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Epoxidation of C-branched glycals: unexpected stereochemical results and their theoretical rationale

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Dedicated to Professor Hans Paulsen in the year of his 80th birthday.

Abstract

This paper describes the synthesis of C-3 methyl-branched glycosides by epoxidation of partially unblocked L-configured glycals. The stereochemical result depends on the orientation of the allylic hydroxyl group. A theoretical explanation is presented, based on the conformational preferences of the respective glycal half-chair conformations that were estimated by applying the BP density functional and a valence triple-ζ basis set. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: C-Branched sugars; BP density functional; Epoxidation; Glycal

1. Introduction

1,2-Anhydro sugars have proven to be invaluable tools for the synthesis of glycosides[1,2] and nucleoside diphosphates.[3] Transformation into Brigl's anhydride prior to glycosylation, however, has been limited to protected glycals, and, moreover, the biologically interesting family of C-branched sugar glycosides has been omitted in previous synthetic papers. Here, we wish to report on the epoxidation of L-mycaral and L-olivomycal as prototypes for C-3-branched deoxy sugars. It was our intention to utilise the glycal route for the synthesis of the respective activated sugars. Since the outcome of the epoxidation step seemed stereochemically not uniform, we embarked on this experimental and theoretical study to shed some light on the attack by dimethyldioxirone (DMDO) on the enol ether double bond.

2. Results and discussion

Starting from the easily accessible 3-C-branched glycals, L-olivomycal (**1**) and L-mycaral (**2**),[4] acetylation gave the monoesters **3** and **4** (cf Scheme 1). Both derivatives were reacted with freshly prepared dimethyldioxirane[5] (DMDO) in a solution of acetone and dichloromethane. In the case of L-olivomycal, an expected β-facial epoxidation, which occurred *cis* to the allylic hydroxy group, furnished β-L-manno-configured **5**. Nucleophilic attack by methanol resulted in a selective *trans* opening of the epoxide to yield α-L-mannopyranoside **6**. Interestingly, polymerization of this bifunctional substrate could not be detected.

In the case of L-mycaral, a similar *cis* epoxidation was expected as well. However, in contrast the preferred attack took place from the β-face and occurred *trans* to the allylic hydroxy group. The β-L-altro-configured isomer **10** was formed in a 4:1 ratio compared to **11**. The configurations of both products were proven again using methanolysis to form methyl 4-*O*-acetyl-6-deoxy-3-*C*-methyl-α-L-altropyranoside (**12**) and methyl 4-*O*-acetyl-6-deoxy-3-*C*-methyl-β-L-allopyranoside (**13**), respectively. The products could not be separated from one another, but their ^{1}H NMR and GCOSY spectra gave clear signals and coupling con-

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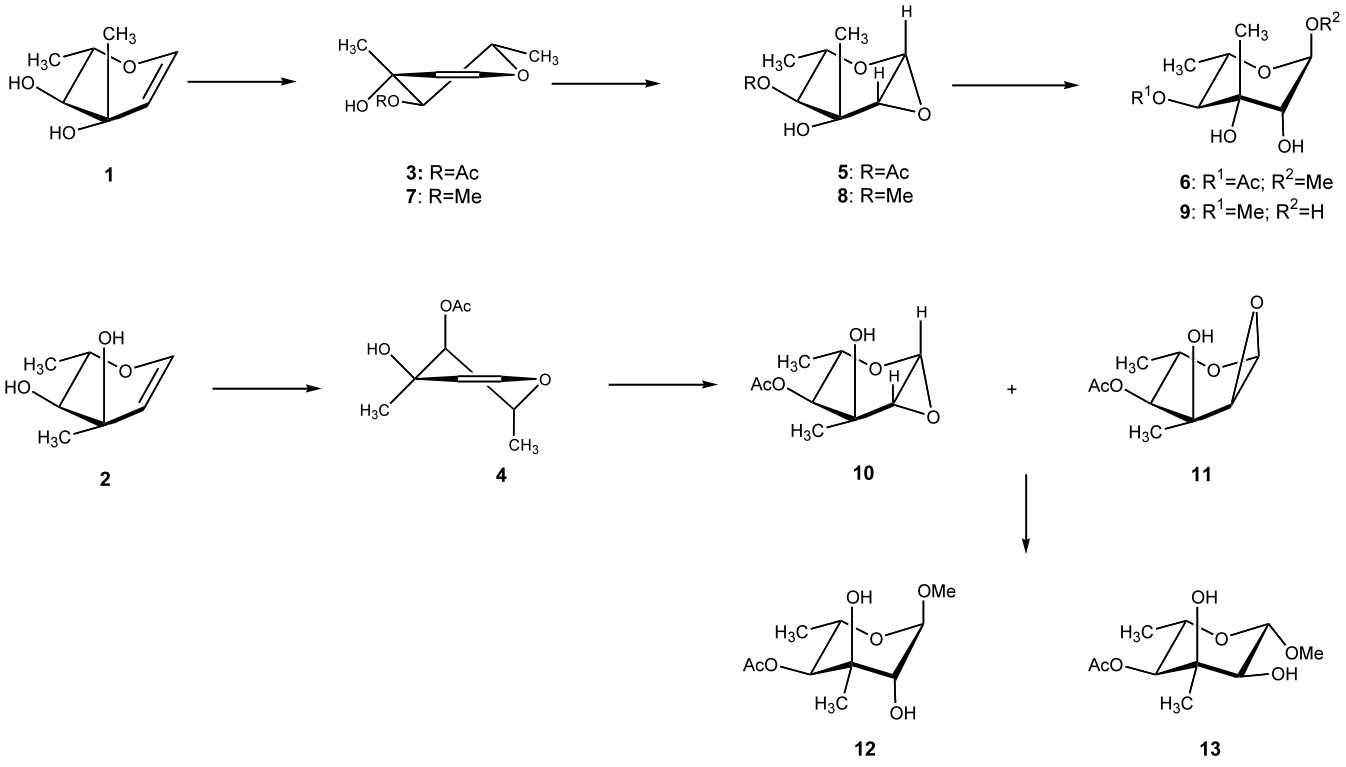
stants for both products [**12**: $J_{1,2}$ 1.4 Hz (eq, eq); **13**: $J_{1,2}$ 7.8 Hz (ax,ax)].

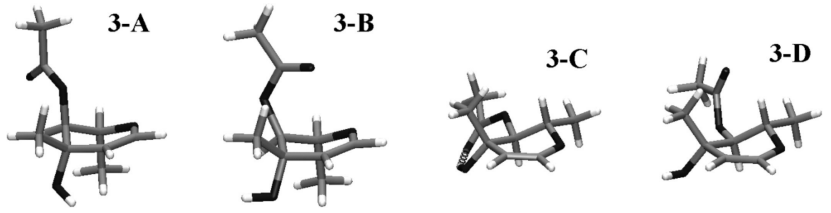
The literature offers mainly two explanations on the diastereoselectivity of epoxidations employing DMDO: steric effects[6,7] and hydrogen-bonding effects.[8–10] The hydroxy group exerts a stabilizing effect through hydrogen bonding on the dipolar DMDO transition state. This effect is more pronounced in nonpolar solvents (acetone/CCl_4 mixtures) than in polar environments (methanol), where in the latter case the solvent stabilises the transition state, and, therefore, steric interactions prevail. Studies by Adam and co-workers discussed the importance of the size of the dihedral angle α between the allylic hydroxy group and the epoxidised double bond in cyclohexenols.[10] The explanation offered by these authors is that dihedral angles larger than 130° favour in the transition state hydrogen bonding between the allylic hydroxy group and the dioxirane reagent. This furnishes a *cis* relationship between the 3-hydroxy group and the formed epoxide. The further rationale is that with smaller angles severe steric interference would lead to *anti* epoxidations.

Thus, a better understanding of the ground-state conformations of the glycal should offer a reliable prediction of the expected stereocontrol. A computational study was carried out at the Density Functional Theory (DFT) level of theory. The ground-state geometries of **3**, **4**, and **7** were considered for the $^4H_5$ and $^5H_4$ conformers, respectively. Two additional starting geometries to compensate for the high rotational barrier of the acetyl group were taken into account for each conformer of **3** and **4**: (i) the carbonyl oxygen situated on the α-face, above the six-membered ring (endo) and (ii) the carbonyl oxygen pointing away from the ring (exo). The results of the calculations for olivomycal **3** are illustrated in Fig. 1. Compound **3-C**, which has a $^5H_4$-half-chair conformation is calculated to be of the lowest energy. For both endo conformers **3-B** and **3-D**, the relative energies are found to be substantially higher (6.3 and 10.3 kcal/mol). Although the dihedral angle of **3-C** (127°) is very close to the optimal angle calculated by Adam and co-workers,[10] the predicted hydrogen bond prevents an effective *cis* stereocontrol brought about by the allylic OH group. Therefore, the *cis*-stereoselectivity of this reaction is exclusively due to steric restrictions. Both the axially configured methyl group and the acetate at the C-4 position favour a β-facial dioxirane attack.

The exclusive steric control should be maintained even if the protecting group at C-4 is changed to a smaller substituent not capable of hydrogen bonding. Thus, alcohol **1** was etherified with iodomethane to yield glycal **7**. Epoxidation and subsequent hydrolysis proved to be equally stereoselective as was the case with compound **3**. Computation for **7** (cf. Fig. 2) revealed the $^5H_4$-half-chair conformation to be energetically favoured. Here, the methyl ether blocks the intramolecular hydrogen-bond interaction with the tertiary OH

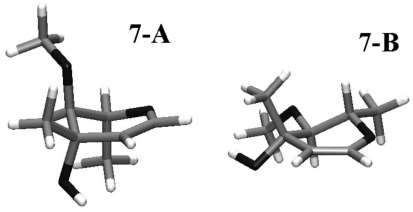


Scheme 1.



Geometry	Conformation	Relative Energy [kcal/mol]	Dihedral Angle α [°]
3-A	$^{4}\mathbf{H}_{5}$ (OAc *exo*)	+1.40	100.7
3-B	$^{4}\mathbf{H}_{5}$ (OAc *endo*)	+10.33	110.1
3-C	$^{5}\mathbf{H}_{4}$ (OAc *exo*)	+0.00	127.0
3-D	$^{5}\mathbf{H}_{4}$ (OAc *endo*)	+6.30	120.0

Fig. 1. Optimised structures of **3** and relative energies of four low-lying conformers. The dihedral angle α refers to the atoms C-1–C-2–C-3–OH.



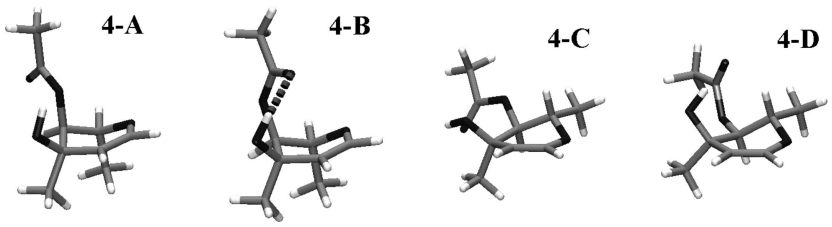
Geometry	Conformation	Relative Energy [kcal/mol]	Dihedral Angle α [°]
7-A	$^{4}\mathbf{H}_{5}$	+0.22	99.4
7-B	$^{5}\mathbf{H}_{4}$	+0.00	131.7

Fig. 2. Optimised structures of **7** and relative energies of two low-lying conformers. The dihedral angle α refers to the atoms C-1–C-2–C-3–OH.

group, and the pseudo equatorial position of the hydroxyl group bends the dihedral angle to a value of 131.7°.

Though the two conformers are energetically almost equal, **7-B** seems to be the more reactive species due to the larger dihedral angle of 131.7°. As predicted, this angle favours the association between the hydroxy group and the attacking dioxirane, and it may be therefore safe to assume that the *cis* selectivity in this reaction can be attributed to a pre-association between the reagent and the HO-3 group.

The calculations for L-mycaral (**4**) indicated the $^{4}H_{5}$-half-chair conformation (**4-A**) to be energetically favoured (cf. Fig. 3). In the favoured conformer **4-A** all substituents, except for the allylic hydroxyl group, are in a pseudoaxial position, with a dihedral angle α of about 129°. This would favour the *cis* transition state; however, the steric effect excerted by the pseudoaxial ester is prevailing and counteracting. As it is known that DMDO is very sensitive to steric factors,[7] the steric effect seems to influence the favoured transition state more than the directive effect of the allylic OH group. In the experiment these competing effects lead to a preferred *trans* epoxidation with a minor part of *cis* epoxidation. An increased steric demand of the substituent would conclusively overrule any other effect and shift the ratio entirely in favour of the β-facial and thus *trans* epoxide.



Geometry	Conformation	Relative Energy [kcal/mol]	Dihedral Angle α [°]
4-A	$^{4}\mathbf{H}_{5}$ (OAc exo)	+0.00	129.4
4-B	$^{4}\mathbf{H}_{5}$ (OAc endo)	+6.37	124.7
4-C	$^{5}\mathbf{H}_{4}$ (OAc exo)	+3.26	138.0
4-D	$^{5}\mathbf{H}_{4}$ (OAc endo)	+0.86	118.3

Fig. 3. Optimised structures of **4** and relative energies of four low-lying conformers. The dihedral angle α refers to the atoms C-1–C-2–C-3–OH.

3. Conclusions

It has been shown by the above experiments and subsequent calculations that H-bonding between the ester carbonyl and the tertiary hydroxyl group has a paramount effect on the stability of the relative conformers. Small changes in the substitution patterns have large effects on the conformational preferences of the glycal half-chairs, which consequently results in a specific product distribution. On the computational side the need of sufficiently large basis sets to allow definite conclusions became evident, a fact which has been also identified by Allinger and co-workers.[11] Synthetically this paper describes the generation of novel C-3 methyl-branched glycosides and comprises the first example of the dioxirane reaction with a partially unblocked glycal without any side reaction.

4. Experimental

4.1. Instrumentation and general methods

^{1}H and ^{13}C NMR spectra were recorded with a Bruker WM 300 (^{1}H, 300.1 MHz; ^{13}C, 75.7 MHz) or with a Bruker AMX 400 (^{1}H, 400 MHz; ^{13}C, 100.6 MHz). Two-dimensional correlation spectra (GCOSY and GHSQC) were measured with the Bruker AMX 400. Chemical shifts (δ) are given in ppm relative to the signal for internal Me_4Si. Optical rotations were measured at 20 °C at 589 nm (Na) with a Perkin–Elmer 241 polarimeter using a 10-cm, 1-mL cell. Electrospray ionisation mass spectra (ESIMS) were recorded with a Micromass Quattro LC-Z spectrometer. Melting points were determined on a Ta Instruments 2010 Differential Scanning Calorimeter. Reactions were monitored by TLC on silica gel plates (E. Merck Kieselgel 60 F_{254}) and detected by spraying with a solution of naphthoresorcinol (200 mg) in sulfuric acid (2N, 100 mL) and ethanol (100 mL) with subsequent heating. Medium-pressure liquid chromatography (MPLC, 3–5 bars) was performed on Kieselgel (E. Merck, 230–400 mesh, 0.040–0.063 μm). Anhydrous solvents (CH_2Cl_2, MeOH) were prepared by passing solvents (analytical grade, p.a.) through molecular sieves (4 Å) under argon.

4.2. General procedure for epoxidation

The glycal (1 mmol) was dissolved in anhydrous CH_2Cl_2 (2 mL) under Ar, and the resulting solution was cooled to 0 °C. A freshly prepared solution of dimethyldioxirane in acetone (20 mL) was added, and the reaction mixture was stirred at 0 °C for 1 h or until TLC indicated complete consumption of the glycal. The solution was evaporated with a stream of dry Ar, and the residue was dried in vacuo to afford the 1,2-anhydro sugar(s) in quantitative yield.

4.3. 4-*O*-Acetyl-1,5-anhydro-2,6-dideoxy-3-*C*-methyl-L-*arabino*-hex-1-enitol (3)

A solution of compound **1** (412 mg, 2.86 mmol) in anhyd pyridine (15 mL) was treated with Ac_2O (325 μL, 3.4 mmol, 1.2 equiv) at room temperature and stirred overnight. The pyridine was evaporated, and the crude

product was three times codistilled using toluene. The resulting residue was purified by MPLC (9:1 cyclohexane–EtOAc) to obtain 465 mg (87%) of compound **3** as a white powder: mp 168 °C; $[\alpha]_D^{20}$ −60.5° (*c* 1.4, Et_2O); ^1H NMR ($CDCl_3$): δ 6.24 (d, 1H, H-1), 4.93 (d, 1H, H-4), 4.77 (d, 1H, H-2), 3.97 (dq, 1H, H-5), 2.55 (bs, 1H, OH), 2.16 (s, 3H, Ac), 1.31 (s, 3H, 3-CH_3), 1.29 (d, 3H, 6-CH_3); $J_{1,2}$ 6.1 Hz, $J_{4,5}$ 9.9 Hz, $J_{5,CH3}$ 6.3 Hz; ^{13}C NMR ($CDCl_3$): δ 171.35 (C=O), 142.56 (C-1), 108.15 (C-2), 79.15 (C-4), 72.11 (C-5), 69.82 (C-3), 24.82 (C-6), 20.89 (Ac), 17.45 (3-CH_3); ESIMS (positive-ion): *m*/*z* 209 $[M + Na]^+$.

4.4. 4-*O*-Acetyl-1,5-anhydro-2,6-dideoxy-3-*C*-methyl-L-*ribo*-hex-1-enitol (4)

A solution of compound **2** (452 mg, 3.14 mmol) in anhyd pyridine (30 mL) was treated with Ac_2O (712 μL, 7.5 mmol, 2.4 equiv) and a catalytic amount of DMAP under Ar, with cooling in an ice bath. After stirring the resulting mixture at room temperature for 2 days, the solvent was evaporated, and the crude product was dried in vacuo. The resulting residue was purified by MPLC (12:1 cyclohexane–EtOAc) to yield 362 mg (62%) of compound **4** as a white powder: mp: 124 °C; ^1H NMR (C_6D_6): δ 5.44 (dd, 1H, H-1), 5.34 (d, 1H, H-4), 5.28 (d, 1H, H-2), 4.22 (dq, 1H, H-5), 1,70 (s, 3H, Ac), 1.49 (d, 3H, 3-CH_3), 1.25 (d, 3H, 6-CH_3); $J_{1,2}$ 3.3 Hz, $J_{1,3\text{-}CH3}$ 1.3 Hz, $J_{4,5}$ 8.9 Hz, $J_{5,CH3}$ 6.2 Hz; ^{13}C NMR (C_6D_6): δ 170.69 (C=O), 125.53 (C-1), 89.74 (C-2), 73.16 (C-4), 72.07 (C-3), 65.95 (C-5), 20.66 (Ac), 18.57 (C-6), 18.24 (3-CH_3); ESIMS (positive-ion): *m*/*z* 209 $[M + Na]^+$.

4.5. 4-*O*-Acetyl-1,2-anhydro-6-deoxy-3-*C*-methyl-β-L-mannopyranose (5)

Compound **5** was prepared according to the general epoxidation protocol. The regio- and stereoselective product formation was proven by methanolysis to compound **6**.[16]

4.6. Methyl 4-*O*-acetyl-6-deoxy-3-*C*-methyl-α-L-mannopyranoside (6)

The formerly prepared 1,2-anhydro sugar **5** (101 mg, 0.5 mmol) was dissolved in anhyd MeOH (5 mL) and stirred for 3 h at room temperature. The solvent was evaporated, and the residue was purified by MPLC (4:1 cyclohexane–EtOAc) to yield 34 mg (30%) of compound **6** as a colourless oil. $[\alpha]_D^{20}$ −75.0° (*c* 1.0, MeOH); ^1H NMR (MeOD): δ 4.91 (d, 1H, H-4), 4.63 (d, 1H, H-1), 3.73 (dq, 1H, H-5), 3.48 (d, 1H, H-2), 3.36 (s, 3H, OCH_3), 2.09 (s, 3H, Ac), 1.29 (s, 3H, 3-CH_3), 1.19 (d, 3H, 6-CH_3); $J_{1,2}$ 1.4 Hz, $J_{4,5}$ 9.9 Hz, $J_{5,CH3}$ 6.2 Hz; ^{13}C NMR (MeOD): δ 172.96 (C=O), 103.68 (C-1), 77.85, 76.52, 73.34, 67.44 (C-2, C-3, C-4, C-5), 55.91 (OCH_3), 21.35 (C-6), 20.04 (Ac), 18.20 (3-CH_3); ESIMS (positive-ion): *m*/*z* 257 $[M + Na]^+$.

4.7. 1,5-Anhydro-2,6-dideoxy-3-*C*-methyl-4-*O*-methyl-L-*arabino*-hex-1-enitol (7)

L-Olivomycal (**3**) (600 mg, 4.2 mmol) was dissolved in anhydrous DMF (30 mL) under Ar, and the solution was cooled using an ice bath. NaH (167 mg, 4.2 mmol, 1 equiv, 60% dispersion in mineral oil) was added, and the resulting mixture was stirred for 1.5 h. The mixture was treated with MeI (259 μL, 4.2 mmol, 1 equiv) and stirred overnight. The solvent was then evaporated, and the residue was dissolved in CH_2Cl_2 and extracted with water. The organic layer was dried over $MgSO_4$, the solvent evaporated, and the crude residue was purified by MPLC (9:1 cyclohexane–EtOAc) to give 194 mg (30%) of compound **7** as a colourless oil. ^1H NMR ($CDCl_3$): δ 6.19 (d, 1H, H-1), 4.65 (d, 1H, H-2), 3.81 (dq, 1H, H-5), 3.36 (s, 3H, OCH_3), 3.19 (d, 1H, H-4), 1.37 (d, 3H, 6-CH_3), 1.33 (s, 3H, 3-CH_3); $J_{1,2}$ 6.0 Hz, $J_{4,5}$ 10.0 Hz, $J_{5,CH3}$ 6.1 Hz; ^{13}C NMR ($CDCl_3$): δ 142.56 (C-1), 108.33 (C-2), 86.94 (C-4), 73.45 (C-5), 71.74 (C-3), 61.06 (OCH_3), 24.26 (C-6), 17.80 (3-CH_3).

4.8. 1,2-Anhydro-6-deoxy-3-*C*-methyl-4-*O*-methyl-β-L-mannopyranose (8)

Compound **8** was prepared according to the general epoxidation protocol. The regio- and stereoselective product formation was proven by hydrolysis to compound **9**.

4.9. 6-Deoxy-3-*C*-methyl-4-*O*-methyl-α-L-mannopyranose (9)

The formerly prepared 1,2-anhydro sugar **8** (87 mg, 0.5 mmol) was dissolved in water and stirred for 1 h at room temperature. The solvent was evaporated, and the residue was purified by MPLC (1:3 cyclohexane–EtOAc) to yield 58 mg (60%) of compound **9** as a white powder: mp 156 °C (dec.); $[\alpha]_D^{20}$ −9.0° (*c* 1.0, MeOH); ^1H NMR (MeOD): δ 4.76 (d, 1H, H-1), 3.48 (s, 3H, OCH_3), 3.33 (d, 1H, H-2), 3.24 (dq, 1H, H-5), 2.99 (d, 1H, H-4), 1.19 (d, 3H, 6-CH_3), 1.10 (s, 3H, 3-CH_3); $J_{1,2}$ 1.2 Hz, $J_{4,5}$ 9.5 Hz, $J_{5,CH3}$ 6.0 Hz; ^{13}C NMR (MeOD): δ 94.43 (C-1), 87.05 (C-2), 78.43 (C-4), 72.16 (C-3), 62.18 (C-5), 49.9 (OCH_3), 19.12, 19.02 (C-6, 3-CH_3); ESIMS (positive-ion): *m*/*z* 215 $[M + Na]^+$.

4.10. 4-*O*-Acetyl-1,2-anhydro-6-deoxy-3-*C*-methyl-β-L-altropyranose (10) and 4-*O*-acetyl-1,2-anhydro-6-deoxy-3-*C*-methyl-α-L-allopyranose (11)

Compound **4** was treated with DMDO according to the general epoxidation protocol. The configuration of the formed epimers was proven by methanolysis to compounds **12** and **13**.

4.11. Methyl 4-*O*-acetyl-6-deoxy-3-*C*-methyl-α-L-altropyranoside (12) and methyl 4-*O*-acetyl-6-deoxy-3-*C*-methyl-β-L-allopyranoside (13)

The mixture of 1,2-anhydro sugars **10** and **11** (92 mg, 0.5 mmol) was dissolved in anhydrous MeOH (2 mL) and stirred for 3 h at room temperature. The solvent was evaporated, and the residue was purified by MPLC (5:2 cyclohexane–EtOAc) to yield 61 mg (57%) of compounds **12** and **13**[16] as a colourless oil. The two epimers could not be separated by MPLC. NMR analysis gave a 4:1 ratio of **12**:**13**. Data for **12**: ^{1}H NMR ($CDCl_3$): δ 4.90 (d, 1H, H-4), 4.73 (d, 1H, H-1), 3.97 (dq, 1H, H-5), 3.58 (d, 1H, H-2), 3.46 (s, 3H, OCH_3), 2.15 (s, 3H, Ac), 1.21 (s, 3H, 3-CH_3), 1.21 (d, 3H, 6-CH_3); $J_{1,2}$ 1.4 Hz, $J_{4,5}$ 10.0 Hz, $J_{5,CH3}$ 6.3 Hz. Data for **13**: ^{1}H NMR ($CDCl_3$): δ 4.64 (d, 1H, H-4), 4.49 (d, 1H, H-1), 3.96 (dq, 1H, H-5), 3.55 (s, 3H, OCH_3), 3.27 (d, 1H, H-2), 2.17 (s, 3H, Ac), 1.26 (s, 3H, 3-CH_3), 1.18 (d, 3H, 6-CH_3); $J_{1,2}$ 7.8 Hz, $J_{4,5}$ 9.7 Hz, $J_{5,CH3}$ 6.3 Hz.

5. Theoretical methods

All ground-state structures were fully optimised using the BP[12,13] density functional and a valence triple-ζ basis set (TZVP[14]) on all atoms. On oxygen a TZVPP[15] basis, which includes more polarisation functions (2d1f), was applied. The calculations were performed with the TURBOMOLE 5.3[15] program suite on a 600 MHz LINUX-PC-Cluster (2GB RAM).

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