohexane-3,4,5-triol-1,5′-[1,3]oxazolidine]]-2′,4′-dione*, was formed from methyl (-)-quinate in 10% yield. Decarbamoylation of the compounds is possible by heating in methanolic sodium methoxide.

Keywords: Cyclitols; Methyl quinate; Methyl shikimate; Epimerisation; Chloral acetals

Recently, we reported a convenient one-pot method for acetalation of sugars which is a selective non-classical '*Domino* Reaction' [2]. Thus, pyranosides having a *cis*, *trans* sequence of three contiguous hydroxyl groups react with electron-deficient aldehydes or ketones (chloral [3], perfluoroalkanals [1,4], hexafluoroacetone [5]) in the presence of dicyclohexylcarbodiimide (DCC) to give cyclic acetals. These acetalation reactions are accompanied by inversion of configuration at the middle chiral carbon atom of the triol unit and, moreover, a carbamoyl function is simultaneously introduced next to the acetal moiety. The mechanism of this reaction has been elaborated [1,3c].

(−)-Quinic acid is commercially available and its abundance in the chiral pool has made it an attractive starting material for asymmetric multistep syntheses of naturally occurring substances and related compounds [6]; shikimic acid can be used as a chiral template in a similar manner. We report in this paper about '*Domino* Reactions' with methyl (−)-quinate (**1**) and methyl (−)-shikimate (**6**).

In order to prevent reactions of the carboxylic acid function with the co-agent DCC (see e.g. ref. [7]), the (−)-quinic acid and the (−)-shikimic acid were esterified with methanol to form **1** and **6**, respectively, using the convenient procedure reported for the methyl shikimate with the acidic ion exchange resin Amberlite IR-120 as catalyst [8]. The physical data of the methyl quinate (**1**) prepared in this way correspond to the published data

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[1] Epimerisation of carbohydrates and cyclitols, Part 14. For Part 13 see ref. [1].

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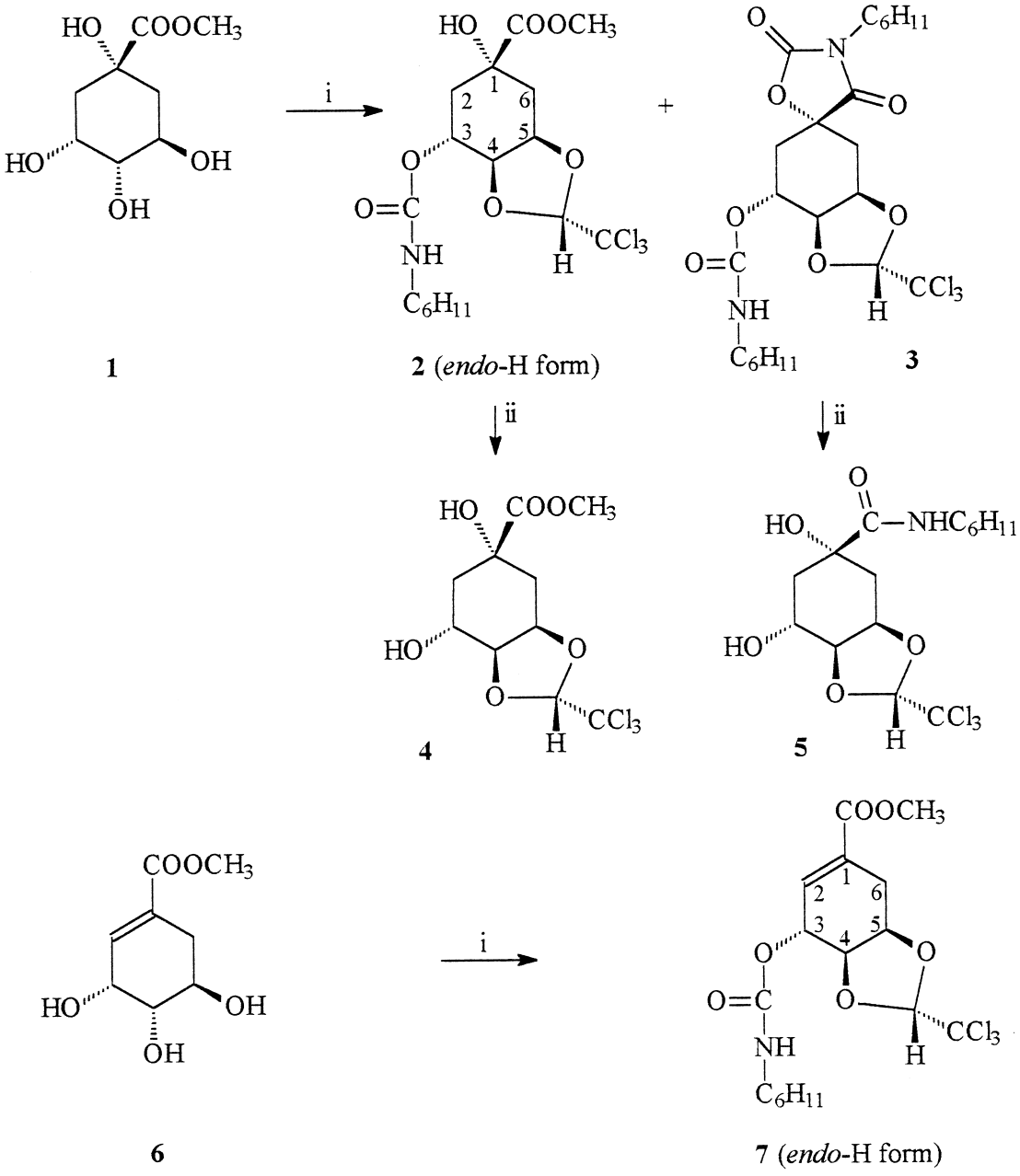

Scheme 1.

[9–11]. Methyl quinate (**1**) and methyl shikimate (**6**) were acetalated by heating with chloral/DCC in 1,2-dichloroethane generating the 4-*epi*-derivatives **2** and **7**, respectively (Scheme 1). Compounds **2** and **7** were isolated in yields of 54–55% after column chromatography. However, the cyclic acetals **2** and **7** are mixtures of the corresponding *endo*-H/*exo*-H diastereomers. The *endo*-H isomer predominated over the *exo*-H diastereomer 16:1 and 3:1, respectively. In the case of **2**, the pure *endo*-H form was obtained by recrystallisation of the diastereomeric mixture from ethyl acetate.

In spite of esterification of the (−)-quinic acid, the OH-function and the ester group at C-1 of methyl quinate (**1**) reacted under the acetalation conditions in parts with DCC generating the spiro-compound

3, (Scheme 1). This byproduct was isolated in a yield of 10% from the first eluate during the chromatographic purification of **2**. It is suggested that addition of the acidic OH-group of **2** to DCC occurs, followed by an intramolecular amidation with elimination of methanol. Hydrolysis of the exocyclic *N*-cyclohexylimido group with loss of cyclohexylamine gives compound **3** during the work-up procedure. For a similar product obtained from a steroid-based α-hydroxy carboxylic acid and DCC, see ref. [7].

A convenient procedure of decarbamoylation was reported for various carbohydrate derivatives [3a,3b,12] which involved heating the compounds in methanolic sodium methoxide. The decarbamoylation of the 4-*epi*-quinate **2** in this way is shown in Scheme 1 generating the hydroxy derivative **4**. Furthermore, the byproduct **3** was heated in methanolic sodium methoxide. Both decarbamoylation and opening of the oxazolidine moiety was observed in this case generating the crystalline amide **5** in a yield of 90% (Scheme 1). The X-ray analysis of **5** shows a $^1C_4$ conformation of the compound with an equatorial arrangement of the cyclohexylaminooxo function. The two OH-groups axially disposed participate in intramolecular hydrogen bonds [13]. To remove the acid-stable 2,2,2-trichloroethylidene acetal function, it must first be converted into an ethylidene acetal, e.g. by treatment with tributyltin hydride and 2,2′-azobisisobutyronitrile (AIBN) [12,14], before acid-catalysed deacetalation can be carried out by analogy with ref. [14].

The structures of the 4-*epi* derivatives **2**–**5** and **7** are supported by their ^{1}H and ^{13}C NMR spectral data. The assignment of the signals has been achieved unambiguously by correlation experiments (H,H-COSY and C,H-COSY). The assignment of the H-3 signal of **2** (δ 5.18) is additionally confirmed by the high field shift of this proton after the decarbamoylation of **2** to **4** (δ 4.35). The ^{1}H NMR spectrum of compound **2** shows, besides the two large *geminal* couplings $J_{2a,2b}$ 14.9 Hz and $J_{6a,6b}$ 13.7 Hz, only one large *vicinal* coupling between H-2 and H-3 (12.2 Hz). It is noticeable that the decarbamoylated 4-*epi*-quinate **4** shows a remarkable change of optical rotation and a significant change of the $J_{2,3}$ and some other couplings compared to the carbamoyl derivative **2**. This indicates a change in conformation. Because of the similar design, compounds **4** and **5** could adopt similar conformations. As already mentioned, the amide **5** adopts a $^1C_4$ conformation in crystals. The ^{1}H NMR spectra recorded in $CDCl_3$ (**4**) and Me_2SO-d_6 (**5**), respectively, show certainly in both cases large H-5–H-6 couplings (**4**: $J_{5,6a}$ 9.8 Hz, $J_{5,6b}$ 7.0 Hz; **5**: $J_{5,6a}$ 9.6 Hz, $J_{5,6b}$ 6.9 Hz) indicating a vicinal diaxial pair of protons, but the different H-2–H-3 couplings (**4**: $J_{2a,3}$ 4.0 Hz, $J_{2b,3}$ 7.0 Hz; **5**: $J_{2a,3}$ 5.0 Hz, $J_{2b,3}$ 9.2 Hz) indicate that the conformations of **4** and **5** can be different in solution.

As already reported for numerous cyclic chloral acetals of carbohydrates [3], the singlet of the endo-H acetal proton is characteristically shifted downfield in comparison with the corresponding signal of the *exo*-H form (**2**: $\delta_{endo\text{-H}}$ 5.42; $\delta_{exo\text{-H}}$ 5.30), **3**: $\delta_{endo\text{-H}}$ 5.49; $\delta_{exo\text{-H}}$ 5.31, **7**: $\delta_{endo\text{-H}}$ 5.42; $\delta_{exo\text{-H}}$ 5.08). The integrals of these signals were used to determine the endo-H/exo-H ratio of the diastereomeric mixtures.

The structure of compound **3** is supported by the following NMR data and arguments. The spectra of the product show the characteristic signals of a carbamoyl- and a chloral acetal function as in **2**. However, the signal for the methyl group of the ester function is missing and three carbonyl functions (δ 173.9, 153.8, and 153.7) and a second *N*-cyclohexyl group are found. The methine proton of the second *N*-cyclohexyl group (δ 3.85) couples only with two *vicinal* methylene groups (tt, $J_{C-H,CH2a}$ 12.2 Hz, $J_{C-H,CH2b}$ 3.9 Hz), whereas the methine proton of the *N*-cyclohexyl carbamoyl group (δ 3.53–3.35) shows as expected, additional coupling with the NH-proton. The chemical shifts of these signals correspond also with the assumed structure.

1. Experimental

General.—Column chromatography used Silica Gel 60 (63–200 μm) [E. Merck]; thin layer chromatography (TLC), Silica Gel foils 60 F_{254} [E. Merck]. NMR measurements used: AC 250 and ARX 300; equipments with internal standard TMS. Melting points were taken using a polarising microscope Leitz (Laborlux 12 Pol) equipped with a hot stage (Mettler FP 90). (−)-Quinic acid was from Aldrich, and Amberlite IR 120 from Fluka.

Methyl quinate (**1**).—A mixture of (−) quinic acid (5,0 g, 26 mmol), Amberlite IR 120 (5.0 g) in dry MeOH (50 mL) was refluxed for 10 h. After

cooling, the solution was filtered and concentrated under reduced pressure. Yield: 5,3 g (99%); mp 126–127 °C (EtOH); lit. [10] mp 124–127 °C, lit. [9] mp 127–128 °C.

*(1*R, *3*R, *4*R, *5*R*)-Methyl 3*-O-*(cyclohexylcarbamoyl)-4,5*-O-*(2,2,2-trichloroethylidene)-1, 3, 4, 5-tetrahydroxycyclohexane-1-carboxylate* (**2**) *and (1*R, *3*R, *4*R, *5*R*)-3′*-N-*cyclohexyl-3*-O-*(cyclohexylcarbamoyl)-4,5*-O-*(2,2,2-trichloroethylidene)spiro[[cyclohexane-3,4,5-triol-1,5′-[1,3]oxazolidine]]-2′,4′-dione* (**3**).—To a solution of methyl quinate (**1**) (1.0 g, 4.85 mmol) in dry 1,2-dichloroethane (15 mL), DCC (2.51 g, 12.12 mmol) and chloral (2.50 g, 16.97 mmol) were added and the mixture was refluxed with stirring for 5 h. After cooling to room temperature and addition of CH_2Cl_2 (20 mL) and 10% aq AcOH (30 mL), the reaction mixture was shaken for about 30 min to destroy excess of DCC. The precipitated *N*,*N*′-dicyclohexyl urea was removed by filtration, the organic phase was separated, and the aq phase was washed twice with CH_2Cl_2 (15 mL). The combined extracts were washed twice with water (20 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by column chromatography (2:1 toluene–EtOAc, R_f 0.43) giving 1.21 g (54%) of the diastereomeric endo-H/exo-H mixture of **2** (ratio 16:1). The amorphous solid was recrystallized from EtOAc giving the pure endo-H diastereomer **2** as colourless crystals, mp 132–134 °C, $[\alpha]_D^{24}$ −5.9° ($c = 1.04$, $CHCl_3$). Additionally, 0.26 g (10%) of the colourless, crystalline byproduct **3** (mp 246–248 °C dec.) were obtained in pure form by slow evaporation of the first eluate fractions. The spiro-derivative **3** (endo-H/exo-H diastereomeric mixture; ≈12:1) was recrystallized from EtOH.

2 *(*endo-*H form)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.42 (s, 1 H; *endo*-Cl_3C-C*H*), 5.18 (ddd, 1 H, $J_{3,4}$ 5.9 Hz, $J_{2a,3}$ 5.7 Hz, $J_{2b,3}$ 12.2 Hz, H-3), 4.90 (ddd, 1 H, $J_{4,5}$ 5.9 Hz, H-5), 4.78 (d, 1 H, $J_{NH,CH}$ 7.9 Hz, N–H), 4.63 (dd, 1 H, $J_{3,4}$ 5.9 Hz, H-4), 3.80 (s, 3H, O–CH_3), 3.51–3.38 (m, 1 H, cyclohexyl–C–H), 3.34 (br, 1 H, OH), 2.45 (dd, 1H, $J_{2a,2b}$ 14.9 Hz, H-2a), 2.19 (ddd, 1 H, $J_{6a,6b}$ 13.7 Hz, $J_{5,6b}$ 6.4 Hz, $^4J_{2a,6b}$ 1.5 Hz, H-6b), 2.00 (dd, 1 H, $J_{5,6a}$ 8.5 Hz, H-6a), 1.68 (ddd, 1 H, 2b), 1.63–1.53 (m, 4 H, cyclohexyl–CH_2), 1.39–1.05 (m, 6 H, cyclohexyl–CH_2). ^{13}C NMR data (63 MHz, $CDCl_3$): δ 175.3 (CH_3O–*C*=O), 154.4 (HN–C=O), 106.7 (acetal-C), 99.7 (CCl_3), 78.1 (C-1) 74.6 (C-4), 72.7 (C-5), 68.9 (C-3), 53.3 (CH_3O), 50.0 (cyclohexyl–CH), 35.6 (C-6), 35.2 (C-2), 33.3, 25.4, 25.4, 24.7, 24.7 (5×cyclohexyl–CH_2). Anal. Calcd for $C_{17}H_{24}Cl_3NO_7$ (460.7): C, 44.32; H, 5.25; N, 3.04. Found: C, 44.29; H, 5.33; N, 2.99.

3. ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.49 (s, 1 H, *endo*-Cl_3C–C*H*), 5.31 (s, 1 H, *exo*-Cl_3C–C*H*), 5.29 (ddd, 1 H, $J_{3,4}$ 4.3 Hz, H-3), 4.90 (ddd, 1H, $J_{5,6a}$ 6.1 Hz, $J_{5,6b}$ 7.9 Hz, H-5), 4.73 (d, 1 H, $J_{N-H,C-H}$ 8.2 Hz, N–H), 4.64 (dd, 1H, $J_{4,5}$ 5.2 Hz, H-4), 3.85 (tt, 1 H, $J_{C-H,CH2a}$ 12.2 Hz, $J_{C-H,CH2b}$ 3.9 Hz, NC–H), 3.53–3.35 (m, 1 H, NHC–*H*), 2.38 (dd, 1 H, $J_{2a,3}$ 8.2 Hz, $J_{2a,2b}$ 15.6 Hz, H-2a), 2.20 (ddd, 1 H, $J_{6a,6b}$ 14.9 Hz, $^4J_{2b,6b}$ 1.5 Hz, H-6b), 2.07 (dd, 1 H, H-6a), 2.05 (m, 1 H, H-2b), 1.99–1.79 (m, 4 H, CH_2), 1.76–1.51 (m, 6 H, CH_2), 1.43–1.03 (m, 10 H, CH_2). ^{13}C NMR data (63 MHz, $CDCl_3$): δ 173.9 (C=O), 153.8, 153.7 (2×C=O), 106.7 (acetal-C), 99.3 (CCl_3), 81.6 (C-1), 76.1, 73.2, 67.0 (C-3, C-4, C-5), 53.1, 50.1 (2×C–H), 33.2, 32.1 (C-2, C-6), 31.2, 28.9, 28.9, 25.5, 25.5, 25.4, 25.4, 24.7, 24.7, 24.7 (10×CH_2). Anal. Calcd for $C_{23}H_{31}Cl_3N_2O_7$ (553.9): C, 49.88; H, 5.64; N, 5.06. Found: C, 49.99; H, 5.58; N, 5.06. MS (70 eV): *m*/*z* 554, isotopic ratio corresponds to 3 Cl-atoms.

*(1*S, *3*R, *4*S, *5*R*)-Methyl 4,5*-O-*(2,2,2-trichloroethylidene)-1, 3, 4, 5-tetrahydroxy-cyclohexane-1-carboxylate* (**4**).—A solution of **2** (1.0 g, 2.17 mmol) in methanolic NaOMe (1.0%, 40 mL) was refluxed for 6–7 h (TLC control). The reaction mixture was subsequently cooled and neutralized with an acidic ion exchanger (Amberlite IR-120). After evaporation of the solvent, **4** was separated from the methyl urethane by column chromatography (R_f 0.26, 2:1 toluene–EtOAc) yielding 0.61 g (84%) of **4** (colourless needles); mp 126–127.5 °C (EtOH); $[\alpha]_D^{25}$ + 59.8° (*c* 1.01, $CHCl_3$).

4 *(*endo-*H form)*. ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.40 (s, 1 H, *endo*-Cl_3C–C*H*), 4.91 (ddd, 1 H, $J_{5,6a}$ 9.8 Hz, $J_{5,6b}$ 7.0 Hz, H-5), 4.70 (dd, 1 H, $J_{4,5}$ 4.8 Hz, H-4), 4.35 (ddd, 1 H, $J_{2a,3}$ 4.0 Hz, $J_{2b,3}$ 7.0 Hz, $J_{3,4}$ 2.7 Hz, H-3), 3.83 (s, 3 H, OCH_3), 2.23 (dd, 1 H, $J_{2a,2b}$ 15.0 Hz, H-2a), 2.18 (ddd, 1 H, $J_{6a,6b}$ 13.7 Hz, H-6a), 1.91 (ddd, 1 H, H-2b), 1.82 (dd, 1 H, H-6b). ^{13}C NMR data (63 MHz, $CDCl_3$): δ 175.2 (CH_3O–C=O), 106.0 (acetal-C), 99.4 (CCl_3), 78.8, 73.7, 67.0 (C-3, C-4, C-5), 74.8 (C-1), 53.6 (OCH_3), 34.8, 34.0 (C-2, C-6). Anal. Calcd for $C_{10}H_{13}Cl_3O_6$ (335.6): C, 35.79; H, 3.90. Found: C, 35.7; H, 3.93.

*(1*S, *3*R, *4*S, *5*R*)-*N*-Cyclohexyl 4,5*-O-*(2,2,2-trichloroethylidene)-1, 3, 4, 5-tetrahydroxycyclohexane-1-carboxamide* (**5**).—A solution of **3** (200 mg, 0.36 mmol) in methanolic NaOMe (1.0%,

10 mL) was refluxed for 6–7 h (TLC control). The reaction mixture was subsequently cooled and neutralized with an acidic ion exchanger (Amberlite IR-120). After evaporation of the solvent, **5** was separated from the methyl urethane by column chromatography (R_f 0.42, 2:1 toluene–EtOAc) yielding 131 mg (90.3%) of **5** (colourless crystals); mp 223–225 °C (EtOAc); $[\alpha]_D^{23}$ + 24.5° (*c* 0.97, MeOH).

5 *(*endo-*H form)*. ^{1}H NMR (250 MHz, Me_2SO-d_6): δ 7.37 (d, 1 H, $J_{N-H,C-H}$ 8.4 Hz, N–H), 5.58 (s, 1 H, *endo*-Cl_3C-C*H*), 5.35 (d, 1 H, $J_{OH,H-3}$ 5.0 Hz, OH), 4.79 (ddd, 1 H, $J_{5,6b}$ 6.9 Hz, $J_{5,6a}$ 9.6 Hz, H-5), 4.40 (dd, 1 H, $J_{4,5}$ 6.4 Hz, H-4), 4.00–3.88 (m, 1 H, H-3), 3.59–3.42 (m, 1 H, C–H), 2.05 (dd, 1 H, $J_{2a,3}$ 5.0 Hz, $J_{2a,2b}$ = 14.0 Hz, H-2a), 1.92 (dd, 1 H, $J_{6a,6b}$ 13.4 Hz, H-6a), 1.85 (dd, 1 H, H-6b), 1.39 (dd, 1 H, $J_{2b,3}$ 9.2 Hz, H-2b), 1.77–1.60 (m, 5 H, CH_2), 1.30–1.20 (m, 5 H, CH_2). ^{13}C NMR data (63 MHz, Me_2SO-d_6): δ 174.2 (HN–C = O), 106.0 (acetal-C), 100.5 (CCl_3), 81.9, 75.1, 67.2 (C-3, C-4, C-5), 79.1 (C-1), 47.4 (C–H), 38.5, 35.2 (C-2, C-6), 32.1, 32.1, 25.1, 24.6, 24.6 (5×CH_2). Anal. Calcd for $C_{15}H_{22}Cl_3NO_5$ (402.7): C, 44.74; H, 5.51; N, 3.48. Found: C, 44.83; H, 5.59; N, 3.48.

*(3*R*, 4*R*, 5*R*)-Methyl 3-*O*-(cyclohexylcarbamoyl)-4,5-*O*-(2,2,2-trichloroethylidene)-3, 4, 5-trihydroxycyclohex-1-ene-1-carboxylate* (**7**).—A mixture of methyl shikimate (**6**) [8,15] (2.0 g, 10.6 mmol), chloral (5.47 g, 37.2 mmol), and DCC (5.50 g, 26.6 mmol) in dry 1,2-dichloroethane (20 mL) was reacted and worked up as described for the methyl quinate **1**. The residue was purified by column chromatography (2:1 heptane–EtOAc, R_f 0.42) giving 2.56 g (54.4%) of a syrupy diastereomeric mixture of **7** (*endo*-H/*exo*-H ratio 3:1).

7 *(*endo-*H form)*. ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.96 (ddd, 1 H, $J_{2,3}$ 4.0 Hz, H-2), 5.42 (s, 1 H, Cl_3C–C*H*), 5.31 (dd, 1 H, $J_{3,4}$ 4.9 Hz, H-3), 4.95 (ddd, 1 H, $J_{5,6a}$ 5.8 Hz, $J_{5,6b}$ 4.3 Hz, H-5), 4.71 (dd, 1 H, $J_{4,5}$ 6.7 Hz, H-4), 4.67 (d, 1 H, $J_{NH,CH}$ 7.9 Hz, N–H), 3.75 (s, 3 H, OCH_3), 3.45 (m, 1 H, cyclohexyl–C–H), 2.89 (dd, 1 H, $J_{6a,6b}$ 17.1 Hz, H-6a), 2.71 (ddd, 1 H, $J_{2,6b}$ 1.5 Hz, H-6b), 2.39–2.21 (m, 2 H, cyclohexyl–CH_2), 2.14–1.89 (m, 3 H, cyclohexyl–CH_2), 1.81–1.40 (m, 5 H, cyclohexyl–CH_2). ^{13}C NMR data (63 MHz, $CDCl_3$): δ 165.7 (CH_3O–C = O), 154.2 (NH–C = O), 136.6 (C-2), 130.6 (C-1), 107.7 (acetal-C), 100.1 (CCl_3), 79.4 (C-3), 75.3, 69.4 (C-4, C-5), 52.2 (OCH_3), 50.1 (cyclohexyl–CH), 33.3, 25.4, 25.4, 24.7, 24.7 (5×cyclohexyl–CH_2), 27.2 (C-6). Anal. Calcd for $C_{17}H_{22}Cl_3NO_6$ (442.7): C, 46.12; H, 5.01 N, 3.16. Found: C, 45.69; H, 5.13; N, 3.07.

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