of $PdCl_2$ (40 mg mL^{-1}, 0.665 mmol) at 20—30 °C. The reaction mixture was stirred for 30 min. The precipitate that formed was filtered off, washed with water, and dried in air. Compound **2** was obtained in a yield of 0.3 g (75%). Recrystallization from Me_2CO gave coffee-colored crystals, m.p. 167—168 °C. Found (%): C, 31.67; H, 2.45; Cl, 11.64; N, 9.09. $C_{16}H_{16}Cl_2N_4O_{10}Pd$. Calculated (%): C, 31.94; H, 2.68; Cl, 11.78; N, 9.31. IR, ν/cm^{-1}: 690, 745 (CH in Py); 860 (O—NO_2); 1040, 1145 (C—O); 1270, 1620 (ONO_2); 1365, 1435, 2296, 2931, 2944, (CH_2); 1530, 1580, 1605 (C—C and C—N in Py); 1730 (C=O); 3075 (CH).

X-ray diffraction analysis of compounds 1 and 2. Crystals of **1** are monoclinic, M = 212.16, a = 5.997(4) Å, b = 7.782(2) Å, c = 20.771(10) Å, β = 90.66(5)°, V = 969.3(5) Å^3, d_{calc} = 1.453(5) g cm^{-3}, λ = 1.5418 Å, space group $P2_1/n$, Z = 4.

Crystals of complex **2**, $[PdCl_2(N_2O_5C_8H_8)_2]$, are monoclinic, M = 601.65, a = 23.112(25) Å, b = 12.003(3) Å, c = 4.341(6) Å, β = 89.72°, V = 1204.2(9) Å^3, d = 1.659(3) g cm^{-3}, λ = 0.70926 Å, space group $P2_1/a$, Z = 2.

Intensities of 464 (for **1**) and 2131 (for **2**) observed unique reflections were measured on a four-circle KM-4 diffractometer (KUMA-Diffraction, Poland) in the range $0.02 < \sin\theta/\lambda < 0.50$ using the $\omega/2\theta$ scanning technique. The structures were solved by direct methods using the SHELX-86 program package on a PC computer. The atomic coordinates in the structure of **1** (see Table 1) were refined by full-matrix least squares to R = 0.11. Temperature factors of the nonhydrogen atoms were refined anisotropically. The high value of the R factor is attributable to the fact that the X-ray diffraction data were collected from layered crystals prepared by low-temperature crystallization. We failed to improve the quality of the crystals by using other solvents and temperature conditions of crystallization. The atomic coordinates in the structure of **2** (see Table 2) were refined by full-matrix least squares using the SHELX-93 program to R = 0.10. The nonhydrogen atoms were refined anisotropically, and the H atoms were refined isotropically. When absorption correction was applied using the DIFABS program, the refinement converged to the R factor of 0.079.

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Glycosylation of betulin acetates with glycals

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Betulin 2-deoxy-α-D-, 2-deoxy-α-L-, and 2,6-dideoxy-α-L-*arabino*-hexopyranosides were synthesized by acid-catalyzed glycosylation (cationite in the H^+ form, LiBr) of betulin 3- and 28-monoacetates with glycal acetates.

Key words: 3-*O*-acetylbetulin, 28-*O*-acetylbetulin, glycal acetates, stereoselective glycosylation, acid catalysis, betulin 2-deoxy-α-D-, 2-deoxy-α-L, and 2,6-dideoxy-α-L-*arabino*-hexopyranosides.

The birch bark is rich in pentacyclic triterpenoids. The content of betulin (**1**) in it reaches 35—40%, depending on the species.[1] Derivatives of betulin and betulinic acid have a broad range of biological activity, including antiviral[2] and antitumor[3] action.

We carried out the glycosylation of betulin monoacetates (**2, 3**) with acetylated glycals (**4—6**) under acid catalysis conditions, using the KU-2-8 cationite (H^+ form) in combination with LiBr as the activator (Scheme 1). We have used this method of glycosylation[4]

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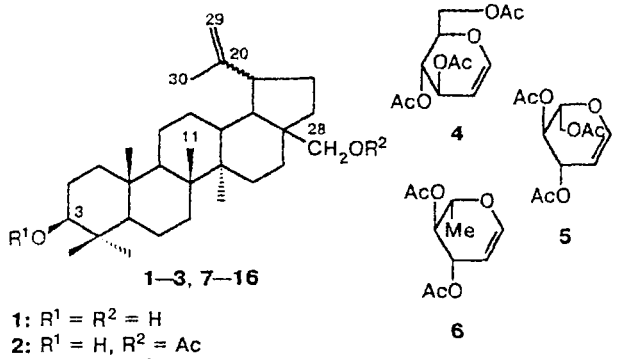
for the synthesis of 2-deoxy-α-glycosides of triterpene alcohols of the oleanane series and some steroids.[5,6] It is necessary to note that the glycosylation of betulin monoacetates with acetobromoglucose gave a mixture of α- and β-glycosides and was accompanied by rearrangements in the aglycone.[7,8]

Scheme 1

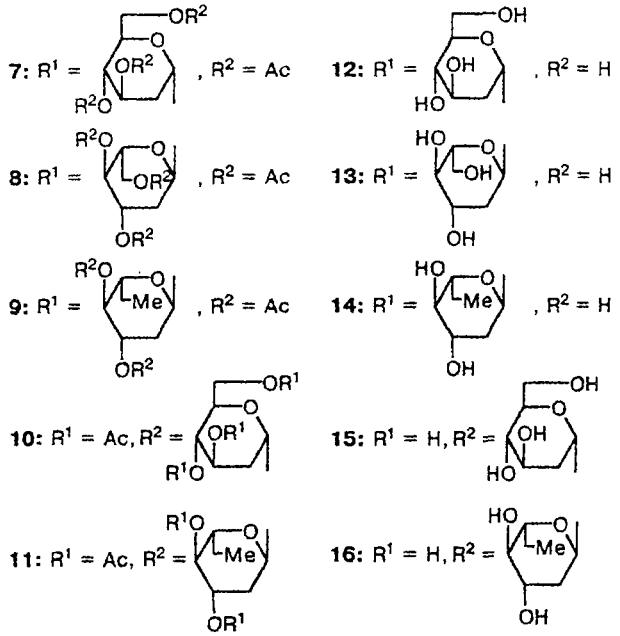
2 + **4** $\xrightarrow{i}$ **7** $\xrightarrow{ii}$ **12**
2 + **5** $\xrightarrow{i}$ **8** $\xrightarrow{ii}$ **13**
2 + **6** $\xrightarrow{i}$ **9** $\xrightarrow{ii}$ **14**
3 + **4** $\xrightarrow{i}$ **10** $\xrightarrow{ii}$ **15**
3 + **6** $\xrightarrow{i}$ **11** $\xrightarrow{ii}$ **16**

Reagents: *i.* KU-2-8 cationite (H^+), LiBr; *ii.* 5% KOH/MeOH.



1—**3**, **7**—**16**

1: $R^1 = R^2 = H$
2: $R^1 = H$, $R^2 = Ac$
3: $R^1 = Ac$, $R^2 = H$



The glycosylation of 28-*O*-acetylbetulin **2** with the acetates of D-glucal (**4**), L-glucal (**5**), and L-ramnal (**6**) gave acetylated 2-deoxy-α-D-, 2-deoxy-α-L, and 2,6-dideoxy-α-L-*arabino*-hexopyranosides (**7**—**9**) in 78—82% yields. The glycosylation of the primary alcohol group of 3-*O*-acetylbetulin (**3**) with the acetates of D-glucal (**4**) and L-ramnal (**6**) gave 2-deoxy-α-D- (**10**) and 2,6-dideoxy-α-L-*arabino*-hexopyranosides (**11**) in a higher yield (~90%). Treatment of compounds **7**—**11** with methanolic KOH resulted in the formation of betulin 2-deoxy-α-glycosides (**12**—**16**) incorporating a carbohydrate substituent at position 3 or 28.

The structures of the compounds synthesized (**7**—**16**) were established by ^1H NMR (see Experimental) and ^{13}C NMR spectroscopy (Table 1). Literature data for betulin, its acetates,[8,9] and 2-deoxy-α-glycosides[10,11] were used for comparison. The introduction of a carbohydrate residue in the molecule of 28-*O*-acetylbetulin results in a downfield shift of the C(3) signal by 4—10 ppm, while the signals of anomeric C(1′) carbon atoms are observed at δ 93.1 and 99.1—99.5, as in the spectra of 2-deoxy-α-glycosides of glycyrrhetic acid and allobetulin.[10,11] The formation of an α-glycoside bond follows from the magnitudes of the coupling constants, $^1J_{C(1'),H(1')}$ = 168.3—170.0 Hz, in the ^{13}C NMR spectra of compounds **7**—**9**.[12] The exact assignment of the signals of carbon and hydrogen atoms in the ^{13}C NMR and ^1H NMR spectra of glycoside **8** was carried out by two-dimensional heteronuclear ^{13}C—^1H COSY NMR spectrum. It follows from this spectrum that the signal of the H(1′) proton at δ 4.93 correlates with the signal of the C(1′) carbon at δ 99.5, while the signals of olefin protons H(29) at δ 4.51 and 4.63 have a cross-peak with the C(29) signal at δ 109.8. The signal of the C(3) aglycone atom at δ 89.3 correlates with the signal of the H(3) atom at δ 2.98. The mutual arrangement of hydrogen atoms determined from ^1H NMR and ^{13}C—^1H COSY spectra indicates that glycoside **8** has the structure of 2-deoxy-α-L-*arabino*-hexopyranoside.

The formation of the glycoside bond in 3-*O*-acetylbetulin through the primary hydroxyl group resulted in a downfield shift of the C(28) signal by 6 and 10 ppm, respectively, in the spectra of compounds **10** and **11**. The signal of the anomeric C(1′) atom in the spectrum of glycoside **10** is observed at δ 97.7, as in the spectrum of 1,2-ethanediol 2-deoxy-α-D-*arabino*-hexopyranoside.[13] The constants $^1J_{C(1'),H(1')}$ = 168.1 and 167.9 Hz in the ^{13}C NMR spectra of compounds **10** and **11** also indicated the presence of an α-glycoside bond.[12]

Thus, glycosylation of primary and secondary hydroxyl groups in betulin monoacetates under conditions of acid catalysis stereoselectively gave 2-deoxy-α-hexopyranosides in high yields.

Experimental

TLC was carried out on Silufol plates (Chemapol, Czech Republic) using $CHCl_3$—MeOH (20 : 1) as the eluent. Compounds were visualized using a 20% solution of phosphotung-

Table 1. ^{13}C NMR spectroscopis data for glycosides **7**—**16** ($CDCl_3$, δ, *J*/Hz)*

Compound	C(2)	C(3)	C(11)	C(20)	C(28)	C(29)	C(30)	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)	OCOCH$_3$	OCOCH$_3$
7	25.1	82.8	20.7	150.0	62.4	109.8	19.0	93.1	35.6	69.2	68.2	69.5	62.7	20.7, 20.8, 20.9, 20.9	169.9, 170.1, 170.6, 171.5
8	25.2	89.3	20.5	149.8	62.4	109.8	18.9	99.5	35.4	69.0	67.7	70.8	62.5	20.6, 20.7, 20.7, 20.9	169.7, 169.9 170.1, 171.2
9	24.2	88.7	20.4	149.6	62.3	109.6	18.8	99.1	35.6	68.9	74.8	65.3	17.6	20.5, 20.6, 20.9, 21.5	169.8, 170.4, 171.0
10	23.6	80.7	20.6	150.1	66.4	109.7	19.0	97.7	35.0	69.1	67.9	69.3	62.1	20.7, 20.8, 21.1	169.7, 170.0, 170.6, 170.7
11	23.6	80.8	20.7	150.3	70.8	109.6	19.0	103.8	35.3	69.1	74.9	64.8	17.9	20.9, 21.2, 21.2	170.3, 170.8
12	24.7	81.7	20.3	149.9	60.5	108.8	19.1	92.7	36.5	71.4	68.5	72.1	62.5		
13	25.1	88.4	20.5	150.1	60.8	109.8	19.0	100.0	36.4	69.3	68.3	71.6	61.8		
14	25.1	88.7	20.8	150.4	60.4	109.6	19.0	100.0	39.0	69.2	78.1	67.5	17.5		
15	27.1	78.9	20.8	150.4	65.8	109.6	19.0	98.2	35.0	71.1	69.0	72.0	61.8		
16	27.1	79.0	20.8	150.5	65.6	109.7	19.1	97.8	35.0	69.3	78.0	67.6	17.8		

* $^1J_{C(1'),H(1')}$ = 169.5 (**7**), 170.0 (**8**), 168.3 (**9**), 168.1 (**10**), 167.9 (**11**).

stic acid in EtOH followed by heating at 100—120 °C for 2—3 min. Column chromatography was performed on silica gel L (40/100 mm) (Chemapol, Czech Republic).

^{13}C and ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer (75.5 and 300 MHz, respectively) in $CDCl_3$ using $SiMe_4$ as the internal standard. Melting points were determined on a Boetius hot micro stage.

MeCN and CH_2Cl_2 used for the syntheses were distilled two times over P_2O_5. Molecular sieves (4 Å) were activated at 180—190 °C for 2 h (1—5 Torr). The KU-2-8 cationite (H^+ form) was dried by a reported procedure.[4] 3-*O*-Acetylbetulin was synthesized by a procedure reported previously.[14] Glycals **4**—**6** were synthesized using a known procedure.[15]

Extraction of betulin from the bark of the *Betula pendula* birch. A Pr^iOH—water mixture (7 : 3, 700 mL) containing dry crushed bark (70 g) was refluxed for 2 h. The bark was filtered off, and the hot solution was kept for 12 h at 0—5 °C. The precipitate that formed was filtered off, and the mother liquor was again used for extraction, which was repeated two times. The yield of dry extract was 24.7 g (35.3%). Betulin was obtained by chromatography of the extract using benzene as the eluent, yield ~75—80%, m.p. 251 °C.

28-Acetoxy-3β-hydroxy-20(29)-lupene (2). A solution of betulin (4.42 g, 10 mmol) in 150 mL of glacial AcOH was refluxed for 1 h, concentrated to half the volume, and the residue was poured into 300 mL of cold water. The precipitate that formed was filtered off and washed to a neutral pH. The dry residue was chromatographed using benzene as the eluent. Yield 3.68 g (76%). M.p. 203—205 °C (*cf.* Ref. 16: m.p. 205 °C).

Synthesis of glycosides 7—11 (general procedure). Glycal **4** (0.27 g), **5** (0.27 g), or **6** (0.22 g), molecular sieves (0.3 g), anhydrous cationite (0.8 g), and LiBr (0.6 g) were added to a solution of betulin monoacetate **2** or **3** (1 mmol, 0.48 g) in 40 mL of a CH_2Cl_2—CH_3CN mixture (1 : 1). The mixture was stirred for 4—5 h (TLC monitoring) and filtered. The filtrate was concentrated, and the residue was chromatographed using a heptane—AcOEt mixture, 7 : 1 → 2 : 1, as the eluent. The 5 : 1 → 3 : 1 mixtures were used to obtain a TLC-homogeneous product.

28-Acetoxy-3β-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranosyloxy)-20(29)-lupene (7). Yield 0.59 g (78.3%). R_f 0.75, m.p. 171—173 °C. Found (%): C, 70.08; H, 9.31. $C_{44}H_{68}O_{10}$. Calculated (%): C, 69.81; H, 9.05. ^1H NMR, δ: 0.78, 0.80, 0.93, 0.95, 1.00 (all s, 15 H, 5 CH_3); 1.00—1.95 (m, 26 CH_2, CH of aglycone, H(2′)); 1.65 (s, 3 H, CH_3); 1.98, 2.01, 2.04, 2.06 (all s, 12 H, 4 Ac); 2.42 (ddd, 1 H, H(19), *J* = 5.4, 11.7, 11.7 Hz); 3.12 (dd, 1 H, H(3), *J* = 5.8, 10.5 Hz); 3.70—3.74 (m, 1 H, H(6′)); 3.82 (d, 1 H, H(28), *J* = 11.0 Hz); 3.98—4.08 (m, 1 H, H(5′)); 4.18—4.32 (m, 2 H, H(28), H(6′)); 4.55 and 4.66 (both br. signals, 2 H, H(29)); 4.96 (t, 1 H, H(4′), *J* = 9.9 Hz); 5.11 (d, 1 H, H(1′), *J* = 2.6 Hz); 5.27 (ddd, 1 H, H(3′), *J* = 5.2, 11.2, 9.9 Hz).

28-Acetoxy-3β-(3,4,6-tri-*O*-acetyl-2-deoxy-α-L-*arabino*-hexopyranosyloxy)-20(29)-lupene (8). Yield 0.61 g (80.1%). R_f 0.73, m.p. 105—107 °C. Found (%): C, 70.11; H, 8.95. $C_{44}H_{68}O_{10}$. Calculated (%): C, 69.81; H, 9.05. ^1H NMR, δ: 0.73, 0.77, 0.81, 0.90, 0.96 (all s, 15 H, 5 CH_3); 1.00—1.90 (m, 26 CH_2, CH of aglycone, H(2′)); 1.63 (s, 3 H, CH_3); 1.90, 1.96, 1.99 (all s, 12 H, 4 Ac); 2.38 (ddd, 1 H, H(19), *J* = 5.5, 11.7, 11.7 Hz); 2.98 (dd, 1 H, H(3), *J* = 5.9, 10.6 Hz); 3.78 (d, 1 H, H(28), *J* = 11.0 Hz); 3.97 (dd, 1 H, H(6′$_a$), *J* = 2.0, 12.0 Hz); 4.06 (ddd, 1 H, H(5′), *J* = 9.8, 2.0, 6.2 Hz); 4.19 (dd, 1 H, H(6′$_b$), *J* = 6.2, 12.0 Hz); 4.21 (d, 1 H, H(28), *J* = 11.0 Hz); 4.51 and 4.63 (both d, 2 H, H(29), *J* = 2.0 Hz); 4.88 (t, 1 H, H(4′), *J* = 9.8 Hz); 4.93 (d, 1 H, H(1′), *J* = 2.8 Hz); 5.25 (ddd, 1 H, H(3′), *J* = 5.3, 11.8, 9.8 Hz).

28-Acetoxy-3β-(3,4-di-*O*-acetyl-2,6-dideoxy-α-L-*arabino*-hexopyranosyloxy)-20(29)-lupene (9). Yield 0.57 g (82%). R_f 0.77, m.p. 98—100 °C. Found (%): C, 72.45; H, 9.73. $C_{42}H_{66}O_8$. Calculated (%): C, 72.17; H, 9.51. ^1H NMR, δ: 0.75, 0.82, 0.88, 0.97, 1.05 (all s, 15 H, 5 CH_3); 1.00—2.15 (m, 26 CH_2, CH of aglycone, H(2′)); 1.29 (d, 3 H, H(6′), *J* = 6.3 Hz); 1.60 (s, 3 H, CH_3); 1.95, 1.96, 1.98 (all s, 9 H,

3 Ac); 2.32—2.40 (m, 1 H, H(19)); 2.93 (dd, 1 H, H(3), J = 6.0, 10.1 Hz); 3.77 (d, 1 H, H(28), J = 11.0 Hz); 3.96 (dq, 1 H, H(5′), J = 9.7, 6.3 Hz); 4.16 (d, 1 H, H(28), J = 11.0 Hz); 4.48—4.53 and 4.58—4.62 (both m, 2 H, H(29)); 4.64 (t, 1 H, H(4′), J = 9.7 Hz); 4.82 (d, 1 H, H(1′), J = 2.1 Hz); 5.20 (ddd, 1 H, H(3′), J = 5.5, 11.7, 9.7 Hz).

3β-Acetoxy-28-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranosyloxy)-20(29)-lupene (10). Yield 0.68 g (89.2%). R_f 0.72, m.p. 93—95 °C. Found (%): C, 70.13; H, 8.81. $C_{44}H_{68}O_{10}$. Calculated (%): C, 69.81; H, 9.05. ^{1}H NMR, δ: 0.77, 0.78, 0.79, 0.92, 0.96 (all s, 15 H, 5 CH_3); 1.00—1.95 (m, 26 CH_2, CH of aglycone, H(2′)); 1.62 (s, 3 H, CH_3); 1.95, 1.98, 1.99, 2.03 (all s, 12 H, 4 Ac); 2.35 (ddd, 1 H, H(19), J = 5.5, 11.1, 11.1 Hz); 2.96 and 3.80 (both d, 2 H, H(28), J = 9.4 Hz); 3.87 (ddd, 1 H, H(5′), J = 9.7, 3.2, 2.1 Hz); 3.96 (dd, 1 H, H(6′$_a$), J = 2.1, 12.3 Hz); 4.34 (dd, 1 H, H(6′$_b$), J = 3.6, 12.3 Hz); 4.41 (dd, 1 H, H(3), J = 5.6, 10.1 Hz); 4.52 and 4.62 (both d, 2 H, H(29), J = 1.7 Hz); 4.85 (d, 1 H, H(1′), J = 2.8 Hz); 4.96 (t, 1 H, H(4′), J = 9.7 Hz); 5.23 (ddd, 1 H, H(3′), J = 5.2, 11.4, 9.7 Hz).

3β-Acetoxy-28-(3,4-di-*O*-acetyl-2,6-dideoxy-α-L-*arabino*-hexopyranosyloxy)-20(29)-lupene (11). Yield 0.63 g (90.1%). R_f 0.76, m.p. 111—113 °C. Found (%): C, 71.85; H, 9.24. $C_{42}H_{66}O_8$. Calculated (%): C, 72.17; H, 9.51. ^{1}H NMR, δ: 0.76, 0.77, 0.90, 0.98 (all s, 15 H, 5 CH_3); 1.00—2.15 (m, 26 CH_2, CH of aglycone, H(2′)); 1.15 (d, H(6′), J = 6.3 Hz); 1.61 (s, 3 H, CH_3); 1.96, 1.97, 2.01 (all s, 9 H, 3 Ac); 2.25—2.32 (m, 1 H, H(19)); 3.10 and 3.64 (both d, 2 H, H(28), J = 9.5 Hz); 3.73 (dq, 1 H, H(5′), J = 9.2, 6.3 Hz); 4.40 (dd, 1 H, H(3), J = 5.3, 10.1 Hz); 4.50 and 4.64 (both br. signals, 2 H, H(29)); 4.68 (t, 1 H, H(4′), J = 9.2 Hz); 4.85 (br. signal, 1 H, H(1′)), 5.01 (ddd, 1 H, H(3′), J = 5.5, 11.2, 9.2 Hz).

Glycosides **7**—**11** were deacetylated with methanolic KOH by the reported procedure[10] to give glycosides **12**—**16** in yields of 87—92%.

3β-(2-Deoxy-α-D-*arabino*-hexopyranosyloxy)-28-hydroxy-20(29)-lupene (12). R_f 0.35, m.p. 170—172 °C. Found (%): C, 73.78; H, 9.95. $C_{36}H_{60}O_6$. Calculated (%): C, 73.42; H, 10.27.

3β-(2-Deoxy-α-L-*arabino*-hexopyranosyloxy)-28-hydroxy-20(29)-lupene (13). R_f 0.33, m.p. 184—186 °C. Found (%): C, 70.21; H, 9.88. $C_{36}H_{60}O_6$. Calculated (%): C, 73.42; H, 10.27.

3β-(2,6-Dideoxy-α-L-*arabino*-hexopyranosyloxy)-28-hydroxy-20(29)-lupene (14). R_f 0.36, m.p. 186—188 °C. Found (%): C, 75.85; H, 10.81. $C_{36}H_{60}O_5$. Calculated (%): C, 75.48; H, 10.56.

28-(2-Deoxy-α-D-*arabino*-hexopyranosyloxy)-3β-hydroxy-20(29)-lupene (15). R_f 0.32, m.p. 145—147 °C. Found (%): C, 73.11; H, 10.61. $C_{36}H_{60}O_6$. Calculated (%): C, 73.42; H, 10.27.

28-(2,6-Dideoxy-α-L-*arabino*-hexopyranosyloxy)-3β-hydroxy-20(29)-lupene (16). R_f 0.34, m.p. 168—170 °C. Found (%): C, 75.75; H, 10.34. $C_{36}H_{60}O_5$. Calculated (%): C, 75.48; H, 10.56.

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