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ORIGINAL ARTICLE

Towards fuel antioxidants of new types

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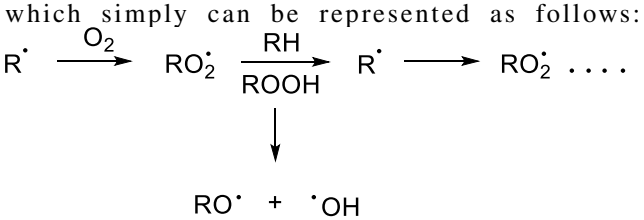
Abstract
To find novel classes of potential fuel additives of multivalent activity, particularly antioxidants, a series of recently synthesized ethyl-6-amino-5-cyan-methyl-4-aryl-4H-pyran-3-carboxylates have been investigated using model oxidative reactions. The compounds studied appear to be prospective inhibitors of hydrocarbons oxidation. Some of them are antioxidants of combined action, breaking the chains of the oxidative reactions with cumene peroxide radicals and catalytically decomposing cumene hydroperoxide.

Keywords Multivalent · Inhibitor · Cumene peroxide · Radical · Antioxidant

Introduction

Resistance to oxidation is one of the most important performance characteristics of fuel and lubrication materials since many undesirable processes occurring in machines and mechanisms are associated with the formation of different oxidation products [1]. Therefore, the design of novel antioxidants of a higher efficiency represents an urgent challenge in the chemistry of additives.

The oxidation of hydrocarbons is known to be a radical-chain and degenerate-branched process, which simply can be represented as follows:

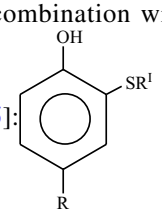


To inhibit this process, one should employ the compounds that would quickly react with the forming radicals (R^* or RO_2^*) or destroy the hydroperoxide without generating other free radicals [2].

Since the antioxidant properties of additives are due to the presence of certain functional groups in their composition, the investigations into the synthesis and mechanism of the antioxidant action of organic compounds containing two or more functional groups in the molecule, which allow combining various types of antioxidants in one structure, is of undoubted research and practical interest [3].

On the basis of the foregoing, we conducted studies on the synthesis, study of the mechanism of action, as well as the relationship between the structure and the effectiveness of the antioxidant action of sulfur-containing polyfunctional antioxidants [4].

When choosing sulfur-containing polyfunctional antioxidants, we proceeded from combining the properties of two types of antioxidants in the molecule of the compound: an antioxidant that effectively breaks oxidation chains by reaction with peroxide radicals, and an antioxidant that decomposes hydroperoxides. As you know, the first type of antioxidants includes mainly phenols and aromatic amines, and the second type—sulfides. Therefore, they initially synthesized and investigated compounds containing a sulfide sulfur atom in a molecule in combination with phenolic fragments—phenolsulfides [5]:



The mechanism of the antioxidant action of sulfur-containing antioxidants was studied using the well-known

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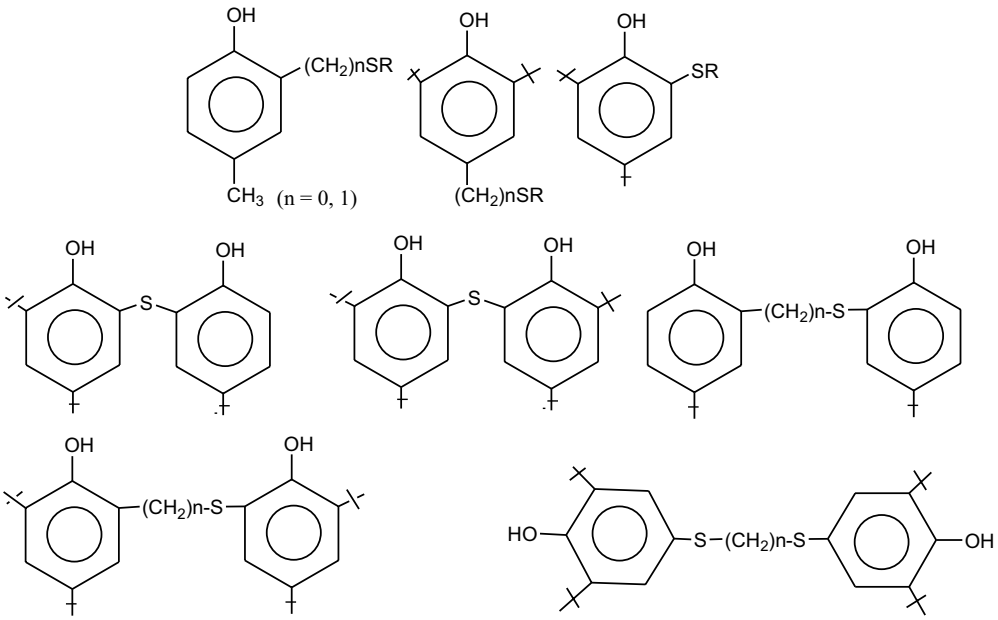
kinetic method, the essence of which is to study the key reactions that determine the inhibitory effect of antioxidants: the termination of oxidation chains in the reaction with peroxide radicals and the decomposition of hydroperoxides. Isopropylbenzene (cumene) was used as a model hydrocarbon, the oxidation mechanism of which has been studied in detail [6, 7].

Studies have shown that the studied antioxidants inhibit the initiated oxidation of cumene by reacting with cumyl peroxide radicals. At the same time, these sulfur-containing antioxidants are at the level of known alkylphenol antioxidants in terms of the effectiveness of the termination of oxidation chains by reaction with peroxide radicals.

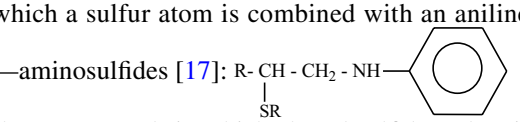
The presence of a sulfide fragment in the molecules of the synthesized antioxidants suggested their interaction with hydroperoxides. The very first studies of the reaction of phenolsulfides with cumyl hydroperoxide showed that their activity in the decomposition of hydroperoxides is incomparably higher than that of sulfides and other types of hydroperoxide breakers. It was found that phenolsulfides catalytically decompose hydroperoxides: one phenol sulfide molecule decomposes tens of thousands of hydroperoxide molecules.

Thus, the study of the antioxidant properties of phenolsulfides showed that they are antioxidants of combined action: they terminate oxidation chains by reaction with peroxide radicals and catalytically destroy hydroperoxides into molecular products.

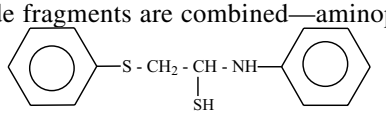
Further, phenol sulfides were synthesized and investigated, in which a sulfur atom is combined with one phenolic fragment (monophenol sulfides) [8–11] and with two phenolic fragments (bisphenol sulfides) [12–16], which differ in the relative position of the sulfur atom and hydroxyl groups, the number substituents in the benzene ring of the phenol fragment and the nature of the substituent at the sulfur atom:

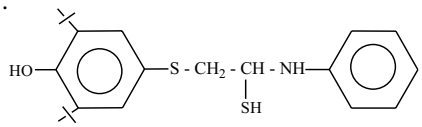


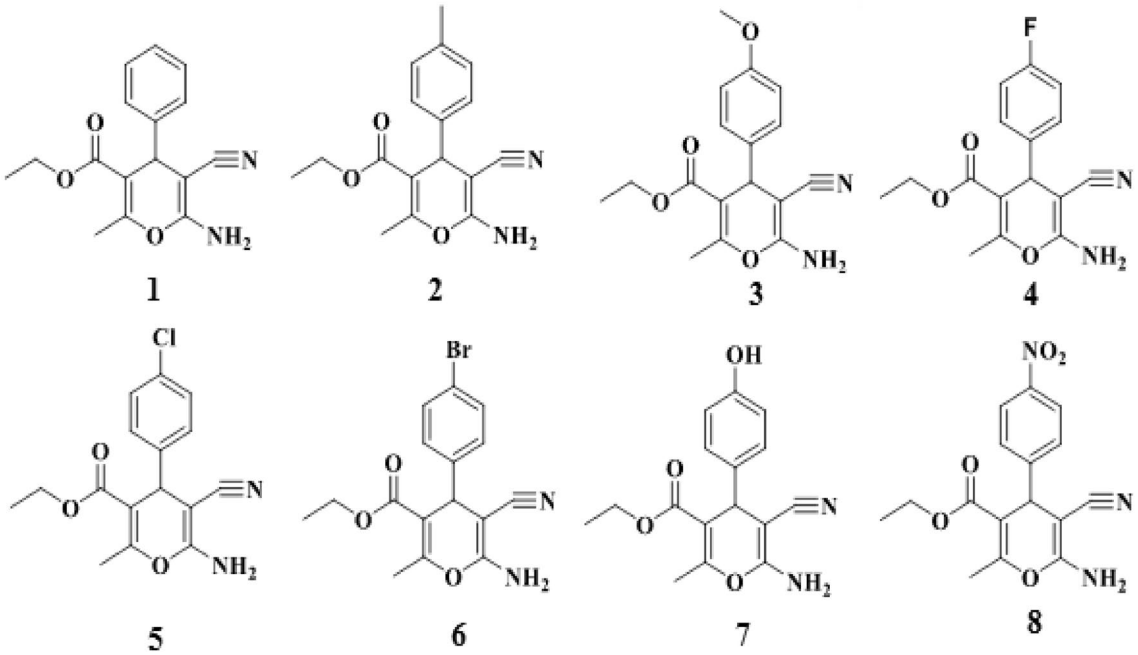
In addition, compounds were synthesized and investigated in which a sulfur atom is combined with an aniline fragment—aminosulfides [17]:



As well as compounds in which phenol sulfide and aminosulfide fragments are combined—aminophenol sulfides [18]:







Scheme 1 Synthesized compounds **1–8**

All of these compounds also turned out to be antioxidants with a combined effect.

In order to search for new antioxidants with a combined effect, a number of nitrogen-sulfur-containing compounds have been synthesized—thiourea derivatives [19–20] nitrogen-sulfur-containing heterocyclic compounds [21–22], which also turned out to be antioxidants with a combined effect.

In the present work, we have studied a series of recently synthesized, earlier unknown ethyl-6-amino-5-cyan-methyl-4-aryl-4H-pyran-3-carboxylates as potential polyfunctional multivalent fuel additives. Mechanism of their action was investigated and relationship between structure and efficiency of their antioxidant activity was estimated.

When selecting compounds for the study, it was assumed that the molecules should combine the properties of two types of antioxidants. The first one should effectively break the oxidation chains via the reaction with peroxide radicals, and the second one should decompose hydroperoxides. As is known, the first type of antioxidants includes mainly phenols and aromatic amines, and the second type consists of polyfunctional compounds.

Previously, antioxidants of combined action were found among thiourea derivatives and polyfunctional heterocycles.

Results and discussion

Chemistry

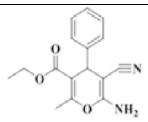
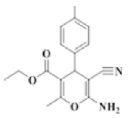
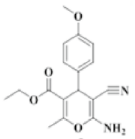
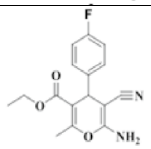
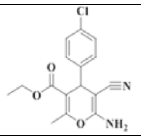
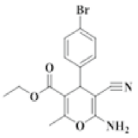
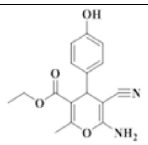
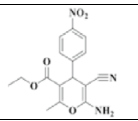
Multicomponent domino reactions have become a useful method in the field of environ-mental and organic synthesis, which is due to their compliance with the requirements of green chemistry [22–26]. Polyfunctional substitute benzo-γ-pyrans synthesized by this method are important heterocyclic compounds. It has also been established that some 2-amino-4H-pyranes are important photoactive materials [27].

For the study, we have chosen eight representatives of the recently synthesized classes of ethyl-6-amino-5-cyan-methyl-4-aryl-4H-pyran-3-carboxylate compounds 1–8 as the antioxidant of combined action (Scheme 1).

All compounds are synthesized by original straightforward methods from available starting materials. When selecting the compounds for the study, we consider that if some of them would show promising performance characteristics, the synthetic procedures might be easily scaled up.

Given the important features of multifunctional 4H-pyran has, it is natural that there are many synthetic attempts to achieve the goal by applying simple reaction

Table 1 The values of the induction time of cumene autooxidation in the presence of the synthesized compounds **1–8**, as well as the kinetic parameters of their reaction with cumene peroxide radicals and cumene hydroperoxide

Compound	Formula	Induction time of cumene autooxidation (T=110°C), τ, min	Reaction with RO_2^* (T=60°C)		Reaction with CHP (T=110°C)	
			f	$K_7.10^{-4}$ l/mol·s	K, l/mol·s	ν
1		250	2.6	3.6	15	12000
2		220	2.2	3.2	13	10000
3		130	1.59	1.92	8	6000
4		210	1.81	2.88	-	-
5		260	2.73	3.84	6	4500
6		280	4.24	4.32	10	7000
7		200	1.97	3.12	11	8000
8		170	1.72	2.04	-	-
Ionol		150	2.10	2.00	-	-

strategies. Given the successful application of these compounds in a different field, the synthesis of their optical isomers on the basis of enantioselective synthesis is one of the most pressing issues (Table 1).

Given the successful application of 4H-pyran has in a different field, which contain different functional groups, we have synthesized them. Various aromatic aldehydes, acetic acid ether and malonnitrile were used as the object of research. Optically active α-amino acid (L-glutamic acid.) were used as chiral organic catalysts. The course of the reaction and the purity of the obtained substance were monitored by NTX chromatography. The scheme of the reaction is as follows (Scheme 2):

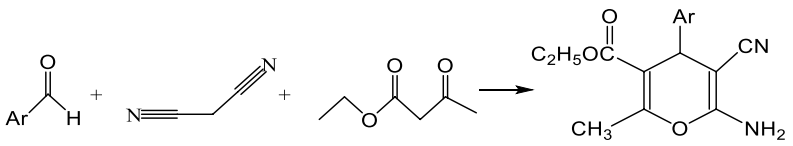
Antioxidant activity

The study of cumene auto-oxidation in the presence of compounds **1–8** has shown that they effectively inhibit this process. The kinetic curves of auto-oxidation at 110 °C in the presence of compounds **1–8** are shown in Fig. 1, and the values of auto-oxidation induction period are given in Table.

To establish the mechanism of the antioxidant action of the synthesized compounds, the kinetics of their reaction with cumene peroxide radicals and cumene hydroperoxide (CHP) has been investigated.

To evaluate the ability of the studied compounds **1–8** to break the oxidation chains via the reaction with cumene

Scheme 2. Synthesis of ethyl-6-amino-5-cyan-methyl-4-aryl-4H-pyran-3-carboxylates (**1–8**)



Ar= - C_6H_5 (1), p-$CH_3C_6H_4$ (2), p-$CH_3OC_6H_4$ (3), p-FC_6H_4 (4), p--ClC_6H_4 (5), p-BrC_6H_4 (6), -C_6H_4-OH (7), p-NO_2 C_6H_4 (8); Kat = L-glutamic acid.

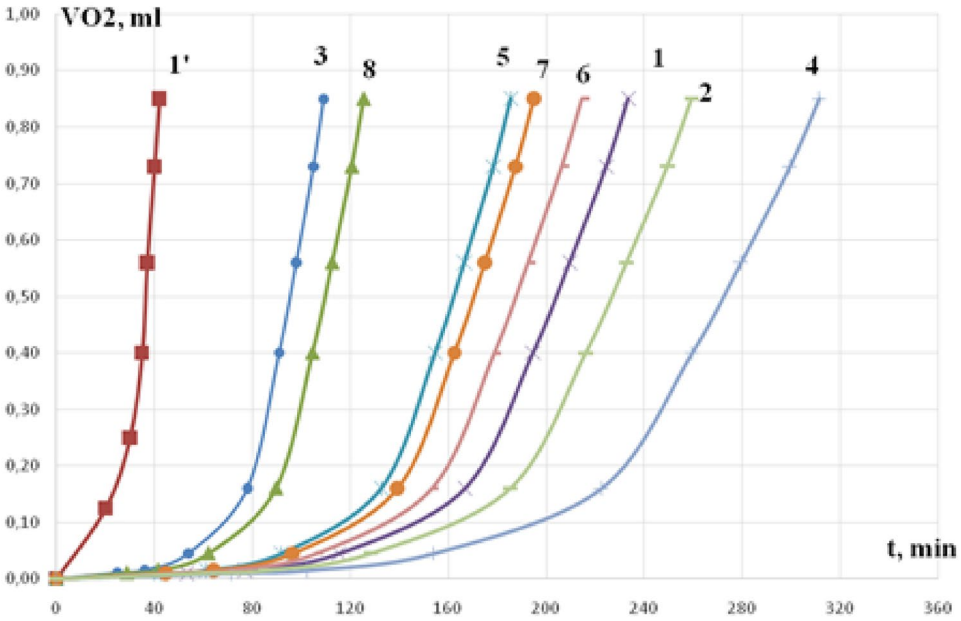


Fig. 1 Kinetic curves of cumene auto-oxidation in the presence of the synthesized compounds: T = 110 °C, V_{O2} is a volume of oxygen (ml), τ is a time (min); [InH] = 0 (1^{I}) [InH] = **1–2–3–4–5–6–7–8** = $5 \cdot 10^{-4}$ mol/l

peroxide radicals, the oxidation of cumene was initiated by azodiisobutyronitrile (AIBN) at 60 °C in the presence of these inhibitors. In all experiments, the concentration of the initiator was $2 \cdot 10^{-2}$ mol/l, and content of the inhibitor was $5 \cdot 10^{-4}$ mol/l. It was found that all studied compounds, to one degree or another, inhibited the initiated oxidation of cumene (Fig. 2):

Using the value of the induction time (τ) of the initiated cumene oxidation, the stoichiometry coefficient *f* was calculated. The latter is equal to the number of oxidation chains breaking under the action of one inhibitor molecule and products of its conversion:

$$f = \frac{\tau \cdot w_i}{[\ln H]_0}$$

where $\tau_{ind.}$ is induction time, W_i is initiation rate, $[InH]_0$ is initial concentration of the inhibitor.

To determine the value of the rate constant of the interaction of inhibitor with cumene peroxide radicals (κ_7), the kinetic curves of the initiated oxidation of cumene were transformed from $\Delta[O_2]$-τ coordinates to $\Delta[O_2]^{-1}$-τ^{-1}coordinates. Using the slope of the straight line

$$tg\alpha = \frac{fk_7[InH]_0}{(k_2[RH]W_i)}$$

it was found that

$$k_7 = \frac{tg\alpha k_2[RH]W_i}{f.[InH]_0}$$

where: $k_2 = 1{,}51$ $mol^{-1 \cdot} s^{-1}$, $[RH] = 7{,}17$ $mol^{-1 \cdot} s^{-1}$ [18].

The values of the kinetic parameters of the reaction of the synthesized compounds with cumene peroxide radicals are given in Table.

To evaluate the ability of the synthesized compounds **1–8** to decompose CHP, the reaction of cumene hydroperoxide with inhibitors has been implemented at 110 °C in chlorobenzene under nitrogen atmosphere (at this temperature, CHP is thermally stable). The studies have shown that the inhibitors, which contain a sulfur atom in the molecule, effectively decompose CHP (Fig. 3). Moreover, one molecule of the studied inhibitors is capable of decomposing several thousand CHP molecules, that is, the reaction has a catalytic character.

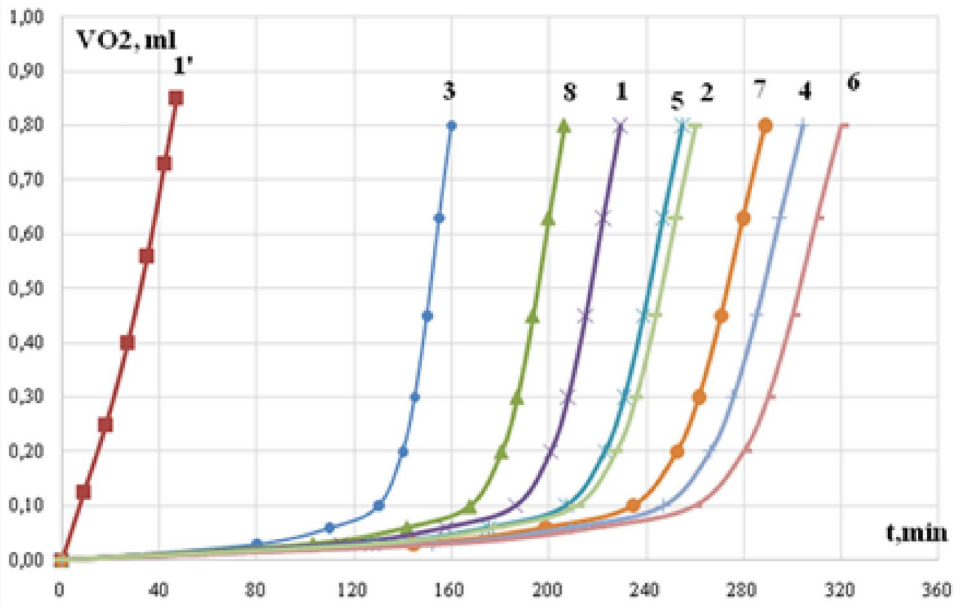


Fig. 2 Kinetic curves of initiated cumene oxidation in the presence of synthesized compounds **1–8**: T = 60ºC; V_{O2} is the volume of oxygen (ml), τ is the time (min.), [InH] = 0 (1') [InH] = $5 \cdot 10^{-4}$ mol/l = **1–8**

The number of CHP molecules (ν), decomposed under the action of one molecule of the studied compounds, was calculated by the formula:

$$\nu = \frac{[CHP]_0 - [CHP]_\infty}{[InH]_0}$$

where $[CHP]_0$ and $[CHP]_\infty$ are the initial and final concentration of CHP, respectively;$[InH]_0$ is the initial concentration of the antioxidant.

It is found that for all compounds, the reaction with CHP is of the first order both in terms of antioxidant and CHP, and the initial reaction rate of the catalytic decomposition of CHP follows the equation:

$$w_0 = K[InH]_0 \cdot [CHP]$$

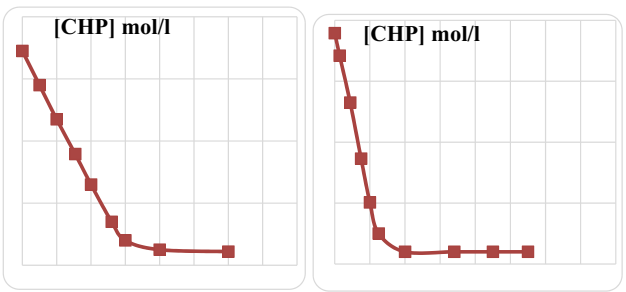


Fig. 3 Kinetic curves of decomposition of CHP **a** under the action of compound **7** $[InH]_{(IV)} = 5.10^{-4}$ mol/l at110°C, initial concentration of [CHP] = 0.34 mol/l, τ is time (min). **b** under the action of compound **1** $[InH]_{(IV)} = 5.10^{-4}$ mol/l at 110 °C, initial concentration of [CHP] = 0.37 mol/l, τ is time (min)

The values of the rate constant of CHP decomposition under the action of the studied compounds (K) and catalytic factor (ν) are given in Table.

The Table also contains values of the induction time (τ) of cumene autooxidation in the presence of the synthesized compounds, as well as the kinetic parameters of their reaction with cumene peroxide radicals and cumeme hydroperoxide.

As shown from Table, all the studied compounds, except for compound **3**, exhibit quite high antioxidant properties and surpass the well-known antioxidant like ionol (2,5-di-tert-butyl-4-methylphenol) in terms of antioxidant activity.

Compounds **5, 6** and **1** possess the highest antioxidant activity. The latter is likely due to the fact that these compounds suppress peroxide radicals and very effectively break the oxidation chains. In addition, unlike ionol, they efficiently decompose hydroperoxides into molecular products. In the reaction with peroxide radicals, the stoichiometry coefficient (f) for these compounds is ~ 4, i.e. one molecule of these compounds breaks about four oxidation chains, while one molecule of ionol breaks only 2 oxidation chains. The reaction rate constant with peroxide radicals for these compounds is also higher than that for ionol.

Conclusion

In conclusion, a specially selected range of heterocyclic compounds **(1–8)**, prospective multivalent fuel antioxidants of a new type, has been synthesized. The composition and structure of the compounds have been proved by modern physical–chemical methods.

It is established that these compounds are effective inhibitors of hydrocarbon oxidation. The mechanism of their antioxidant action involves the breaking of the oxidation chains via the reaction with peroxide radicals, and (for some compounds) catalytic decomposition of hydroperoxides into molecular products.

Materials and methods

Measurements

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker Avance 400 NMR spectrometer (400.13 and 100.6 MHz, respectively). The ^{1}H chemical shifts (δ) were referenced to HMDS (0.05 ppm) in DMSO and the residual deuterated solvent, the ^{13}C chemical shifts were expressed with respect to the deuterated solvent (77.10 ppm for DMSO). Coupling constants in hertz (Hz) were measured from one-dimensional spectra and multiplicities were abbreviated as following: br (broad), s (singlet), d (doublet), dd (doublet of doublets), m (multiplet). The chemical shifts were recorded in ppm, coupling constants (J) in Hz. IR spectra were obtained on a Varian 3100 IF-IR spectrometer (400–4000 cm^{-1}, KBr pellets or films). All spectra are given in Supporting Information (SI).

Experimental

Synthesis of ethyl-6-amino-5-cyan-methyl-4-aryl-4H -pyran-3-carboxylates (1–8)

The corresponding aldehyde (5 mmol), malonnitrile (5.5 mmol), acetoacetic ether (5 mmol), 0.5 mmol optically active α-amino acid is taken as a catalyst in the flask. 8–10 ml of glycerin is used as a solvent. The reaction is carried out in a magnetic stirrer at room temperature. The resulting reaction product is filtered and recrystallized in ethanol.

Ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4H-pyran-3 carboxylate (1)

IR (KBr): 3402.49 (NH_2), 3329.96 (NH_2), 2972.32 (C–H), 2190.34 (C≡N), 1692.10 (C=O), 1652.27, 1609.54, 1375.88, 1259.12, 1120.31, 1062.19 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6) $\delta = 1.21–1.30$ (3H, CH_3, t), 2.50 (3H, CH_3, s), 3.81–4.05 (2H, CH_2, q), 4.60 (H, CH, s), 6.26 (2H, NH_2, s), 7.67–7.88 (5H, H-Ar, m) ppm. ^{13}C-NMR (100 MHz, DMSO-d_6): $\delta = 12.53$, 15.37, 55.53, 61.81, 108.85, 119.22, 125.51, 125.72, 127.53, 127.78, 142.85, 152.53, 154.37, 166.85 ppm.

Ethyl 6-amino-5-cyano-2-methyl-4-(p-tolyl)-4H-pyran-3-carboxylate (2)

^{1}H-NMR (400 MHz, DMSO-d_6) $\delta = 1.31–1.35$ (3H, CH_3, t), 2.12 (3H, CH_3, s), 2.35 (CH_3, s), 3.93–4.05 (2H, CH_2, q), 4.44 (H, CH, s), 6.83 (2H, NH_2, s), 7.07–7.57 (4H, H-Ar, d, d) ppm. ^{13}C-NMR (100 MHz, DMSO-d_6): $\delta = 14.59$, 17.61, 21.43, 38.13, 58.36, 61.48, 107.31, 119.58, 128.36, 135.99, 141.51, 155.63, 159.87, 165.71 ppm.

Ethyl 6-amino-5-cyano-4-(4-methoxyphenyl)-2-methyl-4H-pyran-3-carboxylate (3)

^{1}H-NMR (400 MHz, DMSO-d_6) $\delta = 1.31–1.35$ (3H, CH_3, t), 2.12 (3H, CH_3, s), 3.74 (CH_3, s), 3.93–3.4 (2H, CH_2, q), 4.44 (H, CH, s), 6.83 (2H, NH_2, s), 6.91–7.10 (4H, H-Ar, d, d) ppm. ^{13}C-NMR (100 MHz, DMSO-d_6): $\delta = 14.59$, 17.61, 38.45, 55.25, 56.48, 61.64, 108.25, 114.30, 119.58, 130.90, 136.73, 155.38, 157.85, 159.72, 165.25 ppm.

Ethyl 6-amino-5-cyano-4-(4-fluorophenyl)-2-methyl-4H-pyran-3-carboxylate (4)

^{1}H-NMR (400 MHz, DMSO-d_6) $\delta = 1.13–1.24$ (3H, CH_3, t), 2.46 (3H, CH_3, s), 4.02–4.07 (2H, CH_2, q), 4.34 (H, CH, s), 6.91 (2H, NH_2, s), 7.12–7.43 (4H, H-Ar, d, d) ppm. ^{13}C-NMR (100 MHz, DMSO-d_6): $\delta = 13.81$, 17.61, 37.93, 56.81, 61.48, 107.31, 115.77, 119.14, 130.90, 139.45, 155.72, 159.12, 159.26, 165.14 ppm.

Ethyl-6-amino-4-(4-chlorophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (5)

IR (KBr): 3409.17 (NH_2), 3332.69 (NH_2), 2979.48 (C–H), 2193.69 (C≡N), 1693.41 (C≡O), 1650.55, 1609.34, 1489.39, 1335.42, 1266.26, 1174.09, 1120.47 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6) $\delta = 1.01–1.09$ (3H, CH_3, t), 2.50 (3H, CH_3, s), 3.81–4.03 (2H, CH_2, q), 4.28 (H, CH, s), 6.26 (2H, NH_2, s), 7.29–7.52 (4H, H-Ar, d, d) ppm. ^{13}C-NMR (100 MHz, DMSO-d_6): $\delta = 14.33$, 17.37, 38.18, 58.53, 61.65, 107.85, 118.82, 128.54, 128.72, 130.53, 130.78, 131.51, 141.88, 155.55, 158.67, 165.85 ppm.

Ethyl 6-amino-4-(4-bromophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (6)

IR (KBr): 3408.10 (NH_2), 3330.18 (NH_2), 2979.27 (C–H), 2194.09 (C≡N), 1689.50 (C≡O), 1645.77, 1608.19, 1483.62, 1374.06, 1262.54, 1180.44, 1068.31 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6) $\delta = 1.31–1.39$ (3H, CH_3, t), 2.29 (3H, CH_3, s), 3.88–4.00 (2H, CH_2, q), 4.55 (H, CH, s), 6.96 (2H, NH_2, s), 7.29–7.89 (4H, H-Ar, d, d) ppm. ^{13}C-NMR (100 MHz, DMSO-d_6): $\delta = 14.39$, 17.33, 38.15, 58.42,

61.54, 107.84, 119.15, 131.25, 131.51, 143.58, 156.50, 159.25, 165.41 ppm.

Ethyl 6-amino-5-cyano-4-(4-hydroxyphenyl)-2-methyl-4H-pyran-3-carboxylate (7)

^{1}H-NMR (400 MHz, DMSO-d_6) $\delta = 0.84–0.89$ (3H, CH_3, t), 2.25 (3H, CH_3, s), 3.77–3.87 (2H, CH_2, q), 4.24 (H, CH, s), 6.59 (2H, NH_2, s), 6.71–6.90 (4H, H-Ar, d, d), 9.09 (OH, s) ppm. ^{13}C-NMR (100 MHz, DMSO-d_6): $\delta = 14.25$, 17.00, 37.52, 58.29, 61.48, 107.87, 115.31, 119.15, 131.24, 136.61, 155.14, 156.77, 159.20, 164.92 ppm.

Ethyl 6-amino-5-cyano-2-methyl-4-(4-nitrophenyl)-4H-pyran-3-carboxylate (8)

^{1}H-NMR (400 MHz, DMSO-d_6) $\delta = 1.13–1.24$ (3H, CH_3, t), 2.40 (3H, CH_3, s), 3.94–4.01 (2H, CH_2, q), 4.28 (H, CH, s), 6.88 (2H, NH_2, s), 7.50–8.11 (4H, H-Ar, d, d) ppm. ^{13}C-NMR (100 MHz, DMSO-d_6): $\delta = 14.84$, 17.61, 38.47, 58.05, 61.48, 107.91, 119.58, 124.03, 127.03, 144.60, 150.69, 155.74, 159.68, 165.58 ppm.

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Declarations

Conflict of interest The authors declare that there are no conflicts of interest.

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