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通体结香技术产沉香的2-(2-苯乙基)色酮类化合物及其抗炎活性研究

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摘　要:对通体结香技术诱导白木香形成的沉香化学成分及其抗炎活性进行研究。采用液相和色谱技术进行分离纯化,从沉香中得到10个2-(2-苯乙基)色酮类化合物,通过理化常数和波谱分析分别鉴定为:2-(2-phenylethyl)chromone(**1**)、6-methoxy-2-(2-phenylethyl)chromone(**2**)、5-hydroxy-6-methoxy-2-(2-phenylethyl) chromone(**3**)、6,7-dimethoxy-2-[2-(4′-methoxyphenyl)ethyl]chromone(**4**)、7-Hydroxy-6-methoxy-2-[2-(4′-methoxyphenyl)ethyl]chromone(**5**)、2-[2-(4′-methoxyphenyl)ethyl]chromone(**6**)、6,7-dimethoxy-2-[2-(3′-hydroxy-4′-methoxyphenyl)ethyl]chromone(**7**)、6,7-dimethoxy-2-(2-phenyl ethyl)chromone(**8**)、6,8-dihydroxy-2-[2-(3′-hydroxy-4′-methoxyphenyl)ethyl] chromone(**9**)、6-hydroxy-2-[2-(4′-methoxyphenyl)ethyl]chromone(**10**)。结合脂多糖介导RAW 264.7细胞模型评价其抗炎活性。其中,化合物**2**~**4**和**10**具有显著的抗炎活性,IC_{50}值分别为5.31±0.75,5.57±0.62,0.57±0.02,3.78±0.64 μM。化合物**5**为首次从白木香产沉香中分离得到,所有化合物均为首次从通体结香技术所产沉香中所得,为其品质评价提供了基础依据。

关键词:通体结香技术;2-(2-苯乙基)色酮;沉香;抗炎活性

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2-(2-Phenylethyl) chromones and Anti-inflammation of Agarwood Produced via Whole-tree Agarwood-inducing Technique from *Aquilaria sinensis*

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Abstract: To investigate the chemical constituents and anti-inflammation of agarwood produced via whole-tree agarwood-inducing technique (Agar-Wit) from *Aquilaria sinensis*. The constituents from agarwood were isolated and purified by the chromatographic technique and Semi preparation HPLC. Ten 2-(2-Phenylethyl) chromones were isolated from the agarwood produced by Agar-Wit, their structures were identified on the basis of physiochemical characteristics and spectroscopic data analysis as 2-(2-phenylethyl)chromone (**1**), 6-methoxy-2-(2-phenylethyl)chromone (**2**), 5-hydroxy-6-methoxy-2-(2-phenylethyl) chromone (3), 6,7-dimethoxy-2-[2-(4′-methoxyphenyl)ethyl]chromone (**4**), 7-Hydroxy-6-methoxy-2-[2-(4′-methoxyphenyl) ethyl]chromone (**5**), 2-[2-(4′-methoxyphenyl)ethyl]chromone (**6**), 6,7-dimethoxy-2-[2-(3′-hydroxy-4′-methoxyphenyl)ethyl]chromone (**7**), 6,7-dimethoxy-2-(2-phenyl ethyl)chromone (**8**), 6,

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8-dihydroxy-2-[2-(3′-hydroxy-4′-methoxyphenyl) ethyl] chromone (**9**), 6-hydroxy-2-[2-(4′-methoxyphenyl) ethyl] chromone (**10**). All of the isolates were then assessed for their anti-inflammatory activities on lipopolysaccharide (LPS)-induced nitric oxide (NO) production in RAW264.7. Compounds **2-4** and **10** showed significant anti-inflammatory activities with IC_{50} values 5.31 ± 0.75, 5.57 ± 0.62, 0.57 ± 0.02, 3.78 ± 0.64 μM, respectively. Compound **5** was reported from agarwood of *A. sinensis* for the first time, all the compounds were isolated from the agarwood produced by Agar-Wit for the first time, and has provided scientific foundation for quality evaluation of the agarwood produced by Agar-Wit.

Key words: whole-tree agarwood-inducing technique; 2-(2-Phenylethyl) chromones; agarwood; anti-inflammation

国产药用沉香为瑞香科(Thymelaeaceae)植物白木香[*Aquilaria sinensis* (Lour.) Gilg]含有树脂的木材[1],主产于我国海南、广东等地。针对全世界野生沉香资源濒危、沉香形成机理不清、缺乏产业化结香技术等问题,魏建和等提出并阐明"白木香防御反应诱导结香机制"[2],且在此基础上开发了"通体结香技术"[3]。采用"通体结香技术"极大地提高了沉香产量,且结香 6 个月的沉香药材可满足《中国药典》的要求[3],结香 20 个月的沉香品质不低于野生沉香[4]。极大地解决了沉香产业化生产中所面临的结香技术瓶颈问题,产业化、规范化生产沉香可能变为现实。

沉香自古以来就有"行气止痛、温中止呕、纳气平喘"功效,主要活性成分为 2-(2-苯乙基)色酮类和倍半萜类化合物[5,6]。其中,2-(2-苯乙基)色酮类化合物为沉香的特征性成分。本文针对通体结香技术产沉香的主要成分进行研究,从中分离鉴定了 10 个 2-(2-苯乙基)色酮类化合物,分别为:2-(2-phenylethyl) chromone (**1**)、6-methoxy-2-(2-phenylethyl) chromone (**2**)、5-hydroxy-6-methoxy-2-(2-phenylethyl) chromone (**3**)、6,7-dimethoxy-2-[2-(4′-methoxyphenyl) ethyl] chromone (**4**)、7-Hydroxy-6-methoxy-2-[2-(4′-methoxyphenyl) ethyl] chromone (**5**)、2-[2-(4′-methoxyphenyl) ethyl] chromone (**6**)、6,7-dimethoxy-2-[2-(3′-hydroxy-4′-methoxyphenyl) ethyl] chromone (**7**)、6,7-dimethoxy-2-(2-phenyl ethyl) chromone (**8**)、6,8-dihydroxy-2-[2-(3′-hydroxy-4′-methoxyphenyl) ethyl] chromone (**9**)、6-hydroxy-2-[2-(4′-methoxyphenyl) ethyl] chromone (**10**)。其中,化合物 **5** 为首次从沉香中分离得到,所有化合物均为首次从通体结香技术产沉香中分得。此外,化合物 **2**~**4** 和 **10** 具有显著的抗炎活性,IC_{50} 值分别为 5.31 ± 0.75、5.57 ± 0.62、0.57 ± 0.02、3.78 ± 0.64 μM。

1 仪器与材料

XRC-1 型显微熔点仪(四川科仪厂);旋光度测定仪(Perkin-Elmer 341);Shimadzu UV-2550 分光光度计(日本 Shimadzu 公司);Shimadzu FTIR-8400S 红外光谱仪(日本 Shimadzu 公司);Bruker AV III 600 核磁共振仪(瑞士 Bruker 公司);LTQ-Obitrap 高分辨质谱(Thermo 公司);Lumtech K-1001 半制备液相色谱系统(德国 Lumtech 公司);250 mm × 10 mm, i.d., 5 μM C18 柱(日本 YMC 公司);ODS 填料(12 nm ~ 50 μm,日本 YMC 公司);Sephadex LH-20 凝胶(美国 Pharmacia 公司);柱色谱硅胶(100 ~ 200、300 ~ 400 目)和薄层色谱硅胶(青岛海洋化工厂产品),所用试剂均为分析纯,购于西陇化工股份有限公司。

实验材料为 7 年生白木香采用通体结香技术结香 18 个月后所产沉香,结香基地位于广东省化州市平定镇,结香技术[3]由中国医学科学院药用植物研究所海南分所提供,凭证标本保存于中国医学科学院药用植物研究所海南分所沉香鉴定中心标本馆。

2 提取与分离

干燥沉香粉末 5.0 kg,经 95% 乙醇(25.0 L × 3)加热回流提取,减压浓缩得 850.3 g 浸膏。将浸膏混悬于水中,依次以石油醚、二氯甲烷、乙酸乙酯、正丁醇溶剂萃取,得到不同极性部位。

将二氯甲烷部位(86.5 g)进行硅胶(100 ~ 200 目)柱层析,以石油醚-二氯甲烷(100∶0至 1∶20)以及二氯甲烷-甲醇(100∶0至 0∶100)梯度洗脱,得到 20 个组分(Fr. 1 ~ Fr. 20)。将 Fr. 1 ~ Fr. 10(Fr. A, 10.5 g)再次经硅胶(200 ~ 300 目)柱层析,以石油醚-二氯甲烷(10∶0至 1∶1)及二氯甲烷-甲醇(100∶0至 0∶100)梯度洗脱,获取 9 个组分(Fr. A-1 ~ Fr. A-9)。Fr. A-3(3.0g)通过半制备液相色谱,以乙腈-水(V∶V = 60∶40)等度洗脱,获得化合物 **1**(9.0 mg, t_R = 22.9 min)、**2**(12.3 mg, t_R = 24.2 min)及 **3**(18.1 mg, t_R = 32.8 min)。

将乙酸乙酯部位(35.1 g)进行硅胶(100 ~ 200 目)柱层析,以二氯甲烷-甲醇(100∶0至 0∶100)梯度

洗脱,得7个组分(Fr. A ~ Fr. G)。Fr. A(8.1 g)再次进行常压硅胶(100 ~ 200目)柱层析,以石油醚-二氯甲烷(1∶1、1∶3),二氯甲烷-甲醇(100∶0至0∶100)梯度洗脱,得6个组分(Fr. A-1 ~ Fr. A-6)。Fr. A-3(2.5 g)进行ODS柱层析,以甲醇-水(V∶V=30∶70)逐次梯度洗脱得8个组分(Fr. A-3-1 ~ Fr. A-3-8)。Fr. A-3-5(0.6 g)进行半制备液相色谱,以乙腈-水(V∶V=60∶40)等度洗脱,得化合物**4**(13.3 mg,t_R = 16.0 min)、**5**(29.4 mg,t_R = 19.2 min)及**6**(8.4 mg,t_R = 29.8 min)。Fr. A-3、Fr. A-4(0.9 g)经过Sephadex LH-20凝胶色谱,以甲醇洗脱,获得19个组分。Fr. A-3、Fr. A-5(90 mg)进行半制备液相色谱,以乙腈-水(V∶V =48∶52)等度洗脱,得化合物**7**(9.0 mg,t_R = 14.9 min)和**8**(6.5 mg,t_R = 32.6 min)。Fr. A-3-4-18(110 mg)进行半制备液相色谱,以乙腈-水(V∶V=50∶50)等度洗脱,得化合物**9**(8.7 mg,t_R = 16.0 min)和**10**(9.3 mg,t_R = 20.6 min)。

3　结构鉴定

化合物1　淡黄色针状晶体($CHCl_3$);mp. 65 ~ 66 ℃;IR (KBr) ν_{max}:1663,1640,1600,1460,1561,1384 cm^{-1};^1H NMR ($CDCl_3$, 600 MHz) δ: 8.17 (1H,dd,J=8.0,1.5 Hz,H-5),7.65 (1H,m,H-7),7.44 (1H,d,J=8.4 Hz,H-8),7.37 (1H,t,J=7.2 Hz,H-6),7.33 (2H,t,J=7.2 Hz,H-2′,H-6′),7.30 (1H,m,H-4′),7.23 (2H,t,J=7.2 Hz,H-3′,H-5′),6.12 (1H,s,H-3),3.08 (2H,t,J=7.2 Hz,H-7′),2.92 (2H,t,J=7.2 Hz,H-8′);^{13}C NMR ($CDCl_3$,150 MHz) δ:178.0 (s,C-4),167.5 (s,C-2),157.1 (s,C-9),140.2 (s,C-1′),133.8 (d,C-7),128.4 (d,C-2′,C-6′),128.1 (d,C-3′,C-5′),126.5 (d,C-4′),125.8 (d,C-6),124.0 (s,C-10),124.5 (d,C-5),116.9 (d,C-8),110.0 (d,C-3),32.7 (t,C-7′),36.4 (t,C-8′)。以上数据与文献报道的数据一致[7]。因此,化合物**1**鉴定为2-(2-phenylethyl)chromone [2-(2-苯基乙基)色酮]。

化合物2　淡黄色针状晶体;mp. 89 ~ 90 ℃;IR (KBr) ν_{max}:1652,1638,1604,1597,1562,1480,1434 cm^{-1},表明其结构中存在苯环及吡喃酮;^1H NMR ($CDCl_3$,600 MHz) δ:8.17 (1H,dd,J=8.0,1.5 Hz,H-5),7.66 (1H,m,H-7),7.44 (1H,d,J=8.4 Hz,H-8),7.39 (1H,t,J=7.2 Hz,H-6),7.33 (2H,t,J=7.2 Hz,H-2′,6′),7.30 (1H,m,H-4′),7.23 (2H,t,J=7.2 Hz,H-3′,5′),6.11 (1H,s,H-3),3.69 (3H,s,6-OCH_3),3.06 (2H,t,J=7.2 Hz,H-7′),2.92 (2H,t,J=7.2 Hz,H-8′);^{13}C NMR ($CDCl_3$,150 MHz) δ:177.6 (s,C-4),168.3 (s,C-2),157.0 (s,C-6),151.7 (s,C-9),141.0 (s,C-1′),128.9 (d,C-2′,C-6′),128.4 (d,C-3′,C-5′),126.2 (d,C-4′),123.9 (s,C-10),123.4 (s,C-7),119.3 (d,C-8),109.7 (d,C-3),105.7 (d,C-5),55.7 (q,6-OCH_3),36.5 (t,C-8′),32.4 (t,C-7′)。以上数据与文献报道的数据一致[8]。因此,化合物**2**鉴定为6-methoxy-2-(2-phenylethyl) chromone [6-甲氧基-2-(2-苯基乙基)色酮]。

化合物3　淡黄色针状晶体;mp. 128 ~ 129 ℃;IR (KBr) ν_{max}:2930,1650,1628,1604,1587,1562,1480,1434 cm^{-1},表明其结构中存在羟基、苯环及吡喃酮;^1H NMR ($CDCl_3$,600 MHz) δ:7.33 (2H,t,J=7.2 Hz,H-2′,6′),7.30 (1H,m,H-4′),7.27 (1H,dd,J=12.0,9.0 Hz,H-7),7.23 (2H,t,J=7.2 Hz,H-3′,5′),6.89 (1H,d,J=9.0 Hz,H-8),6.06 (1H,s,H-3),3.97 (3H,s,6-OCH_3),3.09 (2H,t,J=7.2 Hz,H-7′),2.96 (2H,t,J=7.2 Hz,H-8′);^{13}C NMR ($CDCl_3$,150 MHz) δ:184.2 (s,C-4),170.3 (s,C-2),150.6 (s,C-5),149.7 (s,C-9),143.5 (s,C-6),139.7 (s,C-1′),128.9 (d,C-2′,C-6′),128.4 (d,C-3′,C-5′),126.8 (d,C-4′),119.3 (d,C-7),111.0 (s,C-10),108.0 (s,C-3),105.9 (s,C-8),57.2 (q,6-OCH_3),36.3 (t,C-8′),33.1 (t,C-7′)。以上数据与文献报道的数据一致[9]。因此,化合物**3**鉴定为5-hydroxy-6-methoxy-2-(2-phenylethyl) chromone [5-羟基-6-甲氧基-2-(2-苯基乙基)色酮]。

化合物4　无色针状晶体;mp. 139 ~ 140 ℃;IR (KBr) ν_{max}:1645,1628,1600,1575,1560,1485,1430 cm^{-1},表明其结构中存在苯环及吡喃酮;^1H NMR ($CDCl_3$,600 MHz) δ:7.75 (1H,s,H-5),7.28 (2H,dd,J=9.0,3.0 Hz,H-2′,6′),7.07 (1H,s,H-8),6.97 (2H,dd,J=9.0,3.0 Hz,H-3′,5′),6.32 (1H,s,H-3),3.97 (3H,s,4′-OCH_3),3.78 (3H,s,7-OCH_3),3.67 (3H,s,6-OCH_3),3.04 (2H,t,J=7.2 Hz,H-7′),2.93 (2H,t,J=7.2 Hz,H-8′);^{13}C NMR ($CDCl_3$,150 MHz),δ:184.0 (s,C-4),170.0 (s,C-2),157.1 (s,C-7),152.7 (s,C-9),149.8 (s,C-

4′),148.5 (s,C-6),132.7 (s,C-1′),129.9 (d,C-2′,C-6′),118.0 (s,C-10),115.4 (d,C-3′,C-5′),109.3 (d,C-3),104.6 (d,C-5),101.1 (d,C-8),57.2 (q,4′-OCH_3),56.5 (q,7-OCH_3),55.1 (q,6-OCH_3),36.3 (t,C-8′),32.1 (t,C-7′)。以上数据与文献报道的数据一致[10]。因此,化合物**4** 鉴定为6, 7-dimethoxy-2-[2-(4′-methoxyphenyl) ethyl] chromone [6,7-二甲氧基-2-[2-(4′-甲氧基苯基)乙基]色酮]。

化合物 5 淡黄色粉末;mp. 131 ~ 132 ℃;IR (KBr) ν_{max}: 2920, 1635, 1628, 1600, 1515, 1485, 1435,1380 cm^{-1},表明其结构中存在羟基、苯环及吡喃酮;^{1}H NMR ($CDCl_3$,600 MHz) δ:7.54 (1H,s,H-5),7.08 (2H,d,J=9.0 Hz,H-2′,6′),6.92 (1H,s,H-8),6.80 (2H,d,J=9.0 Hz,H-3′,5′),6.06 (1H,s,H-3),3.96 (3H,s,6-OCH_3),3.77 (3H,s,4′-OCH_3),2.96 (2H,m,H-7′),2.89 (2H,m,H-8′);^{13}C NMR ($CDCl_3$,150 MHz) δ: 184.0 (s,C-4),168.0 (s,C-2),157.8 (s,C-4′),152.7 (s,C-9),151.0 (s,C-7),145.5 (s,C-6),132.2 (s,C-1′),129.2 (d,C-2′,C-6′),118.0 (s,C-10),114.4 (d,C-3′,C-5′),109.3 (d,C-3),104.6 (d,C-5),101.9 (d,C-8),56.5 (q,6-OCH_3),55.1 (q,4′-OCH_3),32.1 (t,C-7′),36.3 (t,C-8′)。以上数据与文献报道的数据一致[11]。因此,化合物**5** 鉴定为7-Hydroxy-6-methoxy-2-[2-(4′-methoxyphenyl) ethyl] chromone [7-羟基-6-甲氧基-2-[2-(4′-甲氧基苯基)乙基]色酮]。

化合物 6 淡黄色粉末;mp. 131 ~ 132 ℃;IR (KBr) ν_{max} 1640,1600,1560,1485,1435,1380 cm^{-1},表明其结构中存在苯环及吡喃酮;^{1}H NMR ($CDCl_3$,600 MHz) δ:8.17 (1H,dd,J=8.0,1.5 Hz,H-5),7.66 (1H,m,H-7),7.46 (1H,d,J=8.4 Hz,H-8),7.36 (1H,t,J=7.2 Hz,H-6),7.30 (2H,t,J=7.2 Hz,H-2′,6′),7.21 (2H,t,J=7.2 Hz,H-3′,5′),6.10 (1H,s,H-3),2.98 (2H,t,J=7.2 Hz,H-7′),3.75 (3H,s,4′-OCH_3),2.92 (2H,t,J=7.2 Hz,H-8′);^{13}C NMR ($CDCl_3$,150 MHz) δ:184.0 (s,C-4),168.0 (s,C-2),158.0 (s,C-4′),156.7 (s,C-9),132.9 (d,C-7),132.2 (s,C-1′),129.8 (d,C-2′,C-6′),125.7 (d,C-6),124.6 (d,C-5),123.1 (s,C-10),118.0 (d,C-8),114.1 (d,C-3′,C-5′),110.1 (d,C-3),55.2 (s,4′-OCH_3),36.3 (t,C-8′),32.1 (t,C-7′)。以上数据与文献报道的数据一致[7]。因此,化合物**6** 鉴定为2-[2-(4′-methoxyphenyl) ethyl] chromone [2-[2-(4′-甲氧基苯基)乙基]色酮]。

化合物 7 淡黄色粉末;mp. 146 ~ 147 ℃;IR (KBr) ν_{max}:3360,1640,1600,1510,1485,1430,1380 cm^{-1},表明其结构中存在羟基、苯环及吡喃酮;^{1}H NMR ($CDCl_3$,600 MHz) δ:7.50 (1H,s,H-5),6.87 (1H,s,H-8),6.79 (1H,d,J = 1.8 Hz,H-2′),6.75 (1H,d, J = 8.4 Hz,H-5′),6.65 (1H,dd,J = 8.4, 1.8 Hz,H-6′),6.11 (1H,s,H-3),3.99 (3H,s,7-OCH_3),3.96 (3H,s,6-OCH_3),3.86 (3H,s,4′-OCH_3),2.97 (2H,t,J = 7.2 Hz,H-7′),2.87 (2H,t,J = 7.2 Hz,H-8′);^{13}C NMR ($CDCl_3$,150 MHz) δ: 178.2 (s,C-4),167.5 (s,C-2),155.6 (s,C-7),152.7 (s,C-9),148.1 (s,C-6),145.4 (s,C-4′),144.7 (s,C-3′),133.5 (s,C-1′),119.7 (d,C-6′),117.1 (s,C-10),115.0 (d,C-2′),111.1 (d,C-5′),110.0 (d,C-3),100.5 (d,C-8),104.6 (d,C-5),57.2 (q,7-OCH_3),56.3 (q,6-OCH_3),55.9 (q,4′-OCH_3),36.2 (t,C-8′),32.1 (t,C-7′)。以上数据与文献报道的数据一致[12]。因此,化合物**7** 鉴定为6, 7-dimethoxy-2-[2-(3′-hydroxy-4′-methoxyphenyl) ethyl]chromone [6,7-二甲氧基-2-[2-(3′-羟基-4′-甲氧基苯基)乙基]色酮]。

化合物 8 淡黄色粉末;mp. 142 ~ 143 ℃;IR (KBr) ν_{max}:1660,1640,1600,1580,1510,1485,1430 cm^{-1},表明其结构中存在苯环及吡喃酮;^{1}H NMR ($CDCl_3$,600 MHz) δ:7.51 (1H,s,H-5),7.32 (2H,t,J = 7.2 Hz,H-2′,6′),7.30 (1H,m,H-4′),7.23 (2H,t,J = 7.2 Hz,H-3′,5′),6.85 (1H,s,H-8),6.11 (1H,s,H-3),3.96 (3H,s,7-OCH_3),3.86 (3H,s,6-OCH_3),3.04 (2H,t,J = 7.2 Hz,H-7′),2.95 (2H,t,J = 7.2 Hz,H-8′);^{13}C NMR ($CDCl_3$,150 MHz) δ:178.4 (s,C-4),167.7 (s,C-2),155.0 (s,C-7),152.7 (s,C-9),148.1 (s,C-6),141.1 (s,C-1′),129.2 (d,C-2′,6′),128.4 (d,C-3′,5′),126.7 (d,C-4′),116.9 (s,C-10),110.1 (d,C-3),105.1 (d,C-5),100.5 (d,C-8),56.3 (q,7-OCH_3),55.9 (q,6-OCH_3),32.1 (t,C-7′),35.9 (t,C-8′)。以上数据与文献报道的数据一致[8]。因此,化合物**8** 鉴定为6,7-dimethoxy-2-(2-phenylethyl) chromone

[6,7-二甲氧基-2-(2-苯基乙基)色酮]。

化合物 9　淡黄色粉末;mp. 140 ~ 141 ℃;IR (KBr) ν_{max}: 3350, 2540, 1660, 1630, 1600, 1580, 1510, 1400, 1300 cm^{-1},表明其结构中存在羟基、苯环及吡喃酮;^{1}H NMR ($CDCl_3$, 600 MHz) δ: 6.78 (1H, d, J = 3.6 Hz, H-5), 6.72 (1H, d, J = 8.4 Hz, H-5′), 6.67 (1H, d, J = 3.6 Hz, H-7), 6.64 (1H, d, J = 2.4 Hz, H-2′), 6.57 (1H, dd, J = 8.4, 2.4 Hz, H-6′), 6.01 (1H, s, H-3), 3.72 (3H, s, 4′-OCH_3), 2.96 (2H, m, H-8′), 2.92 (2H, m, H-7′); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 184.0 (s, C-4), 168.9 (s, C-2), 156.2 (s, C-6), 148.8 (s, C-8), 148.2 (s, C-4′), 147.4 (s, C-3′), 142.1 (s, C-9), 134.2 (s, C-1′), 126.0 (s, C-10), 120.2 (d, C-6′), 116.8 (d, C-2′), 113.0 (d, C-5′), 110.0 (d, C-3), 109.2 (d, C-7), 99.1 (d, C-5), 55.9 (q, 4′-OCH_3), 36.8 (t, C-8′), 32.2 (t, C-7′)。以上数据与文献报道的数据一致[12]。因此,化合物 **9** 鉴定为 6,8-dihydroxy-2-[2-(3′-hydroxy-4′-methoxyphenyl)ethyl]chromone [6,8-二羟基-2-[2-(3′-羟基-4′-甲氧基苯基)乙基]色酮]。

化合物 10　淡黄色粉末;mp. 167 ~ 168 ℃;IR (KBr) ν_{max}: 3310, 1640, 1600, 1585, 1560, 1530 cm^{-1},表明其结构中存在羟基、苯环及吡喃酮;^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.82 (1H, d, J = 3.0 Hz, H-5), 7.37 (1H, d, J = 9.0 Hz, H-8), 7.24 (1H, dd, J = 9.0, 3.0 Hz, H-7), 7.10 (2H, t, J = 7.2 Hz, H-2′, 6′), 6.78 (2H, t, J = 7.2 Hz, H-3′, 5′), 6.12 (1H, s, H-3), 3.76 (3H, s, 4′-OCH_3), 2.98 (2H, t, J = 7.2 Hz, H-7′), 2.92 (2H, t, J = 7.2 Hz, H-8′); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 184.0 (s, C-4), 168.0 (s, C-2), 157.7 (s, C-4′), 154.6 (s, C-6), 149.8 (s, C-9), 131.6 (s, C-1′), 129.4 (d, C-2′, 6′), 124.2 (s, C-10), 122.2 (d, C-7), 118.8 (d, C-8), 114.2 (d, C-3′, 5′), 109.1 (d, C-3), 108.0 (d, C-5), 55.2 (q, 4′-OCH_3), 36.2 (t, C-8′), 32.2 (t, C-7′)。以上数据与文献报道的数据一致[13]。因此,化合物 **10** 鉴定为 6-hydroxy-2-[2-(4′-methoxyphenyl) ethyl] chromone [6-羟基-2-[2-(4′-甲氧基苯基)乙基]色酮]。

4　抗炎活性

体外抗炎活性筛选采用小鼠单核巨噬细胞 Raw264.7 模型[14-16],具体如下:Raw264.7 细胞用含 10% FBS 的 DMEM 培养液于 37 ℃、5% CO_2 培养箱中常规培养。细胞按 1×10^5/mL、200 μL/孔接种于 96 孔板中,置于 37 ℃、5% CO_2 细胞培养箱中贴壁 24 h 后,各组加入终浓度为 1 μg/ml LPS,继续培养 24 h,离心,取上清液按照 Griess 法测定上清液中 NO 的含量。结果发现,化合物 **2** ~ **4** 和 **10** 具有显著的抗炎活性,IC_{50} 值分别为 5.31 ± 0.75, 5.57 ± 0.62, 0.57 ± 0.02, 3.78 ± 0.64 μM,与阳性对照药氨基胍相当(IC_{50} 值 1.80 ± 0.2 μM);化合物 **1**、**5**、**6** 显示较弱的抗炎活性,IC_{50} 值分别为 286.7 ± 3.2、126.1 ± 5.7, 4.75 ± 0.35 mM;其他化合物由于其抗炎活性不明显,未检测出其 IC_{50}(表 1)。

表 1　脂多糖介导的 RAW 264.7 细胞模型抗炎活性

Table 1　Inhibitory activity of compounds on LPS-induced NO production in RAW 264.7 cells

Compound	IC_{50}^{a} (μM)	Compound	IC_{50}^{a} (μM)
1	>40	6	>40
2	5.31 ± 0.75	7	NA
3	5.57 ± 0.62	8	NA
4	0.57 ± 0.02	9	NA
5	>40	10	3.78 ± 0.64
Aminoguanidine[b]	1.8 ± 0.2		

注:[a] 三次实验平均值标准差;[b] 阳性对照药物;NA:无活性。

Note: [a] Value present mean ± SD of triplicate experiments; [b] Positive control substance; NA: No Activity.

5　结论

2-(2-苯乙基)色酮类化合物为沉香的特征性成分,是沉香形成过程中产生的防御性物质[2]。本研究从通体结香技术诱导白木香形成的沉香中分离得到 10 个 2-(2-苯乙基)色酮类化合物,所有化合物均为首次从通体结香技术产的沉香中分离得到,再一次证明采用通体结香技术可诱导白木香产生 2-(2-

苯乙基)色酮类化合物。化合物**1**~**6**和**8**在马来沉香(*A. malaccensis*)产沉香中已有报道,化合物**1**,**6**在越南沉香(*A. crassna*)产沉香中已有报道,化合物**1**~**4**,**6**~**10**在白木香(*A. sinensis*)产沉香中已有报道,化合物**5**为首次从白木香产沉香中分离得到,可见采用通体结香技术诱导白木香形成的2-(2-苯乙基)色酮类化合物与同属其他植物形成的沉香具有相同的化学成分。化合物**2**~**4**和**10**具有显著的抗炎活性,与阳性对照药物氨基胍相当,但其构效关系与作用机制尚不明确,有待于进一步研究。本研究可为通体结香技术所产沉香的品质评价提供基础依据。

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