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苍山香茶菜素的结构更正

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关键词　苍山香茶菜；苍山香茶菜素；结构更正

在编写“天然产贝壳杉烯型二萜成分”一书的过程中，作者对不同结构类型的贝壳杉烯型二萜，各种官能团在不同位置的取代，所引起的^{1}H和^{13}C化学位移的变化，仔细认真地进行了系列对照研究，从中发现了一些规律性（另报）。

本文根据上述规律性，简要阐明苍山香茶菜素的结构更正。

苍山香茶菜素bulleyanin（1），$C_{28}H_{38}O_{10}$，mp 240—244°C；其^{13}C NMR谱表明存在3个CH_3，3个CH_2，8个CH，3个四取代碳，4个Ac，2个烯碳和1个酮碳。其^{13}C NMR δ 205.0（s），147.1（s），116.2（t），27.9（q），22.0（q），14.1（q）信号和^{1}H NMR谱δ5.92，5.27（各1H，br. s），1.49，0.94，0.82（各3H，s）信号建议苍山素具有典型的ent-kaur-16-en-15-one骨架[1]。结合考虑碳谱和质谱可知苍山素分子中含有4个仲乙酰氧基，1个仲羟基。这5个含氧官能团是如何排布呢？首先考察^{13}C NMR谱，C_{10}为43.0，C_{20}为14.1表明1α位有取代[2]；C_4为36.6，C_{18}为27.9，C_5为40.4表明3β位和7β位有取代[3, 4]；C_9为56.8，C_8为50.0表明11β位有取代[4]；C_8为50.0，C_{13}为43.9表明剩下的这取代基只能位于12位[4]。在羟基被氧化为酮的脱氢苍山素 dehydrobulleyanin（3）的^{13}C NMR 谱中，C_{13}向低场位移至53.6，C_{11}向低场位移至78.5，C_{14}向低场位移至36.6，据此可知，羟基应在12α位。苍山素的化学结构应更正为1α，3β，7β，11β-tetraacetoxy-12α-hydroxy-ent-kaur-16-en-15-one（1）。前文[6]的错误在于把11β-OAc误置14β位，把1位和7位的取向颠倒。更正后的苍山素和脱氢苍山素的^{13}C NMR和^{1}H NMR数据的指定如下。苍山素乙酯（2）和苍山素氢化物（4）的^{1}H NMR数据可参照（1）和（3）作出正确的指定。

Bulleyanin（1）　^{1}H NMR ($CDCl_3$) δ: 0.82 (3H, s, 19-CH_3), 0.94(3H, s, 18-CH_3), 1.49 (3H, s, 20-CH_3), 1.86, 2.00, 2.13 and 2.22 (each 3H, s, 4×OAc), 2.94 (1H, d, 3, 12α-OH), 3.70 (1H, br. s, 12β-H), 4.77 (1H, t, 3, 3α-H), 5.10 (1H, dd, 8, 12, 1β-H), 5.17 (1H, t, 3, 7α-H), 5.31 (1H, br. s, 11α-H), 5.27 and 5.92 (each 1H, br. s, 17-H_2).

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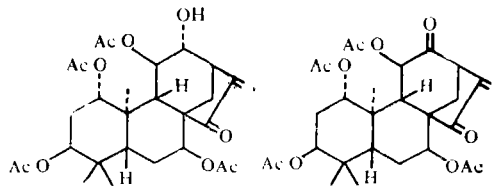
^{13}C NMR ($CDCl_3$) δ：74.6 (1-C), 29.8 (2-C), 78.0 (3-C), 36.6 (4-C), 40.4 (5-C), 24.4 (6-C), 74.6 (7-C), 50.0 (8-C), 56.8 (9-C), 43.0 (10-C), 72.2 (11-C), 79.6 (12-C), 43.9 (13-C), 29.8 (14-C), 205.0 (15-C), 147.1 (16-C), 116.2 (17-C), 27.9 (18-C), 22.0 (19-C), 14.1(20-C), 4 × OAc: 171.0, 171.0, 171.0, 170.4; 22.0, 21.9, 21.7, 21.6.



Dehydrobulleyanin (3) ^1H NMR ($CDCl_3$) δ：0.81 (3H, s, 19-CH_3), 0.93 (3H, s, 18-CH_3), 1.22 (3H, s, 20-CH_3), 1.88, 2.09, 2.13 and 2.22 (each 3H, s, 4 × OAc), 4.79 (1H, t, 3, 3α-H), 5.01 (1H, dd, 6, 12, 1β-H), 5.27 (1H, t, 3, 7α-H), 5.73 (1H, br. s, 11α-H), 5.39 and 5.98 (each 1H, br. s, 17-H_2). ^{13}C NMR ($CDCl_3$) δ：74.6 (1-C), 28.8 (2-C), 77.0 (3-C), 36.3 (4-C), 40.2 (5-C), 23.9 (6-C), 70.1 (7-C), 50.4 (8-C), 54.5 (9-C), 42.8 (10-C), 78.5 (11-C), 201.5 (12-C), 53.6 (13-C), 36.6 (14-C), 201.6 (15-C), 144.5 (16-C), 116.3 (17-C), 27.2(18-C), 21.9 (19-C), 14.7 (20-C), 4 × OAc: 170.4, 170.4, 170.4, 168.5; 21.3, 21.3, 21.2, 21.2.

参 考 文 献

1 Xu Yunlon, Sun Xichang, Sun Handong et al. *Acta Botanica Yunnanica* 1981; 3(3): 283

2 Isao Kubo, Iwao Miura, Tado Kamikawa et al. *Chemistry Letters* 1977; 1289

3 Qin Chonqiu, Liu Chenjiang, Li Jicheng et al. *Acta Botanica Yunnanica* 1984; 6(3): 333

4 Li Jicheng, Liu Chenjiang, Sun Handong et al. *Acta Botanica Yunnanica* 1986; 8(1): 93

5 Sun Handong, Sun Xichang, Lin Zhongwen et al. *Chemistry Letters* 1981; 753

6 Xu Yunlong. *Acta Botanica Yunnanica* 1985; 7(4): 437

STRUCTURAL CORRECTION OF BULLEYANIN

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Abstract Carbon-13 NMR spectra of a number of natural (-) ent-kauranoids have been studied. The rule of change in chemical shifts produced by the change of substituents has been summarized (be published somewhere). By above-mentioned rule, chemical structure of bulleyanin has been altered as 1α, 3β, 7β, 11β-tetra-acetoxy-12α-hydroxy-ent-kaur-16-en-15-one (1).

Key words Bulleyanin; Structural correction