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SYNTHESIS OF ESTERS OF *m*-C(7)-*iso*-PROPYLCARBORAN-C(1)-CARBOXYLIC ACID, NATURAL TERPENE ALCOHOLS, AND PLANT PHENOLS

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*Previously undescribed esters **1b-21b** were prepared by reaction of cetyl alcohol **1a**, terpene alcohols **2a-16a**, plant phenols **17a-19a**, and alcohols **20a** and **21a** with m-C(7)-iso-propylcarboran-C(1)-carboxylic acid.*

Key words: terpenols, alcohols, phenols, *m*-C(7)-*iso*-propylcarboran-C(1)-carboxylic acid, esters.

The use of boron compounds for boron-neutron-capture therapy of malignant neoplasms (cancer) was first proposed in 1936 [1]. This is binary radiotherapy during which thermal neutrons are captured by ^{10}B nuclei and then selectively transferred to cancer cells. Neutron capture leads to formation of an excited ^{11}B nucleus, which splits into high-energy $^{4}He^{2+}$ and $^{7}Li^{3+}$ ions. The cancer cells are killed by the release of these charged particles that create ionization tracks along their trajectories, which lead to cell damage [2-4]. One of the promising modern trends for discovering species for preparing boron clusters for diagnosis and therapy of cancer is the synthesis of carborane derivatives [5-16].

Our goal was to prepare a series of new derivatives of natural terpene alcohols and plant phenols as esters of *m*-C(7)-*iso*-propylcarboran-C(1)-carboxylic acid (**1b**-**21b**) for investigation and screening as antitumor preparations. We selected the following natural compounds for the synthesis: cetyl alcohol (**1a**), terpenols [citronellol (**2a**), elenol (**3a**), geraniol (**4a**), nerol (**5a**), linalool (**6a**), 1*R*,2*S*,5*R*-menthol (**7a**), terpineol (**8a**), 10-hydroxymethylcamphene (**9a**), borneol (**10a**), isoborneol (**11a**), isophenchol (**12a**), nopol (**13a**), *trans*-verbenol (**14a**), 2-*endo*-(2-hydroxyphenyl)-2,3,3-trimethylbicyclo[2.2.1]heptane (**15a**), isocamphyl-2,2-*spiro*-4-(hydroxymethyl)-2,2-dioxolane (**16a**)], plant phenols [eugenol (**17a**), vanillin (**18a**), vanillal (**19a**)], and tetrahydrofurfuryl (**20a**) and furfuryl (**21a**) alcohols. The biological activity and specific sorption by tumor cells of esters **1b**-**21b** that are based on natural compounds **1a**-**21a** may turn out to be higher than for analogous esters of synthetic origin [17, 18]. We envision a synergistic effect caused by the mutual intensification of the pharmacophore fragments in **1b**-**21b**. The esters of *m*-C(7)-*iso*-propylcarboran-C(1)-carboxylic acid (**1b**-**21b**) were prepared by reaction of the corresponding compounds **1a**-**21a** dissolved in absolute pyridine with the acid chloride of *m*-C(7)-*iso*-propylcarboran-C(1)-carboxylic acid without organic solvents (1:1:1 stoichiometric ratio of reagents). This reaction produced **1b**-**21b** in preparative yields of 89-94%.

The structures of the synthesized esters were confirmed by elemental analysis, cryoscopic determination of the molecular weight, and IR, UV, and PMR spectra. The PMR spectra of **1b**-**21b** contain a characteristic elevated baseline from -1.5 to 7.0 ppm for the carborane fragment $C_2B_{10}H_{10}$. The purity of the compounds was 98 ± 1% according to PMR spectroscopy.

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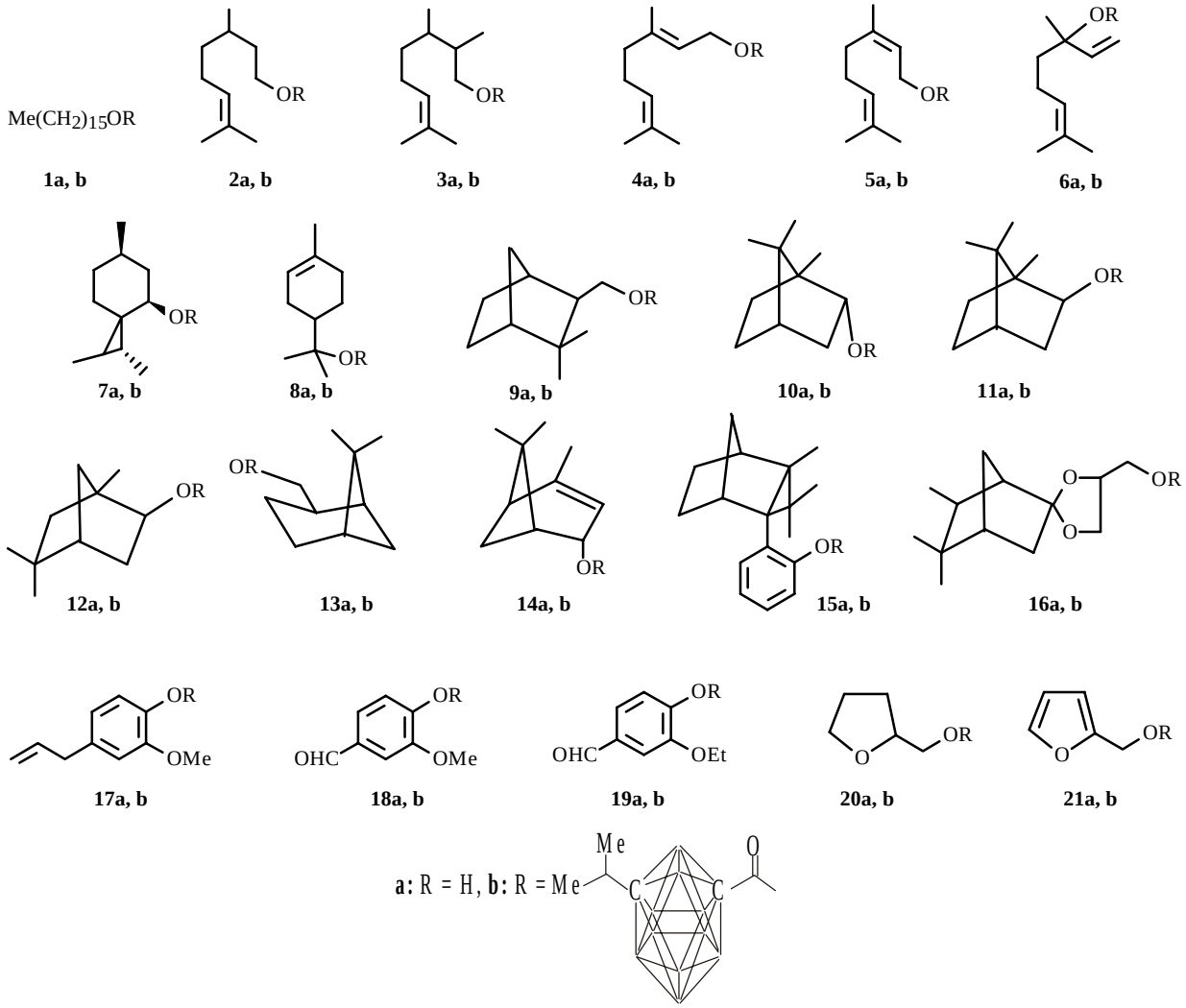

EXPERIMENTAL

IR spectra were recorded on a Protege-460 Fourier spectrophotometer as thin layers. PMR spectra were obtained on a Tesla-567A (100 MHz) spectrometer in $CDCl_3$ solution. Chemical shifts were measured relative to OMTS. UV spectra were obtained on a Specord UV-Vis instrument using $1 \cdot 10^{-3}$ M solutions in *n*-butanol. Molecular weights (M) were determined by cryoscopy in benzene. Column chromatography used silica gel L 100/160 μm with elution by hexane or benzene.

The acid chloride of *m*-C(7)-*iso*-propylcarboran-C(1)-carboxylic acid was prepared as before [19].

Esters of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxylic Acid 1b-21b (General Method). The appropriate alcohol or phenol (5 mmol, **1a-21a**) was dissolved in absolute pyridine (5 mmol). The solution was cooled to 0°C and treated in one portion with the acid chloride of *m*-C(7)-*iso*-propylcarboran-C(1)-carboxylic acid. The reaction mixture was thoroughly mixed and left for 3-5 days at 20-23°C. The products (**1b-21b**) in the mixture with pyridine hydrochloride were dissolved in water, extracted with hexane (**1b-17b**, **20a**, **21a**) or benzene (**18a**, **19a**), washed with water and $NaHCO_3$ solution (5%), and dried over $CaCl_2$. The desiccant was filtered off. The solvent was evaporated. Esters **1b-21b** were purified by column chromatography over silica gel with elution by hexane (**1b-17b**, **20a**, **21a**) or benzene (**18a**, **19a**).

This method produced:

1-Hexadecyl Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxylic Acid (1b). Yield 92%, mp 19-20°C. Found (%): C 58.60, H 11.38, B 23.22. Calc. for $C_{22}H_{50}B_{10}O_2$ (%): C 58.11, H 11.08, B 23.77. M: found 430.2, calc. 454.7.

IR spectrum (ν, cm^{-1}): 2955, 2925, 2855 (CH_{Alk}); 2615 (BH); 1745 (C=O); 1470 (CH_2); 1265 (C–O); 740, 720 (BH). UV spectrum (λ_{max}, ε): 206 (300), 222 (150), 240 (50).

PMR spectrum (δ, ppm, J/Hz): 0.89 (CH_3, t, ^3J = 5.8), 1.06 [$(CH_3)_2C$, d, ^3J = 6.5], 1.15-1.80 [$(CH_2)_{14}$, m], 2.25 (CH, m), 4.11 (CH_2O, t, ^3J = 7.4).

Citronellol Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxlic Acid (2b). Yield 90%, d_{20}^{20} 0.9657, n_D 1.5125. Found (%): C 52.37, H 10.06, B 29.05. Calc. for $C_{16}H_{36}B_{10}O_2$ (%): C 52.12, H 9.84, B 29.32. M: found 356.4, calc. 368.7.

IR spectrum (ν, cm^{-1}): 3050 (=CH); 2966, 2924, 2876, 2854 (CH_{Alk}); 1614 (BH); 1746 (C=O); 1463 (CH_2); 1264 (C–O); 743 (BH). UV spectrum (λ_{max}, ε): 204 (4000).

PMR spectrum (δ, ppm, J/Hz): 0.91 (CH_3 on C-3, d, ^3J = 5.7), 1.06 [$(CH_3)_2C$, d, ^3J = 6.5], 1.60 and 1.68 ($2CH_3$ on C-7, s and s), 2.25 (CH, m), 4.12 (2H-1, t, ^3J = 6.5), 5.05 (H-6, m).

Elenol Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxlic Acid (3b). Yield 92%, d_{20}^{20} 0.9735, n_D 1.5140. Found (%): C 52.30, H 10.03, B 29.09. Calc. for $C_{16}H_{36}B_{10}O_2$ (%): C 52.12, H 9.84, B 29.32. M: found 354.9, calc. 368.7.

IR spectrum (ν, cm^{-1}): 3050 (=CH); 2968, 2925, 2877, 2855 (CH_{Alk}); 1614 (BH); 1746 (C=O); 1465 (CH_2); 1265 (C–O); 744 (BH). UV spectrum (λ_{max}, ε): 204 (4000).

PMR spectrum (δ, ppm, J/Hz): 0.92 (3H-1, d, ^3J = 7.3), 1.05 [$(CH_3)_2C$, d, ^3J = 6.5], 1.32 (CH_3 on C-3, d, ^3J = 7.4), 1.59 and 1.67 ($2CH_3$ on C-7, s and s), 2.25 (CH, m), 4.60 (H-2, m), 5.12 (H-6, m).

Geraniol Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxlic Acid (4b). Yield 92%, d_{20}^{20} 1.0316, n_D 1.5210. Found (%): C 52.74, H 9.48, B 29.33. Calc. for $C_{16}H_{34}B_{10}O_2$ (%): C 52.43, H 9.35, B 29.49. M: found 351.0, calc. 366.6.

IR spectrum (ν, cm^{-1}): 3060, 3025 (=CH); 2970, 2926, 2879, 2856 (CH_{Alk}); 2615 (BH); 1745 (C–O); 1660, 1650 (C=C); 1453 (CH_2); 1260 (C–O); 740 (BH). UV spectrum (λ_{max}, ε): 205 (8000).

PMR spectrum (δ, ppm, J/Hz): 1.06 [$(CH_3)_2C$, d, ^3J = 6.5], 1.61 (CH_3 on C-3, s), 1.69 ($2CH_3$ on C-7, s), 2.25 (CH, m), 4.60 (2H-1, d, ^3J = 6.6), 4.90-5.45 (H-2, H-6, m).

Nerol Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxlic Acid (5b). Yield 93%, d_{20}^{20} 0.9868, n_D 1.5230. Found (%): C 52.69, H 9.44, B 29.37. Calc. for $C_{16}H_{34}B_{10}O_2$ (%): C 52.43, H 9.35, B 29.49. M: found 350.7, calc. 366.6.

IR spectrum (ν, cm^{-1}): 3050, 3025 (=CH); 2971, 2931, 2910, 2880, 2860 (CH_{Alk}); 2615 (BH); 1745 (C=O); 1660 (C=C); 1448 (CH_2); 1255 (C–O); 740 (BH). UV spectrum (λ_{max}, ε): 205 (8000).

PMR spectrum (δ, ppm, J/Hz): 1.05 [$(CH_3)_2C$, d, ^3J = 6.5], 1.60 and 1.69 ($2CH_3$ on C-7, s and s), 1.77 (CH_3 on C-3, br.s), 2.25 (CH, m), 4.55 (2H-1, m), 4.95-5.40 (H-2, H-6, m).

Linalool Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxlic Acid (6b). Yield 90%, d_{20}^{20} 1.0527, n_D 1.5210. Found (%): C 52.66, H 9.49, B 29.30. Calc. for $C_{16}H_{34}B_{10}O_2$ (%): C 52.43, H 9.35, B 29.49. M: found 355.1, calc. 366.6.

IR spectrum (ν, cm^{-1}): 3080 (=CH); 2974, 2933, 2878, 2865 (CH_{Alk}); 2613 (BH); 1744 (C=O); 1675, 1640 (C=C); 1463 (CH_2); 1263 (C–O); 739 (BH). UV spectrum (λ_{max}, ε): 205 (8000).

PMR spectrum (δ, ppm, J/Hz): 1.05 [$(CH_3)_2C$, d, ^3J = 6.4], 1.28 (CH_3 on C-3, s), 1.60 and 1.68 ($2CH_3$ on C-7, s and s), 2.25 (CH, m), 4.90-600 (2H-1, H-6, m).

(-)-1*R*,2*S*,5*R*-Menthol Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxlic Acid (7b). Yield 90%, d_{20}^{20} 0.9719, n_D 1.5115. Found (%): C 52.43, H 10.09, B 29.11. Calc. for $C_{16}H_{36}B_{10}O_2$ (%): C 52.12, H 9.84, B 29.32. M: found 354.7, calc. 368.7.

IR spectrum (ν, cm^{-1}): 2958, 2928, 2872 (CH_{Alk}); 2614 (BH); 1741 (C=O); 1457 (CH_2); 1264 (C–O); 740 (BH). UV spectrum (λ_{max}, ε): 207 (300), 220 (150), 240 (50).

PMR spectrum (δ, ppm, J/Hz): 0.82 (CH_3 on C-3, d, ^3J = 6.9), 0.87 [$(CH_3)_2C$ on C-2, d, ^3J = 6.9], 1.05 [$(CH_3)_2C$, d, ^3J = 6.4], 2.25 (CH, m), 4.58 (H-1, dt, $^3J_{aa}$ = 10.1, $^3J_{ae}$ = 4.7).

Terpineol Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxlic Acid (8b). Yield 91%, d_{20}^{20} 1.0993, n_D 1.5265. Found (%): C 52.71, H 9.55, B 29.24. Calc. for $C_{16}H_{34}B_{10}O_2$ (%): C 52.43, H 9.35, B 29.49. M: found 351.4, calc. 366.6.

IR spectrum (ν, cm^{-1}): 3060 (=CH); 2971, 2929, 2880, 2830 (CH_{Alk}); 2613 (BH); 1739 (C=O); 1650 (C=C); 1460, 1445 (CH_2); 1275 (C–O); 735 (BH). UV spectrum (λ_{max}, ε): 205 (4000).

PMR spectrum (δ, ppm, J/Hz): 1.05 [$(CH_3)_2C$, d, ^3J = 6.4], 1.18 [$(CH_3)_2C$, on C-4, s], 1.64 (CH_3 on C-1, s), 2.25 (CH, m), 5.40 (H-2, m).

10-Methylcamphene Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxlic Acid (9b). Yield 92%, d_{20}^{20} 1.0158, n_D 1.5375. Found (%): C 52.79, H 9.60, B 29.29. Calc. for $C_{16}H_{34}B_{10}O_2$ (%): C 52.43, H 9.35, B 29.49. M: found 350.1, calc. 366.6.

IR spectrum (ν, cm^{-1}): 2970, 2880 (CH_{Alk}); 2614 (BH); 1745 (C=O); 1462 (CH_2); 1256 (C–O); 739 (BH). UV spectrum (λ_{max}, ε): 206 (300), 220 (150), 241 (50).

PMR spectrum (δ, ppm, J/Hz): 1.00 (2CH_3 on C-2, s), 1.05 [$(CH_3)_2C$, d, ^3J = 6.5], 2.25 (CH, m), 2.98 (H-3, br.s), 4.65 (2H-10, d, ^3J = 7.0).

Borneol Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxlic Acid (10b). Yield 92%, d_{20}^{20} 1.0791, n_D 1.5210. Found (%): C 52.77, H 9.51, B 29.20. Calc. for $C_{16}H_{34}B_{10}O_2$ (%): C 52.43, H 9.35, B 29.49. M: found 353.3, calc. 366.6.

IR spectrum (ν, cm^{-1}): 2956, 2879 (CH_{Alk}); 2614 (BH); 1743 (C=O); 1470, 1454 (CH_2); 1268 (C–O); 735 (BH). UV spectrum (λ_{max}, ε): 206 (300), 221 (150), 240 (50).

PMR spectrum (δ, ppm, J/Hz): 0.81 (CH_3 on C-1, s), 0.87 (2CH_2 on C-7, s), 1.06 [$(CH_3)_2C$, d, ^3J = 6.7], 2.25 (CH, m), 4.90 (H-2, m).

Isoborneol Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxlic Acid (11b). Yield 91%, d_{20}^{20} 1.0453, n_D 1.5240. Found (%): C 52.71, H 9.56, B 29.29. Calc. for $C_{16}H_{34}B_{10}O_2$ (%): C 52.43, H 9.35, B 29.49. M: found 350.1, calc. 366.6.

IR spectrum (ν, cm^{-1}): 2955, 2880 (CH_{Alk}); 2615 (BH); 1741 (C=O); 1469, 1456 (CH_2); 1265 (C–O); 740 (BH). UV spectrum (λ_{max}, ε): 206 (300), 220 (150), 240 (50).

PMR spectrum (δ, ppm, J/Hz): 0.83 (CH_3, s), 1.00 (CH_3, s), 1.06 [$(CH_3)_2C$, d, ^3J = 6.7], 1.10 (CH_3, s), 2.25 (CH, m), 4.62 (H-2, m).

Isophenchol Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxlic Acid (12b). Yield 94%, d_{20}^{20} 1.0110, n_D 1.5215. Found (%): C 52.68, H 9.47, B 29.38. Calc. for $C_{16}H_{34}B_{10}O_2$ (%): C 52.43, H 9.35, B 29.49. M: found 358.4, calc. 366.6.

IR spectrum (ν, cm^{-1}): 2967, 2871 (CH_{Alk}); 2614 (BH); 1742 (C=O); 1469, 1453 (CH_2); 1267 (C–O); 739 (BH). UV spectrum (λ_{max}, ε): 205 (300), 220 (150), 240 (50).

PMR spectrum (δ, ppm, J/Hz): 0.92 (CH_3, s), 1.01 (2CH_3, s), 1.06 [$(CH_3)_2C$, d, ^3J = 6.7], 2.25 (CH, m), 4.45 (H-2, m).

Nopol Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxlic Acid (13b). Yield 90%, d_{20}^{20} 1.0936, n_D 1.5320. Found (%): C 52.60, H 9.44, B 29.35. Calc. for $C_{16}H_{34}B_{10}O_2$ (%): C 52.43, H 9.35, B 29.49. M: found 351.8, calc. 366.6.

IR spectrum (ν, cm^{-1}): 2984, 2970, 2917, 2882, 2833 (CH_{Alk}); 2614 (BH); 1747 (C=O); 1468 (CH_2); 1266 (C–O); 742 (BH). UV spectrum (λ_{max}, ε): 207 (350), 221 (150), 240 (50).

PMR spectrum (δ, ppm, J/Hz): 0.81 (CH_3, s), 1.04 [$(CH_3)_2C$, d, ^3J = 6.6], 1.27 (CH_3, s), 2.25 (CH, m), 4.15 (2H-2, t, ^3J = 6.8).

***trans*-Verbenol Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxlic Acid (14b).** Yield 91%, d_{20}^{20} 1.1358, n_D 1.5325. Found (%): C 53.12, H 9.02, B 29.50. Calc. for $C_{16}H_{32}B_{10}O_2$ (%): C 52.72, H 8.85, B 29.66. M: found 340.3, calc. 364.5.

IR spectrum (ν, cm^{-1}): 3040 (=CH); 2974, 2938, 2873 (CH_{Alk}); 2613 (BH); 1739 (C–O); 1652 (C=C); 1469 (CH_2); 1264 (C–O); 745 (BH). UV spectrum (λ_{max}, ε): 205 (4000).

PMR spectrum (δ, ppm, J/Hz): 0.87 (CH_3, s), 1.04 [$(CH_3)_2C$, d, ^3J = 6.6], 1.34 (CH_3, s), 1.75 (CH_3, s), 2.25 (CH, m), 4.70 (H-2, m), 5.28 (H-3, d, ^3J = 4.0).

2-*endo*-[2-Phenyl ester of *m*-C(7)-*iso*-propylcarboran-C(1)-carboxlic acid]-2,3,3-trimethylbicyclo[2.2.1]heptane (15b). Yield 93%, d_{20}^{20} 1.1020, n_D 1.5605. Found (%): C 59.73, H 9.18, B 24.51. Calc. for $C_{22}H_{40}B_{10}O_2$ (%): C 59.42, H 9.07, B 24.31. M: found 419.4, calc. 444.7.

IR spectrum (ν, cm^{-1}): 3090, 3080, 3034, 3010 (CH_{Ar}); 2985, 2954, 2878 (CH_{Alk}); 2614 (BH); 1759 (C=O); 1605, 1481, 1389, 1371 (Ar); 1451 (CH_2); 1246, 1208, 1167, 1115 (C–O); 760, 746, 730, 677 (CH_{Ar}). UV spectrum (λ_{max}, ε): 212 (8000), 260 (1000).

PMR spectrum (δ, ppm, J/Hz): 0.79 (CH_3, s), 0.89 (CH_3, s), 0.95 (CH_3, s), 1.11 [$(CH_3)_2C$, d, ^3J = 6.8], 2.35 (CH, m), 6.80-7.55 (4H_{Ar}, m).

Isocamphyl-2,2-*spiro*-4-[methyl ester of *m*-C(7)-*iso*-propylcarboran-C(1)-carboxlic acid]-2,2-dioxalane (16b). Yield 94%, d_{20}^{20} 1.1473, n_D 1.5250. Found (%): C 52.24, H 9.06, B 24.22. Calc. for $C_{19}H_{38}B_{10}O_4$ (%): C 52.03, H 8.73, B 24.65. M: found 411.2, calc. 438.6.

IR spectrum (ν, cm^{-1}): 2971, 2873 (CH_{Alk}); 2614 (BH); 1751 (C=O); 1472, 1449 (CH_2); 1268, 1109, 1019 (C–O); 739 (BH). UV spectrum (λ_{max}, ε): 205 (400), 220 (200), 243 (100).

PMR spectrum (δ, ppm, J/Hz): 0.89 (2CH_3, s), 1.00 (CH_3, s), 1.04 [$(CH_3)_2C$, d, ^3J = 6.5], 2.25 (CH, m), 3.45-4.45 (2CH_2O and CHO, m).

Eugenol Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxlic Acid (17b). Yield 91%, d_{20}^{20} 1.0862, n_D 1.5550. Found (%): C 51.23, H 7.64, B 28.45. Calc. for $C_{16}H_{28}B_{10}O_3$ (%): C 51.04, H 7.50, B 28.72. M: found 358.6, calc. 376.5.

IR spectrum (ν, cm^{-1}): 3080 (=CH); 3075, 3005 (CH_{Ar}); 2975, 2940, 2913, 2880, 2840 (CH_{Alk}); 2615 (BH); 1770 (C=O); 1639 (C=C); 1607, 1464, 1421 (Ar); 1275, 1249, 1197, 1150, 1124, 1036, 1006 (C–O); 916, 843, 796 (CH_{Ar}); 745 (BH). UV spectrum (λ_{max}, ε): 208 (14000), 218 (8000), 270 (3000).

PMR spectrum (δ, ppm, J/Hz): 1.08 [$(CH_3)_2C$, d, $^3J = 6.7$], 2.25 (CH, m), 3.32 (CH_2, d, $^3J = 6.7$), 3.79 (CH_3O, s), 4.90-5.18 (=CH_2, m), 5.65-6.20 (=CH, m), 6.55-6.95 ($3H_{Ar}$, m).

Vanillin Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxlic Acid (18b). Yield 89%, d_{20}^{20} 1.2554, n_D 1.5655. Found (%): C 46.39, H 6.81, B 29.47. Calc. for $C_{14}H_{24}B_{10}O_4$ (%): C 46.14, H 6.64, B 29.66. M: found 355.2, calc. 364.5.

IR spectrum (ν, cm^{-1}): 3080, 3010 (CH_{Ar}); 2974, 2942, 2880, 2850, 2835, 2735 (CH_{Alk}); 2614 (BH); 1770, 1703 (C=O); 1604, 1503, 1465, 1423, 1391 (Ar); 1277, 1246, 1195, 1146, 1120, 1032, 1005 (C–O); 800, 780, 734 (CH_{Ar}), 745 (BH). UV spectrum (λ_{max}, ε): 206 (9000), 224 (13000), 260 (8000), 308 (4000).

PMR spectrum (δ, ppm, J/Hz): 1.05 [$(CH_3)_2C$, d, $^3J = 6.6$], 2.22 (CH, m), 3.88 (CH_3O, s), 7.00-7.55 ($3H_{Ar}$, m), 9.93 (CHO, s).

Vanillal Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxlic Acid (19b). Yield 89%, d_{20}^{20} 1.2130, n_D 1.5620. Found (%): C 47.93, H 7.12, B 28.34. Calc. for $C_{15}H_{26}B_{10}O_4$ (%): C 47.60, H 6.92, B 28.57. M: found 356.9, calc. 378.5.

IR spectrum (ν, cm^{-1}): 3090, 3080, 3010 (CH_{Ar}); 2982, 2940, 2901, 2881, 2830, 2735 (CH_{Alk}); 2615 (BH); 1769, 1699 (C=O); 1602, 1503, 1441, 1391 (Ar); 1469 (CH_2); 1273, 1245, 1192, 1154, 1120, 1040, 1006 (C–O); 798, 744 (CH_{Ar}). UV spectrum (λ_{max}, ε): 205 (9000), 224 (13000), 260 (8000), 309 (3000).

PMR spectrum (δ, ppm, J/Hz): 1.06 [$(CH_3)_2C$, d, $^3J = 6.7$], 1.45 (CH_3, t, $^3J = 7.4$), 2.23 (CH, m), 4.12 (CH_2, q, $^3J = 7.4$), 6.85-7.50 ($3H_{Ar}$, m), 9.92 (CHO, s).

Tetrahydrofurfuryl Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxlic Acid (20b). Yield 93%, d_{20}^{20} 1.0787, n_D 1.5355. Found (%): C 42.26, H 8.53, B 34.12. Calc. for $C_{11}H_{26}B_{10}O_3$ (%): C 42.02, H 8.33, B 34.38. M: found 292.7, calc. 314.4.

IR spectrum (ν, cm^{-1}): 2975, 2944, 2878 (CH_{Alk}); 2614 (BH); 1749 (C=O); 1464 (CH_2); 1265, 1191, 1132, 1082, 1022 (C–O); 739 (BH). UV spectrum (λ_{max}, ε): 205 (400), 221 (200), 242 (50).

PMR spectrum (δ, ppm, J/Hz): 1.04 [$(CH_3)_2C$, d, $^3J = 6.4$], 2.24 (CH, m), 3.70-4.30 (CHO and $2CH_2O$, m).

Furfuryl Ester of *m*-C(7)-*iso*-Propylcarboran-C(1)-carboxylic Acid (21b). Yield 94%, mp 35-36°C. Found (%): C 42.81, H 7.35, B 34.41. Calc. for $C_{11}H_{22}B_{10}O_3$ (%): C 42.56, H 7.14, B 34.83. M: found 297.7, calc. 310.4.

IR spectrum (ν, cm^{-1}): 3150, 3120 (CH_{Ar}); 2974, 2943, 2880 (CH_{Alk}); 2613 (BH); 1748 (C=O); 1502, 1469, 1392, 1370 (Ar); 1448 (CH_2); 1256, 1192, 1152, 1080, 1016, 950, 921 (C–O); 817, 746, 705, 598 (CH_{Ar}). UV spectrum (λ_{max}, ε): 217 (8000).

PMR spectrum (δ, ppm, J/Hz): 1.05 [$(CH_3)_2C$, d, $^3J = 6.4$], 2.20 (CH, m), 5.08 (CH_2O, s), 6.25-6.45 [2(=CH), m], 7.25-7.48 (=CHO, m).

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REFERENCES

1. G. L. Locher, *Am. J. Roentgenol. Radium Ther.*, **36**, No. 1, 1 (1936).
2. M. Javid, G. L. Brownell, and W. H. Sweet, *J. Clin. Invest.*, **31**, No. 7, 603 (1952).
3. M. F. Hawthorne, *Mol. Med. Today*, 174 (1998).
4. M. F. Hawthorne and A. Maderna, *Chem. Rev.*, **99**, 3421 (1999).
5. M. F. Hawthorne, A. Varadarajan, C. B. Knobler, and S. Chakrabarti, *J. Am. Chem. Soc.*, **112**, 5365 (1990).
6. N. M. Goudgaon, G. F. El-Kattan, and R. F. Schinazi, *Nucleosides Nucleotides*, **13**, No. 1-3, 849 (1994).
7. Y. Endo and Y. Taoda, *Tetrahedron Lett.*, **40**, 9073 (1999).
8. B. Stibr, J. Holub, J. Plesek, T. Jelinek, B. Gruner, F. Teixidor, and C. Vinas, *J. Organomet. Chem.*, **582**, No. 1, 282 (1999).

9. J. M. Oliva and C. Vinas, *J. Mol. Struct.*, **556**, 33 (2000).
10. J. F. Valiant and P. Schaffer, *J. Inorg. Biochem.*, **85**, No. 1, 43 (2001).
11. W. J. Marshall, R. J. J. Young, and V. V. Grushin, *Organometallics*, **20**, 523 (2001).
12. V. I. Bregadze, I. B. Sivaev, D. Gabel, and D. Wohrle, *J. Prophyrins Phthalocyanines*, **5**, 767 (2001).
13. R. Wilko, S. Verbakel, W. Sauerwein, K. Hideghety, and F. Stecher-Rasmussen, *Int. J. Radiat. Oncol. Biol. Phys.*, **55**, No. 3, 743 (2003).
14. P. L. Mauri, F. Basilico, P. G. Pietta, E. Pasini, D. Monti, and W. Saurwein, *J. Chromatogr. B*, **788**, 9 (2003).
15. T. Kuroiwa, S. I. Miyatake, Y. Kajimoto, S. Kawabata, Y. Kuroda, Y. Imahori, M. Kirihata, and K. Ono, *Int. Congress Series*, **1259**, 39 (2004).
16. M. Suzuki, Y. Sakurai, S. Masunaga, Y. Kinashi, K. Nagata, and K. Ono, *Int. J. Radiat. Oncol. Biol. Phys.*, **58**, No. 3, 892 (2004).
17. E. A. Dikusar, A. P. Yuvchenko, T. D. Zvereva, S. A. Makhnach, and S. A. Filanchuk, *Zh. Obshch. Khim.*, **66**, No. 11, 1813 (1996).
18. E. A. Dikusar, T. D. Zvereva, N. G. Kozlov, V. L. Murashko, K. L. Moiseichuk, A. P. Yuvchenko, and V. K. Ol′khovik, *Vestsi Nats. Akad. Navuk Belarusi, Ser. Khim. Navuk*, No. 4, 54 (2002).
19. R. N. Grimes, *Carboranes*, Academic, New York (1970).