油橄榄叶中黄酮类成分的研究

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摘 要:为了充分利用我国油橄榄(*Olea europaea* L.)叶资源,丰富油橄榄叶化学成分的多样性。本文对油橄榄叶的化学成分进行研究,利用硅胶柱层析、重结晶等方法从其乙醇(95%)提取物的乙酸乙酯部位中分离得到了 12 个黄酮类化合物。通过^{1}H NMR 和^{13}C NMR 鉴定了它们的结构,分别为芹菜素(**1**)、木犀草素(**2**)、芦丁(**3**)、芹菜素-7-*O*-葡萄糖苷(**4**)、槲皮素(**5**)、香叶木素-7-*O*-葡萄糖苷(**6**)、香叶木素(**7**)、山柰酚(**8**)、花旗松素(**9**)、木犀草苷(**10**)、异鼠李素(**11**)、表没食子儿茶素没食子酸酯(**12**),其中化合物 **12** 为首次从油橄榄叶中分离得到。本研究为油橄榄叶的进一步开发和合理利用提供了试验基础。

关键词:油橄榄叶;黄酮;化学成分;分离纯化;结构鉴定

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Flavonoids from leaves of *Olea europaea* L.

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Abstract: In order to maximize the potential of *Olea europaea* leaf resources and increase the variety of chemical components found in *O. europaea* leaves. In this study, the chemical makeup of *O. europaea* leaves was examined, and using silica gel column chromatography and other methods, 12 flavonoids were extracted from the ethyl acetate portion of ethanol (95%) extract. Their structures were identified as apigenin (**1**), luteolin (**2**), rutin (**3**), apigenin-7-*O*-glucoside (**4**), quercetin (**5**), diosmetin-7-*O*-glucoside (**6**), diosmetin (**7**), kaempferol (**8**), taxifolin (**9**), luteoloside (**10**), isorhamnetin (**11**), epigallocatechin gallate (**12**), by ^{1}H NMR and ^{13}C NMR, compound **12** was isolated from the leaves of *O. europaea* for the first time. The study has provided test basis for the further development and reasonable application of the *O. europaea* leaves.

Key words: leaves of *Olea europaea*; flavone; chemical composition; isolation and purification; structural identification

油橄榄(*Olea europaea* L.)为木犀科(Oleaceae)木犀榄属(*Olea* L.)常绿乔木,又名齐墩果、木犀榄、欧橄榄、洋橄榄,是世界著名的亚热带果树和重要经济林木,有四千多年的栽培历史。其产地主要集中在地中海沿岸国家,如:西班牙、意大利、希腊、突尼斯、阿尔巴尼亚、土耳其等[1]。甘肃省陇南市武都区是我国油橄榄最佳适宜种植区之一,也是中国四大油橄榄生产基地之一。每年在油橄榄树的修剪和采收过程中会产生大量的油橄榄叶副产物,但大多数都被丢弃或焚烧,甚至许多橄榄油生产商向农户收取油橄榄叶的处理费用,不仅没有充分利用油橄榄叶这一天然植物资源,还对生态环境造成了严重的破坏。油橄榄叶提取物具有抗氧化、抗动脉粥样硬化、抗炎、抗菌、降血糖、降血压等多种功效。在地中海沿岸国家被用于民间医药已经有几千年的历史,且已被写入《欧洲药典》[2]。为了充分利用我国油橄榄叶资源,进一步研究油橄榄叶药理活性的物质基础,本试验对采自甘肃陇南的油橄榄叶进行系统的化学成分研究,以期能够充分利用资源、变废为宝、保护环境。

1 材料与方法

AVANCE III HD 500 型超导核磁共振波谱仪(德国布鲁克);EYELA N-1300 型旋转蒸发仪(上海爱朗);正向柱色谱硅胶(200 ~ 300 目,青岛海洋化工有限公司);薄层层析硅胶板(烟台江友硅胶开发有限公司);D101 型大孔树脂(西安蓝晓科技新材

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料股份有限公司)。试验中所用的试剂均为分析纯。油橄榄叶于2020年10月采自甘肃省陇南市武都区,由青海师范大学确生教授鉴定,均为木犀科木犀榄属植物油橄榄(*Olea europaea* L.)的叶,植物标本(OL-20201008)存放于兰州交通大学六号实验楼519室。

将在室温下阴干的油橄榄叶(0.9 kg)粉碎,用95%乙醇(20 L)冷浸提取三次,每次七天,对得到的提取液通过减压蒸馏回收溶剂,最终得到的总浸膏487.5 g。将得到的总浸膏487.5 g悬浮于蒸馏水(40~50 ℃,2.0 L)中,依次用石油醚、乙酸乙酯、正丁醇溶剂进行萃取。将总浸膏分为极性不同的三个部位,各部位经减压浓缩回收溶剂后,分别得到石油醚部位、乙酸乙酯部位、正丁醇部位和水部位。取乙酸乙酯部位147.5 g,加入适量甲醇溶解,用预先处理好的D101型大孔树脂拌样后,以大孔树脂湿法装柱(规格:60 mm×1 000 mm),干法上样。依次用水、30%、50%、80%、90%、100%体积分数的甲醇进行洗脱,回收溶剂后根据薄层层析检测,将柱层析收集物分为4个部分:F_1~F_4。以30%、50%、80%体积分数的甲醇为洗脱剂得到F_1(3.1 g)、F_2(40.1 g)、F_3(16.7 g),以90%和100%体积分数的甲醇为洗脱剂得到F_4(7.0 g)。由于F_1部分极性较大且量少,暂时没有从中分离得到化合物。F_2部分40.1 g经反向硅胶柱色谱,以甲醇:水(0%→100%)为洗脱剂加压梯度洗脱,经过反复柱层析以及重结晶分离得到化合物**6**(127 mg)、**7**(15 mg)、**8**(10 mg)、**10**(12 mg)、**11**(8 mg)。F_3部分16.7 g经硅胶柱色谱(200~300目),以二氯甲烷:甲醇(100∶1(0∶1)为洗脱剂梯度洗脱,经过反复柱层析以及重结晶分离得到化合物**2**(18 mg)、**3**(11 mg)、**4**(35 mg)、**5**(16 mg)、**9**(10 mg)、**12**(8 mg)。F_4部分7.0 g经硅胶柱色谱(200~300目),以二氯甲烷:甲醇(200∶1→0∶1)为洗脱剂梯度洗脱,经过反复柱层析以及重结晶分离得到化合物**1**(21 mg)。

2 结构鉴定

化合物1 黄色粉末;分子式$C_{15}H_{10}O_5$。^{1}H NMR(500 MHz,$(CD_3)_2CO$)δ:13.01(1H,s,5-OH),7.94(2H,d,J = 8.7 Hz,H-2′,H-6′),7.03(2H,d,J = 8.7 Hz,H-3′,H-5′),6.63(1H,s,H-3),6.54(1H,d,J = 1.6 Hz,H-6),6.25(1H,d,J = 1.6 Hz,H-8);^{13}C NMR(125 MHz,$(CD_3)_2CO$)δ:165.1(C-2),105.3(C-3),183.1(C-4),163.4(C-5),99.8(C-6),165.2(C-7),94.8(C-8),162.0(C-9),104.1(C-10),123.3(C-1′),129.3(C-2′),116.9(C-3′),158.8(C-4′),116.9(C-5′),129.3(C-6′)。以上数据与文献[3]报道的数据基本一致,故鉴定化合物**1**为芹菜素。

化合物2 黄色粉末;分子式$C_{15}H_{10}O_6$。^{1}H NMR(500 MHz,DMSO-d_6)δ:12.95(1H,s,5-OH),7.42~7.38(2H,m,H-2′,H-6′),6.89(1H,d,J = 8.2 Hz,H-5′),6.65(1H,s,H-3),6.44(1H,d,J = 1.8 Hz,H-8),6.18(1H,d,J = 1.9 Hz,H-6);^{13}C NMR(125 MHz,DMSO-d_6)δ:164.0(C-2),103.8(C-3),181.8(C-4),161.6(C-5),99.0(C-6),164.3(C-7),94.0(C-8),157.4(C-9),103.0(C-10),121.6(C-1′),113.4(C-2′),145.9(C-3′),149.8(C-4′),116.2(C-5′),119.1(C-6′)。以上数据与文献[4]报道的数据基本一致,故鉴定化合物**2**为木犀草素。

化合物3 淡黄色粉末;分子式$C_{27}H_{30}O_{16}$。^{1}H NMR(500 MHz,DMSO-d_6)δ:12.58(1H,s,5-OH),7.54(1H,s,H-6′),7.52(1H,s,H-2′),6.84(1H,d,J = 8.2 Hz,H-5′),6.38(1H,s,H-8),6.19(1H,s,H-6),5.33(1H,d,J = 6.9 Hz,H-1″),4.38(1H,s,H-1‴),0.95(3H,d,J = 6.2 Hz,H-6‴);^{13}C NMR(125 MHz,DMSO-d_6)δ:156.9(C-2),133.7(C-3),177.8(C-4),161.7(C-5),99.2(C-6),164.6(C-7),94.1(C-8),157.1(C-9),104.4(C-10),122.1(C-1′),115.7(C-2′),145.2(C-3′),148.9(C-4′),116.7(C-5′),121.6(C-6′),101.6(C-1″),74.5(C-2″),76.9(C-3″),70.5(C-4″),76.3(C-5″),67.4(C-6″),101.2(C-1‴),70.8(C-2‴),71.0(C-3‴),72.3(C-4‴),68.7(C-5‴),18.2(C-6‴)。以上数据与文献[5]报道的数据基本一致,故鉴定化合物**3**为芦丁。

化合物4 黄色粉末;分子式$C_{21}H_{20}O_{10}$。^{1}H NMR(500 MHz,DMSO-d_6)δ:12.94(1H,s,5-OH),7.95(2H,d,J = 8.7 Hz,H-2′,H-6′),6.93(2H,d,J = 8.7 Hz,H-3′,H-5′),6.84(1H,s,H-3),6.83(1H,d,J = 2.2 Hz,H-8),6.44(1H,d,J = 2.2 Hz,H-6),5.05(1H,d,J = 7.4 Hz,H-1″);^{13}C NMR(125 MHz,DMSO-d_6)δ:164.5(C-2),103.2(C-3),182.2(C-4),161.6(C-5),100.1(C-6),163.1(C-7),95.0(C-8),157.1(C-9),105.5(C-10),121.2(C-1′),128.8(C-2′),116.2(C-3′),161.2(C-4′),116.2(C-5′),128.8(C-6′),99.7(C-1″),73.2(C-

2″),76.5(C-3″),69.7(C-4″),77.3(C-5″),60.8(C-6″)。以上数据与文献[6]报道的数据基本一致,故鉴定化合物**4**为芹菜素-7-*O*-葡萄糖苷。

化合物 5　黄色粉末;分子式 $C_{15}H_{10}O_7$。^{1}H NMR(500 MHz,CD_3OD)δ:7.73(1H,d,J = 2.1 Hz,H-2′),7.63(1H,dd,J = 8.5,2.2 Hz,H-6′),6.88(1H,d,J = 8.5 Hz,H-5′),6.38(1H,d,J = 2.1 Hz,H-8),6.18(1H,d,J = 2.0 Hz,H-6);^{13}C NMR(125 MHz,CD_3OD)δ:148.8(C-2),137.2(C-3),177.3(C-4),162.5(C-5),99.2(C-6),165.6(C-7),94.4(C-8),158.2(C-9),104.5(C-10),124.1(C-1′),116.0(C-2′),146.2(C-3′),148.0(C-4′),116.2(C-5′),121.7(C-6′)。以上数据与文献[7]报道的数据基本一致,故鉴定化合物**5**为槲皮素。

化合物 6　黄色粉末;分子式 $C_{22}H_{22}O_{11}$。^{1}H NMR(500 MHz,DMSO-d_6)δ:12.99(1H,s,5-OH),7.45(1H,dd,J = 8.3,2.3 Hz,H-6′),7.42(1H,d,J = 2.3 Hz,H-2′),6.90(1H,d,J = 8.3 Hz,H-5′),6.79(1H,d,J = 2.2 Hz,H-8),6.75(1H,s,H-3),6.44(1H,d,J = 2.2 Hz,H-6),5.08(1H,d,J = 7.5 Hz,H-1″),3.16(3H,s,-OCH_3);^{13}C NMR(125 MHz,DMSO-d_6)δ:164.5(C-2),103.2(C-3),181.9(C-4),161.2(C-5),99.5(C-6),163.0(C-7),94.7(C-8),157.0(C-9),105.4(C-10),121.4(C-1′),113.6(C-2′),145.8(C-3′),150.0(C-4′),116.0(C-5′),119.2(C-6′),48.6(C-OCH_3),99.9(C-1″),73.1(C-2″),76.4(C-3″),69.6(C-4″),77.2(C-5″),60.6(C-6″)。以上数据与文献[8]报道的数据基本一致,故鉴定化合物**6**为香叶木素-7-*O*-葡萄糖苷。

化合物 7　黄色粉末;分子式 $C_{16}H_{12}O_6$。^{1}H NMR(500 MHz,DMSO-d_6)δ:12.93(1H,s,5-OH),7.54(1H,dd,J = 8.3,2.3 Hz,H-6′),7.42(1H,d,J = 2.3 Hz,H-2′),7.08(1H,d,J = 8.6 Hz,H-5′),6.75(1H,s,H-3),6.46(1H,d,J = 2.1 Hz,H-8),6.19(1H,d,J = 2.1 Hz,H-6),3.86(3H,s,-OCH_3);^{13}C NMR(125 MHz,DMSO-d_6)δ:163.5(C-2),103.5(C-3),181.7(C-4),161.5(C-5),98.9(C-6),164.2(C-7),93.9(C-8),157.3(C-9),103.8(C-10),123.0(C-1′),113.0(C-2′),146.8(C-3′),151.1(C-4′),112.2(C-5′),118.7(C-6′),55.8(C-OCH_3)。以上数据与文献[9]报道的数据基本一致,故鉴定化合物**7**为香叶木素。

化合物 8　黄色粉末;分子式 $C_{15}H_{10}O_6$。^{1}H NMR(500 MHz,$(CD_3)_2CO$)δ:12.17(1H,s,5-OH),8.17~8.13(2H,m,H-2′,H-6′),7.03~6.99(2H,m,H-3′,H-5′),6.53(1H,d,J = 2.1 Hz,H-8),6.27(1H,d,J = 2.1 Hz,H-6);^{13}C NMR(125 MHz,$(CD_3)_2CO$)δ:147.0(C-2),136.7(C-3),176.6(C-4),162.4(C-5),99.2(C-6),165.0(C-7),94.5(C-8),160.2(C-9),104.2(C-10),123.4(C-1′),130.5(C-2′),116.4(C-3′),157.8(C-4′),116.4(C-5′),130.5(C-6′)。以上数据与文献[10]报道的数据基本一致,故鉴定化合物**8**为山柰酚。

化合物 9　白色粉末;分子式 $C_{15}H_{12}O_7$。^{1}H NMR(500 MHz,$(CD_3)_2CO$)δ:11.71(1H,s,5-OH),7.07(1H,d,J = 2.0 Hz,H-2′),6.92(1H,dd,J = 8.1,2.1 Hz,H-6′),6.86(1H,d,J = 8.1 Hz,H-5′),5.99(1H,d,J = 2.1 Hz,H-6),6.95(1H,d,J = 2.1 Hz,H-8),5.02(1H,d,J = 11.4 Hz,H-2),4.61(1H,d,J = 11.4 Hz,H-3);^{13}C NMR(125 MHz,$(CD_3)_2CO$)δ:84.5(C-2),73.2(C-3),198.2(C-4),165.2(C-5),97.1(C-6),167.8(C-7),96.0(C-8),164.2(C-9),101.6(C-10),129.8(C-1′),115.8(C-2′),145.8(C-3′),146.6(C-4′),115.9(C-5′),120.9(C-6′)。以上数据与文献[11]报道的数据基本一致,故鉴定化合物**9**为花旗松素。

化合物 10　黄色粉末;分子式 $C_{21}H_{20}O_{11}$。^{1}H NMR(500 MHz,DMSO-d_6)δ:12.99(1H,s,5-OH),7.45(1H,dd,J = 8.3,2.3 Hz,H-6′),7.42(1H,d,J = 2.3 Hz,H-2′),6.90(1H,d,J = 8.4 Hz,H-5′),6.79(1H,d,J = 2.2 Hz,H-8),6.75(1H,s,H-3),6.44(1H,d,J = 2.1 Hz,H-6),5.08(1H,d,J = 7.4 Hz,H-1″);^{13}C NMR(125 MHz,DMSO-d_6)δ:164.5(C-2),103.2(C-3),181.9(C-4),161.1(C-5),99.5(C-6),163.0(C-7),94.7(C-8),157.0(C-9),105.3(C-10),121.4(C-1′),113.6(C-2′),145.8(C-3′),150.0(C-4′),116.0(C-5′),119.2(C-6′),99.9(C-1″),73.1(C-2″),76.4(C-3″),69.6(C-4″),77.2(C-5″),60.6(C-6″)。以上数据与文献[12]报道的数据基本一致,故鉴定化合物**10**为木犀草苷。

化合物 11　黄色粉末;分子式 $C_{16}H_{12}O_7$。^{1}H NMR(500 MHz,DMSO-d_6)δ:12.46(1H,s,5-OH),7.75(1H,t,J = 1.6 Hz,H-2′),7.69(1H,dt,J = 8.5,1.6 Hz,H-6′),6.94(1H,dd,J = 8.5,1.1 Hz,

H-5′),6.49 ~ 6.46(1H,m,H-8),6.19(1H,t,J = 1.6 Hz,H-6),3.84(3H,d,J = 1.1 Hz,-OCH_3);^{13}C NMR(125 MHz,DMSO-d_6)δ:146.6(C-2),135.8(C-3),175.9(C-4),160.7(C-5),98.2(C-6),164.0(C-7),93.6(C-8),156.2(C-9),103.0(C-10),122.0(C-1′),111.7(C-2′),148.8(C-3′),147.4(C-4′),115.4(C-5′),121.7(C-6′),55.8(C-OCH_3)。以上数据与文献[13]报道的数据基本一致,故鉴定化合物**11**为异鼠李素。

化合物 12 白色粉末;分子式 $C_{22}H_{18}O_{11}$。^{1}H NMR(500 MHz,$(CD_3)_2CO$)δ:7.02(2H,s,H-2″,H-6″),6.62(2H,s,H-2′,H-6′),6.06(1H,d,J = 2.3 Hz,H-6),6.03(1H,d,J = 2.3 Hz,H-8),5.56(1H,ddd,J = 4.5,2.6,1.4 Hz,H-3),5.07(1H,s,H-2),3.04(1H,dd,J = 17.4,4.6 Hz,H-4a),2.91(1H,dd,J = 17.4,2.6 Hz,H-4b);^{13}C NMR(125 MHz,$(CD_3)_2CO$)δ:78.1(C-2),69.2(C-3),26.7(C-4),157.8(C-5),96.5(C-6),157.5(C-7),95.8(C-8),157.1(C-9),99.0(C-10),130.7(C-1′),106.8(C-2′),146.3(C-3′),133.2(C-4′),146.3(C-5′),106.8(C-6′),121.9(C-1″),110.0(C-2″),145.9(C-3″),138.7(C-4″),145.9(C-5″),110.0(C-6″),166.0(C-7″)。以上数据与文献[14]报道的数据基本一致,故鉴定化合物**12**为表没食子儿茶素没食子酸酯。

化合物**1 ~ 12**的结构见图1。

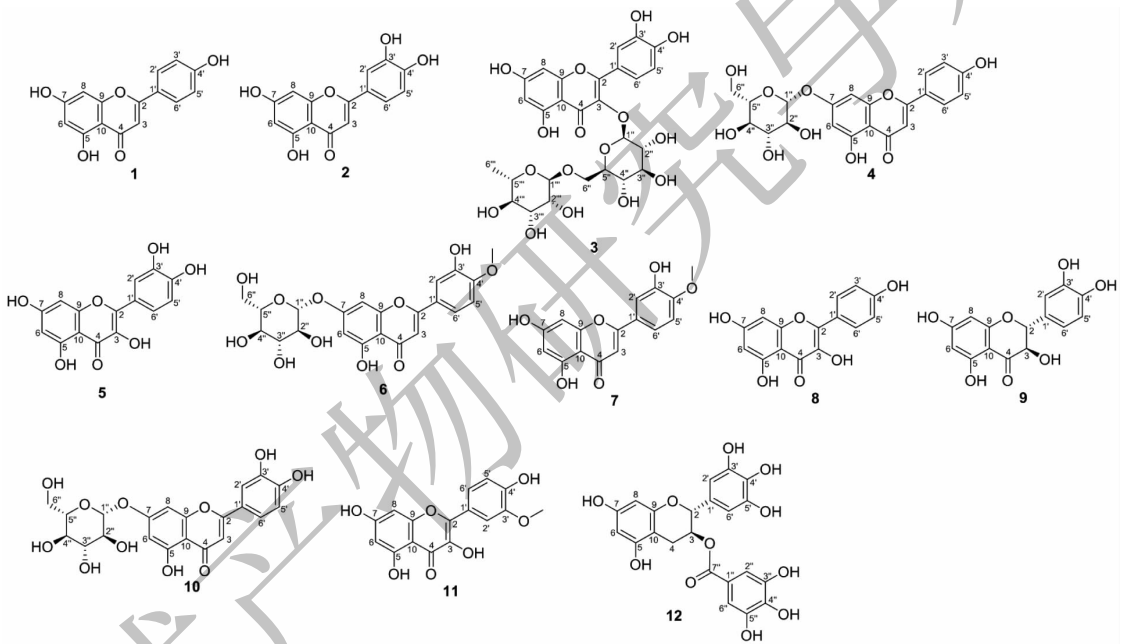

图1 化合物1 ~ 12的化学结构

Fig. 1 Chemical structures of compounds **1-12**

3 讨论与结论

本试验对采自甘肃陇南的油橄榄叶乙醇(95%)提取物的乙酸乙酯部位进行了系统的化学成分研究,从中分离得到了12个黄酮化合物。其中包括3个黄酮类,4个黄酮醇类,3个黄酮苷类,1个双氢黄酮醇类以及1个儿茶素类化合物。并采用^{1}H NMR、^{13}C NMR鉴定了它们的结构。其中化合物**12**表没食子儿茶素没食子酸酯为首次在油橄榄叶中分离得到。本研究丰富了油橄榄叶的化学成分,同时也为我国油橄榄叶资源的进一步开发和利用提供了试验基础。

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