

Reactions of Diols with Dimethyl Carbonate in the Presence of $W(CO)_6$ and $Co_2(CO)_8$

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Abstract—Dimethoxyalkanes and dimethyl alkanediyl biscarbonates were synthesized by reactions of diols with dimethyl carbonate in the presence of tungsten and cobalt carbonyls. Optimal reactant and catalyst ratios and reaction conditions were found to ensure selective formation of dimethoxyalkanes or dimethyl alkanediyl biscarbonates.

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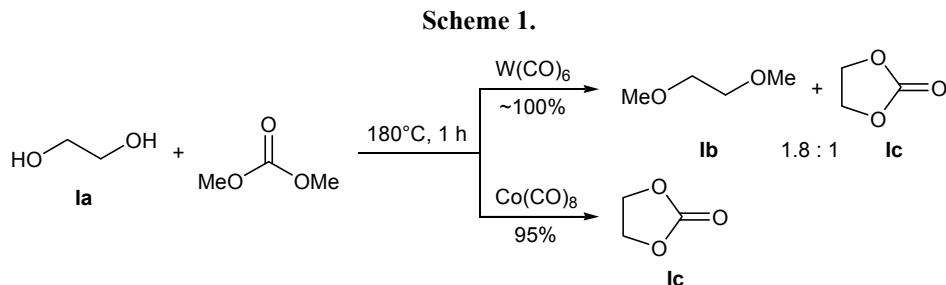
Dimethyl carbonate is a known “green” reagent which is widely used as organic solvent and synthetic equivalent of phosgene in the synthesis of alkyl and aryl carbonates and in the methylation and carbonylation processes in the manufacture of isocyanates, carbamates, and polycarbonates [1–3]. Dimethyl carbonate is increasingly used as methylating agent toward alcohols. Successful methylation of alcohols with dimethyl carbonate requires the presence of a stoichiometric amount of a catalyst (Al_2O_3 , MgO , K_2CO_3 , or KF/Al_2O_3) with respect to alcohol [4–6], and this factor together with harsh reaction conditions (200°C) hampers wide application of dimethyl carbonate as methylating agent in synthetic practice.

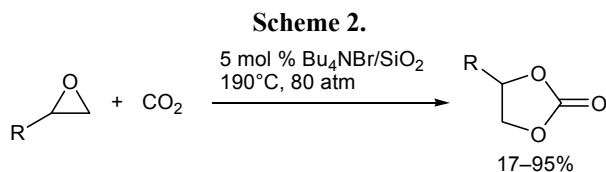
We recently found that tungsten and cobalt carbonyls $W(CO)_6$ and $Co_2(CO)_8$ catalyze methylation of primary, secondary, and tertiary alcohols with dimethyl carbonate, as well as partial or complete transesterification of the latter with those alcohols [7]. The present study was aimed at extending the scope of metal carbonyl-catalyzed reactions of dimethyl carbon-

ate and revealing general and specific features of its reactions with diols in the presence of $W(CO)_6$ and $Co_2(CO)_8$.

The reaction of dimethyl carbonate with ethylene glycol (**Ia**) in the presence of $W(CO)_6$ [$W(CO)_6$ –**Ia**– $(MeO)_2CO$ molar ratio 3:100:400; 180°C, 1 h] gave a mixture of 1,2-dimethoxyethane (**Ib**) and 1,3-dioxolan-2-one (**Ic**) at a ratio of 1.8:1, the conversion of **Ia** being complete. Analogous reaction catalyzed by $Co_2(CO)_8$ selectively afforded 1,3-dioxolan-2-one (**Ic**) in quantitative yield. Here, excess dimethyl carbonate was used since it acts simultaneously as reagent and solvent (Scheme 1). The known method for the synthesis of 1,3-dioxolan-2-ones is based on the reaction of 1,2-epoxyalkanes with carbon dioxide under pressure (82 atm) in the presence of tetrabutylammonium halide [8, 9] (Scheme 2).

Propane-1,3-diol (**IIa**) reacted with dimethyl carbonate in the presence of $W(CO)_6$ under the optimal conditions (180°C, 1 h) to produce 1,3-dimethoxypropane (**IIb**) and methyl 3-methoxypropyl carbonate





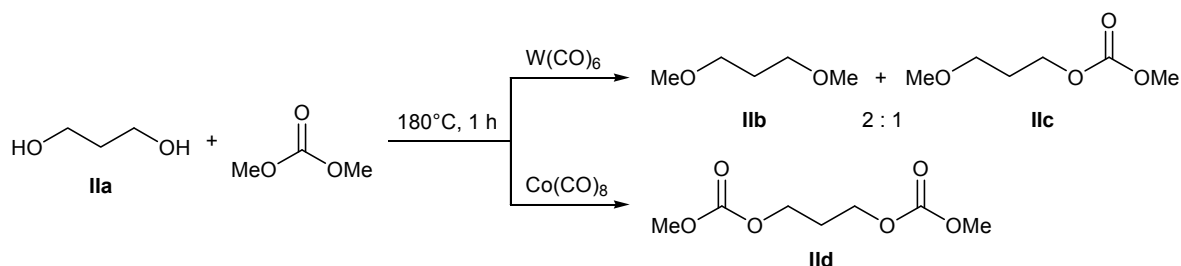
(**IIc**) at a ratio of 2:1. When $\text{W}(\text{CO})_6$ was replaced by $\text{Co}_2(\text{CO})_8$, dimethyl propane-1,3-diyl biscarbonate (**IIId**) was formed as the only product (Scheme 3).

The behavior of butanediols in the reaction under study essentially depended on the position of hydroxy groups. By reaction of butane-1,4-diol (**IIIIa**) with dimethyl carbonate in the presence of $\text{W}(\text{CO})_6$ we obtained 40% of methyl 4-hydroxybutyl carbonate (**IIIb**) as the only product. In the reaction of **IIIIa** with

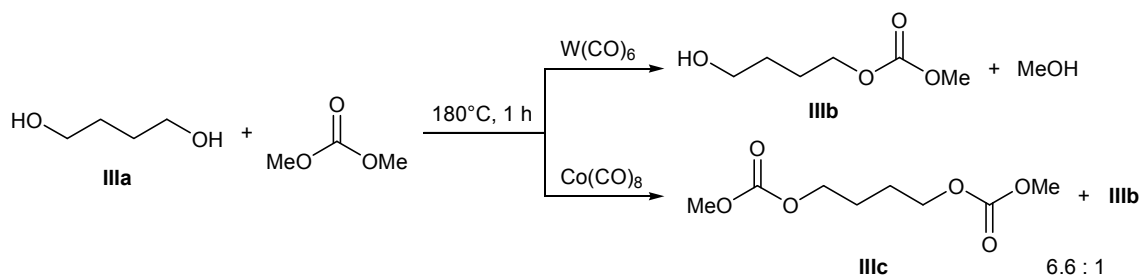
$(\text{MeO})_2\text{CO}$ catalyzed by $\text{Co}_2(\text{CO})_8$ the major product was butane-1,4-diyl dimethyl biscarbonate (**IIIIc**, 85%), and the reaction mixture also contained 15% of ester **IIIIb** (Scheme 4).

Butane-1,3-diol (**IVa**) reacted with dimethyl carbonate in the presence of $\text{W}(\text{CO})_6$, selectively yielding 1,3-dimethoxybutane (**IVb**). The reaction under analogous conditions in the presence of $\text{Co}_2(\text{CO})_8$ led to the formation of an equimolar mixture of methyl 4-methoxybut-2-yl carbonate (**IVc**) and butane-1,3-diyl dimethyl biscarbonate (**IVd**) with an overall yield of 100% (Scheme 5). In the reaction of butane-2,3-diol (**Va**) with dimethyl carbonate the only product was 4,5-dimethyl-1,3-dioxolan-2-one (**Vb**), regardless of the catalyst used (Scheme 6). Pentane-1,2-diol (**VIa**)

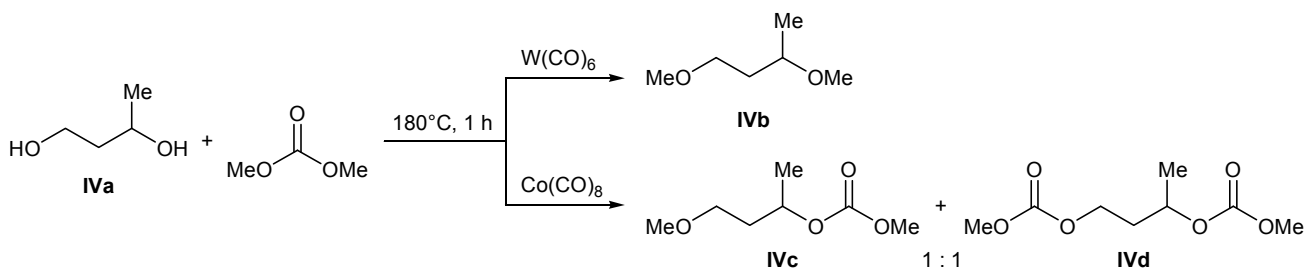
Scheme 3.



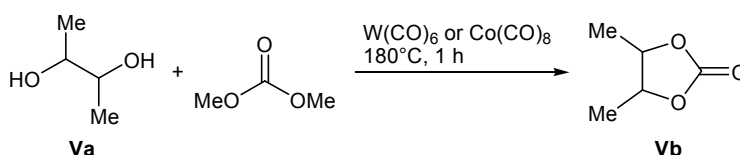
Scheme 4.



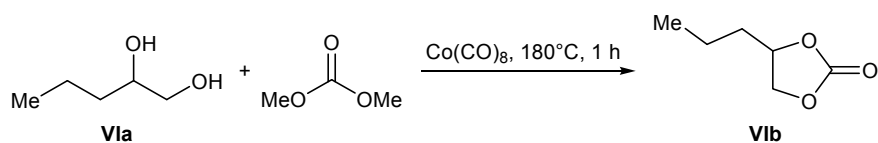
Scheme 5.



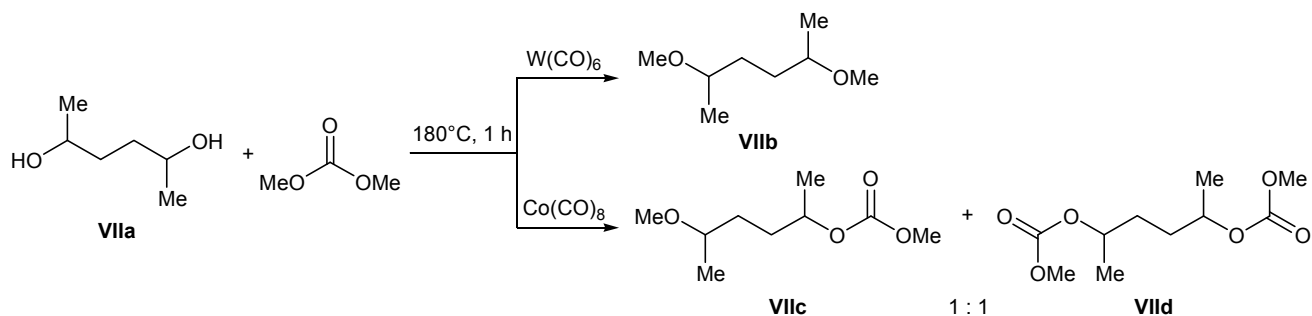
Scheme 6.



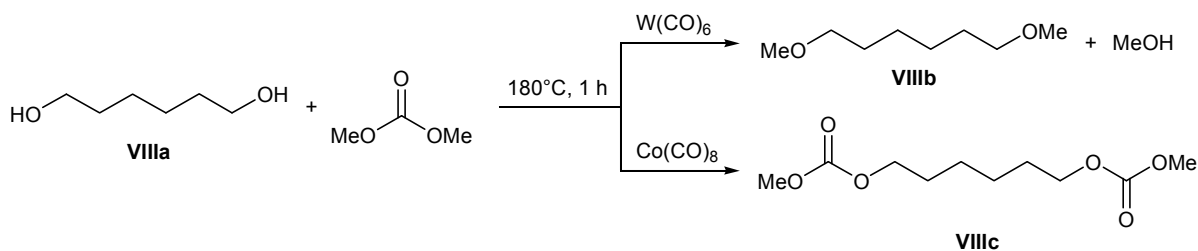
Scheme 7.



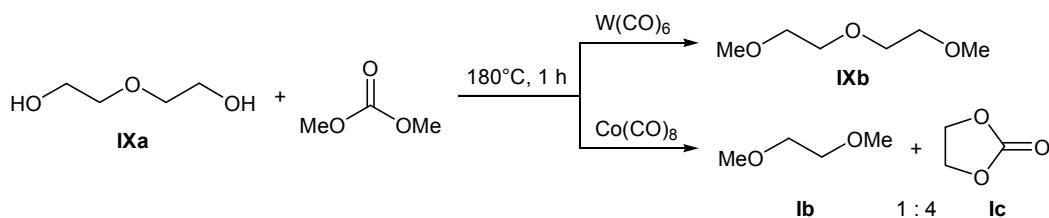
Scheme 8.



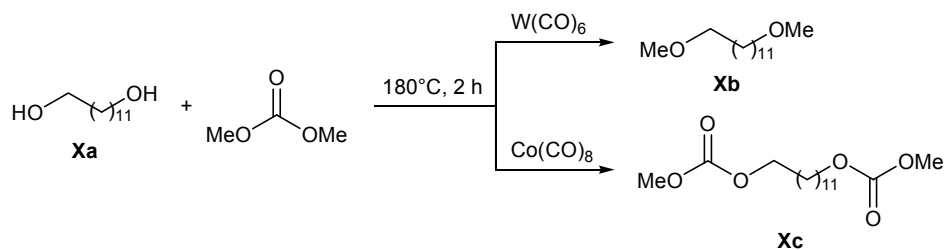
Scheme 9.



Scheme 10.



Scheme 11.



reacted with $(\text{MeO})_2\text{CO}$ in a similar way (Scheme 7). 2,5-Dimethoxyhexane (**VIIb**) was obtained by the reaction of hexane-2,5-diol (**VIIa**) with dimethyl carbonate in the presence of $\text{W}(\text{CO})_6$, whereas $\text{Co}_2(\text{CO})_8$ as catalyst gave rise to the formation of an equimolar mixture of methyl 5-methoxy-2-yl carbonate (**VIIc**) and hexane-2,5-diyl dimethyl biscarbonate

(**VIId**), their overall yield being quantitative (100%) (Scheme 8). 1,6-Dimethoxyhexane (**VIIIb**) was formed as the only product in the reaction of hexane-1,6-diol (**VIIIa**) with dimethyl carbonate in the presence of $\text{W}(\text{CO})_6$, while in the presence of $\text{Co}_2(\text{CO})_8$ selective formation of hexane-1,6-diyl dimethyl biscarbonate (**VIIIc**) was observed (Scheme 8).

Diethylene glycol (**IXa**) reacted with dimethyl carbonate in the presence of $W(CO)_6$ to give diethylene glycol dimethyl ether (**IXb**), whereas $Co_2(CO)_8$ promoted cleavage of the initial glycol molecule at the C–O bond with formation (as in the reaction with ethylene glycol) of 1,2-dimethoxyethane (**Ib**) and 1,3-dioxolan-2-one (**Ic**) at a ratio of 1:4 (Scheme 10). 1,12-Dimethoxydodecane (**Xb**) was formed in the reaction of dodecane-1,12-diol with dimethyl carbonate catalyzed by $W(CO)_6$, and $Co_2(CO)_8$ forced the reaction toward formation of dodecane-1,12-diyl dimethyl biscarbonate (**Xc**) (Scheme 11).

Thus, tungsten and cobalt carbonyls catalyze methylation of diols with dimethyl carbonate, as well as partial or complete transesterification of dimethyl carbonate with the diols. The products were identified by spectral methods and by comparing their spectral parameters with those of authentic samples [10–12].

EXPERIMENTAL

The ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer at 100.62 MHz using $CDCl_3$ as solvent. The mass spectra were obtained on a Shimadzu GCMS-QP2010Plus instrument (SPB-5 capillary column, 30 m \times 0.25 mm; carrier gas helium; oven temperature programming from 40 to 300°C at a rate of 8 deg/min; injector temperature 280°C, ion source temperature 200°C; electron impact, 70 eV). The elemental compositions were determined on a Carlo Erba 1106 analyzer.

The progress of reactions and the purity of products were monitored by GLC on Shimadzu GC-9A and GC-2014 instruments (2 m \times 3-mm column packed with 5% of SE-30 on Chromaton N-AW-HMDS; oven temperature programming from 50 to 270°C at a rate of 8 deg/min; carrier gas helium, flow rate 47 mL/min).

General procedure for the reaction of diols with dimethyl carbonate. A 17-mL stainless steel high-pressure micro reactor was charged with 3 mmol of $W(CO)_6$ or $Co_2(CO)_8$, 100 mmol of the corresponding diol, and 400 mmol of dimethyl carbonate. The reactor was hermetically closed, and the mixture was heated for 1 h at 180°C. When the reaction was complete, the reactor was cooled to room temperature and opened, the reaction mixture was filtered through a layer of alumina, unreacted dimethyl carbonate was distilled off, and the residue was distilled under atmospheric or reduced pressure or crystallized from ethanol.

1,2-Dimethoxyethane (Ib). Yield 64%, bp 84.5–85°C (85°C [10]).

1,3-Dioxolan-2-one (Ic). Yield 95%, mp 39.5–40°C (39°C [10]). ^{13}C NMR spectrum, δ_C , ppm: 64.47 (CH_2), 156.12 (C=O). Found, %: C 40.88; H 4.55. $C_3H_4O_3$. Calculated %: C 40.92; H 4.58.

1,3-Dimethoxypropane (IIb). Yield 63%, bp 102.4–103°C.

Methyl 3-methoxypropyl carbonate (IIc). Yield 31%, bp 77.4–77.8°C (30 mm). ^{13}C NMR spectrum, δ_C , ppm: 29.57 (C^2), 55.17 and 55.27 (OCH_3), 64.84 (C^1), 70.61 (C^3), 155.43 (C=O). Found, %: C 54.28; H 8.91. $C_6H_{12}O_3$. Calculated, %: C 54.53; H 9.15.

Dimethyl propane-1,3-diyl biscarbonate (IIId). Yield 98%, bp 94.5–95°C (6 mm). ^{13}C NMR spectrum, δ_C , ppm: 30.83 (C^2), 54.97 (OCH_3), 64.76 (C^1 , C^3), 155.76 (C=O). Found, %: C 43.68; H 6.05. $C_7H_{12}O_6$. Calculated, %: C 43.75; H 6.29.

4-Hydroxybutyl methyl carbonate (IIIb). Yield 40%, bp 86–87°C (5 mm). ^{13}C NMR spectrum, δ_C , ppm: 25.05 (C^3), 29.27 (C^2), 54.63 (OCH_3), 61.99 (C^1), 67.90 (C^4), 155.82 (C=O). Found, %: C 48.55; H 8.09. $C_6H_{12}O_4$. Calculated, %: C 48.64; H 8.11.

Butane-1,4-diyl dimethyl biscarbonate (IIIc). Yield 85%, bp 87–87.8°C (2 mm). ^{13}C NMR spectrum, δ_C , ppm: 25.17 (C^2 , C^3), 54.83 (OCH_3), 67.43 (C^1 , C^4), 155.76 (C=O). Found, %: C 46.52; H 6.79. $C_8H_{14}O_6$. Calculated, %: C 46.60; H 6.84.

1,3-Dimethoxybutane (IVb). Yield 95%, bp 116.5–117°C. Found, %: C 60.82; H 11.89. $C_6H_{14}O_2$. Calculated, %: C 60.98; H 11.94.

Methyl 4-methoxybut-2-yl carbonate (IVc). Yield 50%, bp 70.5–71°C (12 mm). ^{13}C NMR spectrum, δ_C , ppm: 20.86 (C^1), 34.63 (C^3), 54.51 (OCH_3), 58.30 (OCH_3), 71.37 (C^4), 72.56 (C^2), 155.51 (C=O). Found, %: C 51.76; H 8.62. $C_7H_{14}O_4$. Calculated, %: C 51.84; H 8.70.

Butane-1,3-diyl dimethyl biscarbonate (IVd). Yield 50%, bp 71.5–72°C (1 mm). ^{13}C NMR spectrum, δ_C , ppm: 19.98 (CH_3), 37.71 (C^2), 54.41 and 54.51 (OCH_3), 64.06 (C^1), 71.86 (C^3), 155.80 (C=O). Found, %: C 46.49; H 6.77. $C_8H_{14}O_6$. Calculated, %: C 46.60; H 6.84.

4,5-Dimethyl-1,3-dioxolan-2-one (Vb). Yield 98%, bp 68–69°C (2 mm). ^{13}C NMR spectrum, δ_C , ppm: 16.28 (CH_3), 72.02 (C^4 , C^5), 154.70 (C=O). Found, %: C 51.63; H 6.88. $C_5H_8O_3$. Calculated, %: C 51.72; H 6.94.

4-Propyl-1,3-dioxolan-2-one (VIb). Yield 98%, bp 86–87°C (2 mm). ^{13}C NMR spectrum, δ_C , ppm:

13.58 (CH₃), 17.76 (C²), 35.83 (C¹), 69.39 (C⁵), 76.85 (C⁴), 155.11 (C=O). Found, %: C 55.23; H 7.68. C₆H₁₀O₃. Calculated, %: C 55.37; H 7.74.

2,5-Dimethoxyhexane (VIIb). Yield 98%, bp 78.5–79°C (80 mm). ¹³C NMR spectrum, δ_C, ppm: 23.31 (C¹, C⁶), 31.60 (C³, C⁴), 56.98 (OCH₃), 75.57 (C², C⁵). Found, %: C 65.64; H 12.37. C₈H₁₈O₂. Calculated, %: C 65.71; H 12.41.

Methyl 5-methoxypent-2-yl carbonate (VIIc). Yield 50%, bp 77.2–78°C (4 mm). ¹³C NMR spectrum, δ_C, ppm: 23.14 (C¹), 31.23 (C⁴), 35.93 (C³), 54.43 (OCH₃), 56.73 (OCH₃), 67.43 (C²), 75.29 (C⁵), 155.44 (C=O). Found, %: C 56.69; H 9.48. C₉H₁₈O₄. Calculated, %: C 56.82; H 9.54.

Hexane-2,5-diyl dimethyl biscarbonate (VIIId). Yield 50%, bp 94–95°C (1 mm). ¹³C NMR spectrum, δ_C, ppm: 23.55 (C¹, C⁶), 34.78 (C³, C⁴), 54.43 (OCH₃), 68.02 (C², C⁵), 155.76 (C=O). Found, %: C 51.05; H 7.69. C₁₀H₁₈O₆. Calculated, %: C 51.27; H 7.75.

1,6-Dimethoxyhexane (VIIIb). Yield 97%, bp 74–74.5°C (30 mm). ¹³C NMR spectrum, δ_C, ppm: 28.23 (C³, C⁴), 32.29 (C², C⁵), 61.60 (OCH₃), 72.43 (C¹, C⁶). Found, %: C 65.65; H 12.38. C₈H₁₈O₂. Calculated, %: C 65.71; H 12.41.

Hexane-1,6-diyl dimethyl biscarbonate (VIIIc). Yield 98%, bp 102–103°C (1 mm). ¹³C NMR spectrum, δ_C, ppm: 25.23 (C³, C⁴), 32.14 (C², C⁵), 54.34 (OCH₃), 67.86 (C¹, C⁶), 155.98 (C=O). Found, %: C 51.08; H 7.67. C₁₀H₁₈O₆. Calculated, %: C 51.27; H 7.75.

1,5-Dimethoxy-3-oxapentane (IXb). Yield 95%, bp 80–80.5°C (60 mm) {bp 162°C [11]}.

1,12-Dimethoxydodecane (Xb). Yield 95%, bp 102–103°C (2 mm). ¹³C NMR spectrum, δ_C, ppm: 26.05 (C³, C¹⁰), 29.65 (C⁶, C⁷), 29.90 (C⁵, C⁸), 30.05 (C⁴, C⁹), 30.24 (C², C¹¹), 58.40 (OCH₃), 72.85 (C¹,

C¹²). Found, %: C 72.81; H 13.05. C₁₄H₃₀O₂. Calculated, %: C 72.99; H 13.12.

Dodecane-1,12-diyl dimethyl biscarbonate (Xc). Yield 80%, bp 167–168°C (1 mm). ¹³C NMR spectrum, δ_C, ppm: 25.47 (C³, C¹⁰), 28.43 (C², C¹¹), 29.05 (C⁴, C⁶, C⁷, C⁹), 29.52 (C⁵, C⁸), 54.34 (OCH₃), 67.75 (C¹, C¹²), 155.59 (C=O). Found, %: C 60.18; H 9.42. C₁₆H₃₀O₆. Calculated, %: C 60.35; H 9.50.

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