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Dedicated to Professor Mihaela Hillebrand on the occasion of her 85th anniversary

THE SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF A THIO-DEBRANONE STRIGOLACTONE MIMIC CONTAINING A BENZOTHIAZOLE RING

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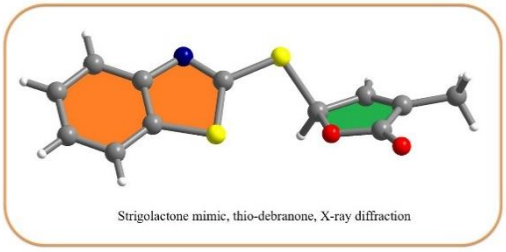
The first thio-debranone strigolactone mimic containing a hetaryl moiety was obtained by S-alkylation of 2-mercaptobenzothiazole with 5-bromo-3-methylfuran-2(5*H*)-one in the presence of potassium carbonate. The structure of the S-alkylation product was deduced by NMR spectroscopy and confirmed by X-ray analysis.



INTRODUCTION

Strigolactones is the generic name of a family of carotenoid derived molecules which act as exogenous signals in the plants rhizosphere[1–9] as phytohormones controlling plant architecture[9–16] and plant metabolism in response to biotic and abiotic environmental stress.[17,18]

Natural strigolactones have complex structures with tricyclic ABC lactone ring system core linked to an unsaturated furan-2-one D-ring by an enol-ether bridge. Stereochemistry is important in the fine-tuning of the biological properties of strigolactones (Fig. 1).[7–9,12–16] The strigolactones which exhibit the A-, B-, C- tricyclic core structure have been designated as canonical strigolactones to distinguish them from strigolactone-like compounds that do not have the canonical A-, B-, and/or C-part and are termed as non-canonical strigolactones.[16] Canonical strigolactones have been classified into two major classes based on stereochemistry (Figure 1). In all canonical and non-canonical strigolactone molecules, the furan-2-one D-ring is connected to the rest of the molecule through an enol ether bridge with a *E* stereochemistry at the double bond.

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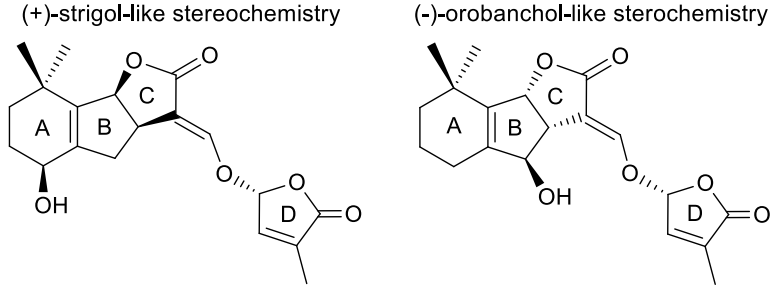


Fig. 1 – The two major classes of naturally canonical strigolactones.

Natural strigolactones are obtained from root exudates of mono- and dicotyledonous plants only in very small amounts. The complex structures of naturally occurring strigolactones and their laborious total syntheses on a multi-gram scale stimulated the interest in syntheses of simplified molecules showing the various bioactivities of naturally strigolactones. Therefore, synthetic strigolactone analogues contain the bioactive CD part of natural compounds,[12,20–25] while strigolactone mimics have the D-ring directly linked to (het)aroyloxy, (het)aryloxy or even heteroaryl moieties (Fig. 2).[25–33] Among these, strigolactone mimics derived from substituted phenols and thiophenols, so-called debranones and thio-debranones, respectively, are easier to synthesize and have remarkable biologic activities.[12,27–31] The multiple and versatile roles of strigolactone analogues and mimics make them interesting not only for plant protection but also for medicinal chemistry.[34–36]

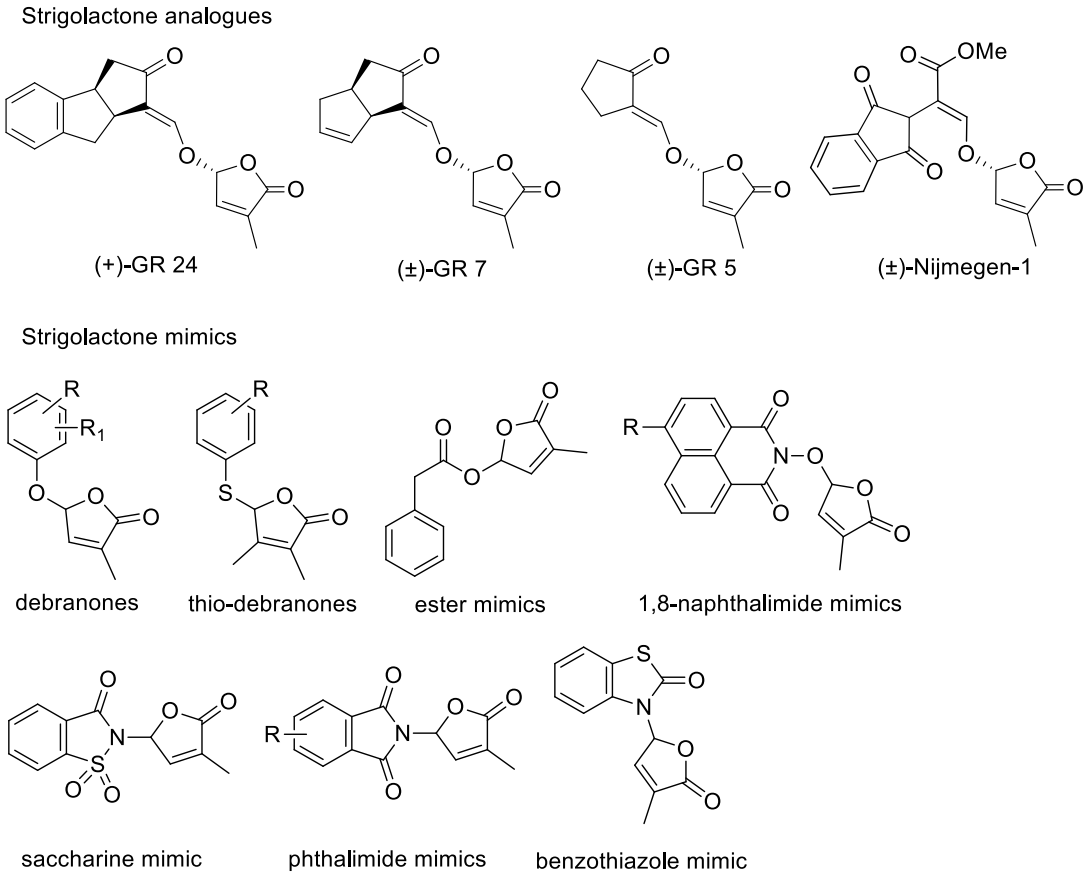


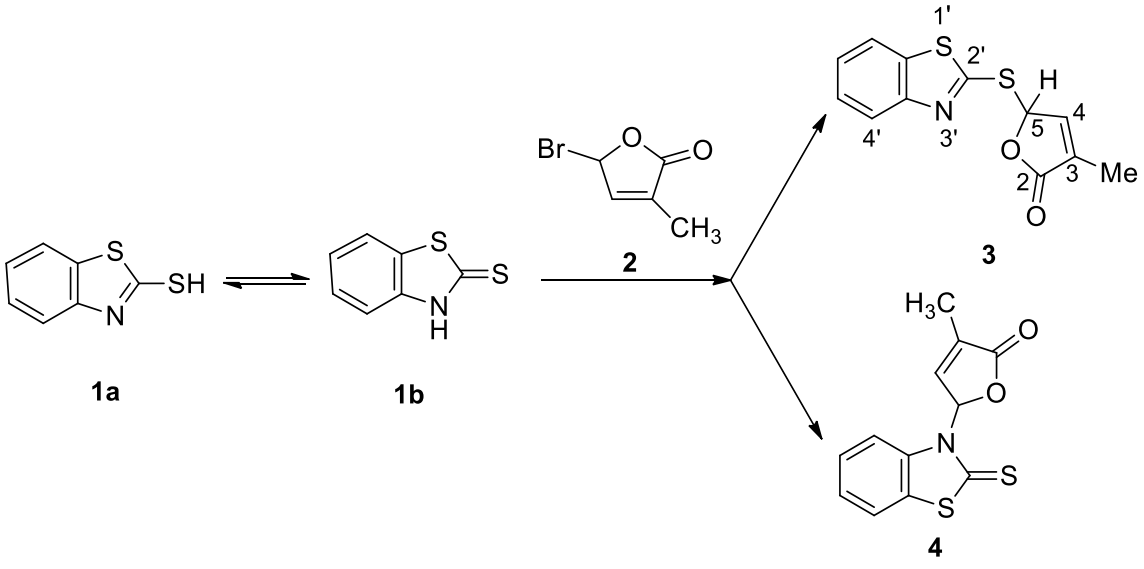
Fig. 2 – Examples of strigolactone analogues and mimics.

Our group was interested in syntheses of simplified bioactive strigolactone mimics accessible on a multi-gram scale and in investigation of their potential applications. A number of synthesized strigolactone mimics containing a 1,8-naphthalimide ring system connected with a 3-methylfuran-2(5*H*)-one *via* an ether bond proved interesting biostimulant properties for plants,[37–39] and microalgae.[40]

Strigolactone mimics that contain a piperidine-substituted 1,8-naphthalimide ring system linked by an ether bond to 3-methylfuran-2(5*H*)-one unit are fluorescent probes for water detection in organic solvents.[41,42] Chitosan-1,8-naphthalimide strigolactone mimics multifunctional plant biostimulant formulations with synergistic effect on plants were developed.[43] New debranone-type strigolactone mimics containing 3,5-disubstituted aryloxy groups linked to the bioactive 3-methylfuran-2(5*H*)-one unit or benzothiazole-derived strigolactone mimics in which the benzothiazole ring is directly linked *via* the cyclic nitrogen atom to the bioactive 3-methylfuran-2(5*H*)-one ring have been synthesized.[44] Biological studies reveal their efficient biostimulant properties on microalgae.[44] Expanding the scope of strigolactone mimics we have synthesized a new thio-debranone-like compound starting from 2-mercaptobennzothiazole and 5-bromo-3-methylfuran-2(5*H*)-one aiming to investigate its physicochemical and biological properties. Herein, we present the synthesis of a new thio-debranone-type strigolactone mimic 5-(benzo[*d*]thiazol-2-ylthio)-3-methylfuran-2(5*H*)-one. The synthesized thio-debranone mimic was structurally characterized by NMR spectroscopy, the single-crystal X-ray diffraction and the Hirshfeld Surface analysis.

RESULTS AND DISCUSSION

A new thio-debranone-type strigolactone mimic containing the benzothiazole ring connected to the bioactive 3-methylfuran-2(5*H*)-one structure *via* a thioether bond was synthesized. The bioactive bicyclic planar molecule of 2-mercapto benzothiazole **1** could exists in the thiol form as benzo[*d*]thiazole-2-thiol **1a** and the thione form as benzo[*d*]thiazole-2(3*H*)-thione **1b** (Scheme 1).[45] The reaction of 2-mercaptobenzothiazole **1** with 5-bromo-3-methylfuran-2(5*H*)-one **2** can lead to two different reaction products. The first one, 5-(benzo[*d*]thiazol-2-ylthio)-3-methylfuran-2(5*H*)-one **3** in which the two bioactive structural units, benzothiazole and 3-methylfuran-2(5*H*)-one, are connected through a thioether link is the condensation reaction product of the thiol tautomeric form **1a** with 5-bromo-3-methylfuran-2(5*H*)-one **2**. The second reaction product, 3-methyl-5-(2-thioxobenzo[*d*]thiazol-3(2*H*)-yl)furan-2(5*H*)-one **4** in which the 3-methylfuran-2(5*H*)-one unit is directly linked with the nitrogen atom from the benzotiazole ring could be formed by the alkylation reaction of the thione tautomeric form **1b** with 5-bromo-3-methylfuran-2(5*H*)-one **2**. By the reaction of 2-mercaptobenzothiazole **1** with 5-bromo-3-methylfuran-2(5*H*)-one **2** in anhydrous acetone, in the presence of anhydrous potassium carbonate at room temperature, we have isolated and completely characterized only the 5-(benzo[*d*]thiazol-2-ylthio)-3-methylfuran-2(5*H*)-one **3**, the condensation product of the thiol tautomeric form **1a** with 3-methylfuran-2(5*H*)-one **2**. The second reaction product, 3-methyl-5-(2-thioxobenzo[*d*]thiazol-3(2*H*)-yl)furan-2(5*H*)-one **4** was detected by NMR analyses during the reaction time but could not be isolated to be completely characterized (Scheme 1).



Scheme 1 – Synthesis of 5-(benzo[*d*]thiazol-2-ylthio)-3-methylfuran-2(5*H*)-one **3**.

There are some interesting synthetic aspects of this synthesis as there is a competition between N- and S-alkylation. For both 2-hydroxybenzothiazole and 2-mercaptobenzothiazole the keto/thione forms are more stables. The alkylation of 2-mercaptobenzothiazole occurs preferentially to the S atom which will better accommodate as thiolate anion being more polarisable. The mild reaction conditions, base and polar aprotic solvent also favour S-alkylation. In the case of 2-hydroxybenzothiazole the alkylation goes to N atom as there is a competition between N and O to accommodate the negative charge. R-S^- anions are also more reactive compared to R-O^-. This is in good accordance with literature on alkylation with allyl halides.[46] Literature data also confirm the preference of the S-alkylation in mild reaction conditions.[46]

The compound 5-bromo-3-methylfuran-2(5*H*)-one **2** was obtained by the brominating of commercially available 3-methylfuran-2(5*H*)-one in carbon tetrachloride with *N*-bromosuccinimide in the presence of catalytic amounts of a radical initiator such as dibenzoyl peroxide or 2,2′-azobis(isobutyronitrile).[47]

The structure of 5-(benzo[*d*]thiazol-2-ylthio)-3-methylfuran-2(5*H*)-one **3** was confirmed by the NMR and IR spectroscopy, the single crystal X-ray.

In the NMR spectrum of compound **3**, the protons H-4, H-5 and the protons of the methyl group belonging to the furanone moiety are coupled with each other. Thus, the protons of methyl group are coupled with H-5 with 5J homoallylic coupling constant over five bonds and with H-4 with a 4J allylic coupling constant over four bonds. The coupling constant of the protons H-4 and H-5 is over three bonds, having a ^3J value of ca. 3.2 Hz.

The ^{13}C-NMR spectrum confirms the proposed structure for the strigolactone mimic **3**. The carbon atom in the carbonyl group of the lactone appears at 172.1 ppm. The carbon atom at position 5 of the furanone ring appears at 83.7 ppm, with ca. 16 ppm lower than when it is bonded to an oxygen atom from like in the case of debranones. The carbon atoms of the double C=C bond from furanone residue appear at 133.3 ppm and 143.9 ppm, respectively. The chemical shifts of the carbon atoms from benzothiazole moiety are in good agreement to those of S-alkylated 2-mercaptobenzothiazoles described in the literature. The first proof of the S-alkylation is given by the chemical shift of the atom C-5, involved in the thioether bond. The chemical shift of C-5 is at ~84 ppm which is with ~3 ppm more deshielded than in the case of the N-alkylated minor isomer **4**.

In the IR spectrum the strong C=O stretch band which has a wavenumber of 1758 cm^{-1} is characteristic for a lactone functional group.

X–Ray crystallography. X-ray diffraction measurements were performed on a Rigaku XtaLAB Synergy-S diffractometer operating with Mo-Kα (λ = 0.71073 Å) micro-focus sealed X-ray tube. The structure was solved by direct methods and refined by full-matrix least squares techniques based on F^2. The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-2019 crystallographic software package. A summary of the crystallographic data and the structure refinement are given in Table 1. CCDC reference number: 2524404.

Table 1

Crystallographic data, details of data collection and structure refinement parameters for compound **3**

Compound	**3**
Chemical formula	$C_{12}H_9NO_2S_2$
M (g mol^{-1})	263.32
Temperature, (K)	293(2)
Wavelength, (Å)	0.71073
Crystal system	*Monoclinic*
Space group	$P2_1/c$
a (Å)	13.0017(5)
b (Å)	8.1419(3)
c (Å)	11.2578(5)
α (°)	90
β (°)	92.868(4)
γ (°)	90
V ($Å^3$)	1190.24(8)
Z	4
D_c (g cm^{-3})	1.469
μ (mm^{-1})	0.434
F(000)	544
Goodness-of-fit on F^2	1.034
Final R_1, wR_2 [I>2σ(I)]	0.0280, 0.0708
R_1, wR_2 (all data)	0.0343, 0.0760

The structural characterization by single-crystal X-ray diffraction confirms the NMR data. Compound **3** crystallizes in the $P2_1/c$ monoclinic space group with one molecule in the asymmetric unit. The molecular structure of the compound **3** is presented in Fig. 3a and consists in a benzothiazole fragment linked through a thioether group to a 3-methylfuran-2(5*H*)-one moiety. The S-C bond lengths for the thioether group are: S2-C7 = 1.7508(17) and S2-C8 = 1.8048(18) Å, while for the benzothiazole moiety are slightly shorter: S1-C1 = 1.7322(17) and S1-C7 = 1.7457(17) Å. The C-N bond lengths are: C6-N1 = 1.391(2) and C7-N1 = 1.292(2)

Å. Within the 3-methylfuran-2(5*H*)-one moiety the bond lengths are: C8-C9 = 1.488(2), C9-C10 = 1.309(3), C10-C11 = 1.496(2), C10-C12 = 1.470(3), C8-O1 = 1.428(2), C12-O1 = 1.371(2) and C12-O2 = 1.192(2) Å. The dihedral angle between the mean planes of the benzothiazole fragment and the five-member ring of the 3-methylfuran-2(5*H*)-one moiety is 33.4º (Fig. 3b).

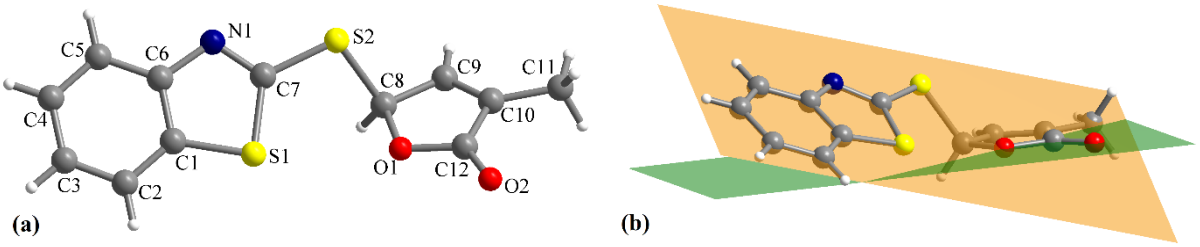


Fig. 3 – Perspective views showing the molecular structure of the compound **3** (a) and the dihedral angle made by the mean planes of the two rings within the structure (b).

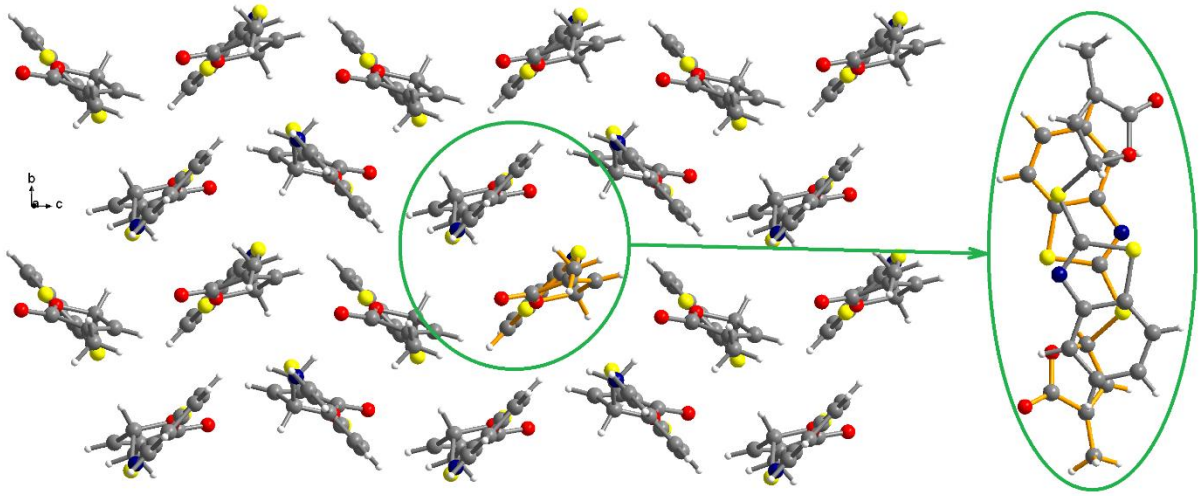


Fig. 4 – View of the packing diagram along the crystallographic *a* axis showing the organization in pairs of the molecules. The inset presents details of the overlapping mode in the pair. In orange is depicted the asymmetric unit.

The analysis of the packing diagrams shows organization of the molecules in pairs with the benzothiazole fragments placed in parallel planes. In Fig. 4 is presented a packing diagram illustrating the pairs association of the molecules in the crystallographic *bc* plane. The N···S contact length between the thiazole fragments within a pair is 3.63 Å (see the inset of the Fig. 4). The N1 and O2 atoms are involved in weak hydrogen interactions (Fig. 5). The (C8'-)H8'···N1 and (C4"-)H4"···O2 distances are: 2.473 and 2.627 Å, and corresponding angles, C8'-H8'···N1 and C4"-H4"···O2, are: 171.4 and 163.0° (symmetry codes: ' = 1–x, 0.5+y, 1.5–z; " = –1+x, y, z).

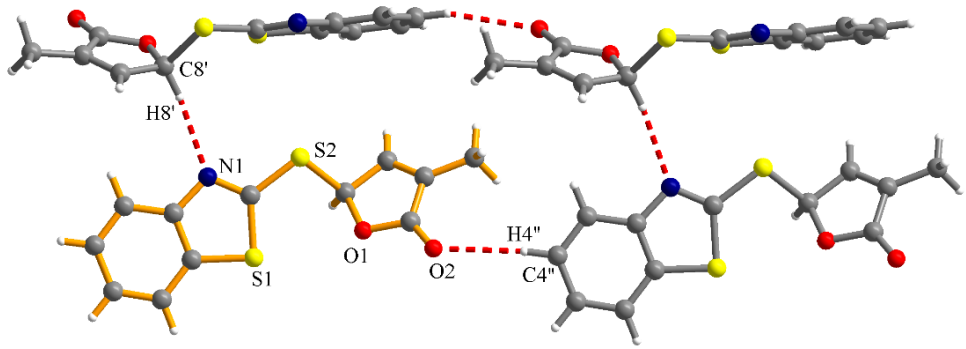


Fig. 5 – View of the packing diagram showing the hydrogen interactions (symmetry codes: ' = 1-x, 0.5+y, 1.5-z; " = -1+x, y, z). In orange is depicted the asymmetric unit.

Hirshfeld surface (HS) analysis (performed using Crystal Explorer 21) is a very good graphical method used for visualization of intramolecular and intermolecular contacts.[48] The two-dimensional fingerprint plots mapped over d_{norm} and the interaction percentage (Fig. 6) sustains the role of different intermolecular and intramolecular interactions in the crystal molecular organization.

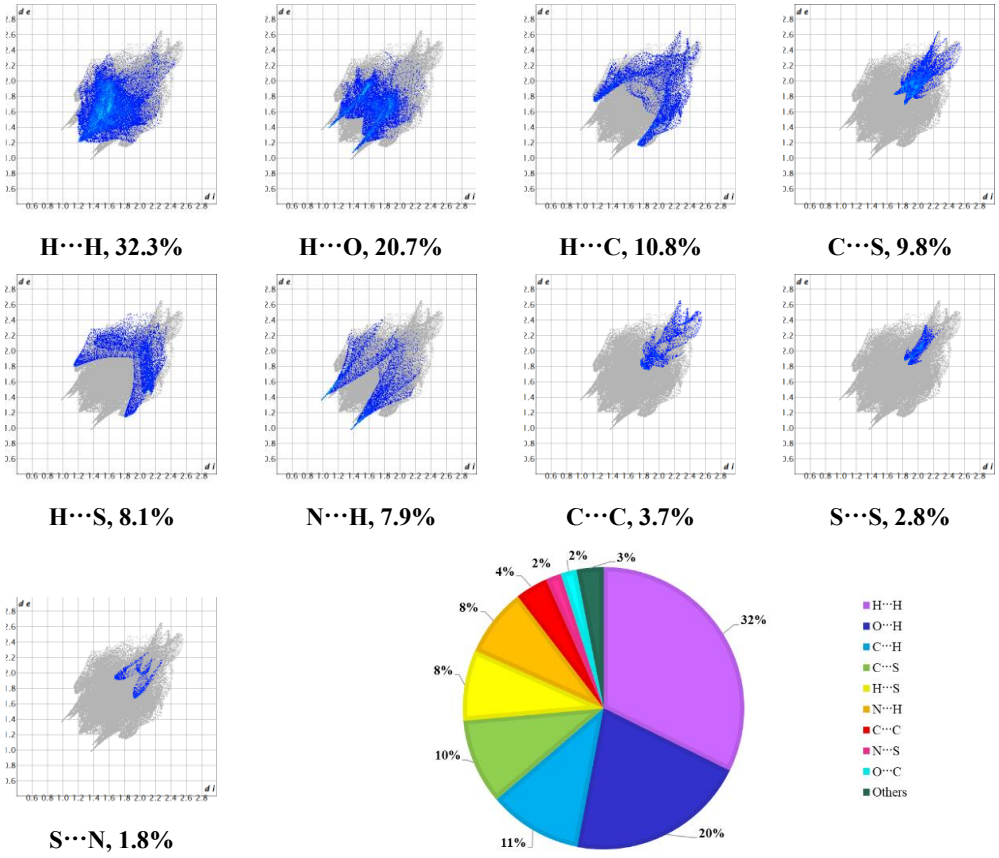


Fig. 6 – The fingerprint mapping and the interaction percentages of different intermolecular contacts obtained from 2D fingerprint plots.

The red regions on a dnorm map represent close intermolecular contacts, where the distance between atoms of adjacent molecules is less than the combined van der Waals radii of those atoms. By analyzing the positions of the red regions, it is possible to accurately determine where hydrogen bond donors and acceptors interact with neighboring molecules within the crystal lattice.

The d_{norm} representation for HS analysis generated for compound **3** reveals a number of 6 red spots (Fig. 7) characteristic for intermolecular close contacts and their reciprocals: $H_4\cdots O_2$, $H_8\cdots N_1$ and $H_2\cdots N_1$ (see Fig. 3 and Fig. 5).

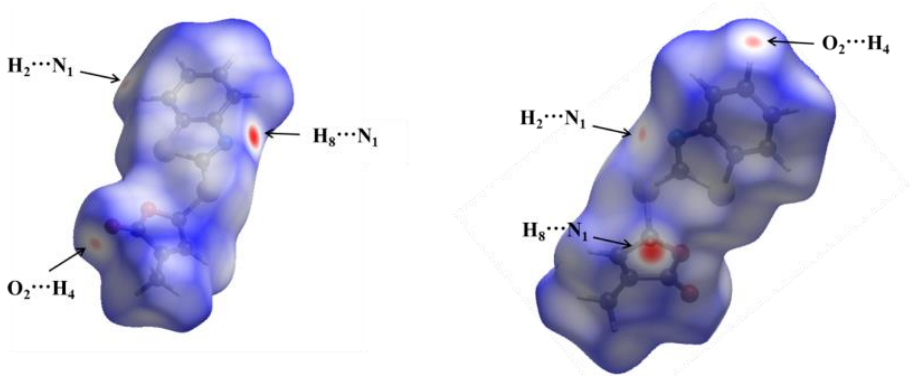


Fig. 7 – The Hirshfield analysis plotted over d_{norm} and the visualization of intermolecular contacts for compound **3**.

The percentage interactions given by the fingerprint plots suggest a dispersion driven supramolecular network directed by weak C-H···N and C-H···O contacts. The sum of C···C, S···N, C···S and S···S contacts which account togheter for about 18% of the total Hirshfeld surface might suggest a possible weak interaction between the thiazole moieties. This is still possible even at the distance of 3.88 Å between the centroids of the thiazole rings. Also the C···S percentage of 9.8% might come for the packing induced approach of the exocyclic sulfur atom to the benzene or thiazole rings of adjacent molecules which can suggest that the lone pair electrons of the sulphur interacts with the neighbouring π-systems. Thus the introduction of a benzothiazole ring to the bioactive furanone moiety can lead to interesting binding modes to desired targets.

EXPERIMENTAL

Melting point, determined on a Boetius apparatus, is uncorrected. The IR spectrum was registered on a Fourier-transform (FT)-IR Vertex 70 spectrometer (Bruker Optik GmbH, Ettlingen, Germany) in ATR modes. The NMR spectra were recorded on a Varian Gemini 300 BB instrument, at 300.1 MHz and 75.5 MHz for ^{1}H and ^{13}C nuclei respectively. Chemical shifts are reported as δ (ppm) and are referenced to internal TMS for ^{1}H chemical shifts and to the internal deuterated solvent for ^{13}C chemical shifts ($CDCl_3$ referenced at 77.0 ppm) The elemental analysis was carried out on a COSTECH Instruments EAS32 apparatus and satisfactory microanalyses were obtained. The 5-bromo-3-methylfuran-2(5*H*)-one **2** was obtained in good yield by the brominating of commercial 3-methylfuran-2(5*H*)-one, technical grade, with *N*-bromosuccinimide in carbon tetrachloride, at reflux temperature, in the presence of catalytic amounts of dibenzoyl peroxide or 2,2′-azobis(isobutyronitrile).[46] and it was used as crude reaction product (94–95 %). All reagents and solvents were commercially products (Sigma-Aldrich) and have been used without purification.

Synthesis of 5-(benzo[*d*]thiazol-2-ylthio)-3-methylfuran-2(5*H*)-one (3).To a solution of 1.67 g (10 mmol) of 2-mercaptobenzothiazole **1** in 20 mL acetone 2.1 g (15 mmol) anhydrous potassium carbonate catalyst was added, then 2.4 g (15 mmol) of crude 5-bromo-3-methylfuran-2(5*H*)-one **2** dissolved in 20 mL of acetone was slowly added under stirring at room temperature. The stirring was continued for 20 hours at room temperature. The reaction mixture was filtered off after cooling to remove the inorganic waste, the acetone was evaporated and the residue was chromatographed on an alumina 70–230 mesh packed column by eluting with dichloromethane and the desired compound **3** was filtered off. The compound was obtained by crystallization from isopropanol as a pale yellow (0.82 g, 31% yield) with mp 104–106 °C. Anal. Calcd. for $C_{12}H_9NO_2S_2$ (263.34): C, 54.73; H, 3.44; N, 5.32. Found: C, 54.79; H, 3.40; N, 5.28. ATR-FTIR (solid): 1758 cm^{-1} (CO). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 1.98 (t, 3H, *J*= 1.3 Hz, Me) 6.95 (quint., 1H, *J* = 1.3, 2.3, 3.2 Hz, H-5), 7.18 (quint., 1H, *J*= 1.3, 2.3, 3.2 Hz, H-4), 7.34–7.40 and 7.44–7.49 (2m, 2H, H-5', H-6'), 7.79–7.82, 7.93–7.96 (2m, 2H, H-4', H-7'). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 10.8 (Me), 83.7 (C-5), 121.3, 122.5 (C-4', C-7', benzothiazole), 125.3, 126.6 (C-5', C-6', benzothiazole), 133.3 (C-3), 136.0 (C-7a', benzothiazole), 143.9 (C-4), 152.9 (C-3a', benzothiazole), 160.8 (C-2', benzothiazole), 172.1 (C=O).

CONCLUSION

In conclusion we have efficiently synthesized a new thio-debranone, 5-(benzo[*d*]thiazol-2-ylthio)-3-methylfuran-2(5*H*)-one, a potential strigolactone mimic. We have expanded the scope of thio-debranones by grafting a benzothiazole moiety to the bioactive furanone scaffold. The synthesized S-alkylation product was structurally characterized by NMR, single crystal X-ray diffraction and Hirshfeld surface analysis. The supramolecular structure of compound was described also. The biological activity of new synthesized thio-debranone follows to be evaluated.

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