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Reduction of Diene Adducts of Laevopimaric Acid

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Summary. Diene adducts of laevopimaric acid with maleic anhydride or fumaric acid were reduced with $LiAlH_4$. Besides a triol, a monoacid and the corresponding lactone were obtained from the maleic acid adduct. The fumaric acid adduct afforded two triols with different configuration at C-16. Regioselective reduction of the maleic anhydride adduct with $NaBH_4$ gave a lactone.

Keywords. Diene adducts; Fumaric acid; Laevopimaric acid; Maleic anhydride; Selective reduction.

Reduktion von Dienaddukten der Lävopimarsäsure

Zusammenfassung. Bei der Reduktion mit $LiAlH_4$ gingen die Addukte der Lävopimarsäure mit Maleinsäureanhydrid bzw. Fumarsäure in ein Triol, eine Monocarbonsäure und das entsprechende Lacton über. Das Fumarsäureaddukt lieferte zwei Triole mit unterschiedlicher Konfiguration an C-16. Regioselektive Reduktion des Maleinsäureanhydridaddukts mit $NaBH_4$ ergab ein Lacton.

Introduction

The *Diels-Alder* adduct of abietic acid and maleic anhydride is used in technical chemistry for paper sizing. During the reaction, abietic acid is isomerized to laevopimaric acid. The corresponding methyl ester adduct **1** has been reduced with $LiAlH_4$ by *Sandermann* and *Striesow* [1]. They obtained triol **2** and a dihydroxy carboxylic acid in which one of the anhydride carboxyl groups was selectively converted to an alcohol. However, the authors could not determine the structure unambiguously; therefore, formulae **3** and **4** were given for the product. In order to clarify this point, we treated maleopimaric anhydride (**1**) and fumaropimaric acid (**7**) with lithium aluminum hydride and determined the structure of the reaction products.

Results and Discussion

Reduction of **1** *with* $LiAlH_4$

Reduction of **1** with $LiAlH_4$ in dimethoxyethane gave a mixture of triol **2** and two other compounds. **2** has already been described in the literature [1, 2]. We

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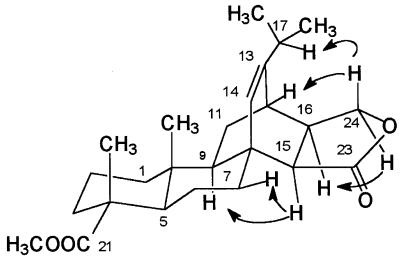
identified one of the two byproducts as the acid **3** on account of its ^{1}H NMR spectrum. Since H-15 gave a dublet, it was obvious that the carboxyl group was attached to C-15. This was confirmed by NOE experiments. Irradiation of the resonance of the protons at C-24 gave NOE signals at H-17 and CH_3-18/19, clearly demonstrating the hydroxymethyl group being attached to C-16. We therefore assigned structure **3** to the hydroxy acid described in Ref. [1]. During the NMR experiments we observed that **3** is slowly converted to a new compound which could be shown to be identical with the third product (**5**) obtained in this reaction.

Compound **5** exhibits an IR absorption at 1756 cm^{-1}, indicating a tricylic γ-lactone [3]. Likewise, a lactone has been discussed [1] as an intermediate during reduction of **1** with $LiAlH_4$ similar to the reduction of citraconopimarate with $NaBH_4$ [2]. The ^{1}H NMR spectrum of **5** shows two AB spin systems in the region between 3.0 and 3.4 ppm. Both have a coupling constant typical for a geminal arrangement of the protons. One of them has no further coupling and was therefore assigned to CH_2OH-21. The second one shows couplings to H-16 in a COSY experiment and was assigned to CH_2OH-24. With the aid of NOE experiments we could distinguish between the two diastereotopic protons of CH_2OH-24. Saturation of the resonance of H-17 gave an NOE at the high field part of this AB system (3.81 ppm); from a molecular model one can assign this resonance to H(pro-*R*)-24. Irradiation of H-16 gave an NOE at the corresponding low field part (4.29 ppm); therefore this is the resonance of H(pro-*S*)-24. Further NOE experiments proved that the protons in position 15 and 16 are oriented *cis* with respect to each other. From H-15 we obtained NOE correlations to H-16, H-9, and H-11_{ax}. Starting from H-16, NOE enhancements at H-15 and H-11_{ax} were observed. The mass spectrum shows a base peak at 288 as the result of H_2O elimination and *retro-Diels-Alder* fragmentation of the molecule ion.

Reduction of **1** *with* $NaBH_4$

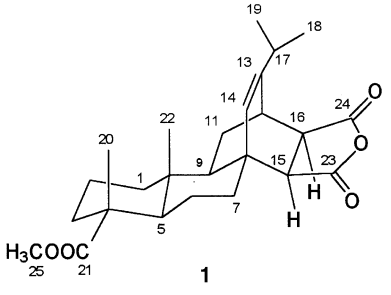
The reaction of **1** with $NaBH_4$ in dioxane has been described by *Maciejewski* et al. [4]. A lactone as product has been reported; however, the structure given indicates that carbonyl group 23 was reduced by the hydride. This is in contrast to our results which show that $LiAlH_4$ attacks the sterically less hindered CO-24 first. Therefore we repeated the reduction of **1** with $NaBH_4$ under the conditions mentioned in Ref. [2]. The product has the same melting point and identical physical constants as described in literature. After assignment of the ^{1}H and ^{13}C resonances we obtained evidence that in fact CO-24 and not CO-23 is reduced by sodium borohydride and that the correct structure for the product is that given in formula **6**. The lactone carbonyl group is attached to C-15. This is indicated by the high frequency shift of H-7_{eq} ($\delta = 2.64$ ppm). This proton is close in space to CO-23, and its resonance is shifted by the anisotropy effect of the carbonyl group. We assume that this steric influence is the origin of the regioselectivity of the hydride reduction of these compounds. These results were corroborated by NOE measurements; the observed correlations are indicated in the following formula.



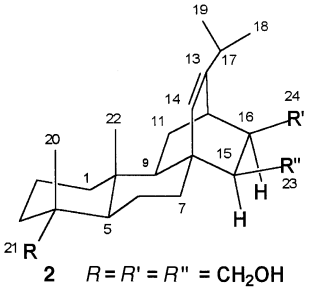
NOE correlations found in **6**

Reduction of **7** *with* $LiAlH_4$

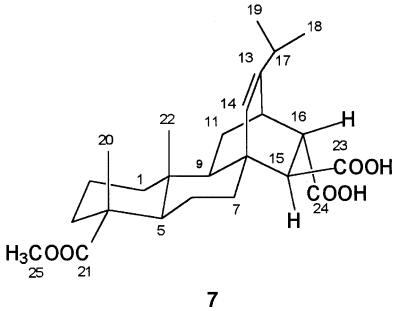
When **7** was reduced with $LiAlH_4$ in dimethoxyethane at 0°C, the *cis*-triol **2** was obtained in 63% yield. This indicates a fast base-catalyzed isomerization at C-16 before reduction of the carboxyl group. However, if a solution of **6** was added to $LiAlH_4$, no *cis*-triol **2** was formed. Instead, the *trans*-triol **8** (51%) was obtained. The ^1H NMR spectrum of **8** showed the typical AB systems for the three CH_2OH groups. NOE experiments allowed to assign the resonances. Irradiation of the proton signals of CH_2-24 gave an NOE enhancement at H-11_{ax}, proving (*R*)



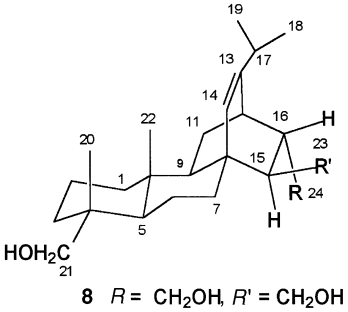
1



2 *R* = *R'* = *R"* = CH_2OH
3 *R* = *R'* = CH_2OH, *R"* = COOH
4 *R'* = COOH, *R* = *R"* = CH_2OH
5 *R* = CH_2OH, *R'*-*R"* = CH_2O-CO
6 *R* = CO_2CH_3 *R'*-*R"* = CH_2O-CO



7



8 *R* = CH_2OH, *R'* = CH_2OH

Scheme

configuration at C-16. NOE correlations between the olefinic proton H-14 and CH_2-23 confirm (*R*) configuration at C-15. α-Orientation of C-24 is also indicated by a low-frequency shift (6.3 ppm) of ^{13}C resonance of C-11 compared to triol **2**. This shift difference is typical for the γ-gauche effect in rigid systems [5].

Experimental

Analytical methods

Melting points: melting point apparatus Dr. Tottoli, uncorrected; optical rotation: polarimeter 241 MC (Perkin Elmer); MS: Varian MAT 711 spectrometer (70 eV electron impact and field desorption); IR spectra; infrared spectrometer System 2000 FT (Perkin Elmer); UV/Vis: Lambda 17 UV/Vis spectrometer (Perkin Elmer); NMR spectra: Varian Inova 400, 600 (297 K), 5 mm tubes, solvent resonance as internal standard. ^1H and ^{13}C resonances were assigned using $^1H,^1H$ and $^1H,^{13}C$ correlation spectra. For NOE measurements, oxygen was carefully removed by bubbling Ar through the solutions. ^1H and ^{13}C resonances are numbered as given in the formulas. Elemental analyses: Laboratory for Microanalysis, Institute of Physical Chemistry, University of Vienna; their found values were in satisfactory agreement with the calculated ones. Thin-layer chromatography (TLC): TLC plates (Merck) Kieselgel 60 F_{254} 0.2 mm 200×200 mm; the substances were detected in UV light at 254 nm and by spraying with MeOH/sulfuric acid (9:1) and subsequent heating with a heat gun. 1,2-Dimethoxyethane was dried by refluxing with CaH_2 and subsequent distillation [6]. Methyl 13-(1-methylethyl)-17,18-dinoratis-13-ene-4,15β,16β-tricarboxylic acid 15,16-anhydride-4-carboxylate (**1**) and 13-(1-methylethyl)-17,18-dinoratis-13-ene-4-methoxycarbonyl-15α,16β-dicarboxylic acid (**7**) were obtained by *Diels-Alder* addition of maleic anhydride and fumaric acid to abietic acid methyl ester, respectively, as described in Refs. [7–9].

15β-Hydroxymethyl-13-(1-methylethyl)-16αH-atis-13-ene-17,19-diol (**2**; $C_{24}H_{40}O_3$), *13-(1-Methylethyl)-16αH-atis-13-ene-17,18-dihydroxy-15β-carboxylic acid* (**3**; $C_{24}H_{38}O_4$) *and 13-(1-Methylethyl)-16αH-atis-13-ene-17,18-dihydroxy-15β-carboxylic acid-15,16-lactone* (**5**; $C_{24}H_{36}O_3$)

2 g (5 mmol) of **1** were dissolved in 100 ml dimethoxyethane; this solution was added dropwise to 3 g (79 mmol) $LiAlH_4$ during cooling with ice. This mixture was stirred and heated on a water bath for 45 min. The mixture was cooled, and ice was added gradually. After addition of conc. HCl and extraction with Et_2O (five times), the organic phases were dried over Na_2SO_4. The solvent was removed by evaporation, and 1.7 g of a white solid were obtained. This solid was dissolved in 250 ml $CHCl_3$, and the solution was extracted five times with 2 *N* NaOH. The organic layer was dried over Na_2SO_4, evaporated, and the residue was recrystallized from acetone. Yield: 380 mg (20.4%) **2** (white crystals).

The aqueous phase was acidified with HCI and extracted four times with Et_2O. Evaporation gave 300 mg **5** (18%) as a pale yellow solid which was recrystallized from EtOH. From the acidified aqueous phase a white solid separated after a few minutes which was recrystallized from EtOH. Yield: 560 mg (29.3%) **3**.

2: M.p.: 170°C (Refs. [1,8]: m.p.: 169–172°C); $R_f = 0.67$ (acetone); $[\alpha]_D^{20} = +5.50°$, $[\alpha]_{546}^{20} = +6.04°$ ($c = 0.9$, CH_3OH); IR (KBr): $\bar{\nu} = 3283$ (s), 2954 (s), 2928 (s), 2867 (s), 1463 (m), 1383 (m), 1358 (m); 1032 (s) cm^{-1}; ^1H NMR (400 MHz, δ, $CDCl_3$): 0.56 (s, 3H, 22-H), 0.70 (s, 3H, 20-H), 0.76–0.83 (m, 1H, 1-H_{ax}), 0.97, 0.98 (2d, $J =$ 6.8 Hz, 6H, 18-H, 19-H), 1.05–1.10 (m, 1H, 11-H_{eq}), 1.15–1.23 (m, 2H, 3-H_{ax}, 5-H), 1.28–1.32 (m, 1H, 9-H), 1.34–1.51 (m, 7H, 1-H_{eq}, 2-H, 3-H_{eq}, 6-H, 7-H_{ax}), 1.62 (ddd, J = 12.5, 9.9, 2.7 Hz, 1H, 11-H_{ax}), 1.83 (dt, $J =$ 9.7, 2.0 Hz, 1H, 15-H),

1.99–2.03 (m, 1H, 7-H$_{eq}$), 2.13–2.25 (m, 2H, 16-H, 17-H), 2.33 (br s, 1H, 12-H), 3.03 (d, $J = 10.9$ Hz, 1H, 21-H), 3.40 (d, $J = 10.9$ Hz, 1H, 21-H), 3.41 (dd, $J = 11.2$, 9.7 H, 1H, 23-H), 3.48 (dd, $J = 11.3$, 3.8 Hz, 1H, 24-H), 3.55 (t, $J = 11.3$ Hz, 1H, 24-H), 3.74 (dd, $J = 11.2$, 2.0 Hz, 1H, 23-H), 5.36 (s, 1H, 14-H) ppm; ^{13}C NMR (100 MHz, δ, $CDCl_3$): 15.91 (C-22), 17.31 (C-2), 17.85 (C-20), 19.37 (C-6), 20.45, 21.12 (C-18, C-19), 30.41 (C-11), 33.14 (C-17), 35.16 (C-3), 36.31 (C-7), 37.24 (C-4), 37.91 (C-10), 38.09 (C-12), 38.80 (C-1), 39.96 (C-8), 45.70 (C-16), 47.51 (C-5), 54.25 (C-15), 55.13 (C-9), 61.00 (C-23), 65.54 (C-24), 71.70 (C-21), 124.86 (C-14), 147.87 (C-13) ppm; MS (70 eV): *m/z* (%) = 376 [M^+] (5.3), 358 (9.5), 327 (1.5), 289 (13.6), 288 (100.0), 271 (13.4), 257 (22.0), 253 (3.0), 215 (3.8), 187 (5.3), 159 (5.7), 133 (18.9), 123 (7.6), 95 (6.8), 91 (9.1), 81 (6.1), 55 (5.3), 43 (9.8).

3: M.p.: 168°C (Ref. [1]: m.p.: 171–173°C); $R_f = 0.58$ (acetone); $[\alpha]_D^{20} = +23.5°$, $[\alpha]_{546}^{20} = +27.5°$ ($c = 0.9$, CH_3OH); IR (KBr): $\bar{\nu} = 3428$ (s), 2934 (s), 2878 (s), 2864 (s), 1708 (s), 1467 (w), 1447 (w), 1382 (w), 1336 (w), 1245 (w), 1194 (m), 1039 (m) cm^{-1}; ^{1}H NMR (400 MHz, δ, CD_3OD): 0.70 (s, 3H, 22-H), 0.78 (s, 3H, 20-H), 0.85–0.91 (m, 1H, 1-H$_{ax}$), 1.11, 1.13 (2d, $J = 6.8$ Hz, 6H, 18-H, 19-H), 1.24–1.68 (m, 10H, 1-H$_{eq}$, 2-H, 3-H, 5-H, 7-H$_{ax}$, 9-H, 11-H), 2.01–2.05 (m, 1H, 7-H$_{eq}$), 2.20–2.26 (m, 1H, 16-H), 2.32 (sept, $J = 6.8$ Hz, 1H, 17-H), 2.54 (d, $J = 10.9$ Hz, 15-H), 2.71 (br s, 1H, 12-H), 3.04 (d, $J = 10.9$ Hz, 1H, 21-H), 3.26 (t, $J = 9.8$ Hz, 1H, 24-H), 3.32–3.36 (m, 1H, 24-H), 3.39 (d, $J = 10.9$ Hz, 1H, 21-H), 5.53 (s, 1H, 14-H) ppm; ^{13}C NMR (100 MHz, δ, CD_3OD): 17.17 (C-22), 18.53 (C-20), 18.71 (C-2), 20.27 (C-6), 20.83, 21.83 (C-18, C-19), 30.19 (C-11), 34.75 (C-17), 36.05 (C-7), 36.75 (C-3), 36.87 (C-12), 38.64 (C-4), 39.50 (C-10), 40.10 (C-1), 41.58 (C-8), 46.99 (C-16), 49.57 (C-5), 57.07 (C-9), 58.13 (C-15), 64.46 (C-24), 72.37 (C-21), 126.80 (C-14), 147.15 (C-13), 176.61 (C-23) ppm; MS (70 eV): *m/z* (%) = 372 (8.3) [M^+-H_2O], 357 (1.5), 341 (7.5), 327 (1.1), 299 (0.8), 289 (15.0), 288 (100.0), 270 (1.5), 257 (7.5), 245 (2.3), 227 (1.5), 215 (2.2), 185 (1.5), 173 (3.0), 146 (6.0), 133 (10.5), 111 (5.3), 95 (4.5), 91 (7.5), 81 (4.5), 55 (3.8), 43 (4.5).

5: M.p.: 164–167°C; $R_f = 0.79$ (acetone); $[\alpha]_D^{20} = +34.2°$, $[\alpha]_{546}^{20} = +38.4°$ ($c = 0.17$, CH_3OH); IR (KBr): $\bar{\nu} =$ 3582 (s), 2954 (s), 1756 (s), 1467 (m), 1381 (m), 1247 (m), 1162 (s), 1047 (s), 1005 (s), 850 (w), 687 (w), 572 (w) cm^{-1}; ^{1}H NMR (400 MHz, δ, CD_3OD): 0.70 (s, 3H, 22-H), 0.79 (s, 3H, 20-H), 0.87–0.95 (m, 1H, 1-H$_{ax}$), 1.11 (d, $J = 6.9$ Hz, 6H, 18-H, 19-H), 1.22 (ddd, $J = 13.0$, 5.8, 3.1 Hz, 1H, 11-H$_{eq}$), 1.25–1.64 (m, 10H, 1-H$_{eq}$, 2-H, 3-H, 5-H, 6-H, 7-H$_{ax}$, 9-H), 1.66 (ddd, $J = 13.0$, 9.6, 2.7 Hz, 1H, 11-H$_{ax}$), 2.35 (sept, $J = 6.7$ Hz, 1H, 17-H), 2.48 (d, $J = 9.9$ Hz, 15-H), 2.62–2.66 (m, 1H, 7-H$_{eq}$), 2.67 (br s, 1H, 12-H), 2.78 (dddd, $J = 9.9$, 9.2, 3.6, 3.1 Hz, 16-H), 3.06 (d, $J = 11.1$ Hz, 1H, 21-H), 3.42 (d, $J = 11.1$ Hz, 1H, 21-H), 3.81 (dd, $J = 9.2$, 3.6 Hz, 1H, 24-H$_{proR}$), 4.29 (t, $J = 9.2$ Hz, 1H, 24-H$_{proS}$), 5.59 (s, 1H, 14-H) ppm; ^{13}C NMR (100 MHz, δ, CD_3OD): 16.78 (C-22), 18.60 (C-20), 18.71 (C-2), 20.26 (C-6), 21.02, 21.87 (C-18, C-19), 29.75 (C-11), 35.35 (C-17), 36.38 (C-7), 36.67 (C-3), 38.63(C-4), 39.26 (C-12), 39.42 (C-10), 40.34 (C-1, C-16), 41.13 (C-8), 49.30 (C-5), 54.24 (C-15), 55.38 (C-9), 72.33 (C-21), 72.95 (C-24), 127.40 (C-14), 149.18 (C-13), 180.79 (C-23) ppm; MS (70 eV): *m/z* (%) = 372 [M^+] (12.1), 357 (3.0), 341 (8.7), 327 (1.5), 299 (0.8), 289 (12.1), 288 (100.0), 270 (1.9), 257 (12.1), 245 (2.3), 219 (1.5), 215 (2.3), 187 (1.5), 161 (2.6), 146 (4.5), 133 (9.1), 111 (3.8), 91 (3.0), 81 (2.3), 55 (1.5), 43 (2.3).

Preparation of **2** *from* **7**

0.9 g (2.2 mmol) **7** were dissolved in 100 ml dimethoxyethane; this mixture was added dropwise to 3 g (79 mmol) $LiAlH_4$ in undercooling with ice. This mixture was stirred and heated on a water bath for 90 min and then cooled. Ice water and conc. HCl were added before the mixture was extracted five times with $CHCl_3$. The organic phase was dried over Na_2SO_4 and evaporated. The white residue was recrystallized from acetone; yield: 520 mg (63%) **2**. The substance was identical with the product obtained from **1** (see above) as established by means of a mixed melting point and spectroscopic data.

Methyl 13-(1-methylethyl)-16αH-18-noratis-13-ene-17,18-dihydroxy-4,15β-dicarboxylic-acid-15,16-lactone-4-carboxylate (**6**; $C_{25}H_{38}O_3$)

Preparation according to Ref. [2]; m.p.: 165.5–166.5°C (Ref. [2]: 166–167°C); ^{1}H NMR (400 MHz, δ, $CDCl_3$): 0.56 (s, 3H, 22-H), 0.86–0.95 (m, 1H, 1-H_{ax}), 1.01, 1.02 (2d, $J = 6.8$ Hz, 6H, 18-H, 19-H), 1.08–1.17 (m, 5H, 2-H, 11-H_{eq}, 20-H), 1.32–1.60 (m, 8H, 1-H_{eq}, 2-H, 3-H_{ax}, 6-H, 7-H_{ax}, 9-H, 11-H_{ax}) 1.66 (dd, $J = 13.4$, 4.6 Hz, 1H, 3-H_{eq}), 1.71 (dd, 11.7, 1.8 Hz, 1H, 5-H), 2.23 (sept, $J = 6.8$ Hz, 1H, 17-H), 2.55 (br s, 1H, 12-H), 2.58–2.68 (m, 2H, 7-H_{eq}, 16-H), 3.63 (s, 3H, 25-H), 3.69 (dd, $J =$ 9.4, 3.9 Hz, 1H, 24-H_{proR}), 4.18 (t, $J = 9.4$ Hz, 1H, 24-H_{proS}), 5.51 (s, 1H, 14-H) ppm; ^{13}C NMR (100 MHz, δ, $CDCl_3$): 15.49 (C-22), 16.73 (C-20), 17.03 (C-6), 20.16, 20.97 (C-18, C-19), 21.74 (C-2), 27.89 (C-11), 33.80 (C-17), 34.63 (C-7), 36.64 (C-3), 37.39 (C-12), 37.59 (C-10), 38.12 (C-1), 38.73 (C-16), 39.74 (C-8), 47.13 (C-4), 49.59 (C-5), 51.87 (C-25), 52.19 (C-15), 53.92 (C-9), 70.78 (C-24), 125.81 (C-14), 147.05 (C-13), 177.59 (C-23), 179.18 (C-21) ppm.

13-(1-Methylethyl)-15β-hydroxymethyl-atis-13-ene-17,18-diol (**8**; $C_{24}H_{40}O_3$)

1.1 g (2.6 mmol) **7** were dissolved in 55 ml dimethoxyethane; this solution was added dropwise to 1.5 g (40 mmol) $LiAlH_4$ under cooling with ice. After heating for 15 min on a water bath and recooling, ice and water were added, and the mixture was acidified with conc. HCl and extracted three times with Et_2O. The organic phase was dried over Na_2SO_4 and evaporated. A white residue was obtained and recrystallized from acetone.

Yield: 503 mg (51%); $R_f = 0.76$ (acetone); m.p.: 205°C (acetone); $[\alpha]_D^{20} = -16.3°$, $[\alpha]_{546}^{20} = -19.9°$, ($c = 0.9$, CH_3OH); IR (KBr): $\bar{\nu} = 3303$ (s), 3265 (s), 2943 (s), 2902 (s), 2889 (s), 2852 (s), 1462 (m), 1442 (m), 1383 (m), 1078 (m), 1042 (s), 1007 (s), 841 (m), 664 (m) cm^{-1}; ^{1}H NMR (400 MHz, δ, CD_3OD): 0.71 (s, 3H, 22-H), 0.78 (s, 3H, 20-H), 0.84–0.92 (m, 1H, 1-H_{ax}), 0.98–1.05 (m, 2H, 11-H_{eq}, 15-H), 1.10 (d, $J = 6.5$ Hz, 6H, 18-H, 19-H), 1.23–1.27 (m, 2H, 5-H, 9-H), 1.37–1.63 (m, 7H, 1-H_{eq}, 2-H, 6-H, 7-H_{ax}, 16-H), 1.78 (ddd, $J =$ 13.3, 9.9, 2.8 Hz, 1H, 11-H_{ax}) 1.92–1.96 (m, 1H, 7-H_{eq}), 2.39 (sept, $J = 6.5$ Hz, 1H, 17-H), 2.60 (br s, 1H, 12-H), 2.92 (t, $J = 9.9$ Hz, 1H, 23-H), 3.05 (d, $J = 10.9$ Hz, 1H, 21-H), 3.38 (d, $J = 10.9$ Hz, 1H, 21-H), 3.51 (dd, $J = 10.0$, 8.8 Hz, 1H, 24-H), 3.64 (dd, $J = 10.0$, 7.4 Hz, 1H, 24-H), 3.70 (dd, $J = 9.9$, 4.8 Hz, 1H, 23-H), 5.40 (s, 1H, 14-H) ppm; ^{13}C NMR (100 MHz, δ, CD_3OD): 17.10 (C-22), 18.56 (C-20), 18.73 (C-2), 20.51 (C-6), 21.48, 21.52 (C-18, C-19), 24.09 (C-11), 34.32 (C-17), 35.79 (C-12), 36.76 (C-3), 37.00 (C-7), 38.59 (C-4), 39.39 (C-10), 40.32 (C-1), 41.43 (C-8), 46.36 (C-16), 49.30 (C-5), 56.37 (C-15), 57.53 (C-9), 65.63 (C-23), 66.68 (C-24), 72.41 (C-21), 126.06 (C-14), 151.43 (C-13) ppm; MS (70 eV): *m/z* (%) = 376 [M^+] (13.6), 358 (1.9), 343 (2.3), 315 (1.5), 297 (2.3), 290 (2.3), 288 (100.0), 271 (18.1), 257 (17.4), 245 (1.5), 227 (2.6), 215 (3.8), 187 (6.0), 173 (11.3), 148 (12.1), 146 (16.2), 133 (37.4), 123 (20.4), 95 (14.3), 91 (21.1), 81 (14.3), 55 (9.1), 43 (12.8).

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