Pergamon

Tetrahedron: Asymmetry Vol. 5, No. 5, pp. 879-886, 1994

0957-4166/94 $7.00+0.00

0957-4166(94)E0116-R

Highly Diastereoselective Addition of Photochemically Generated Radicals to (5R)-(-)-Menthyloxy-2[5H]-furanone - Synthesis of (-)-Terebic Acid

Norbert Hoffmann[x]

Institut für Organische Chemie der RWTH Aachen, Prof.-Pirlet-Str. 1, D-52054 Aachen, Germany.

***Abstract*:** Photochemically generated ketyl and 2-dioxolanyl radicals are added with high diastereoselectivity (de > 95 %) to (5R)-(-)-5-menthyloxy-2[5H]-furanone. This reaction is used for the asymmetric synthesis of (-)-terebic acid. The double bond is attacked by the radicals on the ul-side.

Introduction

In the methodology of organic synthesis, the addition of radicals to α,β-unsaturated carbonyl and carboxyl compounds is an interesting complement to the Michael addition[1]. Therefore the stereoselectivity of this reaction has been investigated intensively[2]. This publication reports upon high diastereoselectivity in the addition of photochemically generated radicals to (5R)-(-)-5-menthyloxy-2[5H]-furanone 1[3] (Figure 1). Whilst 1 reacts with high diastereoselectivity in Diels-Alder reactions, polar Michael-additions, additions of carbenoid species and 1,3-dipolar addition reactions[4], the addition of ethylene to ($^3\pi\pi^*$)-excited 1 and other alkoxyfuranones proceeds with low diastereoselectivity[3c,5]. Because of its multifunctionality, 1 is an interesting synthon for the synthesis of natural products and compounds with biological activity[3c,4,5b].

Hydroxyalkyl radicals are easily generated from alcohols by H-abstraction with ($^3\pi\pi^*$)-excited carbonyl compounds. The addition reaction of these radicals to derivatives of fumaric and maleic acid has been used in the synthesis of racemic terebic acid and enantiomerically enriched derivatives of terebic acid[7].

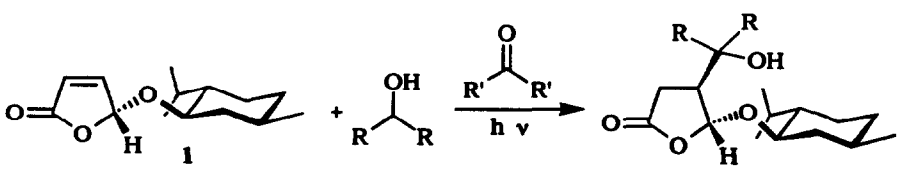
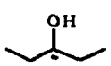


Figure 1: Diastereoselective photochemical addition of secondary alcohols to (5R)-(-)-5-menthyloxy-2[5H]-furanone 1 on the ul-side.

Results and discussion

1 and a small quantity of ketone (in most cases acetone) were dissolved in the corresponding secondary alcohol or in 1,3-dioxolane. The solutions were irradiated through a pyrex filter. The diastereoselectivity as well as the product ratio, which results from the competive reactions of two different ketyl radicals (generated from the alcohol and the ketone), were measured by ^{13}C-NMR spectroscopy from samples of the crude products. In all cases, the diastereoselectivity was >95%. The products were purified for further characterization (Table 1).

Table 1: Reaction of photochemically generated radicals to (5R)-(-)-5-menthyloxy-2[5H]-furanone **1**.

n°	R·	yield[1]	formation of **2**[2]	mp	[α]
1		93 %	100%	85 - 87 °C	$[\alpha]_D^{21}$ = -150 (C = 1.056, $CHCl_3$)
2		51 %	12 %	syrup	$[\alpha]_D^{21}$ = -141 (C = 1.036, $CHCl_3$)
3		82 %	< 3 %	121 °C	$[\alpha]_D^{21}$ = -143 (C = 0.970, $CHCl_3$)
4		62 %	5.5 %	128 - 130 °C	$[\alpha]_D^{22}$ = -103 (C = 0.991, $CHCl_3$)
5		70 %	6 %	108 °C	$[\alpha]_D^{21}$ = -144 (C = 1.006, $CHCl_3$)

[1]yield of purified products, [2] ratio of the products from the radical addition

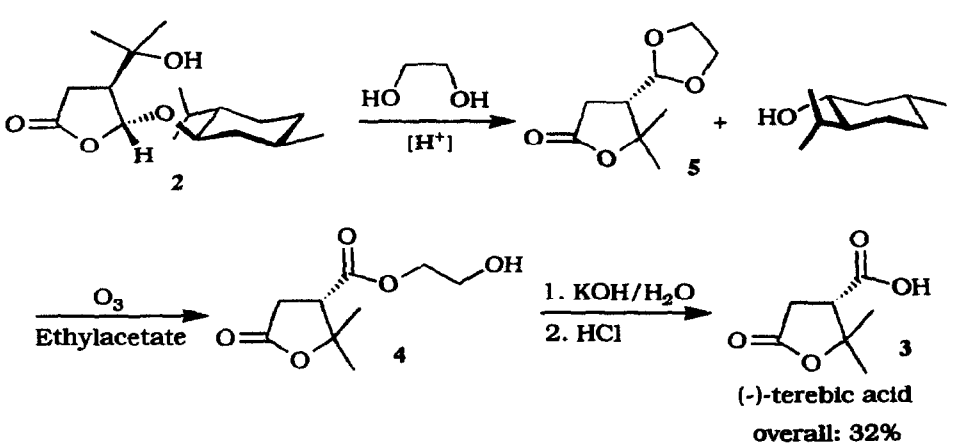
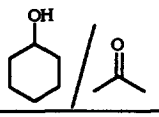
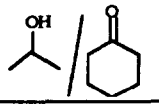


Figure 2: Synthesis of (-)-terebic acid **3** from 4-(2'-hydroxy-2'-propyl)-5-(-)-menthyloxyfuranone **2**.

In order to determine the side of the attack, **2** was converted into (-)-terebic acid **3** (Figure 2). The sense of optical rotation and the absolute configuration are known for this compound[8]. After reaction of **2** with glycol, the glycol ester **4** of the terebic acid was obtained by ozonolysis[9] of the dioxolane **5**. Saponification yielded the (-)-terebic acid **3**. These reactions can be carried out without isolation of the intermediate products. Thus **1** is attacked at the ul-side by the radicals.

Table 2: Competition reaction of hydroxy alkylradicals resulting from the alcohol and the sensitizer (ketone).

	volumes (ml)	competition products[1]
	80/20	13 %
	100/1	5.5 %
	95/5	< 3 %

[1]portion of the products from the addition of radicals resulting from the ketone sensitizer.

In all investigated cases, acetone was used as the sensitizer. Consequently **2** was observed as a competitive product (n° 2,4,5, Table 1). The resulting ratios of products (Table 1) correlate with the reactivity of the different radicals. The formation of **2** is also enhanced by increasing the concentration of acetone. To show these relationships, cyclohexanone has also been used as sensitizer in the reaction of **1** with isopropanol (Table 2). The side product, which results from the reaction of **1** with 1-hydroxy-1-cyclohexyl radicals (n° 4, Table 1), was not observed in this case.

From this results, it can be concluded, that 2-hydroxy-isopropyl radicals are more reactive than the 1-hydroxy-1-cyclohexyl radicals. Consequently, the enhanced formation of **2** in the reaction of **1** with 3-pentanol (n° 2, Table 1) can be attributed to the relatively low reactivity of the corresponding 3-hydroxy-3-pentyl radicals in the addition to **1**. 1-Hydroxy-1-cyclopentyl radicals (n° 3, Table 1) has the same or a higher reactivity as 2-hydroxyisopropyl radicals. Since the electronic effects of radical stabilization are comparable in the investigated systems (n° 1 - 4, Table 1), the different reactivities are a consequence of the different steric and entropic effects (degrees of freedom in the substituents)[10]. The degree of reactivity of 1,3-dioxolan-1-yl radicals (n° 5, Table 1) is about the same as that of 1-hydroxy-1-cyclohexyl radicals (n° 4, Table 1). Kinetic studies of the reaction of 5-ethoxy-2[5H]-furanone **6** with isopropanol (Figure 3) have proved that the time for complete conversion is decoupled in the absence of acetone. The remaining reactivity may result from sensitization by the furanones **1** or **6**. The investigated substrates don't react in the dark.

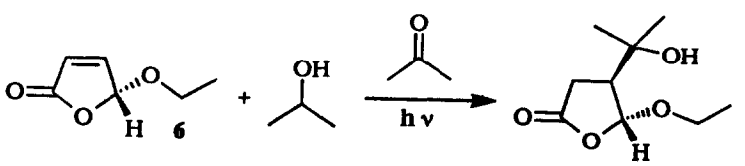


Figure 3: Photosensitized addition of isopropanol to 5-ethoxy-2[5H]-furanone **6**.

This result as well as the fact that the reaction is also very efficient if acetone is used in low concentrations and that the starting solutions can be irradiated trough a pyrex filter are arguments for a radical chain mechanism[11] (Figure 4), as was pointed out by Pitts et al.[12]

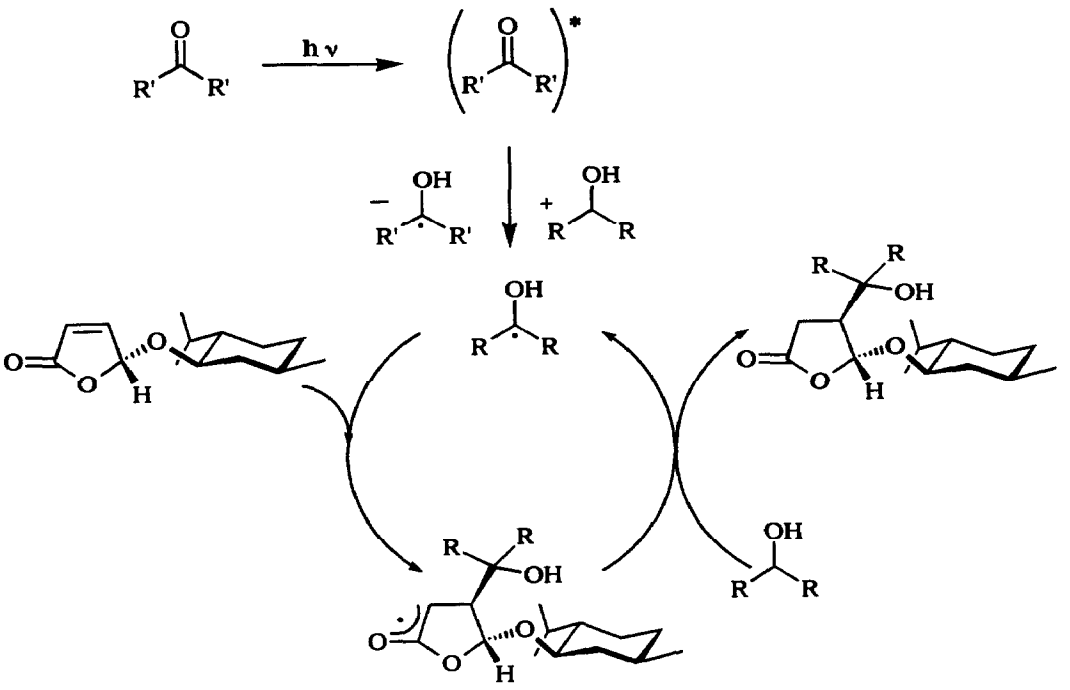


Figure 4: Radical chain mechanism of the reaction of hydroxyalkyl radicals generated by photochemical H-abstraction at secundary alcohols.

ACKNOWLEDGEMENTS

I am grateful to Prof. Dr. Hans-Dieter Scharf for an employment after finishing my Ph.D.-thesis, which enabled me to accomplish this research. I thank cand.-chem. Athanasios Kokorakis and cand.-chem. Robert Sauer for their assistance and Dipl.-Chem. Peter Esser and Désirée Gilliam for their help with the large scale synthesis of 1.

Experimental Section

General remarks

NMR-spectra: Varian VXR 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz, internal standard: TMS, solvent $CDCl_3$); IR-spectra: Perkin Elmer PE 1750 FT; mass spectra: Varian MAT 212 (70 eV); specific rotation: Perkin Elmer 241; melting points: Büchi 510; gas chromatography (determination of conversion): Hewlett Packard 5890 Series II (column: HP-FFAP, 25 m x 0.3 mm); TLC: Merck DC-Alufolien Kieselgel 60 F_{254}.

Irradiations were carried out under nitrogen with a high pressure mercury lamp (HPK 150 W, Philips) in a

photoreactor fitted with a pyrex immersion well. The solutions were flushed with nitrogen for about 0.5 h before the irradiation started. The temperature of the solutions was about 15 °C.

General procedure for hydroxyalkyl radical addition to **1** *(Table 1)*

1 g of **1** and 1 ml acetone were dissolved in 100 ml of the secondary alcohol or 1,3-dioxolane. The solutions were irradiated for 1 h. The solvent was evaporated in vacuo. Small quantities of cyclohexanol or cyclopentanol were removed by azeotropic distillation with water. The product ratios were determined by ^{13}C-NMR spectroscopy of the crude material. The solid products were recrystallized from cyclohexane. The reaction product from pentanol-3 was chromatographed (100 ml Kieselgel 60, (Merck) eluent: 10% ethyl acetate/hexane).

General procedure for the competition experiments (Table 2)

1 g of **1** was dissolved in a mixture of alcohol and ketone. The reaction mixture was irradiated until the conversion was complete (as indicated by TLC, eluent: 20 % ethyl acetate/hexane). The ratio of products was determined from the crude material as described above.

Reaction of **5** *with isopropanol*

2.56 g of **5** and 1 ml acetone were dissolved in 140 ml isopropanol. The conversion was complete afer 50 min of irradiation. 2.56 g of **5** was dissolved in 140 ml isopropanol without addition of acetone. 7 h of irradiation were needed for complete conversion.

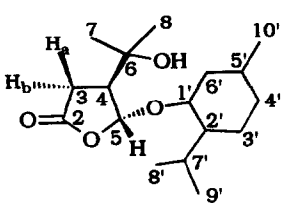
5.1 g of **5** in 140 ml isopropanol with 1 ml of acetone needed 120 min for complete conversion, while the same quantities of **5** and isopropanol with 2 ml acetone needed only 70 min . The conversion was followed by GC.

Synthesis of terebic acid **3**

23.8 g of **1** was dissolved in 140 ml isopropanol an 50 ml acetone. The mixture was irradiated for 4.8 h. After evaporation, 29.4 g of crude material was obtained. Recrystallization from n-hexane gave 25.7 g (86 %) of pure product.

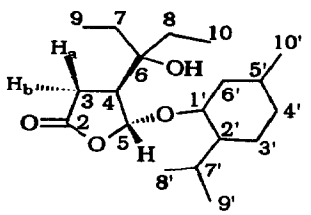
3.1 g of **2** and a catalytic amound of p-toluenesulfonic acid were dissolved in 50 ml glycol. The mixture was heated to 110 °C for about 14 h. After cooling to room temperature, the mixture was treated with saturated $NaHCO_3$-solution and ether. The aqueous phase was extracted 12 times with ether. The organic phases were dried with $MgSO_4$. The crude material obtained after evaporation of the ether was dissolved in 50 ml ethylacetate. The resulting solution was ozonized for 100 min at -78 °C. After the excess ozone had been removed by N_2-stream, the solvent was evaporated (T < 45 °C). The resulting mixture was added to 30 ml of 1-N-KOH-solution and stirred for about 14 h at room temperature. The mixture was extracted four times with ether to remove the (-)-menthol (yield of recovery: 1.3 g (80 %)). The aqueous solution was acidified with dilute HCl and saturated with NaCl. The resulting mixture was percolated with ether for three days. The ethereal solution was dried with $MgSO_4$. The residue after concentration, was recrystallized from water and a small quantity of ethanol. Yield: 0.55 g (32%), mp: 198°C,

$[\alpha]_D^{19}$ = -13.7 (C = 1.052, acetone).

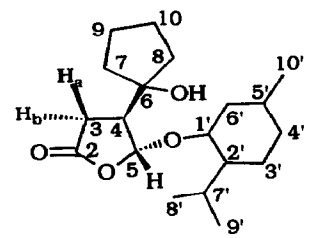


^{1}H-NMR: δ = 5.70 (d, J = 3.0 Hz, H-5), 3.55 (d/t, J = 4.0/10.5 Hz, H-1'), 2.70 (d/d J = 9.5/18.0 Hz, H_b-3), 2.53 (d/d J = 5.5/18.0 Hz, H_a-3), 2.32 (d/d/d, J = 3.0/5.5/9.5 Hz, H-4), 2.16 (m, H_{eq}-6'), 2.14 (d/sep, J = 2.5/7.0 Hz, H-7'), 1.66 (m, 3 H, H_{eq}-3',4', OH), 1.38 (m, H-5'), 1.28 (s, H-7,8), 1.21 (s, H-7,8), 0.94 (d, J = 6.5 Hz, H-10'), 0.88 (d, J = 7.0 Hz, H-8',9'), 0.79 (d, J = 7.0 Hz, H-8',9'), 0.8 - 1.08

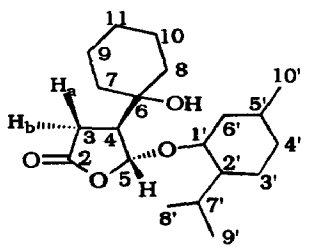
(m, 3 H, H_{ax}-3',4',6') ppm. - ^{13}C-NMR: δ = 176.37 (C-2), 102.26 (C-5), 77.32 (C-1'), 69.94(C-6), 51.86 (C-4), 47.85 (C-2'), 39.85 (C-6'), 34.35 (C-4'), 31.41 (C-5'), 30.13 (C-3), 27.82 (C-7,8), 27.76 (C-7,8), 25.41 (C-7'), 23.11 (C-3'), 22.29 (C-10'), 20.94 (C-8',9'), 15.71 (C-8',9') ppm. - IR (KBr): ν = 3550, 2960, 2950, 2925, 1790, 1645, 1180, 1100, 940 cm^{-1}. - MS: m/z (%) = 298 (M^+, 0.3), 280 (0.7), 241 (1), 221 (2), 213 (4), 161 (12), 143 (63), 139 (81), 138 (87), 125 (31), 115 (48), 97 (76), 95 (44), 83 (100), 81 (69), 71 (35), 69 (65), 59 (47), 57 (34), 55 (52), 43 (36), 41 (55). - Anal. Calcd. C, 68.46; H, 10.07; Found C, 67.79; H, 10.08.



^{1}H-NMR: δ = 5.74 (d, J = 4.0 Hz, H-5), 3.55 (d/t, J = 4.0/10.5 Hz, H-1'), 2.61 (d, J = 9.0 Hz, H-3), 2.61 (d, J = 9.0 Hz, H'-3), 2.42 (d/d/d, J = 4.0/8.0/9.0 Hz, H-4), 2.16 (m, H_{eq}-6'), 2.14 (d/sep, J = 2.5/7.0 Hz, H-7'), 1.30 - 1.72 (m, H-7,8,5', H_{eq}-3',4'), 1.16 - 1.27 (m, H-2'), 0.94 (d, J = 6.5 Hz, H-10'), 0.89 (t, J = 7.5 Hz, H-9,10), 0.86 (t, J = 7.5 Hz, H-9,10), 0.88 (d, J = 7.0 Hz, H-8',9'), 0.80 (d, J = 7.0 Hz, H-8',9') ppm. - ^{13}C-NMR: δ = 175.76 (C-2), 101.77 (C-5), 77.30 (C-1'), 74.18 (C-6), 48.13 (C-2',4), 47.98 (C-2',4), 39.74 (C-6'), 34.39 (C-4'), 31.44 (C-5'), 29.65 (C-3), 29.00 (C-7,8), 28.39 (C-7,8), 25.43 (C-7'), 23.13 (C-3'), 22.33 (C-10'), 20.97 (C-8',9'), 15.76 (C-8',9'), 7.71 (C-9,10), 7.52 (C-9,10) ppm. - IR ($CDCl_3$): ν =3484, 2958, 2927, 2872, 1768 cm^{-1}. - MS: m/z (%) = 326 (M^+, 0.14), 171 (36), 153 (57), 142 (32), 139 (76), 138 (51), 124 (24), 98 (27), 97 (23), 95 (24), 87 (38), 83 (100), 81 (45), 69 (32), 57 (53), 55 (43), 41 (33). - Anal. Calcd. C, 69.99; H, 10.43; Found C, 69.72; H, 10.32.

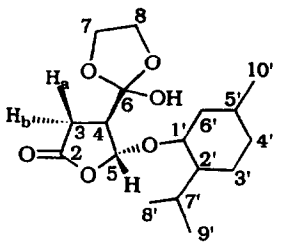


^{1}H-NMR: δ = 5.71 (d, J = 3.0 Hz, H-5), 3.54 (d/t, J = 4.0/10.5 Hz, H-1'), 2.71 (d/d J = 9.5/18.0 Hz, H_b-3), 2.54 (d/d J = 5.5/18.0 Hz, H_a-3), 2.36 (d/d/d, J = 3.0/5.5/9.5 Hz, H-4), 2.05 - 2.19 (m, 2H, H_{eq}-6', H-7'), 1.99 (s, OH), 1.60 - 1.90 (m, 9H, H-7,8,9,10, H_{eq}-3',4'), 1.50 (m, 1H, H-7,8,9,10), 1.37 (m, H-5'), 1.21 (s, H-2'), 1.00 (d/q, J = 3.0/12.5 Hz, H_{ax}-3'), 0.94 (d, J = 6.5 Hz, H-10'), 0.89 (d, J = 7.0 Hz, H-8',9'), 0.79 (d, J = 7.0 Hz, H-8',9') ppm. - ^{13}C-NMR: δ = 176.47 (C-2), 102.74 (C-5), 81.62 (C-6), 77.32 (C-1'), 50.84 (C-4), 47.89 (C-2'), 39.92 (C-6'), 38.87 (C-7,8), 38.32 (C-7,8), 34.38 (C-4'), 31.43 (C-5'), 30.54 (C-3), 25.46 (C-7'), 23.86 (C-9,10), 23.46 (C-9,10), 23.16 (C-3'), 22.30 (C-10'), 20.94 (C-8',9'), 15.72 (C-8',9') ppm. - IR (KBr): ν = 3495, 2959, 2935, 2865, 1770, 1457, 1375, 1190, 965 cm^{-1}. - MS: m/z (%) = 325 (M^++1, 0.34), 169 (43), 151 (60), 140 (37), 139 (67), 138 (61), 123 (36), 96 (31), 95 (40), 83 (100), 81 (57), 69 (28), 67 (37), 57 (39), 55 (46), 41 (32). - Anal. Calcd. C, 70.37; H, 9.88; Found C, 70.49; H, 10.12.

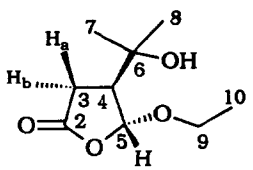


^{1}H-NMR: δ = 5.74 (d, J = 3.5 Hz, H-5), 3.53 (d/t, J = 4.0/10.5 Hz, H-1'), 2.605 (d, J = 6.5 Hz, H_a-3), 2.610 (d, J = 10.0 Hz, H_b-3), 2.35 (d/d/d, J = 3.5/6.5/10.0 Hz, H-4), 2.05 - 2.21 (m, 2H, H_{eq}-6', H-7'), 2.05 (s, OH), 1.70 (m, 9H, H-7,8,9,10,11, H_{eq}-3',4'), 1.10 - 1.40 (m, 4 H, H-7,8,9,10,11,5'), 1.00 (d/q, J = 3.0/12.5 Hz, H_{ax}-3'), 0.93 (d, J = 6.5 Hz, H-10'), 0.88 (d, J = 7.0 Hz, H-8',9'), 0.79 (d, J = 7.0 Hz, H-8',9') ppm. - ^{13}C-NMR: δ = 176.18 (C-2), 101.78 (C-5), 77.28 (C-1'), 70.76 (C-6), 50.75 (C-4), 47.89 (C-2'), 39.80 (C-6'), 35.58 (C-7,8), 35.54 (C-7,8), 34.37 (C-4'), 31.42 (C-5'), 29.43 (C-3), 25.41 (C-7'), 25.35 (C-11), 23.13 (C-3'), 22.30

(C-10'), 21.61 (2C, C-9,10), 20.94 (C-8',9'), 15.74 (C-8',9') ppm. - IR (KBr): ν = 3470, 2950, 2850, 1763, 1449, 1385, 1185, 1125, 955 cm^{-1}. - MS: m/z (%) = 338 (M^+, 0.11), 183 (30), 165 (59), 154 (37), 139 (49), 138 (54), 136 (32), 110 (33), 99 (35), 95 (36), 83 (100), 81 (85), 69 (32), 57 (44), 55 (52), 41 (43). - Anal. Calcd. C, 71.01; H, 10.06; Found C, 70.91; H, 10.14.



^{1}H-NMR: δ= 5.63 (d, J = 1.5 Hz, H-5), 4.91 (d, J = 3.5 Hz, H-6), 3.84 - 4.06 (m, 4 H, H-7,8), 3.53 (d/t, J = 4.0/10.5 Hz, H-1'), 2.71 (d/d J = 9.5/16.5 Hz, H_b-3), 2.65 (d/d/d/d, J = 1.5/2.5/3.5/9.5 Hz, H-4), 2.48 (d/d J = 2.5/10.5 Hz, H_a-3), 2.16 (m, 2 H, H_{eq}-6',7'), 1.63 (m, 3 H, H_{eq}-3',4', ...), 1.38 (m, H-5'), 1.22 (m, H-2'), 0.98 (m, H_{ax}-3'), 0.94 (d, J = 6.5 Hz, H-10'), 0.88 (d, J = 7.0 Hz, H-8',9'), 0.78 (d, J = 7.0 Hz, H-8',9') ppm. - ^{13}C-NMR: δ = 175.66 (C-2), 102.43 (C-5), 100.79 (C-6), 77.14 (C-1'), 65.52 (C-6,7), 65.33 (C-6,7), 47.71 (C-2'), 45.06 (C-4), 39.82 (C-6'), 34.33 (C-4'), 31.39 (C-5'), 28.31 (C-3), 25.47 (C-7'), 23.13 (C-3'), 22.26 (C-10'), 20.89 (C-8',9'), 15.65 (C-8',9') ppm. -IR (KBr): ν = 2963, 2931, 2890, 2865, 1788, 1458, 1420, 1398, 1300, 1245, 1168, 1110, 949 cm^{-1}. - MS: m/z (%) = 312 (M^+, 0.29), 175 (3), 157 (2), 138 (12), 128 (4), 95 (4), 83 (7), 81 (7), 73 (100), 57 (4), 55 (7), 41 (7). - Anal. Calcd. C, 65.38; H, 9.25; Found C, 65.44; H, 8.97.



^{1}H-NMR: δ = 5.52 (d, J = 3.5 Hz, H-5), 3.87 (d/q, J = 9.5/7.0 Hz, H-9), 3.66 (d/q, J = 9.5/7.0 Hz, H'-9), 2.75 (s, OH) 2.67 (d/d J = 18.0/10.0 Hz, H_b-3), 2.58 (d/d, J = 18.0/6.5 Hz, H_a-3), 2.32 (d/d/d, J = 3.5/6.5/10.0 Hz, H-4), 1.26 (s, H-7, 8), 1.25 (t, J = 7.0 Hz, H-10), 1.20 (s, H-7,8) ppm. - ^{13}C-NMR: δ = 176.43 (C-2), 106.02 (C-5), 69.61 (C-6), 65.65 (C-9), 51.88 (C-4), 30.01 (C-3), 27.83 (C-7,8), 27.73 (C-7,8), 15.02 (C-10) ppm. - IR (kap): ν = 3475, 2978, 2937, 1775, 1380, 1179, 1119, 946 cm^{-1}. - MS: m/z (%) = 189 (M^+ + 1, 0.2), 143 (3), 130 (7), 114 (10), 97 (16), 85 (28), 75 (34), 71 (37), 70 (37), 69 (53), 59 (100), 57 (30), 47 (32), 43 (50), 41 (23). - Anal. Calcd. C, 57.45; H, 8.51; Found C, 56.44; H, 8.51.

Terebic acid **3**: ^{1}H-NMR (DMSO-d_6): δ = 3.23 (t, J = 8.5 Hz, 1H, C*H*), 2.84 (d/d, J = 8.5/18.0 Hz, 1H, C*H* H), 2.72 (d/d, J = 8.5/18.0 Hz, 1H, CH*H*), 1.51 (s, 3H, C*H* $_3$), 1.29 (s, 3H, C*H* $_3$) ppm. - ^{13}C-NMR (DMSO-d_6): δ = 174.29 (*C* OOR), 171.74 (*C* OOH), 83.89 (*C* -O), 49.53 (*C* H), 31.49 (*C* H_2), 27.79 (*C* H_3), 23.05 (*C* H_3) ppm.

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[x]present address (for correspondence): Laboratoire de Réarrangements Thermiques et Photochimiques associé au CNRS, Université de Reims - UFR Science, B.P. 347, F-51062 Reims, France

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(*Received in UK* 1 *March* 1994)