Tetrahedron Letters 49 (2008) 5580–5582

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis and stereochemistry of (−)-rosiridol and (−)-rosiridin

Elisabeth Schöttner, Kristina Simon, Manuel Friedel, Peter G. Jones, Thomas Lindel *

Technische Universität Braunschweig, Institutes of Organic, Inorganic and Analytical Chemistry, 38106 Brunswick, Germany

ARTICLE INFO

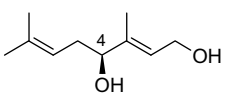
Article history:
Received 16 April 2008
Revised 27 June 2008
Accepted 1 July 2008
Available online 4 July 2008

Keywords:
Monoterpenoids
DIP–Cl
Mosher method
Prenyl nucleophiles
Natural products

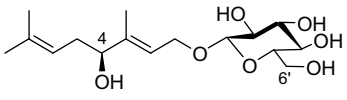
ABSTRACT

The plant-derived monoterpenoids (−)-rosiridol and (−)-rosiridin can be assembled in an enantioselective manner via DIP–Cl reduction of a ketone precursor obtained by BCl_3-mediated C–C coupling of prenyl stannane and an α,β-unsaturated C_5 aldehyde. On the basis of Mosher analyses, the absolute stereochemistry 4*S* was assigned to (−)-rosiridol; this was confirmed by X-ray structure analysis of pentaacetylrosiridin. Glucosylation of (4*S*)-4-acetoxygeraniol proceeds under Koenigs–Knorr conditions in diethyl ether. (−)-Rosiridin was synthesized for the first time.

Exploring the synthesis of cladiellane diterpenoids,[1] we became interested in the hydroxylated monoterpenoid (−)-rosiridol [(−)-**1**, (−)-4-hydroxygeraniol]. (−)-Rosiridol [(−)-**1**] has been isolated as a natural product from the rhizome of the medicinal plant *Rhodiola rosea*[2–4] (Crassulaceae, roseroot), from the leaves of *Cunila spicata* (Lamiaceae),[5] and was detected in petals of the rose *Rosa damascena*.[6]



(−)-rosiridol ((−)-**1**)



(−)-rosiridin ((−)-**2**)

Glycosylated derivatives of (−)-rosiridol [(−)-**1**] include the major component (−)-rosiridin [(−)-**2**] from *Rh. rosea*[2,7] and rhodiolosides B and C from *Rhodiola sachalinensis*.[8,9] A rosiridyl side chain occurs in the tyramine derivative acidissiminol from the wood apple tree *Limonia acidissima*[10] and in a 5-methylcoumarin from *Mutisia orbignyana* (Asteraceae).[11] The carbon skeleton of the marine triterpenoid glycoside xestovanin A contains a 4-hydroxygeranyl partial structure.[12]

There are contradicting reports on the absolute stereochemistry of (−)-rosiridol. While Kadota et al.[7] and Koike et al.[8] concluded that (−)-rosiridol [(−)-**1**] should have 4*R* configuration, Hong et al.[13] and Yoshikawa et al.[9] derived 4*S* configuration. An independent synthesis of (−)-rosiridol and a first synthesis of (−)-rosiridin [(−)-**2**] might shed some light on that issue.

Hong et al. published the only total synthesis of (−)-**1** by coupling prenylzinc to a C_5 aldehyde in the presence of HMPA and a norbornene-derived chiral auxiliary under precisely defined conditions strongly dependent on the reaction time.[13]

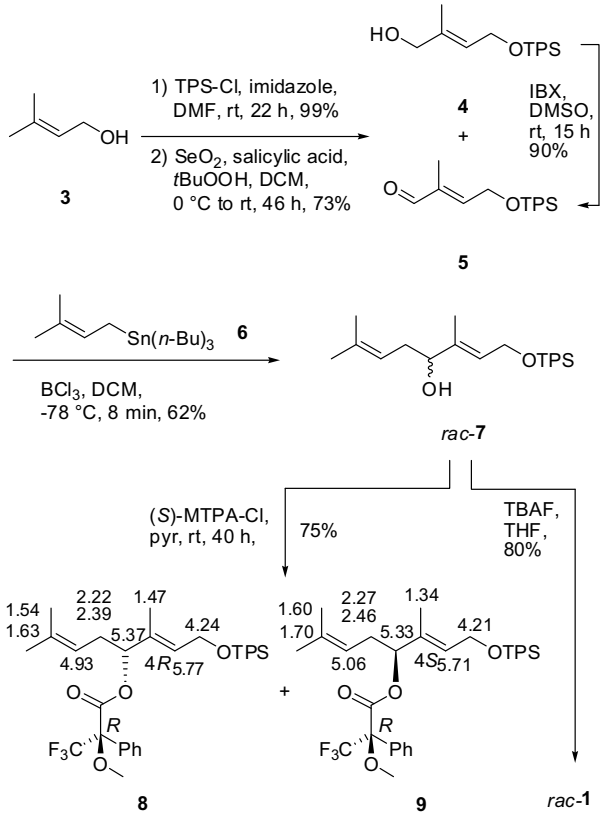
Synthesis of rac-rosiridol. We first synthesized *rac*-rosiridol (*rac*-**1**) to obtain NMR data of both Mosher esters. Aldehyde **5** was prepared from prenol (**3**) in three steps (Scheme 1).[14] The concomitantly formed allylic alcohol **4** was oxidized to **5** with IBX. Regarding the regioselective S_N2 addition of the prenyl nucleophile to a carbonyl group,[15] a procedure first employed by Danishefsky and co-workers worked best.[16] BCl_3 was rapidly added to a cooled solution of aldehyde **5** and stannane **6** leading to the desired alcohol *rac*-**7** via transmetalation of the prenyl moiety from tin to boron (Scheme 1). We observed formation of the regioisomeric S_N2' product when the stannane **6** was prepared from prenyl bromide, whereas use of prenyl chloride led to complete S_N2 regioselectivity.[17]

Removal of tin containing impurities was possible by column filtration on KF–silica (1:9) leaving the OTPS group intact.[18] Deprotection under standard conditions afforded *rac*-rosiridol (*rac*-**1**) in 80% yield.[19]

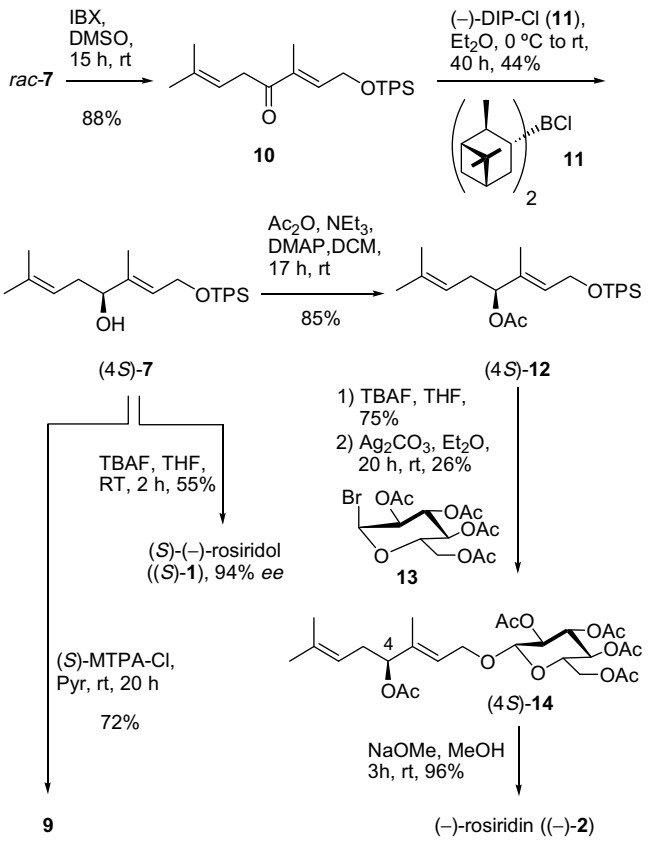
Diastereomeric (*R*)-Mosher esters **8** and **9** were synthesized from *rac*-**7** (Scheme 1, Fig. 1) employing (*S*)-MTPA–Cl[20] and were analyzed by ^{1}H NMR spectroscopy (**8**: (*R*,4*R*), **9**: (*R*,4*S*)).[21] The (*R*,*R*)-diastereomer **8** must exhibit the same ^{1}H NMR chemical shifts as the (*S*,*S*)-compound, which are to be compared with that of (*S*,*R*)-diastereomer **9**. We also desilylated **8** and **9** affording the 4-*O*-MTPA esters of *rac*-**1**, which exhibited ^{1}H NMR chemical shifts

* Corresponding author. Tel.: +49 531 391 7300; fax: +49 531 391 7744.
E-mail address: th.lindel@tu-bs.de (T. Lindel).

0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.07.018



Scheme 1. Synthesis and Mosher analysis of *rac*-rosiridol (*rac*-**1**). ^{1}H NMR chemical shifts were obtained in $CDCl_3$.



Scheme 2. Synthesis of (–)-rosiridol [(–)-**1**] and (–)-rosiridin [(–)-**2**].

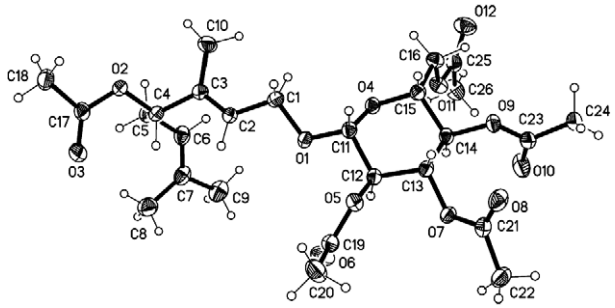


Figure 1. Structure of pentaacetylrosiridol [(4*S*)-**14**] in the crystal, obtained by recrystallization from EtOH.[29]

corresponding well to those of **8** and **9**. The bulky TPS group does not appear to substantially change the average conformation of the Mosher esters.

Enantioselective synthesis of (–)-rosiridol. Alcohol *rac*-**7** was oxidized with IBX affording ketone **10** (Scheme 2). For the reduction of **10** we employed (–)-DIP–Cl (**11**)[20] and obtained alcohol (4*S*)-**7**. Removal of the TPS group afforded (–)-rosiridol [(–)-**1**] with negative optical rotation ($[\alpha]_D^{20}$ –7.2, *c* 0.36, acetone), proving its identity with the natural product. The enantioselectivity of ketone reductions with (–)-DIP–Cl predicts the formation of the (*S*)-enantiomer.[22] The absolute stereochemistry of (4*S*)-**7** was confirmed by ^{1}H NMR spectroscopy of the (*R*)-Mosher ester **9** and comparison with the data obtained on derivatization of *rac*-**7**. The enantiomeric ratio of (4*S*)-**7** and (4*R*)-**7** obtained by the (–)-DIP-Cl reduction was about 97:3 (^{1}H NMR analysis). We additionally confirmed this by using (*R*)-MTPA–Cl.[20]

Koike et al. obtained rosiridyl 1-*O*-pivaloate by enzymatic hydrolysis of the diglycoside rhodioloside B, followed by esterification.[8] The ^{1}H NMR chemical shift differences reported for the Mosher esters of rosiridyl 1-*O*-pivaloate almost exactly mirror our data, but with opposite sign. The ^{1}H NMR chemical shift differences observed for the 4,6′-bis-Mosher esters of (–)-rosiridin [(–)-**2**] obtained by Kadota et al. are quite small and difficult to compare with our values.[7] The Kadota and Koike groups both conclude that (–)-rosiridol [(–)-**1**] has *R* configuration. Contrastingly, Hong et al. base their opposite 4*S* assignment for (–)-rosiridol [(–)-**1**] not only on the Mosher esters of the TBS-protected analog of [(–)-**1**], but also on the conversion of the compound to the pheromone (–)-eldanolide.[13] The absolute stereochemistry of (–)-eldanolide had been proven earlier by total synthesis.[23] Our own Mosher analysis, in accordance with the expected stereoselectivity of the (–)-DIP–Cl reduction, lets us draw the same conclusion as the Hong and Yoshikawa groups proposing 4*S* configuration for (–)-rosiridol [(–)-**1**].

Glucosylation. (4*S*)-4-*O*-Acetylrosiridol[24] was obtained from (4*S*)-**7** in the presence of DMAP, followed by desilylation of (4*S*)-**12** (Scheme 2).[25] Koenigs–Knorr glucosylation employing tetraacetylated α-glucopyranosyl bromide (**13**) in the presence of Ag_2CO_3 in Et_2O[26] provided the peracetylated compound (4*S*)-**14** in 26% isolated yield after chromatography with 15% recovered starting material.[27] Glucosylations carried out in DMF as described, for example, for xylosylations by Satgé et al.[28] were unsatisfactory in our hands. In a prior model reaction, glucosylation of geraniol provided the β-glucoside in an isolated yield of 34% after chromatography with 20% recovered starting material. These non-optimized yields are within the range of expectation for glucosylations of geraniol derivatives. We were able to determine the stereochemical outcome of the (–)-DIP–Cl reduction independently by X-ray analysis of crystalline pentaacetylrosiridin [(4*S*)-**14**, Fig. 1]; the absolute configuration was determined on the basis

of anomalous scattering by oxygen.[29] Saponification with NaOMe/MeOH liberated (−)-(4*S*)-rosiridin (96%).

The maximum deviation of ^{13}C NMR chemical shifts (methanol-d_4) of (−)-(4*S*)-rosiridin, when compared with the data reported by Kadota[7] and, recently, by Yoshikawa,[9] was 0.9 and 0.2, respectively. In a control experiment we synthesized diastereomeric (−)-(4*R*)-rosiridin. Alcohol (4*R*)-**7** was obtained by reduction of **10** with (+)-DIP–Cl, followed by acetylation, glucosylation (30 °C, 44%), and saponification. 4*S*- and 4*R*-rosiridins exhibit very similar ^{13}C NMR chemical shifts, with the largest difference of 0.2 ppm observed for C-3′ (methanol-d_4). Optical activities were also comparable ($[\alpha]_D^{26}$ −33.4 (4*S*), *c* 0.9 (good agreement with Kurkin[2] and Yoshikawa[9]) and −22.5 (4*R*), *c* 1.6, acetone, respectively). For the diastereomeric pentaacetylrosiridins (4*S*)-**14** and (4*R*)-**14**, however, the difference in optical rotation was more significant ($[\alpha]_D^{28}$ −24.5 (4*S*), *c* 1.0 and −4.9 (4*R*), *c* 1.0, acetone, respectively). Kurkin et al. had reported $[\alpha]_D^{20}$ −28.4 (*c* 1.0, acetone) for (4*S*)-**14**.[2] This leads us to conclude that the natural product (−)-rosiridin has 4*S* configuration.

Acknowledgment

Financial support was provided in part by the Fonds der Chemischen Industrie (doctoral stipend to M.F.).

References and notes

1. Friedel, M.; Golz, G.; Mayer, P.; Lindel, T. *Tetrahedron Lett.* **2005**, *46*, 1623–1626.
2. Kurkin, V. A.; Zapesochnaya, G. G.; Shachvlinskii, A. N. *Khim. Prir. Soedin.* **1985**, *5*, 632–636; . *Chem. Nat. Comp.* **1986**, *21*, 593–597.
3. Bykov, V. A.; Zapesochnaya, G. G.; Kurkin, V. A. *Khim. Farm. Zhurn.* **1999**, *33*, 28–39; . *Pharm. Chem. J.* **1999**, *33*, 29–40.
4. Ali, Z.; Fronczek, F. R.; Khan, I. A. *Planta Med.* **2008**, *74*, 178–181.
5. Manns, D. *Planta Med.* **1993**, *59*, 171–173.
6. Knapp, H.; Straubinger, M.; Fornari, S.; Oka, N.; Watanabe, N.; Winterhalter, P. *J. Agric. Food Chem.* **1998**, *46*, 1966–1970.
7. Fan, W.; Tezuka, Y.; Ni, K. M.; Kadota, S. *Chem. Pharm. Bull.* **2001**, *49*, 396–401.
8. Ma, G.; Li, W.; Dou, D.; Chang, X.; Bai, H.; Satou, T.; Li, J.; Sun, D.; Kang, T.; Nikaido, T.; Koike, K. *Chem. Pharm. Bull.* **2006**, *54*, 1229–1233.
9. Yoshikawa, M.; Nakamura, S.; Li, X.; Matsuda, H. *Chem. Pharm. Bull.* **2008**, *5*, 695–700.
10. Ghosh, P.; Sil, P.; Das, S.; Thakur, S.; Kokke, W. C. M. C. *J. Nat. Prod.* **1991**, *54*, 1389–1393.
11. Zdero, C.; Bohlmann, F.; Solomon, J. *Phytochemistry* **1988**, *27*, 891–897.
12. Northcote, P. T.; Andersen, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 6276–6280.
13. Hong, B.-C.; Hong, J.-H.; Tsai, Y.-C. *Angew. Chem.* **1998**, *110*, 482–484; Hong, B.-C.; Hong, J.-H.; Tsai, Y.-C. *Angew. Chem., Int. Ed.* **1998**, *37*, 468–470.
14. Corey, E. J.; Snider, B. B. *J. Am. Chem. Soc.* **1972**, *94*, 2548–2550.
15. Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207–2293.
16. Depew, K. M.; Danishefsky, S. J.; Rosen, N.; Sepp-Lorenzino, L. *J. Am. Chem. Soc.* **1996**, *118*, 12463–12464.
17. Naruta, Y.; Nishigaichi, Y.; Maruyama, K. *Org. Synth.* **1993**, *71*, 118–124.
18. Harrowven, D. C.; Guy, I. L. *Chem. Commun.* **2004**, 1968–1969.
19. *Characterization of rac-***1** *and (−)-***1**: R_f (PE/EtOAc, 1:1) = 0.17. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.67–5.62 (m, 1H, C*H*CH$_2$OH), 5.13–5.09 (m, 1H, (CH$_3$)$_2$CC*H*), 4.24–4.15 (m, 2H, C*H*$_2$OH), 4.02–3.99 (m, 1H, C*H*OH), 2.28–2.19 (m, 3H, C*H*$_2$CHOH, O*H*), 2.07 (br, 1H, O*H*), 1.73 (d, ^4J = 1.1 Hz, 3H, (*C*H$_3$)$_2$C), 1.67 (m, 3H, CC*H*$_3$), 1.64 (s, 3H, (*C*H$_3$)$_2$C). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.2 (1C, CH$_3$*C*), 135.0 (1C, (CH$_3$)$_2$*C*), 124.5 (1C, *C*HCH$_2$OH), 119.8 (1C, (CH$_3$)$_2$*C*CH), 76.4 (1C, *C*HOH), 59.0 (1C, *C*H$_2$OH), 34.1 (1C, *C*H$_2$CHOH), 25.8 (1C, (CH$_3$)$_2$C), 18.0 (1C, (*C*H$_3$)$_2$C), 12.1 (1C, *C*H$_3$C). IR (ATR): $\tilde{\nu}$ = 3319 cm^{-1} (br, m), 2968 (w), 2915 (m), 2876 (m), 2860 (m), 1671 (w), 1441 (m), 1378 (m), 1315 (w), 1096 (w), 1045 (m), 994 (s), 881 (w), 833 (w), 569 (m). UV–vis (MeOH): λ_{max} (lg ε) = 202 nm (3.97). HRMS (GC–MS): calcd $C_{10}H_{16}O$ [M−H$_2$O]$^+$: 152.1201; found: 152.1215. $[\alpha]_D^{25}$ −7.2 (*c* 0.36, acetone). CD (TFE): λ_{max} ($\Delta\varepsilon$) = 192 (−8.49), 206 (1.41), 212 nm (−0.38 mol^{-1} dm^3 cm^{-1}).
20. (−)- and (+)-MTPA–Cl were purchased from Acros. (−)-DIP–Cl and (+)-DIP-Cl were purchased from Sigma Aldrich.
21. Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092–4096.
22. Brown, H. C.; Chandrasekharan, J.; Ramachandran, P. V. *J. Am. Chem. Soc.* **1988**, *110*, 1539–1546.
23. Vigneron, J. P.; Méric, R.; Larchevêque, M.; Debal, A.; Kunesch, G.; Zagatti, P.; Gallois, M. *Tetrahedron Lett.* **1982**, *23*, 5051–5054.
24. Iriye, R.; Uno, T.; Ohwa, I.; Konishi, A. *Agric. Biol. Chem.* **1990**, *54*, 1841–1843.
25. *Characterization of (−)-(4S)-***12**: R_f (PE/EtOAc, 40:1) = 0.14. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.66 (m, 4H, *o*-Ph-*H*), 7.44–7.35 (m, 6H, *m*-Ph-*H*, *p*-Ph-*H*), 5.66–5.62 (m, 1H, OCH$_2$C*H*), 5.09 (t, ^3J = 6.9 Hz, 1H, C*H*O), 5.04–4.99 (m, 1H, (CH$_3$)$_2$CC*H*), 4.24 (d, ^3J = 5.9 Hz, 2H, OC*H*$_2$CH), 2.37–2.20 (m, 2H, C*H*$_2$CHOH), 2.03 (s, 3H, C*H*$_3$CO), 1.68 (d, ^4J = 1.1 Hz, 3H, (*CH*$_3$)$_2$C), 1.61 (d, ^4J = 0.6 Hz, 3H, (*CH*$_3$)$_2$C), 1.43 (d, ^4J = 1.1 Hz, 3H, CC*H*$_3$), 1.04 (s, 9H, (CH$_3$)$_3$C). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2 (1C, CH$_3$*C*OO), 135.6 (4C, *o*-Ph-*C*), 134.2 (1C, CHCCH$_3$), 134.2 (1C, (CH$_3$)$_2$*C*), 133.8 (2C, PhC$_q$), 129.6 (2C, *p*-Ph-*C*), 127.6 (4C, *m*-Ph-*C*), 127.3 (1C, OCH$_2$*C*H), 119.0 (1C, (CH$_3$)$_2$*C*CH), 78.1 (1C, *C*HO), 60.7 (1C, OCH$_2$CH), 31.6 (1C, *C*H$_2$CHOH), 26.8 (3C, (CH$_3$)$_3$C), 25.8 (1C, (CH$_3$)$_2$C), 21.2 (1C, *C*H$_3$COO), 19.1 (1C, (CH$_3$)$_3$*C*), 17.9 (1C, (CH$_3$)$_2$C), 12.6 (1C, *C*H$_3$C). IR (ATR): $\tilde{\nu}$ = 3072 cm^{-1} (w), 3050 (w), 2959 (w), 2932 (w), 2893 (w), 2858 (w), 1737 (m), 1471 (w), 1428 (w), 1369 (w), 1237 (s), 1110 (m), 1067(m), 1046 (m), 1019 (m), 938(w), 823 (m), 786 (w), 740 (m), 703 (s), 611 (m). UV–vis (MeOH): λ_{max} (lg ε) = 203 (4.54), 217 nm (4.27). MS (ESI): *m*/*z* (%): 473 (100), 474 (35), 475 (8). HRMS (ESI): calcd $C_{28}H_{38}O_3SiNa$ [M+Na]$^+$: 473.2488, found: 473.2495. $[\alpha]_D^{25}$ −9.6 (*c* 0.48, acetone).
26. (a) Biesalski, H.-K.; Doepner, G.; Kunz, H.; Paust, J.; John, M. *Liebigs Ann. Chem.* **1995**, 717–720; (b) Patov, S. A.; Punegov, V. V.; Kuchin, A. V.; Frolova, L. L. *Chem. Nat. Compd.* **2006**, *42*, 431–433.
27. *Characterization of (−)-(4S)-***14**: R_f (PE/EtOAc, 2:1) = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.53–5.50 (m, 1H, OCH$_2$C*H*), 5.20 (t, ^3J = 9.5 Hz, 1H, 2-*H*), 5.12–5.06 (m, 2H, COOC*H*, 4-*H*), 5.04–4.97 (m, 2H, (CH$_3$)$_2$CC*H*, 3-*H*), 4.51 (d, ^3J = 8.0 Hz, 1H, 1-*H*), 4.26–4.15 (m, 4H, OC*H*$_2$CH, 6-*H*$_2$), 3.69–3.64 (m, 1H, 5-*H*), 2.42–2.24 (m, 2H, C*H*$_2$CHO), 2.09 (s, 3H, 6-OAc), 2.05 (m, 6H, C*H*$_3$COO–CH, 4-OAc), 2.03 (s, 3H, 2-OAc), 2.00 (s, 3H, 3-OAc), 1.70 (m, 3H, (*CH*$_3$)$_2$C), 1.65 (s, 3H, CC*H*$_3$), 1.62 (s, 3H, (*CH*$_3$)$_2$C). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6 (1C, CH$_3$*C*OO–C6), 170.3 (1C, CH$_3$*C*OO–C3), 170.2 (1C, CH$_3$*C*OO–CH), 169.4 (1C, CH$_3$*C*OO–C2), 169.3 (1C, CH$_3$*C*OO–C4), 138.5 (1C, CHCCH$_3$), 134.6 (1C, (CH$_3$)$_2$*C*), 122.4 (1C, OCH$_2$*C*H), 118.7 (1C, (CH$_3$)$_2$*C*CH), 99.1 (1C, *C*1), 77.9 (1C, *C*4), 72.9 (1C, *C*2), 71.8 (1C, *C*5), 71.3 (1C, *C*3), 68.5 (1C, *C*HO), 64.9 (1C, OC*H*$_2$CH), 62.0 (1C, *C*6), 31.6 (1C, *C*H$_2$CHO), 25.8 (1C, (CH$_3$)$_2$C), 21.2 (1C, *C*H$_3$COO–CH), 20.7 (1C, *C*H$_3$COO–C6), 20.7 (1C, CH$_3$*C*OO–C4), 20.6 (1C, *C*H$_3$COO–C3), 20.6 (1C, *C*H$_3$COO–C2), 17.9 (1C, (*C*H$_3$)$_2$C), 12.7 (1C, *C*H$_3$C). IR (ATR): $\tilde{\nu}$ = 2956 cm^{-1} (w), 1743 (m), 1729 (m), 1433 (w), 1369 (m), 1210 (s), 1166 (m), 1032 (s), 962 (m), 905 (m), 824 (w), 600 (m), 559 (w). UV–vis (MeOH): λ_{max} (lg ε) = 202 nm (4.05). MS (ESI): *m*/*z* (%): 565 (100) [M+Na]$^+$, 566 (26), 567 (6). HRMS (ESI): calcd $C_{26}H_{42}O_{12}N$ [M+NH$_4$]$^+$: 560.2702, found: 560.2708. $[\alpha]_D^{25}$ −24.5 (*c* 1.0, acetone). CD (TFE): λ_{max} ($\Delta\varepsilon$) = 192 (−39.40), 208 nm (−5.65 mol^{-1} dm^3 cm^{-1}).
28. Satgé, C.; Le Bras, J.; Hénin, F.; Muzart, J. *Tetrahedron* **2005**, *61*, 8405–8409.
29. X-ray structure analysis of the ethanol solvate of pentaacetylrosiridin [(4*S*)-**14**]. Crystal data: $C_{28}H_{44}O_{13}$, monoclinic, $P2_1$, a = 11.8096(5), b = 7.4452(4), c = 17.3830(6) Å, β = 90.394(2)°, Z = 2, T = 100 K. A colorless plate 0.3 × 0.2 × 0.04 mm was used to record a total of 20,498 data to 2θ (max) 144° (99.9% complete to 135°) using Cu Kα radiation on an Oxford Diffraction Nova O diffractometer. The structure was refined using the program SHELXL-97 (G.M. Sheldrick, University of Göttingen, Germany) to wR_2 0.073, R_1 0.029 (all data) for 5390 independent data and 380 parameters. The ethanol molecule was disordered over two positions. The Flack parameter refined to 0.06 (10), thus determining the absolute configuration on the basis of the anomalous dispersion of oxygen. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-691291. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.camac.uk).