Synthesis and evaluation of some chromene derivatives as antioxidant with surface activity

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Síntesis y evaluación de algunos derivados de cromeno como antioxidantes con actividad superficial

Síntesi i avaluació d'alguns derivats de cromeno com antioxidants amb activitat superficialarrejats amb pneumàtics fora d'ús (GTR) desvulcanitzats mitjançant microones

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SUMMARY

A number of azo heterocyclic derivatives **3a-j** were synthesized by the reaction of chromene derivative **1** with different aryl diazonium chloride **2a-j**. These compounds have an increase antioxidant activity due to increasing the chromophores, which give facility for radical scavengers, and hydroperoxide decomposers, as well as synergistic mixtures of both of them. Condensation of thesecompounds and stearoyl chloride with propoxylated the products by using propylene oxide afforded surface active agents have a pronounced surface activity, which can be serve in the manufacture of antioxidant additives, dyes, drugs and cosmetics.

Keywords: Synthesis; Chromene derivatives; Antioxidants; Surface activity.

RESUMEN

Una serie de derivados azoicos heterocíclicos **3a-j** se sintetizaban por la reacción del derivado de cromeno **1** con distintos cloruros de aril diazonio **2a-j**. Estos compuestos tienen una actividad antioxidante elevada debido a su creciente número de cromóforos, lo que facilita la existencia de antioxidantes y descomponedores o desintegradores de hidroperóxidos, así como de mezclas sinérgicas de ambos. La condensación de estos compuestos y de cloruro de estearoilo con productos propoxilados usando óxido de propileno daba lugar a tensoactivos con una elevada actividad superficial, los cuales pueden servir en la fabricación de aditivos antioxidantes, colorantes, fármacos y cosméticos.

Palabras clave: Síntesis; derivados de cromeno; antioxidantes; actividad superficial.

RESUM

Un grup de derivats azoics heterocíclics **3a-j** es sintetitzaven per la reacció del derivat de cromeno **1** amb diferents clorurs d'aril diazonio **2a-j**. Aquests compostos tenen una activitat antioxidant elevada degut al creixent numero de cromòfors, el que facilita la existència de antioxidants i descomponedors o desintegradors de hidroperòxids, així com de mescles sinèrgiques tots dos. La condensació d'aquests compostos i del clorur de estearoilo amb productes propoxilats fent servir òxids de propilè tenia com resultat tensioactius amb una elevada activitat superficial, molt adients en la fabricació de additius antioxidants, colorants, fàrmacs i cosmètics.

Paraules clau: Síntesi; derivats de cromeno; antioxidants; activitat superficial.

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INTRODUCTION

Mineral lubricating oils are usually used in presence of air, often at elevated temperatures, whereby oxidative chemical reactions can take place.[1-3] The rate of these oxidative processes varies greatly with the nature of oils, the extent of processing in refining, the temperature, and the presence of a metallic catalyst.[4,5] Such oxidations have a drawback on the oil, thus leading to failures in lubrication that accompanied by damage of machines. Large degree of damage is due to the formation of viscous, solid bodies or emulsions, which interfere with the regular distribution of the lubricant. Consequently, antioxidant additives became highly required to decrease oil oxidation, with a secondary effect of reducing corrosion of certain types of sensitive bearing materials.[6] There is still a need to add at least an antioxidant to the mineral oil for most applications, even after employing the most extensive refining techniques.[7] Antioxidants can be considered as free radical inhibitors of peroxide decomposers, and may vary in chemical structures. Thus, various classes of compounds have been used as antioxidant-additives, as aromatics, naphthenes, paraffins, and heterocyclic compounds.[8-11]

Chromene derivatives are widely distributed in nature and have been reported to exhibit diverse extensive applications in different fields, as anticancer, antimicrobial, cosmetics, pigments, and agrochemicals.[12-16] It is interest in the industrial potentialities of oleo-chemicals has resulted in the development of various synthetic procedures for the heterocyclic moiety incorporated with the fatty chain. Because of significant potential therapeutic properties and industrial applications of heterocyclic moieties in the medicinal chemistry and in oleochemical industries has resulted the prominent place and generated much interest in the synthesis of new classes of fatty acid chain containing heterocyclic systems, so called as oleo-chemicals such as oleo-pyrazoles, oleo-triazoles, oleo-oxazoles etc., thereby to explore their industrial applications.[17,18] Oleo-chemicals are essential to a variety of industries such as coatings, surfactants, plasticizers, lubricant additives (antislip and antiblock additives), cosmetics, pharmaceuticals, soaps, detergents, textiles, plastics, organic pesticides and used especially as mild surfactants in cosmetic formulations. [19-22]

The aim of the present work is to find potential oxidation inhibitors to act as antioxidants for industrial lubricating oils such as turbine oils and surface active compounds. The research done in this work could be regarded as an extension to our previous work for constructing phenols containing fused chromeno-pyrimidines heterocycles and other surface active heterocyclic compounds.[23-30] In the present work, new phenols compounds linked to oxygen and nitrogen heterocycles have been synthesized as antioxidants for lubricating oils.

EXPERIMENTAL

IR spectra were recorded on a Pye Unicam SP-1000 cm^{-1} spectrometer using a KBr wafer technique. Faculty of science, Mansoura University. The ^1H NMR spectra were measured on Bruker WP 300 MHz and/or Bruker AC 300 spectrometer (Fällanden, Switzerland) operating at 400 MHz in (DMSO-d_6) as a solvent, using TMS as an internal reference in. Mass spectra were determined on a GC-MS.QP-100 EX Schimadzye (Japan) in the Micro analytical Unit, Faculty of Science, Cairo University, Cairo, Egypt. Elemental analysis were carried out using CHNS elemental analyzer model EA3000 EURO VECTOR instruments and the surface active properties measurements of the prepared surfactants (γ) were made at 25°C with Du Nouy tensiometer (Kruss Type 8451) were carried out at Chemistry Department Faculty of Applied Science, Umm Al-Qura University, Saudi Arabia.

General procedure for the synthesis of 2-amino-6-arylazo-7-hydroxy-4-(4-hydroxy-phenyl)-4H-chromene-3-carbonitrile derivatives (3a-j)

A solution of aryl diazonium chloride **2a-j** [prepared by stirring solution of appropriate arylamine (10 mmol) in 2*N* hydrochloric acid (125 mL) in an ice-bath and diazotized with 0.1*N* nitrite solution (10 mL) with stirring at 0-5°C for 1h] was added dropwise to a stirred cold solution of chormene **1** in sodium hydroxide solution (5%, 30 mL). The reaction mixture was stirred for 2-3h until coupling was complete. The solid precipitate was filtered, dried and recrystallized from a suitable solvent.

2-Amino-7-hydroxy-4-(4-hydroxyphenyl)-6-(phenyldiazenyl)-4H-chromene-3-carbonitrile (3a)

Light brown solid (1,4-dioxane); yield (0.33g, 85%), mp > 300 °C. IR(υ/cm^{-1}): 3400-3350 (2OH), 3342, 3211(NH_2), 2194 (CN). ^1H NMR (DMSO-d_6): δ 4.60 (s, 1H, CH-4 pyran), 6.90 (s, 2H, NH_2), 7.20-8.20 (m, 11H, ArH), 9.10 (s, 1H, OH), and 9.94 (s, 1H, OH). MS (*m/z, %*): 384, 73%. Anal. Calcd. (%) for $C_{22}H_{16}N_4O_3$ (384.39): C, 68.74; H, 4.20; N, 14.58. Found: C, 68.61; H, 4.35; N, 14.43.

2-Amino-7-hydroxy-4-(4-hydroxyphenyl)-6-(p-tolyldiazenyl)-4*H*-chromene-3-carbonitrile (3b)

Red solid (1,4-dioxane); yield (0.3g,72%), m.p.168-170°C. IR (υ/cm^{-1}): 3400-3350 (2OH), 3364, 3309 (NH_2), 2200 (CN).^1H NMR (DMSO-d_6): δ 2.23 (s, 3H,CH_3), 4.60 (s, 1H, CH-4 pyran), 6.86 (s, 2H, NH_2), 7.20-8.20 (m, 10H, ArH), 9.10 (s,1H, OH), and 9.82 (s, 1H,OH). MS (*m/z, %*): 398, 70.52%. Anal. Calcd. (%) for $C_{23}H_{18}N_4O_3$ (398.41): C, 69.34; H, 4.55; N, 14.06. Found: C, 69.25; H, 4.46; N, 13.88.

2-Amino-7-hydroxy-4-(4-hydroxyphenyl)-6-((4-methoxyphenyl)diazenyl)-4*H*-chromene-3-carbonitrile (3c)

Dark brown solid (ethanol); yield (0.33g, 80%), m.p.163-165°C. IR (*υ*/cm^{-1}): 3400-3350 (2OH), 3367, 3305 (NH_2), 2207 (CN). ^1H NMR (DMSO-d_6): δ 3.9 (s, 3H, CH_3), 4.90 (s, 1H, C4-H pyran), 6.87 (s, 2H, NH_2),

7.20-8.20 (m, 10H, ArH), 9.10 (s, 1H, OH), and 9.88 (s, 1H, OH). MS (*m/z, %*): 414, 69.87%. Anal. Calcd. (%) for $C_{23}H_{18}N_4O_4$ (414.41): C, 66.66; H, 4.38; N, 13.52. Found: C, 66.48; H, 4.23; N, 13.67.

Ethyl 4-((2-amino-3-cyano-7-hydroxy-4-(4-hydroxyphenyl)-4*H*-chromen-6-yl)diazenyl)benzo-ate (3d)

Reddish brown solid (1,4-dioxane); yield (0.32g,70%), m.p.123-125°C. IR (υ/cm^{-1}): 3400-3350 (two OH), 3345, 3322 (NH_2), 2206 (CN), 1698 (CO). ^{1}H NMR (DMSO-d_6): δ 1.01 (t, 3H, CH_3), 4.07 (q, 2H, CH_2), 4.64 (s, 1H, CH-4 pyran), 6.86 (s, 2H, NH_2), 7.20-8.20 (m, 10H, ArH), 9.10 (s, 1H, OH), and 9.96 (s, 1H, OH). MS (*m/z, %*): 456, 81.43%. Anal. Calcd. (%) for $C_{25}H_{20}N_4O_5$ (456.45): C, 65.78; H, 4.42; N, 12.27; Found: C, 65.62; H, 4.30; N, 12.18.

2-Amino-7-hydroxy-4-(4-hydroxyphenyl)-6-((4-nitrophenyl)diazenyl)-4*H*-chromene-3-carbo-nitrile (3e)

Light red solid (1,4-dioxane); yield (0.36g, 83%), m.p. 203-205°C. IR (*υ*/cm^{-1}): 3400-3350 (2OH), 3339, 3288 (NH_2), 2211 (CN). ^{1}H NMR (DMSO-d_6): δ 4.88 (s, 1H, CH-4 pyran), 6.90 (s, 2H, NH_2), 7.20-8.40 (m, 10H, ArH), 9.10 (s, 1H, OH), and 9.96 (s, 1H, OH). MS (*m/z, %*): 429, 68.42%. Anal. Calcd. (%) for $C_{22}H_{15}N_5O_5$ (429.39): C, 61.54; H, 3.52; N, 16.31. Found C, 61.36; H, 3.40; N, 16.20.

2-Amino-6-((4-chlorophenyl)diazenyl)-7-hydroxy-4-(4-hydroxyphenyl)-4*H*-chromene-3-carbo-nitrile (3f)

Red solid (ethanol); yield (0.34g, 81%), m.p.123-125°C. IR (υ/cm^{-1}): 3400-3350 (2OH), 3342, 3217(NH_2), 2190 (CN). ^{1}H NMR (DMSO-d_6): δ 4.66 (s, 1H, CH-4 pyran), 6.88 (s, 2H, NH_2), 7.20-8.20 (m, 10H, ArH), 9.07 (s, 1H, OH), and 9.91 (s, 1H, OH). MS (*m/z, %*): 418, 83.65%. Anal. Calcd. (%) for $C_{22}H_{15}ClN_4O_3$ (418.08): C, 63.09; H, 3.61; N, 13.38. Found: C, 62.96; H, 3.43; N, 13.23.

2-Amino-6-((4-bromophenyl)diazenyl)-7-hydroxy-4-(4-hydroxyphenyl)-4*H*-chromene-3-carbo-nitrile (3g)

Red solid (ethanol); yield (0.33g, 78%), m.p.170-172°C. IR (*υ*/cm^{-1}): 3400-3350 (2OH), 3342, 3211 (NH_2), 2212 (CN). ^{1}H NMR (DMSO-d_6): δ 4.60 (s, 1H, CH-4 pyran), 6.89 (s, 2H, NH_2), 7.20-8.20 (m, 10H, ArH), 9.10 (s, 1H, OH), and 9.94 (s, 1H,OH). MS (*m/z,%*): 463, 86.44%. Anal. Calcd. (%) for $C_{22}H_{15}BrN4O_3$ (462.03): C, 57.04; H, 3.26; N, 12.09. Found: C, 56.91; H, 3.32; N, 12.22.

2-Amino-7-hydroxy-4-(4-hydroxyphenyl)-6-((4-hydroxyphenyl)diazenyl)-4*H*-chromene-3-carbo-nitrile (3h)

Reddish brown solid (ethanol); yield (0.3g, 75%), m.p. 233-235°C. IR (*υ*/cm^{-1}): 3400-3330 (3OH), 3333, 3305 (NH_2), 2205 (CN). ^{1}H NMR (DMSO-d_6): δ 4.67 (s, 1H, CH-4 pyran), 6.90 (s, 2H, NH_2), 7.20-8.20 (m, 10H, ArH), 9.10 (s, 1H, OH), 9.34 (s, 1H, OH) and 9.88 (s, 1H, OH). MS (*m/z, %*): 400, 60.90%. Anal. Calcd. (%) for $C_{22}H_{16}N_4O_4$ (400.39): C, 66.00; H, 4.03; N, 13.99. Found: C, 66.18; H, 4.21; N, 13.82.

4-((2-Amino-3-cyano-7-hydroxy-4-(4-hydroxyphenyl)-4*H*-chromen-6-yl)diazenyl)benzoic acid (3i)

Orange solid (1,4-dioxane); yield (0.34g, 79 %), m.p.228-230°C. IR (*υ*/cm^{-1}): 3400-3350 (2OH), 3323, 3301(NH_2), 2500-3100 (OH of carboxylic group), 2205 (CN), 1702 (CO). ^{1}H NMR (DMSO-d_6): δ 4.59 (s, 1H, CH-4 pyran), 6.90 (s, 2H, NH_2), 7.20-8.20 (m, 10H, Ar-H), 9.10 (s, 1H, OH), and 9.92 (s, 1H, OH), 10.52 (s, 1H, OH of carboxylic group). MS (*m/z, %*): 428, 73.81%. Anal. Calcd. (%) for $C_{23}H_{16}N_4O_5$ (428.40): C, 64.48; H, 3.76; N, 13.08. Found: C, 64.31; H, 3.63; N, 12.93.

4-((2-Amino-3-cyano-7-hydroxy-4-(4-hydroxyphenyl)-4*H*-chromen-6-yl)diazenyl)-*N*-(4,6-dimethylpyrimidin-2-yl)benzenesulfonamide (3j)

Orange solid (DMF); yield (0.4g,70%), m.p.101-103°C. IR (υ/cm^{-1}): 3400-3350 (2OH), 3343, 3315 (NH_2), 3199 (NH), 2218 (CN). ^{1}H NMR (DMSO-d_6): δ 2.33 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 4.87 (s, 1H, CH-4 pyran), 6.79 (s, 2H, NH_2), 7.00-8.20 (m, 11H, Ar-H), 9.10 (s, 1H, OH), and 9.90 (s, 1H, OH), 10.98 (s, 1H, NH). MS (*m/z, %*): 555, 24.35%. Anal. Calcd. (%) for $C_{28}H_{23}N_7O_5S$ (569.59): C, 59.04; H, 4.07; N, 17.21; S, 5.63. Found: C, 58.90; H, 3.88; N, 17.13; S, 5.76.

General procedure for synthesis of chromene derivatives (4a-j)

Equimolar amounts of chromene derivatives **(3a-j)** (10 mmol), in each case, and catalytic amount of triethylamine in acetone (25 mL) maintained at -10 °C was added dropwise with stirring a solution of stearoyl chloride (10 mmol) in dry acetone (15 mL) over a period of 1h. The reaction mixture was stirred for overnight, followed by upon pouring onto ice/water mixture containing drops of hydrochloric acid. The obtained product was collected via recrystallization from the proper solvent.

***N*-(3-Cyano-7-hydroxy-4-(4-hydroxyphenyl)-6-(phenyldiazenyl)-4*H*-chromen-2-yl)stearamide (4a)**

Pale yellow solid (ethanol); yield (0.52g, 80%), mp 260-262°C. IR (υ/cm^{-1}): 3410-3325 (2OH and NH), 2916-2849 (aliphatic CH), 2204 (CN) and 1674 (CO). ^{1}H NMR ($CDCl_3$): δ 0.89 (t, 3H, terminal CH_3), 1.29-1.64 (m, 32H, aliphatic CH_2), 4.44 (s, 1H, CH-4 pyran), 7.06-8.92 (m, 12H, ArH and NH), 10.05 (s, 1H, OH), and 10.75 (s, 1H, OH). Anal. Calcd. (%) for $C_{40}H_{50}N_4O_4$ (650.85): C, 73.82; H, 7.74; N, 8.61. Found: C, 73.67; H, 7.59; N, 8.48.

***N*-(3-Cyano-7-hydroxy-4-(4-hydroxyphenyl)-6-(p-tolyldiazenyl)-4*H*-chromen-2-yl)stearamide (4b)**

Reddish brown solid (1,4-dioxane); yield (0.52g, 85%), m.p.124-126°C. IR (υ/cm^{-1}): 3400-3350 (2OH), 3364, 3309 (NH_2), 2200 (CN).^{1}H NMR (DMSO-d_6): δ 0.87 (t, 3H, terminal CH_3), 2.15 (s, 3H, CH_3), 1.15-1.60 (m, 32H, aliphatic CH_2), 4.33 (s, 1H, CH-4 pyran), 7.26-7.98 (m, 11H, ArH and NH), 9.55 (s,1H, OH), and 10.42 (s, 1H,OH). Anal. Calcd. (%) for $C_{41}H_{52}N_4O_4$ (664.88): C, 74.06; H, 7.88; N, 8.43. Found: C, 74.22; H, 8.06; N, 8.59.

***N*-(3-Cyano-7-hydroxy-4-(4-hydroxyphenyl)-6-((4-methoxyphenyl)diazenyl)-4*H*-chromen-2-yl) stearamide (4c)**

Brown solid (1,4-dioxane); yield (0.54g, 82%), m.p.119-121°C. IR (*υ*/cm^{-1}): 3399-3332 (2OH and NH), 2916-2848 (aliphatic CH), 2199 (CN) and 1674 (CO). ^{1}H NMR ($CDCl_3$): δ 0.87 (t, 3H, terminal CH_3), 1.15-1.60 (m, 32H, aliphatic CH_2), 4.22 (s, 1H, C4-H pyran), 7.26-8.11 (m, 11H, ArH and NH), 9.58 (s, 1H, OH), and 9.97 (s, 1H, OH). Anal. Calcd. (%) for $C_{41}H_{52}N_4O_5$ (680.88): C, 72.32; H, 7.70; N, 8.23. Found: C, 72.50; H, 7.88; N, 8.37.

Ethyl 4-((3-cyano-7-hydroxy-4-(4-hydroxyphenyl)-2-stearamido-4*H*-chromen-6-yl) diazenyl) benzoate (4d)

Brown solid (1,4-dioxane); yield (0.51g, 70%), m.p.103-105°C. IR (υ/cm^{-1}): 3400-3350 (2OH), 3345, 3322 (NH_2), 2206 (CN), 1698 (CO). ^{1}H NMR (DMSO-d_6): δ 0.89 (t, 3H, terminal CH_3), 1.21-1.65 (m, 32H, aliphatic CH_2), 4.13 (q, 2H, CH_2), 4.34 (s, 1H, CH-4 pyran), 7.26-8.00 (m, 11H, ArH and NH), 9.35 (s, 1H, OH), and 10.16 (s, 1H, OH). Anal. Calcd. (%) for $C_{43}H_{54}N_4O_6$ (722.91): C, 71.44; H, 7.53; N, 7.75; Found: C, 71.28; H, 7.38; N, 7.58.

***N*-(3-Cyano-7-hydroxy-4-(4-hydroxyphenyl)-6-((4-nitrophenyl)diazenyl)-4*H*-chromen-2-yl) stearamide (4e)**

Orange solid (ethanol); yield (0.53g, 76%), m.p. 135-137°C. IR (*υ*/cm^{-1}): 3391-3342 (2OH and NH), 2917-2849 (aliphatic CH), 2195 (CN) and 1678 (CO). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, terminal CH_3), 1.33-1.66 (m, 32H, aliphatic CH_2), 4.47 (s, 1H, CH-4 pyran), 7.26-8.82 (m, 11H, ArH and NH), 9.95 (s, 1H, OH), and 11.27 (s, 1H, OH). Anal. Calcd. (%) for $C_{40}H_{49}N_5O_6$ (695.85): C, 69.04; H, 7.10; N, 10.06. Found: C, 68.89; H, 6.96; N, 9.89.

***N*-(6-((4-Chlorophenyl)diazenyl)-3-cyano-7-hydroxy-4-(4-hydroxyphenyl)-4*H*-chromen-2-yl) stearamide (4f)**

Reddish yellow solid (1,4-dioxane); yield (0.56g, 82%), m.p.103-105°C. IR (υ/cm^{-1}): 3398-3338 (2OH and NH), 2917-2848 (aliphatic CH), 2201 (CN) and 1669 (CO). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, terminal CH_3), 1.25-1.65 (m, 32H, aliphatic CH_2), 4.46 (s, 1H, CH-4 pyran), 7.03-8.20 (m, 11H, ArH and NH), 9.46 (s, 1H, OH), and 10.36 (s, 1H,OH). Anal. Calcd. (%) for $C_{40}H_{49}ClN_4O_4$ (685.29): C, 70.11; H, 7.21; N, 8.18. Found: C, 69.88; H, 6.94; N, 8.39.

***N*-(6-((4-Bromophenyl)diazenyl)-3-cyano-7-hydroxy-4-(4-hydroxyphenyl)-4*H*-chromen-2-yl) stearamide (4g)**

Reddish yellow solid (1,4-dioxane); yield (0.58g, 79%), m.p.146-147 °C. IR (*υ*/cm^{-1}): 3402-3346 (2OH and NH), 2919-2848 (aliphatic CH), 2200 (CN) and 1670 (CO). ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, terminal CH_3), 1.32-1.67 (m, 32H, aliphatic CH_2), 4.16 (s, 1H, CH-4 pyran), 7.16-7.98 (m, 11H, ArH and NH), 9.95 (s,1H, OH), and 11.15 (s, 1H, OH). Anal. Calcd. (%) for $C_{40}H_{49}BrN_4O_4$ (729.75): C, 65.84; H, 6.77; N, 7.68. Found: C, 65.62; H, 6.49; N, 7.91.

***N*-(3-Cyano-7-hydroxy-4-(4-hydroxyphenyl)-6-((4-hydroxyphenyl)diazenyl)-4*H*-chromen-2-yl) stearamide (4h)**

Reddish brown solid (ethanol); yield (0.51g, 76 %), m.p. 166-168°C. IR (*υ*/cm^{-1}): 3405-3356 (2OH and NH), 2915-2849 (aliphatic CH), 2211 (CN) and 1672 (CO). ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, terminal CH_3), 1.30-1.66 (m, 32H, aliphatic CH_2), 4.07 (s, 1H, CH-4 pyran), 7.29-8.20 (m, 11H, ArH and NH), 9.69 (bs, 2H, 2OH), and 10.71 (s, 1H, OH). Anal. Calcd. (%) for $C_{40}H_{50}N_4O_5$ (666.38): C, 72.04; H, 7.56; N, 8.40. Found: C, 72.21; H, 7.71; N, 8.25.

4-((3-Cyano-7-hydroxy-4-(4-hydroxyphenyl)-2-stearamido-4*H*-chromen-6-yl)diazenyl)benzoic acid (4i)

Pale yellow solid (ethanol); yield (0.5g, 75%), m.p.174-176°C. IR (*υ*/cm^{-1}): 3400-3350 (2OH), 3323, 3301 (NH_2), 2500-3100 (OH of carboxylic group), 2205 (CN), 1702 (CO). ^{1}H NMR (DMSO-*d6*): δ 0.88 (t, 3H, terminal CH_3), 1.14-1.63 (m, 32H, aliphatic CH_2), 4.19 (s, 1H, CH-4 pyran), 7.23-8.22 (m, 11H, ArH and NH), 9.22 (s, 1H, OH), and 9.98 (s, 1H, OH), 11.52 (s, 1H, OH of carboxylic group). Anal. Calcd. (%) for $C_{41}H_{50}N_4O_6$ (694.86): C, 70.87; H, 7.25; N, 8.06. Found: C, 70.69; H, 7.09; N, 8.23.

***N*-(3-Cyano-6-((4-(*N*-(4,6-dimethylpyrimidin-2-yl)sulfamoyl)phenyl)diazenyl)-7-hydroxy-4-(4-hydroxyphenyl)-4*H*-chromen-2-yl)stearamide (4j)**

Reddish yellow solid (1,4-dioxane); yield (0.54g, 65%), m.p. 90-92°C. IR (υ/cm^{-1}): 3400-3350(2OH), 3343,3315 (NH_2), 3199 (NH),2218 (CN).^{1}H NMR (DMSO-d_6): δ 0.87 (t, 3H, terminal CH_3), 1.21-1.57 (m, 32H, aliphatic CH_2), 2.11 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 4.13 (s, 1H, CH-4 pyran), 7.23-8.10 (m, 12H, Ar-H and NH), 9.34 (s,1H, OH), and 10.22 (s, 1H, OH), 11.35 (s, 1H, NH). Anal. Calcd. (%) for $C_{46}H_{57}N_7O_6S$ (836.05): C, 66.08; H, 6.87; N, 11.73; S, 3.84. Found: C, 66.22; H, 7.01; N, 11.51; S, 3.66.

Preparation of surface active agents

Addition of propylene oxide (10 moles) to the active hydrogen atom in the synthesized compounds **(4a-j)** was carried out according to the Morgos procedure.[31] 0.5 wt % KOH solution containing 0.01 mol of the synthesized compound was stirred and heated above its melting point, in each case, while passing a slow stream of nitrogen through the system to flush out oxygen and remove the water from the catalyst. The nitrogen stream was then stopped and propylene oxide was added dropwise with continuous stirring and heating under an efficient reflux system to retain the propylene oxide. The reaction was conducted for different intervals of time ranging from 1 to 10 h. The reaction vessel was weighed, and the amount of reacted propylene oxide and average degree of propoxylation were determined from the increment in the mass of the reaction mixture. Normally, addition of propylene oxide gave mixture of propoxylated products and their structures were confirmed based on IR and ^{1}H NMR spectra. IR-spectra revealed a broad band in the region of (3450-2300) cm^{-1} (OH) and two other bands in region of (1170-1020) and (950-900) cm^{-1} for (C-

O-C ether linkage of polypropoxy chain) besides the original bands of these compounds. ^{1}H NMR-spectra showed the protons of the propoxy groups, which appeared as a broad multiple signals in the region of (3.21-3.80) in addition to the other signals of these compounds.

Surface and interfacial tension

Surface and interfacial tension measurements were carried out according to Findlay [32] using a Kru¨ss tensiometer [33] for the synthesized surfactants (0.1 mol/L), using a platinum iridium ring at a constant temperature (25 ± 1°C). Paraffin oil was used for the interfacial tension measurements.

Cloud point

Cloud points was determined by gradually heating a surfactant solution (1.0 wt %) in a bath controlled of the temperature, and recording the temperature at which the clear, or nearly clear solutions become definitely turbid, the cloud point was determined. The reproducibility of this temperature was checked by cooling the solutions until they become clear again.[34]

Wetting time

This property was measured by immersing a cotton skein (1 g) in a solution of the prepared surfactants (1.0 wt %) in distilled water at 25° C. The sinking time measured in seconds.[35]

Foaming properties

The solution of surfactants (1.0 wt%, 25 mL) was shaken vigorously for 10 seconds in a 100 ml graduated cylinder with glass stopper at 25 °C was used. The solution was allowed to stand for 30 seconds; the foam height was measured.[36]

Emulsification stability

Emulsification stability was prepared from aqueous solution of surfactant (20 mmol, 10 mL) and toluene (5 mL) at 25 °C. Emulsion stability was determined as the time, which took 9 mL of aqueous layer into separate from the emulsion counting since cession of shaking.[37]

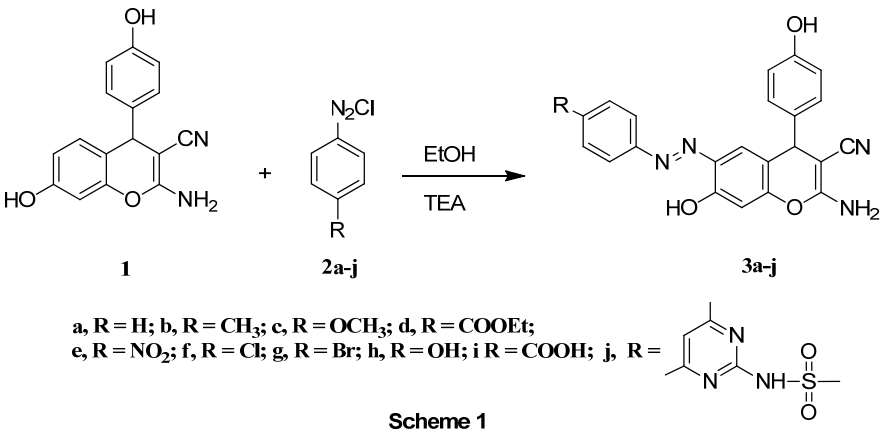
Biodegradability

The biodegradation tests of the synthesized nonionic surfactants were performed according to the river water Die-Away method.[38] In this test, a stirred solution containing the tested surfactant (1,000 ppm) was incubated at 25 °C. Samples were withdrawn daily, filtered using Whatman filter paper and the surface tension was measured using a Du Nouy tensiometer. The process was repeated for 7 days.

RESULTS AND DISCUSSION

Chromene derivative **1** [39], was coupled with various aryl diazonium chloride **2a-j** at the position 6 in the chromene ring and gave a number of valuable azo heterocyclic dyes **3a-j (Scheme 1)**, These compounds expect to increase antioxidant activity due to increasing chromophores that give facility for radical scavengers, and hydroperoxide decomposers, as well as synergistic mixtures of both of them. The IR spectra revealed two broad absorption bands in the region 3300-3400 cm^{-1} for the OH groups, and the characteristic bands of amino group were obtained for stretching at 3000-4000 cm^{-1}. Also, characteristic bands from 1580-1600 cm^{-1} due to the azo group. Moreover, nitrile group characteristic bands were seen at 2250-2100 cm^{-1}, while the general aromatic stretching bands were observed at 3200-3000 cm^{-1}. In addition, characteristic bands for halogen groups like chlorine and bromine were found at 740-700 cm^{-1} & 600-500 cm^{-1}.

While, characteristic stretching frequencies of 1,4-disubstituted phenyl ring were found at 823 cm^{-1} respectively suggesting the correct formation of the desired products. The ^{1}HNMR spectra of compounds **3a-j** showed singlet signal at δ 6.50-6.90 ppm due to amino protons, the methine proton C4-H pyran appeared as singlet at δ 4.50-4.90 ppm. The proton C4-H pyran is a bit downfield as compared to a proton singlet in isolation because of the strong electron-withdrawing group like –CN present on the adjacent carbon, which deshields the proton forcing it to go down field. Moreover, the mass spectra gave supporting evidence for the suggested structure by giving



Scheme 1

the correct molecular ion peak of the proposed structures **3a-j**. These phenol compounds linked to oxygen and nitrogen heterocycles have been synthesized as antioxidants for lubricating oils.

Evaluated of the synthesized compounds (3a-j) as antioxidant activity

The base oil that used for the evaluation of the synthesized **(3a-j)** is turbine oil of viscosity grade 68, which has the required oxidation stability value using the standard international test methods as shown in **(Table 1)**.

Turbine oil is a very high quality, rust and oxidation inhibited circulating oil developed for use in industrial steam turbines, rotary air compressors and many other industrial applications. It is specially formulated to provide a very high level of oxidation resistance for long service life. It must have excellent oxidation resistance and thermal stability at high temperatures to minimize sludge and varnish formation, and provide long service life.

Table 1: *Standard specifications of the base oil with international antioxidant additive.*

Specific Gravity @ 60°F	0.868
TOST, ASTM D943-04a, hours	15000
Density, lbs/gal @ 60°F	7.22
RPVOT, ASTM D2272, minutes	1200
Color, ASTM D1500	0.5
Air Release, ASTM D3427, minutes	2
Flash Point (COC), °C (°F)	243 (469)
Demulsibility, ASTM D1401, minutes to pass	20
Pour Point, °C (°F)	-27 (-17)
Foam Test, ASTM D892	pass
Rust Test, ASTM D665 A&B	Pass
Kinematic viscosity cSt @ 40°C	68.0
Acid Number, ASTM D974, mg KOH/g	0.08
Kinematic viscosity cSt @ 100°C	8.8
Copper Corrosion, ASTM D130	1a
Viscosity Index	100
Viscosity	
Oxidation Stability	

The oxidation stability of the synthesized compounds were evaluated in **(Table 2)**.

Table 2: *The Properties formulated lubricating oil compared with base oil*

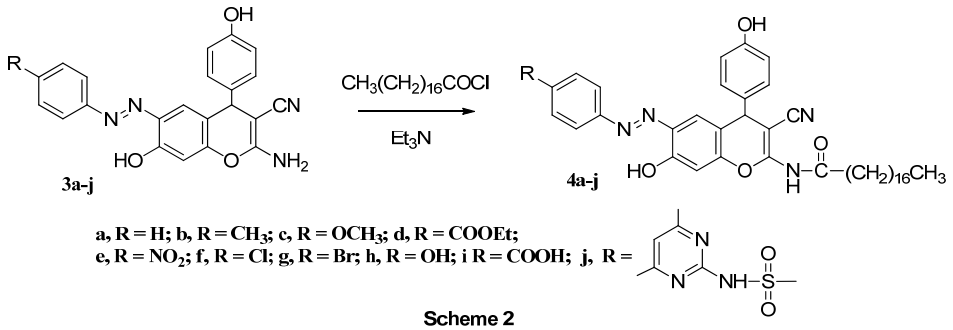
Antioxidant additive	Kinematic viscosity cSt @ 40°C	Kinematic viscosity cSt @ 100°C	RPVOT, minutes
Base oil with commercial antioxidant	68	8.8	1200
3a	68.01	8.77	1204
3b	68.14	8.93	1254
3c	68.12	8.79	1298
3d	68.09	8.81	1175
3e	68.11	8.84	1097
3f	68.01	8.89	1167
3g	67.95	8.91	1122
3h	68.04	8.83	1277
3i	68.13	8.85	1188
3j	67.84	8.02	1304

On addition of antioxidants, it will act to resist oxidation, but once the antioxidant has been consumed, the oil will begin to react with the oxygen and the pressure in the vessel will drop. The time it takes to reach the specified drop in pressure is recorded and compared to new oil specifications. The addition of antioxidant **3a, b, c, h, j** showed marked increase in oxidation stability test especially **3j** compared with the base oil of international commercial antioxidant. For efficiency of compounds **3a, b, c, h, j** as antioxidant may be attributed to presence of electron donating group. Compound **3j** showed highest oxidation stability test (RPVOT) value, this may be attributed to presence of two OH act as hydrogen donor to free radical to act as free radical inhibitor, in addition to presence of NH of sulphonamide which can also, act as free radical inhibitor and radical scavengers. On other hand, compound **3j** has the advantage antioxidant character of hindered phenols and secondary amines, which can explain the high value of RPVOT compared with commercially used antioxidant. The kinematic viscosity is reported at one of two temperatures, either 40°C or 100°C. Likewise, most engine oils are typically measured at 100°C because the engine oil classification system is referenced to the kinematic viscosity at 100°C. Additionally, 100°C reduces the rise of measurement interference for engine oil soot contamination. The kinematic viscosity of formulated oil with antioxidant additives do not showed marked changes in its values than commercially used antioxidant.

Monitoring and trending viscosity is perhaps one of the most important components of any oil analysis program. Even small changes in viscosity can be magnified at operating temperatures to the extent that an oil is no longer able to provide adequate lubrication. Typical industrial oil limits are set at ±5 percent for caution, and ±10 percent for critical, although severe duty applications and extremely critical systems should have even tighter targets. There is a good relation between oxidation stability of oil with value of total acid number (TAN) as shown in **(Table 3)**. It shows that, addition of additives to oil also inhibit the increasing of total acid number by oxidation.

Table 3: *The total acid number (TAN) of base and formulated oil at different temperatures*

Antioxidant additive	Total acid number @ 40°C	Total acid number @ 100°C	Total acid number @ 150°C	Total acid number @ 200°C
Base oil	0.08	0.093	0.12	0.15
3a	0.077	0.090	0.110	0.142
3b	0.08	0.093	0.119	0.146
3c	0.072	0.090	0.114	0.14
3d	0.071	0.087	0.113	0.141
3e	0.078	0.090	0.115	0.143
3f	0.08	0.092	0.116	0.145
3g	0.08	0.093	0.12	0.145
3h	0.072	0.089	0.11	0.139
3i	0.08	0.093	0.12	0.15
3j	0.070	0.089	0.109	0.136

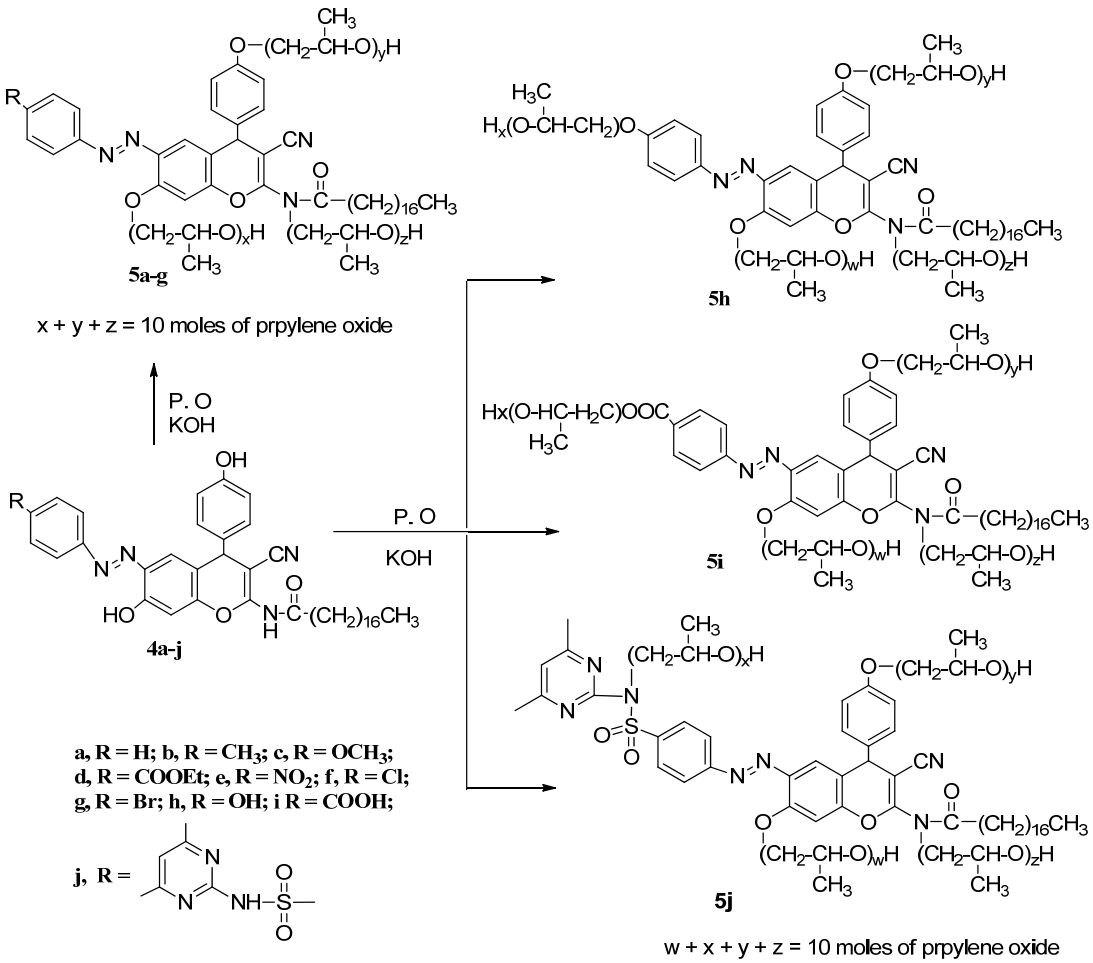


Scheme 2

The total acid number (TAN) as a function of temperature, (TAN) increase as temperature increase. This can be explained that at higher temperature the rate of oxidation of oil increase, and hence formation of free radical, sludge and acidic compounds. But, in generally, the value of TAN decrease on addition of antioxidant especially **3j** which give evidence that additive compounds have effective effect by retarding oxidation of oil and hence decrease formation of acidic compounds.

Conversion of the synthesized compounds (3a-j) to surface active agents (5a-j)

The surface active agents find diverse applications in industry, home and uses to accelerate soaking, and liming is improved by the addition of wetting agents.[40] Herein we continue this works by utilizing fatty acid chloride to prepare a new surface active agents incorporated with heterocyclic derivatives. Thus, condensation of chromene derivatives **(3a-j)** with stearoyl chloride in presence of triethylamine furnished the adducts **(4a-j)**, **(Scheme 2)**. The structure of these products was characterized and identified by their elemental analysis, IR and ^{1}HNMR spectra. IR spectra reveled two bands in the region of (2950-2815) cm^{-1} (CH_2 aliphatic), besides the original bands of these compounds. While, the ^{1}H NMR-spectra showed the protons of aliphatic chain, which appeared as a broad multiple signals in the region of (1.14-1.66) in addition to the other signals of these compounds.



Scheme 3

Table 4: *Surface properties of the surface active agents*

Compounds	Surface tension (dyne/cm) 0.1 m/l	Interfacial tension (dyne/cm) 0.1 m/l	Cloud Point °C	Wetting time (sec.)	Emulsion stability (min.)	Foam height (mm)
5a	33	12.5	92	85	148	33
5b	35	12	86	78	135	25
5c	37	14	94	78	139	29
5d	33	13	89	86	146	34
5e	31	10	91	95	157	37
5f	36	13	94	79	129	30
5g	38	14	99	75	138	29
5h	31	11	86	96	155	35
5i	34	12	85	83	135	32
5j	39	14	96	77	133	28

In order to investigate the synthesized compounds as the surface-active agents, two requirements are needed. The first requirement is the presence of active hydrogen atoms to react with alkylene oxide and the second is the molecular weight should be suitable to have an amphiphilic molecule with the suitable hydrophilic-lipophilic balance. Thus, the reaction of chromene derivatives **(4a-j)** with 10 moles of propylene oxide in presence of KOH as a catalyst affords the corresponding propoxylated products **(5a-j) (Scheme 3)**. The structure of these products was characterized and identified by their IR and ^{1}H NMR spectra (see the experimental part).

Evaluation of the synthesized compounds (5a-j) as surface active agents

The study of the surface active properties of the oxypropylated compounds has been done in aqueous solution (1wt %, pH = 7) at 25°C. The surface active and related properties of the synthesized compounds including, surface and interfacial tension, cloud point, wetting time, foaming, and emulsification properties are given in **(Table 4)**.

Surface and interfacial tension

It is noticeable that the nonionic surfactants incorporating heterocyclic moiety have lower values, which might be due to the electrostatic repulsion between the ionized molecules. In addition, we found that the chromene derivatives **5e** and **5h** have the lower values of surface tension than other compounds that refer to the difference in the surface activity. In general, the obtained results indicated that the synthesized products have prominent surface activity.

Cloud point

The most efficient use of nonionic surfactants in aqueous systems is by understanding a property called cloud point, which is the temperature at which the aqueous solution of the prepared nonionic surfactants shows turbidity on heating. The results showed high cloud points and showed good performance in hot water, which reflects the fact that, it can be used over a wide range of temperatures. General, the synthesized nonionic surfactants bearing heterocyclic moieties showed high values of cloud point, the high values of cloud point that might be attributed to the presence of aromatic ring.

Wetting time

All the product surfactants are good wetting agents and very effective as wetting agents in distilled water, where the prepared compounds showed a decrease of the wetting time. So, the products with effective wetting agents can find a wide application in house hold detergents and in the textile industry.[41]

Foaming power

The results obtained in this work revealed that, the tested compounds yielded low foam, where, the low foaming power compounds have some obvious application in the dyeing and auxiliary industries.[42]

Emulsifying properties

In general, all the prepared surfactants possess high emulsion stability; these results might lead to the application of the surfactants of choice in pesticide and cosmetic formulation. Moreover, the prepared surfactants can be useful in dye baths in the textile industry and as emulsion paints.

Biodegradability

The biodegradability data were given in **(Table 5)**, within the experimental accuracy; all the prepared surfactants seem to degrade easy which means that these compounds are safe for human beings as well as environments.

Table 5: *Biodegradability of the surface active agents*

Compounds	1st day	2nd day	3rd day	4th day	5th day	6th day	7th day
5a	41	47	58	69	80	91	-
5b	43	50	58	69	81	94	-
5c	46	53	65	74	83	94	-
5d	40	47	57	68	80	92	-
5e	38	46	56	65	77	87	94
5f	45	53	62	74	86	94	-
5g	45	52	60	71	83	94	-
5h	39	47	59	61	74	88	94
5i	42	48	59	62	76	89	93
5j	47	55	65	76	86	96	-

CONCLUSIONS

This study reports the successful synthesis of new phenols compounds linked to oxygen and nitrogen heterocycles as antioxidants for lubricating oils and as surface active agents. The prepared surface active agents exhibited emulsifier properties where many textile processes such as scouring and dyeing, it is necessary to introduce surfactants into the bath to remove oily impurities from the fibers. Therefore, their potential use in a non-edible media such as insecticides or pesticides as well as in the manufacturing of antioxidant additives, dyes, drugs and cosmetics.

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