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SYNTHESIS AND CRYSTAL STRUCTURE OF NEW DINITRO DERIVATIVES OF SESQUITERPENE LACTONE ACHILLIN

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Abstract- An unexpected dinitro derivative (**2**) of sesquiterpene lactone achillin (**1**), isolated from the aerial part of *Achillea micrantha* Wild., was formed when this compound was exposed to gaseous NOCl in $CHCl_3$. This derivative was transformed into dinitrocarbonic acid (**3**) in pyridine in 30 minutes and in quantitative yield. The structures of these compounds were unambiguously determined by single-crystal X-Ray diffraction analysis.

INTRODUCTION

Plants of family Asteraceae are the main sources of sesquiterpene γ-lactones.[1-6] These compounds possess a wide range of biological activities including antitumor, antimalarial, antiviral, antibacterial, growth-regulating, repellent, *etc*.[7] Because of the biological importance, the chemical modification of sesquiterpene lactones is a promising direction which allow to synthesize biologically active derivatives and study "structure-activity" relationships. Among the perspective directions of chemical modifications synthesis of water-soluble derivatives, oxidative reactions, for example epoxidation and introduction of halogen atom (chlorination, bromination) are particularly important.

Interestingly, the derivatives of sesquiterpene lactones with nitro group have not been reported in literature. In this paper, the synthesis and formation of new unusual dinitro derivatives of achillin (**1**) through nitrosochlorination reaction is described.

RESULTS AND DISCUSSION

In continuation of our work on halogenation of naturally occurring sesquiterpene lactones with the aim to synthesize new physiologically active compounds,[8-9] we carried out the nitrosochlorination of sesquiterpene lactone achillin (**1**). This compound was originally isolated from the aerial parts of *Achillea micrantha* Wild.[10] usual conditions (passing of purified gaseous NOCl[11] through cooled (0-10° C) solution of lactone (**1**) in $CHCl_3$ until full consumption of initial compound, periodic TLC analysis) were applied out to monitor the progress of this very slow reaction (48 h). According to TLC, only product (**2**) was formed, which was isolated as colourless crystals, insoluble in most of the organic solvents.

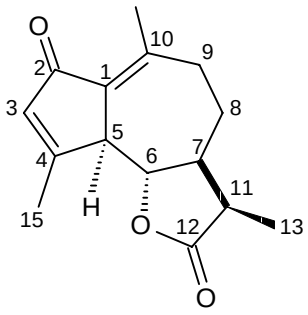
It was found through Beilstein database, that this derivative does not contain chlorine atom and the EI MS spectrum showed peaks, corresponding to ions of initial lactone (**1**). The stereochemistry was determined by the single-crystal X-Ray diffraction analysis of 1,10-dihydro-1α, 10α-dinitroachillin (**2**). Seven-membered ring in the compound (**2**) was found to have a chair conformation (Figure 1), and lactone ring has as envelope conformation with deviation of C(7) atom at a value 0.499(4) Å from the plane of other atoms. The similar conformation of above mentioned rings was found in related compound, guaianolide tetrahydroleucomisine.[12] Cyclopentenone fragment of the compound (**2**) was found to be planar in the range of ±0.039(4) Å. The length of C(2)-C(3) bond in the cyclopentenone fragment (1.429(4) Å) is smaller than the average value 1.464(18) Å[13] for conjugated fragment C=C-C(=O)-C and agreed with the length of same bond in δ-homo-4-norestro-3(5)-ene-2,17-dione.[14] The bond length C(10)-N(2) (1.562(3) Å) of equatorially oriented nitro group was found to be large in comparison with the normal C(1)-N(1) bond (1.537(3) Å). The same difference in the length of axial and equatorial oriented bonds C-NO_2 was observed in 2-hydroxy-2,3,4,5,6-pentamethyl-5,6-dinitrocyclohex-3-enone.[15]

The formation of dinitro derivatives during nitrosochlorination has not been reported earlier in the literature. On the other hand, the interaction of NOCl with unsaturated compounds of various types is well known and has been reviewed.[16] The α-enones present in the lactone (**1**) may be playing a role in the formation of chloroisonitroso ketones (chlorooximes).[17,18]

NOCl through a column filled with humid KCl.[11] For example, slow reaction of NOCl with cholesterol acetate, which give 5α-chloro-6β-nitro derivative, sharply accelerates in the presence of NO_2.[19] The formation of 1,2-dinitro derivative was observed in the reaction of isobutylene with N_2O_4 in ether.[20]

The mechanism of formation of dinitro derivative (**2**) is not clear but it was found that the use of impure

NOCl containing NO_2 noticeably accelerate the formation of derivative (**2**), which on TLC found to be a complicated mixture of products and thus the reaction is not selective in this case.



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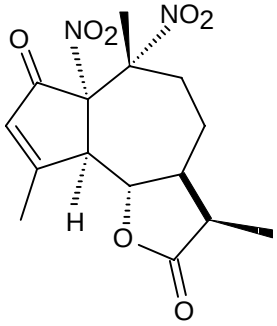

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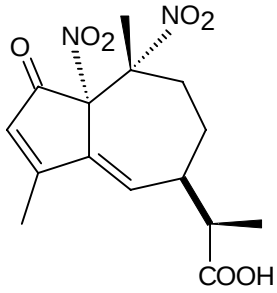

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Table 1. ^{1}H-NMR spectral data of compounds (**2**) and (**3**) (Me_4Si, δ, ppm, *J*/Hz).

Proton	**2**[*]	2[**]	**3**[**]
H (3)	6.31 dq ($J_{3,15}$ = 1.0; $J_{3,5}$ = 2.0)	6.20 dq ($J_{3,15}$ = 1.2; $J_{3,5}$ = 2.5)	6.27 br s
H (5)	3.88 ddq ($J_{5,6}$ = 10.0; 2.0; 1.0)	4.20 d ($J_{5,6}$ = 10.0)	
H (6)	5.00 t ($J_{6,5}$ = 10.0)	4.94 t ($J_{6,5}$ = 10.0)	6.64 d ($J_{6,7}$ = 4.0)
H (7)	3.16 m	3.13 m	3.66 m
H (8A)	1.82 m	1.53 d ($J_{8A,8B}$ = 14.0)	1.80 m
H (8B)	3.15 m	1.75 d ($J_{8B,8A}$ = 14.0)	1.90 m
H (9A)	2.12 m	1.95 m	2.10 ddd ($J_{9A,9B}$ =14.0; $J_{9A,8B}$ = 5.0; $J_{9A,8A}$= 3.0)
H (9B)	3.34 td ($J_{9A,9B}$= 14.0; $J_{9A,8A}$= 5.0)	3.39 td ($J_{9A,9B}$ = 14.0; $J_{9A,8A}$ = 4.0)	3.60 ddd ($J_{9A,9B}$ = 14.0; $J_{9B,8B}$ = 5.0; $J_{9B,8A}$= 3.0)
H (11)	2.84 quint ($J_{11,8}$ = 8.0)	2.75 quint. ($J_{11,8}$ = $J_{11,13}$ = 8.0)	2.81 dq ($J_{11,8}$ = 5.0; $J_{11,13}$ = 7.5)
3H (13)	1.23 d ($J_{13,11}$ = 8.0)	1.11 d ($J_{13,11}$ = 8.0)	1.30 d ($J_{13,11}$ = 7.5)
3H (14)	1.59 br s	1.58 br s	1.49 br s
3H (15)	2.33 br s	2.09 br s	1.94 br s

[*]Solvent - Acetone-d_6 , [**]Solvent - Pyridine-d_5

The ^{1}H-NMR (Table 1) and ^{13}C-NMR (Table 2) spectra of lactone (**2**) in acetone-d_6 is interpreted with the help of two-dimensional ^{1}H-^{1}H-NMR (COSY) and ^{1}H-^{13}C-NMR (HMBC) spectra. These spectra were recorded in pyridine-d_5. However, it was unexpectedly found that the compound (**2**) in this solvent quantitatively and irreversibly changed into acid (**3**), the NMR spectra data of which are given in the Tables 1 and 2. The conversion time during which lactone (**2**) totally and quantitatively isomerizes to **3** at

30° C is about 30 min. In the first 10-15 min it is possible to record ^{1}H-NMR spectra (pyridine-d_5) of the mixture of compounds (**2**) and (**3**) with the noticeable amount (about 50%) of starting material (**2**) (Table 1). After slow evaporation of pyridine-d_5, the crystals of compound (**3**) were formed, which were eventually used in X-Ray analysis.

Table 2. ^{13}C-NMR data of compounds (**2**) and (**3**).

Atom	**2***(δ)	**3****(δ)
C(1)	95.40 (s)	93.23 (s)
C(2)	192.89 (s)	191.45 (s)
C(3)	130.95 (d)	130.67 (d)
C(4)	180.08 (s)	171.74 (s)
C(5)	61.08 (d)	136.92 (s)
C(6)	80.92 (d)	138.90 (d)
C(7)	43.03 (d)	39.55 (d)
C(8)	22.46 (t)	27.09 (t)
C(9)	37.62 (t)	38.96 (t)
C(10)	94.00 (s)	89.67 (s)
C(11)	39.47 (d)	44.53 (d)
C(12)	180.10 (s)	177.25 (s)
C(13)	10.61 (q)	13.76 (q)
C(14)	21.39 (q)	20.25 (q)
C(15)	22.63 (q)	14.34 (q)

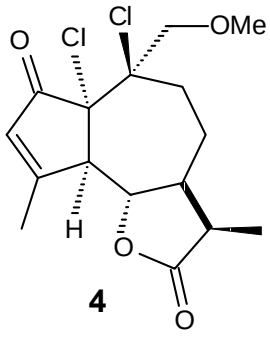
*Solvent - Acetone-d_6 ,**Solvent - Pyridine-d_5

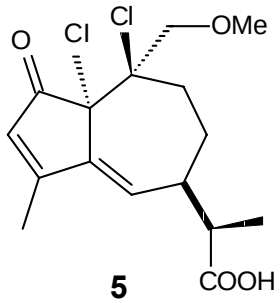
The computer generating X-Ray diffraction model of compound (**3**) is shown in Figure. 2. The seven-membered ring in compound (**3**) has a chair conformation as was observed in the compound (**2**), but with another angle of pseudorotation. Dienone fragment C(1)-C(7)-C(15)-O(3) in compound **(3)** is planar in the range of ±137(2) Å. A hydrogen bond between COOH…N type was observed between the molecule of acid and pyridine with parameters: O(2)…N(1)S 2.677(3) Å; O(2)-H 0.82 Å; H…N(1)S 1.86 Å; O(2)-H…N(1)S 175˚.

The isomerization of compounds (**2**) to **3** is due to presence of an electron acceptor group NO_2 at C(1) (possibly at C(10) too), since the achillin (**1**) itself is inert in pyridine. On the other hand, the isomerization is observed only in pyridine solution, not in the acetone or chloroform.

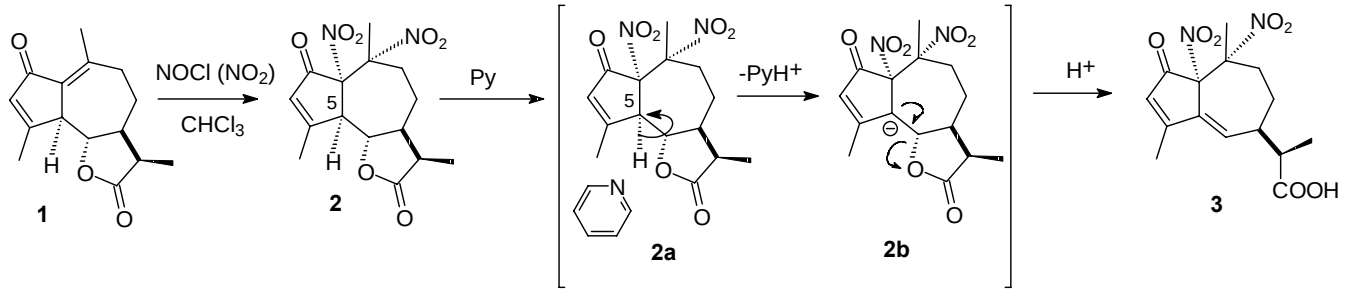
Dichloro derivative (**4**),[8] also used as a model compound, decomposes in pyridine-d_5 but with slow rate. After 1 h at room temperature in NMR tube, the spectrum has not changed noticeably, but after 48 h, a

mixture of two compounds were observed, one of which was identified as acid (**5**). This was further confirmed by ^{1}H-NMR spectral data δ_H 1.30 (3 H, d, $J_{11, 13}$ = 7.0 Hz, C(11)Me); 6.14 (1 H, br s, H(3)); 6.51 (1 H, br d, $J_{6, 7}$ = 4.5 Hz, H(6)), which is similar to protons signals in the spectrum of compound (**3**) (Table 1).





The possible mechanism of isomerization of compound (**2**) to acid derivative (**3**) presented in the Scheme1. Pyridine as a base eliminates acidic H-5 in the molecule of dinitroachillin (**2**) resulted in the formation of a stabilized carbanion (**2b**). Intramolecular nucleophilic "ring-opening" of lactone in the intermediate (**2b**) followed by addition of a proton results in the formation of dinitroacid (**3**).



Scheme 1: The possible mechanism of isomerization of compound (**2**) to acid (**3**).

EXPERIMENTAL

The melting points were determined on a Boetius melting point apparatus. IR spectra were recorded on a Vector 22 apparatus in KBr. UV-spectra were measured on Specord UV-Vis apparatus in EtOH solutions.

NMR spectra were recorded on a Bruker DRX-500 spectrometer (working frequency 500.13 MHz for ^{1}H, 125.76 MHz for ^{13}C and 36.13 MHz for ^{14}N, δ-scale) with standard "Bruker" programs (COSY, COLOC). MS spectra (HR EIMS) (70 eV) were obtained on Finnegan MAT 8200 apparatus.

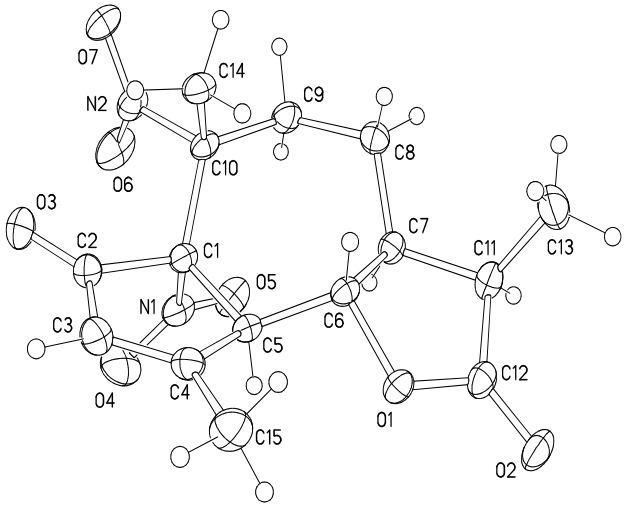


Figure 1: The ORTEP Computer-generated X-Ray diagram of dinitrolactone (**2**).

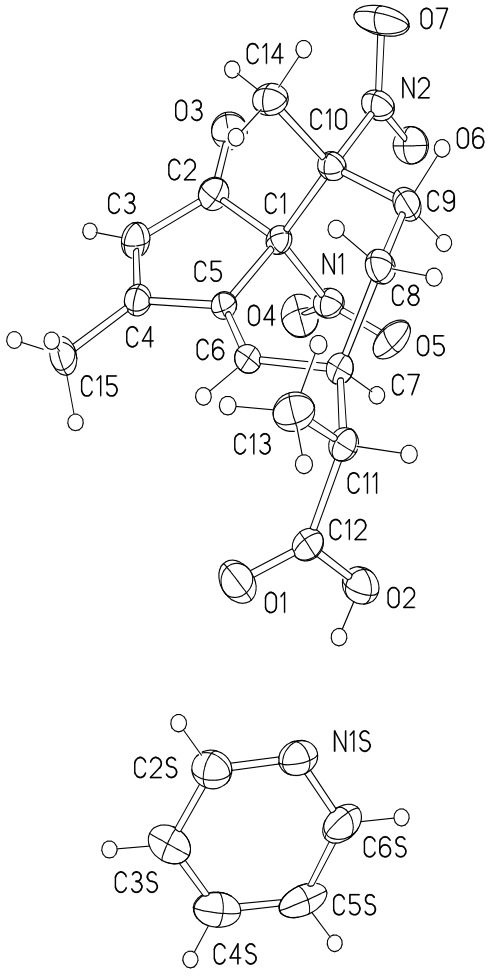


Figure 2: The ORTEP Computer-generated X-Ray diagram of dinitro acid (**3**).

Table 3. Coordinates ($\times 10^4$) and equivalent isotropic parameters (A^2, $\times 10^3$) of non-hydrogen atoms in compound (**2**).

Atom	x	y	z	U(eq)
C1	1817(3)	4738(1)	1177(1)	35(1)
C2	1479(4)	4464(2)	2137(1)	45(1)
C3	363(4)	5155(2)	2541(1)	50(1)
C4	-105(3)	5807(1)	2000(1)	40(1)
C5	910(3)	5698(1)	1137(1)	33(1)
C6	-320(3)	5974(1)	362(1)	33(1)
C7	574(3)	5759(1)	-515(1)	36(1)
C8	42(4)	4825(2)	-829(1)	44(1)
C9	1223(4)	4082(1)	-399(1)	43(1)
C10	963(3)	3997(1)	583(1)	36(1)
C11	-129(4)	6550(2)	-1063(2)	44(1)
C12	-282(3)	7289(1)	-412(2)	42(1)
C13	-2117(6)	6438(2)	-1505(2)	69(1)
C14	-1189(4)	3829(2)	823(2)	43(1)
C15	-1412(5)	6582(2)	2186(2)	58(1)
O1	-389(2)	6947(1)	391(1)	41(1)
O2	-350(3)	8080(1)	-526(1)	58(1)
O3	1989(4)	3752(1)	2427(1)	63(1)
O4	5002(3)	4996(2)	1714(2)	70(1)
O5	4704(3)	4976(1)	342(1)	57(1)
O6	3913(3)	3165(1)	832(2)	71(1)
O7	1221(4)	2430(1)	822(1)	64(1)
N1	4045(3)	4894(1)	1060(1)	46(1)
N2	2134(3)	3124(1)	787(1)	49(1)

Table 4. Coordinates ($\times 10^4$) and equivalent isotropic parameters (A^2, $\times 10^3$) of non-hydrogen atoms in compound (**3**).

Atom	x	y	z	U(eq)
C1	4483(4)	13082(2)	1516(1)	35(1)
C2	4576(4)	14243(2)	1357(1)	45(1)
C3	3663(5)	14343(2)	806(1)	49(1)
C4	2820(4)	13468(2)	638(1)	40(1)
C5	3179(4)	12635(2)	1047(1)	33(1)
C6	2481(4)	11693(2)	1008(1)	36(1)
C7	2809(4)	10812(2)	1411(1)	38(1)
C8	2217(5)	11082(2)	2024(1)	45(1)
C9	3628(5)	11798(2)	2333(1)	45(1)
C10	3670(4)	12906(2)	2118(1)	37(1)
C11	1747(5)	9833(2)	1210(1)	43(1)
C12	2449(5)	9561(2)	619(1)	46(1)
C13	-521(5)	9860(2)	1231(1)	58(1)
C14	1640(4)	13409(2)	2167(1)	50(1)
C15	1597(5)	13326(2)	115(1)	54(1)
N1	6603(4)	12690(2)	1407(1)	45(1)
N2	5105(4)	13455(2)	2538(1)	48(1)
O1	1430(5)	9616(2)	206(1)	92(1)
O2	4303(3)	9257(2)	604(1)	63(1)
O3	5231(4)	14891(2)	1667(1)	65(1)
O4	7708(3)	13242(2)	1140(1)	71(1)
O5	7052(3)	11849(2)	1564(1)	69(1)
O6	6877(3)	13342(2)	2476(1)	61(1)
O7	4387(4)	13923(2)	2926(1)	95(1)
N1(S)	5305(5)	8682(2)	-449(1)	64(1)
C2(S)	4278(6)	9121(3)	-867(1)	67(1)
C3(S)	4765(6)	9026(3)	-1429(2)	75(1)
C4(S)	6372(7)	8441(3)	-1569(2)	79(1)
C5(S)	7447(7)	7979(2)	-1155(2)	79(1)
C6(S)	6854(6)	8117(2)	-593(2)	72(1)

Optical rotations were measured (at 580 nm) on polarimeter Polamat A. "Silufol" plates were used for TLC. Detection of products was performed by spray of 1% solution of vanilline in H_2SO_4 or 1% solution of $KMnO_4$. Achillin (**1**) with mp 145.5-146.5 °C was isolated following the literature procedure[10] from the aerial part of *Achillea micrantha* Wild.

1,10-Dihydro-1α,10α-dinitroachillin (2). Gaseous NOCl obtained as described in literature[11] was passed through cooled (from 0 to –10 °C) solution of lactone (**1**) (0.20 g, 0.8 mmol) in 10 mL of freshly distilled $CHCl_3$ during 48 h (total conversion according to TLC). Then 5 mL of ethanol was added. Small rhombic crystals of compound (**2**) were filtered and recrystallized from MeCN 0.19 g (69.1%) of dinitro derivative (**2**) was obtained with acetonitrile (MeCN) solvent of recrystallization, mp 220° C (decomp) $[\alpha]^{20}_{580}$ + 94.4° (*c* 1.80; acetone), R_f 0.54 (eluent – petroleum ether – EtOAc 2 : 1). UV-spectrum, λ_{max} nm: 233 (shoulder; ε 11900). IR, ν cm^{-1}: 1783 (γ-lactone), 1724 (C=O), 1626 (C=C), 1556 (C-NO_2), 1230, 1150, 1043, 995, 850. MS spectrum, *m/z* ($I_{отн}$ (%)): 292 $[M - NO_2]^+$ (1), 246 $[M – 2\ NO_2]^+$ (100), 217 (13), 173 (22), 172(12), 105 (12), 91 (19). ^{1}H- and ^{13}C-NMR spectra are shown in Tables 1 and 2. ^{14}N NMR spectrum ($CDCl_3$, external standard – formamid, signal of which accepted at 112.4 ppm) δ: 383.0 (m), 390.8 (m). Anal. Calcd for $C_{15}H_{18}N_2O_7$: C, 53.25; H, 5.36; N, 8.28. Found: C, 53.22; H, 5.39; N, 8.23.

(1*S*,7*R*,10*R*,11*R*)-2-Oxo-1, 10-dinitroguaia-3, 5(6)-dien-11-oic acid (3). The lactone (**2**) (0.03g, 0.092 mmol) was dissolved in 0.4 mL of pyridine-d_5 and ^{1}H-NMR spectra were recorded after every 10-15 min. Decrease in content of compound (**2**) and increase of compound (**3**) was clearly observed. After 30 min only signals for compound (**3**) were observed. After ^{1}H-NMR spectra analysis, the solution was poured into small vial, from which pyridine-d_5 was slowly evaporated. The crystals obtained solvent of recrystallization in mixture of acetone-hexane (2:1) with mp 103-106 °C (decomp) were used for X-Ray analysis, after recrystallization from acetone-hexane there was obtained crystals with mp139-142 °C (decomp), $[\alpha]^{22}_{580}$ +52.5° (*c* 0.99; $CHCl_3$). UV, λ_{max} nm: 284 nm (ε 4355). IR (KBr), ν cm^{-1}: 1720 (C=O), 1556 (C-NO_2), 1387, 1339, 1308, 1194, 883, 868, 808, 640. MS spectrum, *m/z* ($I_{отн}$ (%)): 245 $[M-2NO_2]^+$ (14), 189 (10), 173 (14), 161(16), 105 (12), 84 (100). ^{1}H- and ^{13}C-NMR spectra are shown in Tables 1 and 2. Anal. Calcd for $C_{15}H_{18}N_2O_7$: C, 53.25; H, 5.36; N, 8.28. Found: C, 53.18; H, 5.42; N, 8.19.

X-Ray Diffraction Experiments on compounds (**2**) and (**3**) were performed on Bruker P4 diffractometer (Mo Kα-radiation with graphite monochromatic, 2θ/θ-scanning in the range 2θ < 55 и 50°). Colorless crystalline sample of compound (**2**) with dimensions 0.32 × 0.48 × 0.84 mm, and compound (**3**) with dimensions 0.40 × 0.46 × 0.70 mm were selected for diffraction experiments.

The structures were determined by direct methods using SHELXTL-97 program, location of hydrogen atoms were calculated geometrically. Final refinement of structure was performed by Least Square Method in full matrix anisotropic-isotropic approximation (for atoms H) using program SHELXTL-97 all over F^2.

Crystals of **2** are orthorhombic: a = 6.7727(3), b = 14.9825(11), c = 15.5849(8) Å, V = 1581.4(2) Å^3, Space group $P2_12_12_1$, Z = 4, $C_{15}H_{18}N_2O_7$, $d_{calc.}$ = 1.421 g/cm^3, μ = 0.114 mm^{-1}. Intensity of 2096 independent reflections was measured. Finally wR_2 = 0.0951, S = 1.056, 290 parameters (R = 0.0339 for 1897 F > 4σ).

Crystals of **3** are orthorhombic: a = 6.7042(4), b = 13.1091(10), c = 23.554(2) Å, V = 2070.0(3) Å^3, Space group $P2_12_12_1$, Z = 4, $C_{15}H_{18}N_2O_7$ + C_5H_5N, $d_{calc.}$ = 1.339 g/cm^3, μ = 0.103 mm^{-1}. A total of 2022 independent reflections were measured. Finally wR_2 = 0.1028, S = 1.044, 273 parameters (R = 0.0366 for 1846 F > 4σ).

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