96. The Novel Adamantane Isomer 2,5-Trimethylenenorbornane (Tricyclo-[5.3.0.$0^{3,9}$]decane, 4-Homotwistbrendane)

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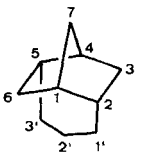
Summary

A synthesis of the novel $C_{10}H_{16}$ hydrocarbon 2,5-trimethylenenorbornane (tricyclo[5.3.0.$0^{3,9}$]decane, **1**), one of the 19 members of the 'adamantaneland', and its *Lewis*-acid-catalyzed rearrangement is described.

2,5-Trimethylenenorbornane (**1**)[1]) belongs to the set of 19 isomeric tricyclic $C_{10}H_{16}$-compounds, known as 'adamantanland' [2]. We describe here a synthesis and its *Lewis*-acid-catalyzed isomerization of the hitherto unknown hydrocarbon **1**.

Scheme 2

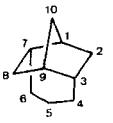


1

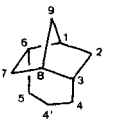
Synthesis of *1*. – The easily available *p*-toluenesulfonate **3** [3] of protoadamant-4-en-10*endo*-ol (**2**) [4] was used as suitable starting material. Solvolysis of **3** in 1N NaOH/THF 3:1 yielded after 3 weeks at 85° a mixture of five alcohols, which were separated by column chromatography: 11% of **2** (corresponding to actual starting material **3**), 1.5% of its epimeric *exo*-alcohol **4** [4] [5], 68% of 5,10-didehydroproto-

[1]) Tricyclo[5.3.0.$0^{3,9}$]decane (**a**), 4-homotwistbrendane (**b**), cristane [1]. In the present communication the numbering of the C-atoms follows the trimethylenenorbornane nomenclature. The correct IUPAC names are added in parentheses in the experimental part.

Scheme 1



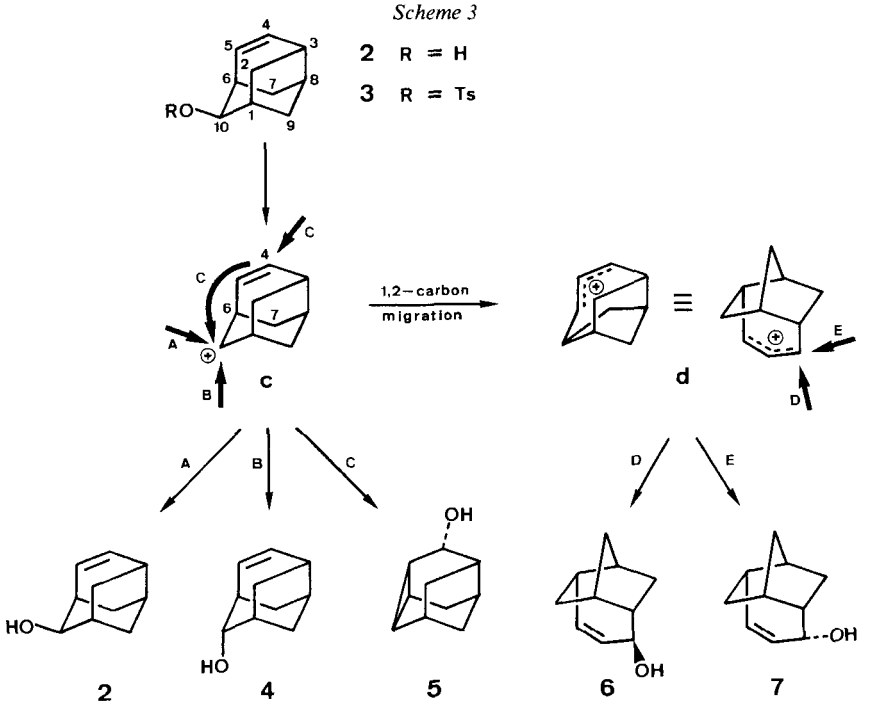
a



b

0018-019X/82/3/1032-06$01.00/0

Scheme 3



adamant-4$^{C(7)}$-ol[2]) (**5**)[3]) [3–5], and 17% of the desired alcohol **6** along with 2.5% of its epimer 7.

Scheme 3 summarizes probable mechanistic pathways from **3** to **2** and **4**–**7**. The alcohols **2** (pathway A) and **4** (pathway B) are directly derived from the primarily formed protoadamant-4-en-10-yl ion (**c**), whereas **5** (pathway C) is the result of C(4), C(5) double bond participation in **c**. Attack of solvent at the allylic ion **d**, obtained by 1,2-carbon migration of the C(6), C(7)-bond in **c**, leads to the rearranged alcohols **6** (pathway D) and **7** (pathway E)[4]).

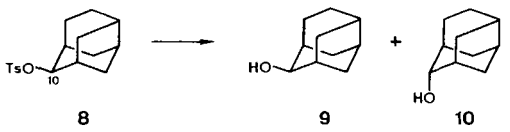
Conversion of the unsaturated alcohol **6** to compound **1** was achieved by the following routes. Ketone **11** or alkene **12** were used as key intermediates. The

[2]) In protoadamantanes and in 2,5-trimethylenenorbornanes the indices indicate the C-atom towards which a substituent is orientated.

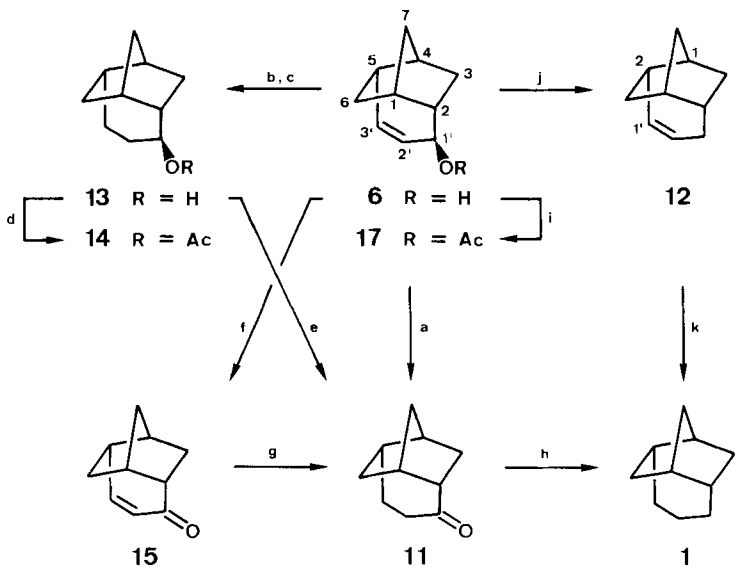
[3]) Compound **5** can easily be converted to **4** in refluxing aqueous acetone in the presence of perchloric acid.

[4]) Neither base- nor acid-catalyzed solvolysis of protoadamantan-10*endo*-yl *p*-toluenesulfonate (**8**), the saturated analogue of **3**, yielded rearranged 2,5-trimethylenenorbornanols, but only *endo*- (**9**) [6] and *exo*-protoadamantan-10-ol (**10**) [6] as the primary products.

Scheme 4



Scheme 5



a) H_2, 10% Pd/C, AcOEt; b) H_2, *Raney*-nickel, MeOH; c) HN=NH (from potassium azodicarboxylate [7]), MeOH; d) Ac_2O, Py; e) Pyridinium dichromate, pyridinium trifluoracetate, CH_2Cl_2 [8]; f) $CrO_3 \cdot Py$, CH_2Cl_2; g) H_2, 10% Pd/C, AcOEt; h) H_2N-NH_2, KOH, glycol, 110–180°; i) AcCl, Et_3N, Et_2O; j) Li/NH_3, Et_2O, –78°; k) H_2, 5% $Pd/CaCO_3$, pentane.

former was prepared in three independent ways: a) in quantitative yield directly by treatment of **6** with hydrogen in the presence of Pd/C; b) reduction of the allylic alcohol **6** to the saturated analogue **13**, also characterized as its acetate **14**, proceeded either by hydrogenation in the presence of *Raney*-nickel (quant.) or by diimide reduction (68%) and was followed by oxidation to **11** (91%)[5]); c) *Collins* oxidation

[5]) Reductions of the ketone **11** in most cases led to a mixture of the two epimeric alcohols **13** and **16** in a proportion depending on the conditions. The results are summarized in the *Table*.

Scheme 6

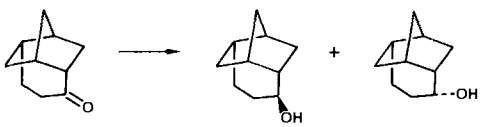


Table. *Reduction of ketone* **11**

Reaction conditions	Isolated yield	Composition 13 : 16
$BH_3 \cdot THF$, THF, 1 h, RT.	89%	10 : 1
$LiAlH_4$, Et_2O, 1 h, RT.	83%	6 : 1
Na, toluene, *i*-C_3H_7OH, 1 day, reflux	95%[a])	1 : 10
$LiAlH(O\text{-}t\text{-}C_4H_9)_3$, THF, 19 h, reflux	no reaction	

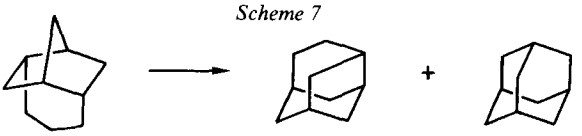
[a]) Yield with respect to converted starting material; isolated yield: 66% **13**+**16** and 30% **11**.

of **6** led to the α,β-unsaturated ketone **15** (69%), which on hydrogenation gave quantitatively ketone **11**. *Wolff-Kishner* reduction of **11** yielded (65%) 2,5-trimethylenenorbornane (**1**). The other access to **1** was by acetylation of **6** (93%), reduction of the allylic acetate **17** with lithium in liquid ammonia to the alkene **12** (50%), and hydrogenation of **12** to the hydrocarbon **1** (93%).

In accordance with the symmetry of **1**, its ^{13}C-NMR. spectrum shows only 6 signals: 19.73 (*t*, C(2')), 26.95 (*t*, C(1') and C(3')), 33.26 (*d*, C(2) and C(5)), 34.10 (*t*, C(3) and C(6)), 42.15 (*d*, C(1) and C(4)), 43.69 (*t*, C(7)).

Adamantane rearrangement of *1*. – Treatment of **1** with aluminum bromide as catalyst (molar ratio approx. 5:1) in carbon disulfide at −70° for 5 min yielded protoadamantane (**18**) and adamantane (**19**) in the ratio of 1:4.5 as the sole products. This result is in agreement with the predictions for the most likely pathway for the rearrangement of **1** to adamantane (**19**) [2b].

Scheme 7



1 **18** **19**

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Analytical and special data[1]). – *General.* Melting points (m.p.) were determined in sealed capillary tubes in an oil bath (*Büchi 510* apparatus) and are uncorrected. The UV. spectrum was measured in pentane on a *Cary 14* spectrophotometer. The absorption maximum λ_{max} is given in nm, the ε-value added in parentheses. IR. spectra were recorded in CCl_4 on a *Perkin-Elmer 297* spectrophotometer, bands are given in cm^{-1}. ^{1}H-NMR. spectra ($CDCl_3$) were measured on a *Varian HA-100* or *Bruker WM-300* and ^{13}C-NMR. spectra (25.5 MHz) on a *Varian XL-100* using $CDCl_3$ as solvent. Chemical shifts are given in ppm relative to TMS as internal standard; J = spin-spin coupling constant (Hz), $w^1/_2$ = half width at half height (Hz). Mass spectra (MS.) were performed on a *Hitachi-Perkin-Elmer RMU-6M* instrument at 70 eV ionizing electron energy, source temperature 180°, inlet temperature 200°. The most important ions are listed as *m/z* values with relative intensities (% of base peak) in parenthesis.

2,5-Trimethylenenorbornane (tricyclo[5.3.0.0^{3,9}]decane, **1**). M.p. 146–149°. – IR.: 1469*m*, 1452*w*, 1326*w*, 1301*w*, 1152*w*, 1010*w*, 948*w*, 847*w*. – ^{1}H-NMR. (300 MHz): 1.31 (*d*×*d*×*d*×*d*, J(gem) = 13, J(2,3*endo*) and J(5,6*endo*), resp. = 9, J(3*endo*,4) and J(1,6*endo*), resp. = 3 or 1.5, J(3*endo*, 7$^{C(5)}$) and J(6*endo*, 7$^{C(3)}$), resp. = 1.5 or 3, H_{endo}–C(3) and H_{endo}–C(6)); 1.41 (*m*, $w^1/_2 \approx 5$, 2 H–C(7)); 1.57 (*d*, J(vic) = 12, $w^1/_2$ each ≈5, 2 H–C(2')); 1.6–1.85 (*m*, H_{exo}–C(3), H_{exo}–C(6), 2 H–C(1') and 2 H–C(3')); 2.1 (*m*, $w^1/_2 \approx 25$, H–C(2) and H–C(5)); 2.15 (*m*, $w^1/_2 \approx 8$, H–C(1) and H–C(4)). – ^{13}C-NMR.: 19.73 (*t*, C(2')); 26.95 (*t*, C(1') and C(3')); 33.26 (*d*, C(2) and C(5)); 34.10 (*t*, C(3) and C(6)); 42.15 (*d*, C(1) and C(4)); 43.69 (*t*, C(7)). – MS.: 136 (32, M^+, $C_{10}H_{16}$), 121 (47), 107 (35), 93 (81), 80 (100), 77 (25), 67 (87), 53 (17), 41 (38), 27 (15).

2,5-Trimethylenenorborn-2'-en-1'$^{C(1)}$-ol (tricyclo[5.3.0.0^{3,9}]dec-5-en-4$^{C(9)}$-ol, **6**). – IR.: 3625*m*, 3400*m* br., 3030*m*, 1634*w*, 1467*m*, 1392*m*, 1321*w*, 1307*w*, 1296*w*, 1221*w*, 1036*s*, 1026*s*, 1011*m*, 973*m*, 962*m*, 943*w*, 877*m*, 846*w*, 715*w*, 679*w*. – ^{1}H-NMR. (100 MHz): 1.1–2.0 (*m*, 2H–C(3), 2H–C(6) and 2H–C(7)); 1.65 (*s*, HO$^{C(1)}$–C(1')); 2.0–2.8 (*m*, H–C(1), H–C(2), H–C(4) and H–C(5)); 4.50 (*d*×*d*, J(2,1') ≈ 6, J(1',2') = 6, H$^{C(3)}$–C(1')); 5.62 (*d*×*d*, J(2',3') = 10, J(1',2') = 6, H–C(2')); 6.21 (*d*×*d*, J(2',3') = 10, J(5,3') = 8, H–C(3')). – MS.: 150 (8, M^+, $C_{10}H_{14}O$), 132 (10), 117 (24), 109 (28), 104 (14), 96 (16), 91 (36), 83 (100), 79 (40), 70 (10), 67 (39), 55 (15), 41 (17), 39 (19), 27 (11).

2,5-Trimethylenenorbornan-1'-one (tricyclo[5.3.0.0^{3,9}]decan-4-one, **11**). M.p. 143–147°. – IR.: 1700*s*, 1475*m*, 1460*m*, 1416*w*, 1348*w*, 1319*w*, 1314*w*, 1297*w*, 1227*m*, 1198*w*, 1136*m*, 1102*w*, 1085*w*, 1011*w*,

1000*w*, 967*m*, 941*m*, 916*w*, 882*w*, 842*w*. – ^{1}H-NMR. (100 MHz): 1.1–1.75 (*m*, 5H); 1.75–2.2 (*m*, 3H); 2.2–2.9 (*m*, H–C(1), H–C(2), H–C(4), H–C(5) and 2H–C(2′)). – MS.: 150 (26, M^+, $C_{10}H_{14}O$), 132 (3), 122 (6), 108 (9), 96 (18), 79 (35), 66 (100), 55 (16), 41 (18), 28 (48).

2,5-Trimethylenenorborn-1′-ene (tricyclo[5.3.0.0^{3,9}]dec-4-ene, **12**). M.p. 115°. – IR.: 3015*m*, 2830*m*, 1627*w*, 1463*m*, 1428*w*, 1380*w*, 1312*w*, 1301*m*, 1259*w*, 1248*w*, 1201*m*, 1185*m*, 1102*w*, 1082*w*, 1051*w*, 1025*w*, 1013*m*, 984*w*, 945*w*, 928*w*, 909*w*, 850*m*, 676*s*. – ^{1}H-NMR. (300 MHz): 1.30 ($d\times d\times d\times d$, J(gem) = 11, J(5,6*endo*) = 9, J(1,6*endo*) = 2 or 1, J(6*endo*, 7$^{C(2)}$) = 1 or 2, H_{endo}–C(6)); 1.4–1.8 (*m*, H_{exo}–C(6), 2 H–C(3) and 2 H–C(7)); 2.13 (*m*, $w^1/_2 \approx 18$, H–C(5)); 2.15–2.3 (*m*, H–C(4) and 2H–C(3′)); 2.3–2.4 (*m*, H–C(1) and H–C(2)); 5.46 ($d\times d\times d\times d$, J(1′,2′) = 10, J(2′,3′$^{C(6)}$) = 6, J(2′,3′$^{C(4)}$) = 2.5, J(2,2′) = 1, H–C(2′)); 5.93 ($d\times d\times d$, J(1′,2′) = 10, J(2,1′) = 7, J(1′,3′) = 2.5, H–C(1′)). – MS.: 134 (42, M^+, $C_{10}H_{14}$), 119 (22), 106 (15), 105 (21), 93 (25), 92 (55), 91 (55), 80 (43), 79 (45), 78 (17), 77 (27), 68 (9), 67 (100), 66 (30), 65 (14), 53 (8), 51 (9), 41 (19), 39 (21), 28 (16).

2,5-Trimethylenenorbornan-1′$^{C(1)}$-ol (tricyclo[5.3.0.0^{3,9}]decan-4$^{C(9)}$-ol, **13**). M.p. 185–186°. – IR.: 3625*m*, 3450*w* br., 1477*m*, 1464*w*, 1366*w*, 1259*w*, 1201*w*, 1136*w*, 1067*w*, 1038*s*, 1018*s*, 969*m*, 948*m*, 940*m*, 918*w*, 862*w*, 613*w*. – ^{1}H-NMR. (300 MHz): 1.2–1.45 (*m*, 5H); 1.49 (*s*, HO$^{C(1)}$–C(1′)); 1.55–1.8 (*m*, 3H); 1.87 (*d*, J = 12, $w^1/_2$ each ≈ 5, 1H); 2.1–2.25 and 2.39 (2*m*, 3H and 1H ($w^1/_2 \approx 10$), H–C(1), H–C(2), H–C(4) and H–C(5)); 2.31 ($d\times d\times d$, J(gem) = 13, J(1′,2′) = 10, J(2′,3′) = 6.5, H–C(2′)); 4.23 ($d\times d\times d$, J(1′,2′) = 10, J = 5, J = 4, H$^{C(3)}$–C(1′)). – MS.: 152 (7, M^+, $C_{10}H_{16}O$), 134 (31), 119 (21), 109 (11), 108 (60), 106 (20), 105 (19), 96 (46), 95 (63), 94 (11), 93 (53), 92 (38), 91 (40), 84 (10), 83 (20), 81 (19), 80 (56), 79 (61), 78 (15), 77 (27), 70 (14), 68 (14), 67 (81), 66 (100), 65 (12), 57 (16), 55 (22), 54 (10), 53 (15), 43 (10), 41 (43), 39 (30), 29 (13), 28 (23).

2,5-Trimethylenenorbornan-1′$^{C(1)}$-yl acetate (tricyclo[5.3.0.0^{3,9}]decan-4$^{C(9)}$-yl acetate, **14**). M.p. 37°. – IR.: 1734*s*, 1476*w*, 1465*w*, 1376*w*, 1364*m*, 1308*w*, 1290*w*, 1246*s*, 1202*w*, 1180*w*, 1146*w*, 1034*w*, 1015*m*, 984*m*, 967*m*, 946*w*, 919*w*, 897*w*. – ^{1}H-NMR. (100 MHz): 1.1–1.5 and 1.5–1.95 (2*m*, 5H and 4H); 1.99 (*s*, $H_3COO^{C(1)}$–C(1′)); 2.05–2.45 (*m*, H–C(1), H–C(2), H–C(4), H–C(5) and H–C(2′)); 5.15 (*m*, $w^1/_2 \approx 20$, H$^{C(3)}$–C(1′)). – MS.: 194 (0.2, M^+, $C_{12}H_{18}O_2$), 152 (12), 135 (17), 134 (89), 119 (37), 107 (10), 106 (26), 105 (28), 95 (11), 93 (50), 92 (60), 91 (42), 81 (17), 80 (41), 79 (37), 78 (17), 77 (16), 67 (38), 66 (32), 55 (10), 53 (78), 43 (100), 41 (23), 39 (14).

2,5-Trimethylenenorborn-2′-en-1′-one (tricyclo[5.3.0.0^{3,9}]dec-5-en-4-one, **15**). M.p. 63–65°. – UV.: 231 (7400). – IR.: 3030*m*, 1676*s*, 1604*w*, 1467*m*, 1450*w*, 1376*m*, 1310*w*, 1304*m*, 1284*m*, 1238*m*, 1161*w*, 1154*w*, 1139*m*, 1099*w*, 1072*w*, 1006*w*, 977*w*, 965*w*, 957*w*, 936*w*, 893*m*, 843*m*, 659*m*. – ^{1}H-NMR. (100 MHz): 1.23 (*d*, J(gem) = 12, $w^1/_2$ each ≈ 6, H_{endo}–C(3)); 1.3–1.8 (*m*, $w^1/_2 \approx 7$, 2 H–C(6) and 2 H–C(7)); 1.92 ($d\times d$, J(gem) = 12, J(2,3*exo*) = 10, $w^1/_2$ each ≈ 5, H_{exo}–C(3)); 2.42 and 2.56 (2*m*, $w^1/_2 \approx 11$ and 12, H–C(1) and H–C(4)); 2.75–3.2 (*m*, H–C(2) and H–C(5)); 5.95 ($d\times d\times d$, J(2′,3′) = 10, J(2,2′) = 2 or 1, J(5,2′) = 1 or 2, H–C(2′)); 7.08 ($d\times d$, J(2′,3′) = 10, J(5,3′) = 8, H–C(3′)). – MS.: 148 (63, M^+, $C_{10}H_{12}O$), 133 (9), 120 (33), 105 (17), 91 (43), 81 (100), 66 (70), 53 (34), 39 (30), 27 (21).

2,5-Trimethylenenorbornan-1′$^{C(3)}$-ol (tricyclo[5.3.0.0^{3,9}]decan-4$^{C(2)}$-ol, **16**). M.p. 149–152°. – IR.: 3620*m*, 3400*w* br., 1473*m*, 1461*m*, 1360*w*, 1315*w*, 1305*w*, 1239*w*, 1201*w*, 1166*w*, 1155*w*, 1068*w*, 1026*s*, 1014*m*, 994*s*, 968*m*, 956*s*, 943*w*, 914*w*, 871*w*, 847*w*. – ^{1}H-NMR. (300 MHz): 1.15–1.55 (*m*, 5H); 1.38 (*s*, HO$^{C(3)}$–C(1′)); 1.64 (*m*, $w^1/_2 \approx 30$, H–C(2′)); 1.7–1.9 (*m*, 3H); 2.0–2.15 and 2.15–2.35 (2*m*, 2H and 3H, H–C(1), H–C(2), H–C(4), H–C(5) and H–C(2′)); 4.25 ($d\times d$, J = 8, J = 6, H$^{C(1)}$–C(1′)). – MS.: 152 (6, M^+, $C_{10}H_{16}O$), 134 (14), 119 (14), 109 (11), 108 (56), 106 (16), 105 (13), 96 (43), 95 (63), 94 (10), 93 (45), 92 (23), 91 (29), 83 (18), 81 (15), 80 (46), 79 (50), 78 (11), 77 (20), 70 (10), 68 (12), 67 (67), 66 (100), 57 (14), 55 (16), 53 (12), 41 (34), 39 (29), 29 (10), 28 (13).

2,5-Trimethylenenorborn-2′-en-1′$^{C(1)}$-yl acetate (tricyclo[5.3.0.0^{3,9}]dec-5-en-4$^{C(9)}$-yl acetate, **17**). – IR.: 3030*w*, 1735*s*, 1471*m*, 1371*m*, 1308*w*, 1296*w*, 1242*s*, 1018*m*, 992*w*, 962*m*, 921*w*, 887*w*, 865*w*. – ^{1}H-NMR. (100 MHz): 1.1–1.9 (*m*, 2H–C(3), 2H–C(6) and 2H–C(7)); 2.07 (*s*, $H_3CCOO^{C(1)}$–C(1′)); 2.05–2.75 (*m*, H–C(1), H–C(2), H–C(4) and H–C(5)); 5.49 ($d\times d$, J(2,1′) ≈ 6, J(1′,2′) = 6, H$^{C(3)}$–C(1′)); 5.62 ($d\times d$, J(2′,3′) = 10, J(1′,2′) = 6, H–C(2′)); 6.27 ($d\times d$, J(2′,3′) = 10, J(5,3′) = 8, H–C(3′)). – MS.: 192 (8, M^+, $C_{12}H_{16}O_2$), 150 (31), 132 (79), 117 (88), 109 (10), 104 (40), 91 (79), 83 (49), 79 (32), 77 (18), 67 (30), 54 (21), 43 (100), 39 (21), 27 (11).

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