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·研究论文·

马来松香酸酰腙类化合物的合成及杀菌活性

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摘 要:以马来松香酸为原料,经酰氯化和肼解反应制备了马来松香酸酰肼(**3**),**3**与取代苯甲醛通过缩合反应合成了11个未见文献报道的马来松香酸酰腙类化合物**4a**～**4k**,其结构均经IR、^{1}H NMR、^{13}C NMR和元素分析表征和确证。初步的生物活性测定结果表明:目标化合物在质量浓度为50 μg/mL下对5种供试植物病原菌均有不同程度的杀菌活性,其中化合物**4e**(R＝4-$CH_3OC_6H_4$)对小麦赤霉病菌 *Gibberella Zeae* 的抑制率达68.3%。

关键词:马来松香酸;酰腙;合成;杀菌活性

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Synthesis and fungicidal activity of maleated rosin acid acylhydrazone compounds

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Abstract: Maleated rosin acid hydrazide (**3**) was prepared via acyl chlorination and hydrazinolysis using maleated rosin acid as starting material, followed by condensation of **3** with phenyl aldehydes to afford eleven novel maleated rosin acid acylhydrazones **4a**－**4k.** Their structures were confirmed by IR, ^{1}H NMR, ^{13}C NMR and elemental analysis. The preliminary bioassay showed that, all the target compounds exhibited different fungicidal activity against five fungi tested at the concentration of 50 μg/mL, in which compound **4e** (R＝4-$CH_3OC_6H_4$) had the best inhibition rate of 68.3% against *Gibberella Zeae*.

Key words: maleated rosin acid; acylhydrazone; synthesis; fungicidal activity

松香是自然界极其丰富的再生性天然资源,主要成分是树脂酸。松香树脂酸具有独特的化学结构和多个手性中心,树脂酸及其衍生物已表现出抗炎、抑菌、杀虫和抗肿瘤等广泛的生物活性,在医药和农药等领域有着重要用途[1]。通过对松香树脂酸的结构进行改造,合成具有更高生物活性的化合物已成为林产化学和有机合成化学当前的研究热点之一[2-8]。酰腙类化合物分子中含有一个很好的活性亚结构基团(－CONHN＝CH－),含有该基团的化合物大多具有良好的除草和杀菌等生物活性,近年

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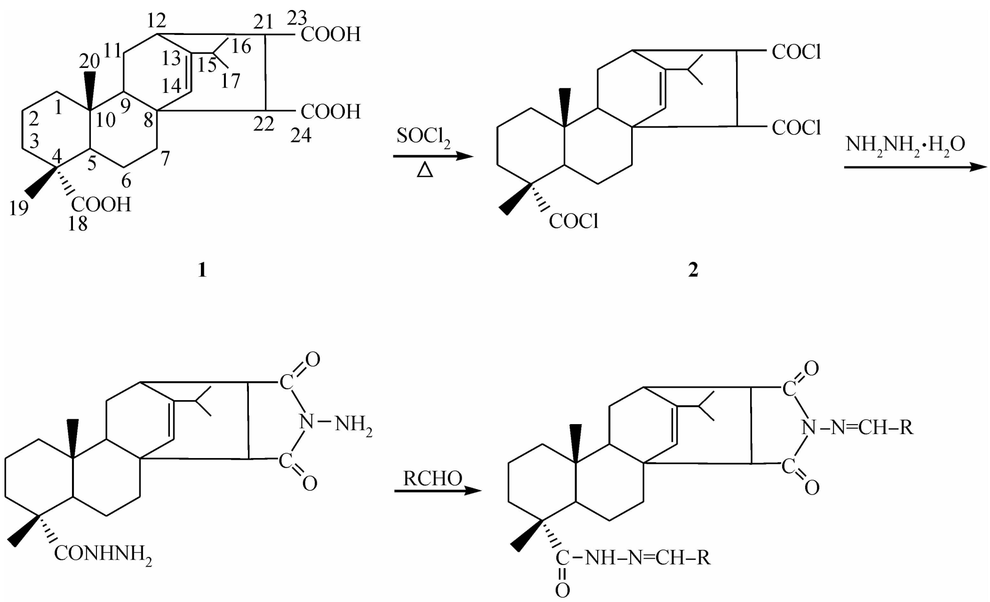
来备受农药和医药界的关注[9-13]。笔者认为若将此基团引入到马来松香酸的骨架中,可望合成出多种马来松香酸酰腙类新型生物活性物质,并可能为新型农药的开发提供新的先导化合物。本文报道以马来松香酸(**1**)为原料,经马来松香酸酰氯(**2**)和马来松香酸酰肼(**3**)中间体,通过酰肼与取代苯甲醛的缩合反应得到了 11 个未见文献报道的马来松香酸酰腙化合物 **4**,对其结构进行了分析和表征,并初步测试了其对植物病原菌的抗菌活性。目标化合物的合成路线见 **Scheme 1**。



Scheme 1

1 实验部分

1.1 仪器及试剂

Nicolet Nexus 470 FT-IR 红外光谱仪(美国 Nicolet 公司); AVANCE AV 600 MHz 超导核磁共振仪(瑞士 Bruker 公司);PE2400 Ⅱ 型元素分析仪(美国 Perkin Elmer 公司);X-4 型显微熔点测定仪(温度计未校正,北京泰克仪器有限公司)。

松香(特级,广西梧州松脂股份有限公司);马来松香酸(**1**)按文献[14]自制;其余试剂均为市售分析纯。5 种供试病原菌由南开大学元素有机化学研究所生物活性测试室提供。

1.2 化合物的合成

1.2.1 中间体 **2** 的合成 参考文献[15]合成得到微黄白色固体 **2**,m. p. 188 ~ 190℃(无文献值),收率约为 70%。

1.2.2 中间体 **3** 的合成 化合物 **3** 为新化合物,参考文献[16]方法合成得到微黄色固体,m. p. 255 ~ 256 ℃,收率约为 80%。IR,ν/cm^{-1}:3 282,2 959,2 868,1 769,1 694,1 507。^{1}H NMR(600 MHz,DMSO),δ:0.53(s,3H,C_{20} − H),0.88 ~ 0.95(m,6H,C_{16} − H,C_{17} − H),1.04(s,3H,C_{19} − H),1.09(s,2H,CH_2),1.24 ~ 1.73(m,10H,CH_2),1.78 ~ 1.81(m,1H,C_9 − H),2.10 ~ 2.13(m,1H,C_{15} − H),2.34(dd,J = 9.6 Hz,3.1 Hz,1H,C_5 − H),2.45(d,J = 7.9 Hz,1H,C_{12} − H),2.81(dd,J = 7.8 Hz,2.8 Hz,1H,C_{22} − H),2.86(d,J = 1.5 Hz,1H,C_{21} − H),4.21(s,2H,NH_2),4.83(d,J = 9.3 Hz,2H,NH_2),5.33(s,1H,CH ═ C),8.81(t,J = 2.3 Hz,1H,NH)。^{13}C NMR(150 MHz,DMSO),δ:177.27,175.24,174.55,146.13,124.29,53.33,53.21,50.24,48.96,45.16,42.78,37.63,37.20,36.44,35.05,34.96,32.22,27.16,20.72,20.66,20.16,16.81,16.28,15.53。

1.2.3 目标化合物 **4** 的合成 将 1.0 g(2 mmol)化合物 **3** 和 30 mL 无水乙醇加入到 250 mL 三口烧瓶中,滴加 3 mL 冰乙酸(作催化剂),在 N_2 保护下加入 9 mmol 取代苯甲醛,78 ℃下反应 4 h, 用硅胶薄层色谱(TLC)监测(展开剂:石油醚/乙酸乙酯)至原料反应完全,得橙红色透明液体,旋干,得黄色粘稠液粗品。柱层析提纯得到 11 个马来松香酸酰腙目标化合物 **4**[**4a** ~ **4k** 所用的洗脱剂依次为

V(石油醚)∶V(乙酸乙酯)=1∶1,1∶1,1∶1,1∶1,4∶9,3∶4,3∶4,5∶7,5∶8,4∶7,2∶1]。

1.3 杀菌活性测定

采用菌丝生长速率法[17]。供试化合物先用丙酮溶解,再用200 μg/mL 的乳化剂 Sorporl-144 稀释成500 μg/mL 的药液。取1 mL 药液于培养皿内,加入9 mL PSA 培养基,制成含供试化合物为50 μg/mL的含药平板。在已培养好的供试菌株上打取直径5 mm 的菌饼,置于含药平板内,每皿3 块。以不加药剂者为空白对照。于温度为(24 ±1) ℃的培养箱内培养48 h 后测量各处理菌丝扩展直径,并与空白对照相比较,由(1)式计算相对抑制率。

相对抑制率/% =(对照菌落直径 - 处理菌落直径)×100/对照菌落直径 (1)

2 结果与讨论

2.1 目标化合物的波谱特征

目标化合物 **4** 的理化数据、红外光谱数据和元素分析结果见表1,核磁数据见表2 和表3。

表1 目标化合物4 的理化、红外光谱和元素分析数据

Table 1 Physico-chemical data,IR and elemental analysis data of target compounds **4**

化合物 Compd.	R	收率 Yield/%	熔点 m. p./℃	物态 State	红外光谱 IR,ν/cm^{-1}	元素分析 Elemental analysis(计算值,Calcd.) C	H	N
4a	C_6H_5	62	185~186	白色晶体 White crystal	3 446,1 771,1 710,1 668	75.40(75.47)	7.40(7.33)	9.20(9.26)
4b	4-FC_6H_4	86	179~180	白色晶体 White crystal	3 446,1 772,1 710,1 652	71.26(71.23)	6.64(6.61)	8.70(8.74)
4c	4-ClC_6H_4	78	175~176	白色晶体 White crystal	3 447,1 775,1 713,1 664	67.96(68.01)	6.64(6.59)	6.93(6.97)
4d	4-BrC_6H_4	84	184~185	白色晶体 White crystal	3 448,1 773,1 712,1 665	60.20(60.24)	5.87(5.83)	7.26(7.21)
4e	4-$CH_3OC_6H_4$	72	177~178	黄色晶体 Yellow crystal	3 447,1 773,1 707,1 654	72.38(72.43)	7.61(7.56)	8.27(8.24)
4f	2-$CH_3OC_6H_4$	73	174~175	黄色晶体 Yellow crystal	3 447,1 775,1 709,1 655	72.45(72.43)	7.54(7.56)	8.21(8.24)
4g	3-$CH_3OC_6H_4$	77	171~172	白色晶体 White crystal	3 449,1 774,1 709,1 655	72.40(72.43)	7.57(7.56)	8.26(8.24)
4h	4-$NO_2C_6H_4$	73	192~193	黄色晶体 Yellow crystal	3 442,1 780,1 716,1 652	66.05(65.99)	6.33(6.39)	11.80(11.84)
4i	2-$NO_2C_6H_4$	88	183~184	黄色晶体 Yellow crystal	3 424,1 775,1 717,1 655	65.93(65.99)	6.45(6.39)	11.78(11.84)
4j	3-$NO_2C_6H_4$	71	175~176	黄色晶体 Yellow crystal	3 449,1 774,1 697,1 648	66.01(65.99)	6.33(6.39)	11.90(11.84)
4k	3-Cl-4-ClC_6H_3	58	183~184	白色固体 White solid	3 449,1 774,1 717,1 648	61.89(61.83)	5.67(5.72)	7.45(7.40)

表2 目标化合物4 的^{1}H NMR 数据

Table 2 ^{1}H NMR spectral data of target compounds **4**

化合物 Compd.	^{1}H NMR(600 MHz,$CDCl_3$/TMS),δ
4a	0.61(s,3H,$C_{20}-H$),0.95~0.97(m,6H,$C_{16}-H$ & $C_{17}-H$),1.26(s,3H,$C_{19}-H$),1.40~1.42(m,2H,CH_2),1.46~1.49(m,4H,CH_2),1.53~1.55(m,2H,CH_2),1.64~1.78(m,2H,CH_2),1.89~1.91(m,2H,CH_2),1.98(d,J=9.8 Hz,1H,C_9-H),2.23~2.25(m,1H,$C_{15}-H$),2.52(d,J=8.2 Hz,1H,C_5-H),2.55~2.58(m,1H,$C_{12}-H$),2.84~2.90(m,1H,$C_{21}-H$),3.12(d,J=2.5 Hz,1H,$C_{22}-H$),5.47(s,1H,HC=C),7.37~7.40(m,5H,Ar),7.44~7.46(m,1H,Ar),7.72(s,2H,Ar),7.78(d,J=7.4 Hz,2H,Ar),8.36(s,1H,N=$\underline{CH}$-Ar),9.01(s,1H,N=$\underline{CH}$-Ar),9.37(s,1H,CONH)

续表(Continued)

化合物 Compd.	^{1}H NMR(600 MHz,$CDCl_3$/TMS),δ
4b	0.65(s,3H,C_{20} – H),0.93 ~ 0.99(m,6H,C_{16} – H & C_{17} – H),1.29(s,3H,C_{19} – H),1.36 ~ 1.82(m,10H,CH_2),1.90 ~ 1.92(m,2H,CH_2),1.96(s,1H,C_9 – H),2.26 ~ 2.27(m,1H,C_{15} – H),2.53(d,*J* = 8.1 Hz,1H,C_5 – H),2.57 ~ 2.59(m,1H,C_{12} – H),2.90 ~ 2.93(m,1H,C_{21} – H),3.14(d,*J* = 3.3 Hz,1H,C_{22} – H),5.48(s,1H,HC = C),7.03 ~ 7.14(m,4H,Ar),7.73(s,2H,Ar),7.80(dd,*J* = 8.6 Hz,5.3 Hz,2H,Ar),8.32(s,1H,N = CH – Ar),8.94(s,1H,N = CH – Ar),8.99(s,1H,CONH)
4c	0.65(d,*J* = 7.4 Hz,3H,C_{20} – H),0.92 ~ 0.99(m,6H,C_{16} – H & C_{17} – H),1.28(s,3H,C_{19} – H),1.37 ~ 1.60(m,8H,CH_2),1.69 ~ 1.81(m,2H,CH_2),1.90 ~ 1.92(m,2H,CH_2),1.95(s,1H,C_9 – H),2.25 ~ 2.28(m,1H,C_{15} – H),2.53(d,*J* = 8.2 Hz,1H,C_5 – H),2.54 ~ 2.59(m,1H,C_{12} – H),2.90 ~ 2.95(m,1H,C_{21} – H),3.14(d, *J* = 2.7 Hz,1H,C_{22} – H),5.48(s,1H,HC = C),7.36 ~ 7.38(m,4H,Ar),7.67(d,*J* = 8.0 Hz,2H,Ar),7.73(dd,*J* = 6.7 Hz,1.9 Hz,2H,Ar),8.32(s,1H,N = CH – Ar),9.01(s,1H,N = CH – Ar),9.04(s,1H,CONH)
4d	0.65(s,3H,C_{20} – H),0.93 ~ 0.98(m,6H,C_{16} – H & C_{17} – H),1.29(s,3H,C_{19} – H),1.36 ~ 1.80(m,10H,CH_2),1.90 ~ 1.92(m,2H,CH_2),1.95(s,1H,C_9 – H),2.24 ~ 2.26(m,1H,C_{15} – H),2.53(d,*J* = 8.2 Hz,1H,C_5 – H),2.56 ~ 2.59(m,1H,C_{12} – H),2.90 ~ 2.93(m,1H,C_{21} – H),3.14(d,*J* = 2.1 Hz,1H,C_{22} – H),5.48(s,1H,HC = C),7.52 ~ 7.55(m,4H,Ar),7.60(d,*J* = 8.2 Hz,2H,Ar),7.66(d,*J* = 8.5 Hz,2H,Ar),8.30(s,1H,N = CH – Ar),8.92(s,1H,N = CH – Ar),9.04(s,1H,CONH)
4e	0.67(s,3H,C_{20} – H),0.96 ~ 1.02(m,6H,C_{16} – H & C_{17} – H),1.30(s,3H,C_{19} – H),1.40 ~ 1.66(m,8H,CH_2),1.69 ~ 1.85(m,2H,CH_2),1.90 ~ 1.95(m,2H,CH_2),2.07(s,1H,C_9 – H),2.25 ~ 2.29(m,1H,C_{15} – H),2.54(d,*J* = 8.1 Hz,1H,C_5 – H),2.58 ~ 2.61(m,1H,C_{12} – H),2.86 ~ 2.96(m,1H,C_{21} – H),3.16(d, *J* = 3.7 Hz,1H,C_{22} – H),3.86(d,*J* = 2.1 Hz,6H,CH_3O),5.51(s,1H,HC = C),6.92 ~ 6.95(m,4H,Ar),7.71(d,*J* = 8.4 Hz,2H,Ar),7.80 ~ 7.83(m,2H,Ar),8.23(s,1H,N = CH – Ar),8.75(s,1H,N = CH – Ar),8.84(s,1H,CONH)
4f	0.65(s,3H,C_{20} – H),0.96 ~ 0.99(m,6H,C_{16} – H & C_{17} – H),1.29(s,3H,C_{19} – H),1.37 ~ 1.65(m,8H,CH_2),1.75 ~ 1.78(m,2H,CH_2),1.90 ~ 1.94(m,2H,CH_2),2.05(s,1H,C_9 – H),2.22 ~ 2.31(m,1H,C_{15} – H),2.53(d,*J* = 7.8 Hz,1H,C_5 – H),2.57 ~ 2.66(m,1H,C_{12} – H),2.85 ~ 2.93(m,1H,C_{21} – H),3.14(d, *J* = 1.9 Hz,1H,C_{22} – H),3.83(s,3H,CH_3O),3.88(s,3H,CH_3O),5.50(s,1H,HC = C),6.88 ~ 6.91(m,2H,Ar),6.93 ~ 7.02(m,2H,Ar),7.36(t,*J* = 6.9 Hz,1H,Ar),7.41(t,*J* = 7.3 Hz,1H,Ar),8.06 ~ 8.09(m,2H,Ar),8.57(s,1H,N = CH – Ar),8.76(s,1H,N = CH – Ar),9.22(s,1H,CONH)
4g	0.65(s,3H,C_{20} – H),0.92 ~ 0.99(m,6H,C_{16} – H & C_{17} – H),1.25(s,3H,C_{19} – H),1.40 ~ 1.66(m,8H,CH_2),1.70 ~ 1.94(m,4H,CH_2),2.05(s,1H,C_9 – H),2.25 ~ 2.28(m,1H,C_{15} – H),2.53(d,*J* = 8.2 Hz,1H,C_5 – H),2.60 ~ 2.65(m,1H,C_{12} – H),2.90 ~ 2.95(m,1H,C_{21} – H),3.15(d,*J* = 2.6 Hz,1H,C_{22} – H),3.83(d,*J* = 2.5 Hz,3H,CH_3O),3.85(s,3H,CH_3O),5.50(s,1H,HC = C),6.96(dd,*J* = 8.2 Hz,2.5 Hz,1H,Ar),7.01(d,*J* = 7.6 Hz,1H,Ar),7.22(d,*J* = 7.5 Hz, 1H,Ar),7.29 ~ 7.33(m,3H,Ar),7.39(s,2H,Ar),8.28(s,1H,N = CH – Ar),8.78(s,1H,N = CH – Ar),8.95(s,1H,CONH)
4h	0.66(d,*J* = 8.5 Hz,3H,C_{20} – H),0.93 ~ 0.99(m,6H,C_{16} – H & C_{17} – H),1.32(s,3H,C_{19} – H),1.39 ~ 1.67(m,10H,CH_2),1.73 ~ 1.84(m,2H,CH_2),1.88 ~ 1.99(m,1H,C_9 – H),2.23 ~ 2.27(m,1H,C_{15} – H),2.52 ~ 2.62(m,2H,C_{12} – H & C_5 – H),2.92 ~ 2.96(m,1H,C_{21} – H),3.17(d, *J* = 2.2 Hz,1H,C_{22} – H),5.50(d,*J* = 5.1 Hz,1H, – HC = C),7.90(d,*J* = 8.7 Hz,2H,Ar),7.95 ~ 8.00(m,2H,Ar),8.26(dd,*J* = 8.9 Hz,1.9 Hz,4H,Ar),8.54(s,1H,N = CH – Ar),9.06(s,1H,N = CH – Ar),9.35(s,1H,CONH)
4i	0.66(d,*J* = 7.6 Hz,3H,C_{20} – H),0.97 ~ 1.01(m,6H,C_{16} – H & C_{17} – H),1.24 ~ 1.26(m,2H,CH_2),1.30(s,3H,C_{19} – H),1.37 ~ 1.60(m,8H,CH_2),1.72 ~ 1.84(m,2H,CH_2),1.90 ~ 1.99(m,1H,C_9 – H),2.25 ~ 2.30(m,1H,C_{15} – H),2.57 ~ 2.60(m,2H C_{12} – H & C_5 – H),2.92 ~ 2.96(m,1H,C_{21} – H),3.16(d, *J* = 3.4 Hz,1H,C_{22} – H),5.52(s,1H,HC = C),7.54(t,*J* = 7.8 Hz,1H,Ar),7.59 ~ 7.71(m,3H,Ar),8.03(d,*J* = 8.2 Hz,1H,Ar),8.09 ~ 8.12(m,2H,Ar),8.30(d,*J* = 7.8 Hz,1H,Ar),8.72 ~ 8.82(m,1H,N = CH – Ar),9.37(s,1H,N = CH – Ar),9.65(s,1H,CONH)

续表(Continued)

化合物 Compd.	^{1}H NMR(600 MHz,$CDCl_3$/TMS),δ
4j	0.64(s,3H,C_{20} − H),0.92 ~ 0.99(m,6H,C_{16} − H & C_{17} − H),1.22 ~ 1.28(s,3H,C_{19} − H),1.42 ~ 1.78(m,10H,CH_2),1.85 ~ 1.90(m,2H,CH_2),1.94(s,1H,C_9 − H),2.15 ~ 2.24(m,1H,C_{15} − H),2.45(d,J = 7.8 Hz,1H,C_5 − H),2.53(d,J = 8.7 Hz,1H,C_{12} − H),2.78 ~ 2.86(m,1H,C_{21} − H),3.08(d, J = 1.8 Hz,1H,C_{22} − H),5.40(s,1H,HC = C),7.54(d,J = 8.1 Hz,1H,Ar),7.61 ~ 7.70(m,3H,Ar),8.03(d,J = 8.2 Hz,1H,Ar),8.11(dd,J = 8.8 Hz,9.5 Hz,2H,Ar),8.30(d,J = 7.8 Hz,1H,Ar),8.77(s,1H,N = CH − Ar),9.37(s,1H,N = CH − Ar),9.66(s,1H,CONH)
4k	0.68(s,3H,C_{20} − H),0.97 ~ 1.01(m,6H,C_{16} − H & C_{17} − H),1.28(s,3H,C_{19} − H),1.31 ~ 1.66(m,10H,CH_2),1.70 ~ 1.83(m,2H,CH_2),1.89 ~ 2.00(m,1H,C_9 − H),2.27 ~ 2.29(m,1H,C_{15} − H),2.57 ~ 2.62(m,2H,C_{12} − H & C_5 − H),2.92 ~ 2.96(m,1H,C_{21} − H),3.18(d, J = 2.7 Hz,1H,C_{22} − H),5.52(s,1H,HC = C −),7.29 ~ 7.31(m,2H,Ar),7.41 ~ 7.43(m,2H,Ar),8.10 ~ 8.12(m,2H,Ar),8.63 ~ 8.65(m,1H,N = CH − Ar),9.03 ~ 9.13(m,1H,N = CH − Ar),9.49(s,1H,CONH)

表 3 目标化合物 4 的 ^{13}C NMR 数据

Table 3 ^{13}C NMR spectral data of target compounds **4**

化合物 Compd.	^{13}C NMR(150 MHz,$CDCl_3$/TMS),δ
4a	175.18,174.79,173.40,161.52,148.72,147.23,134.53,133.82,133.09,132.04,130.42,129.78,129.04,128.73,128.66,127.71,124.87,53.72,50.77,49.68,46.84,43.55,40.96,37.84,37.69,36.91,35.94,35.08,32.84,27.70,21.53,20.85,20.32,17.02,16.64,15.86
4b	174.94,174.69,173.31,164.23,147.41,147.33,130.81,130.75,129.98,129.96,129.58,129.42,124.82,116.05,115.97,115.90,115.82,53.87,50.81,49.70,46.91,43.51,40.97,37.80,37.77,37.12,35.94,35.13,32.84,27.70,21.47,20.84,20.29,17.02,16.68,15.83
4c	174.69,173.30,173.24,159.60,147.36,147.27,138.07,136.36,132.28,131.69,130.76,129.80,129.06,129.02,128.95,128.81,124.83,53.87,50.80,49.72,46.96,43.51,40.98,37.87,37.77,37.01,35.89,35.13,32.86,27.72,21.50,20.86,20.32,17.03,16.70,15.84
4d	175.01,174.68,173.29,159.61,147.44,147.36,132.75,132.70,132.14,132.02,131.97,129.96,129.02,128.98,128.73,126.59,124.84,53.88,50.80,49.71,46.97,43.50,40.98,37.86,37.77,37.00,35.86,35.12,32.84,27.70,21.47,20.84,20.30,17.01,16.69,15.82
4e	174.90,173.50,162.91,161.89,147.45,147.36,130.74,130.71,129.48,125.87,124.97,117.53,117.15,116.97,114.48,114.30,114.27,55.58,55.53,54.12,51.02,49.88,46.75,43.67,41.12,38.06,37.03,36.10,35.27,32.94,29.84,27.82,21.56,20.92,20.51,17.27,16.75,15.92
4f	174.60,173.95,173.23,159.17,147.29,147.18,133.50,131.82,127.44,127.04,124.88,124.77,121.51,121.00,120.73,110.96,110.86,55.63,54.05,53.86,50.92,49.78,46.82,43.56,40.99,37.89,35.91,35.23,35.09,32.86,29.70,27.77,21.43,20.87,20.20,16.99,16.04,15.82
4g	174.68,174.02,173.25,161.70,147.36,147.30,134.44,129.65,124.95,124.79,122.27,122.24,121.14,119.04,111.73,111.70,110.92,55.48,54.02,53.86,50.85,49.74,46.38,43.55,40.98,37.85,36.95,35.91,35.24,35.14,32.87,27.74,21.40,20.87,20.31,16.97,16.05,15.81
4h	174.63,174.15,173.22,156.81,149.60,148.68,147.55,147.50,145.87,139.98,139.19,129.24,128.11,124.89,124.84,124.05,123.92,53.98,50.80,49.71,46.97,43.50,40.98,37.86,37.07,35.89,35.22,35.15,32.83,27.79,21.55,20.86,20.33,17.01,16.16,15.80
4i	174.52,174.31,173.03,157.26,148.60,148.12,147.49,133.82,133.59,131.79,130.47,129.69,129.19,128.76,128.70,124.88,124.73,53.87,50.78,49.73,46.98,43.48,40.97,37.91,37.75,36.91,36.06,35.22,32.89,27.73,21.54,20.86,20.29,17.01,16.69,15.84
4j	175.41,175.14,174.21,156.81,148.61,147.32,146.07,145.99,135.89,135.52,132.84,129.97,129.81,124.73,124.49,122.46,122.39,53.90,50.93,49.80,47.15,43.44,40.69,37.86,35.56,35.21,32.76,31.95,29.72,27.67,21.49,20.84,20.28,17.02,16.70,15.83
4k	174.47,173.20,173.14,156.53,147.38,138.32,136.52,136.42,134.64,129.80,129.70,129.53,128.91,128.66,127.69,127.66,124.90,53.86,50.79,49.73,47.01,43.50,41.00,37.90,37.02,35.95,35.10,32.88,31.46,29.72,27.73,21.53,20.86,17.07,16.77,15.85

化合物**4**的IR谱图中均存在3组典型的酰腙特征吸收峰:3 450 ~ 3 400 cm^{-1}之间显示的中等强度吸收峰为N－H伸缩振动特征吸收峰;1 780 ~ 1 640 cm^{-1}之间显示的3个强吸收峰为目标产物上3个C＝O的伸缩振动吸收峰;在1 600 ~ 1 450 cm^{-1}之间显示的4个吸收峰为与C＝N相连的苯的伸缩振动吸收峰。而在各自的指纹区中,亦能找到相应的特征吸收峰。

化合物**4**的^{1}H NMR谱中,与C＝O和氮相连的氮上的氢化学位移在9.66 ~ 8.84之间;与芳基和氮相连的碳上的氢化学位移在9.37 ~ 8.57和8.65 ~ 8.23之间;芳环氢的化学位移在8.54 ~ 6.88之间,为多组多重峰。^{13}C NMR谱中3个C＝O上的碳的化学位移在175.41 ~ 174.47、175.14 ~ 173.20和174.21 ~ 173.14之间;C＝N上碳的化学位移在165.91 ~ 156.53之间;C＝C上碳的化学位移在149.60 ~ 147.18之间。

2.2 目标化合物的杀菌活性

目标化合物**4a ~ 4k**对5种植物病原菌的杀菌活性测定结果见表4。可以看出,在50 μg/mL下,马来松香酸酰腙类化合物对供试5种病原菌均有一定的杀菌活性,其中对小麦赤霉病菌的活性相对较好。而对于小麦赤霉病菌,化合物**4e**(R＝4-$CH_3OC_6H_4$)的活性最好,抑制率为68.3%,其次是化合物**4i**(R＝2-$NO_2C_6H_4$)和**4a**(R＝C_6H_5),抑制率分别为55.7%和52.6%,其余化合物活性均较低,有待进一步进行结构修饰。

表4 目标化合物4的杀菌活性(50 μg/mL,抑制率/%)

Table 4 Fungicidal activity of target compounds **4**(50 μg/mL, Inhibition rate/%)

化合物 Compd.	黄瓜枯萎病菌 *Fusarium oxysporum* f. *cucumerinum*	苹果轮纹病菌 *Physalospora piricola*	番茄早疫病菌 *Alternaria solani*	花生褐斑病菌 *Cercospora arachidicola*	小麦赤霉病菌 *Fusarium graminearum*
4a	23.6	23.0	20.5	20.5	52.6
4b	14.5	23.0	15.3	15.3	41.0
4c	28.2	27.4	25.8	15.3	48.3
4d	23.6	27.4	20.5	15.3	40.4
4e	28.2	36.1	20.5	20.5	68.3
4f	28.2	36.1	20.5	20.5	43.2
4g	19.1	40.4	25.8	15.3	42.5
4h	23.6	36.1	15.3	20.5	36.1
4i	23.6	31.7	20.5	15.3	55.7
4j	28.2	40.4	20.5	20.5	42.6
4k	30.3	28.2	29.8	19.1	44.9

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