Chinese Chemical Letters Vol. 13, No. 11, pp 1079 – 1082, 2002
http://www.imm.ac.cn/journal/ccl.html

Sebiferone, a New Triterpenoid from Stem Bark of *Sapium sebiferum* (L.) Roxb.

Run Hui LIU, Ling Yi KONG*

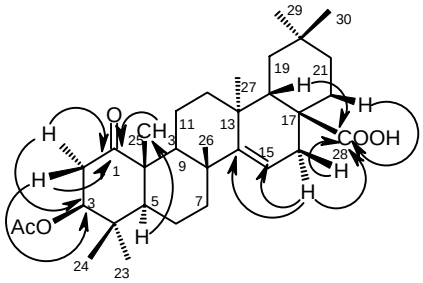
Department of Natural Medicinal Chemistry, China Pharmaceutical University, Nanjing 210038

Abstract: From the stem bark of *Sapium sebiferum* a new triterpenoid, named sebiferone (**1**), was isolated. The structure of the new compound was elucidated as 3β-acetoxy-D-friedoolen-14-en-1-one-28-oic acid on the basis of spectral and chemical methods.

Keywords: *Sapium sebiferum.*, Euphorbiaceae, sebiferone.

Sapium sebiferum (L.) Roxb. (Euphorbiaceae), which was native to China, now spreaded world wide, and very familiar to us as a roadside and garden tree. The root, stem bark and leaves of *Sapium sebiferum* have been used as a purgative and diuretic in traditional chinese medicine. This plant has attracted much attention in 1960s because of its effective activity against schistosoma japonicum[1]. Many triterpenoids have been found previously in this plant[2,3]. We report here the isolation and structural elucidation of a new triterpenoid **1** from the stem bark of *Sapium sebiferum*.

Figure 1 The key correlations of compound **1** in HMBC spectrum



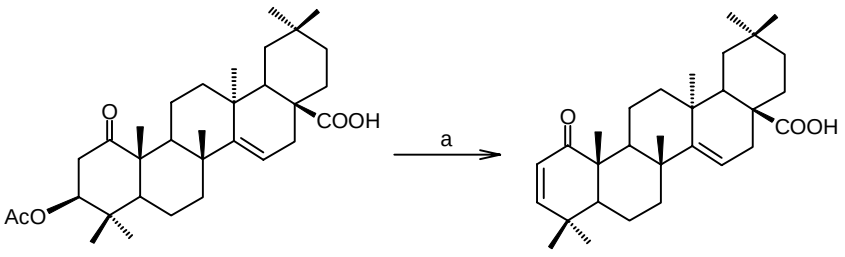
The EtOH extract of the dried and powdered stem bark of *Sapium sebiferum* was partitioned with petroleum ether, EtOAc and n-BuOH. The petroleum ether fraction was further separated by silica gel chromatography and crystallized from petroleum ether/EtOAc to afford **1**. Compound **1** was obtained as a colorless amorphous solid, mp 228-230°C. It gave a positive Liebermann-Burchard test for triterpenoids. The EIMS

*E-mail: lykong@jlonline.com

of **1** revealed the molecular ion peak at *m/z* 512, the ^{13}C NMR and DEPT spectrum exhibited 32 carbon signals (8×CH_3, 9×CH_2, 5×CH, 10×C). Then the molecular formula of **1** was deduced to be $C_{32}H_{48}O_5$. Its IR spectrum showed the presence of three carbonyl groups (1737, 1713, 1690 cm^{-1}). The ^1H NMR spectrum (**Table 1**) was observed the presence of seven tertiary methyl groups on saturated carbons at δ 0.91(s, 3H), 0.94(s, 6H), 0.99(s, 6H), 1.06(s, 3H), 1.34(s, 3H), one acetoxy methyl at δ 2.05(s, 3H), one oxymethine proton was observed as double doublet at δ 4.73(dd, 1H, J=4.7, 11.5Hz), which is due to the axial proton attached to C-3 containing the acetoxy group in equatorial position[4], one olefinic proton appeared as a double doublet at δ 5.51(dd, 1H, J=3.3, 7.8Hz). Two olefinic carbons at δ 160.2 and 116.8 in the ^{13}C NMR (**Table 1**) spectrum indicated that compound **1** belongs to the taraxerane-type triterpenoid, and the double bond is at C-14 and C-15[4]. The position of the carboxylic group at C-17 was confirmed by the HMBC spectrum (**Figure 1**). The correlation of C-28 (-COOH) with H_2-16, H-18 and H-22 were observed in the HMBC spectrum.

The ^1H and ^{13}C NMR data of **1** were similar to those of aleuritolic acid acetate (3 β -acetoxy-D-friedoolean-14-en-28-oic acid)[5], except for the absence of a methylene signal and the appearance of an additional ketone carbonyl signal (δ 210.8) in the ^{13}C NMR spectrum. Thus, compound **1** was considered to be the oxidized derivative of aleuritolic acid acetate. The position of the ketone group at C-1 was determined by the long-range correlation observed in the HMBC spectrum (**Figure 1**). In the HMBC spectra of **1**, H_2-2, H-3 and H_3-25 were observed to be have long-range correlations with the ketone carbon, indicating that the ketone group should be at C-1.

Figure 2 Hydrolysis reaction of compound **1**



1 **2**

a: 10%NaOH /MeOH, reflux, 4 h

Meanwhile, the location of ketone group at C-1 was also further proved by the hydrolysis reaction (**Figure 2**) of **1**. In this reaction the acetoxyl at C-3 and one proton at C-2 were eliminated to give compound **2** with α, β-unsaturated carbonyl function, which is due to the active proton at C-2 neighbouring with the C-1 ketone group. The structure of product **2** was elucidated as D-friedoolen-2, 14-dien -1-one -28-oic acid by spectral methods[6], and confirmed that it is also a new compound. Thus, **1** was finally elucidated as 3β-acetoxy-D-friedoolen-14-en-1- one-28-oic acid, named as sebiferone.

Table 1 ^{1}H and ^{13}C NMR spectrum data of compound **1** in $CDCl_3$ (δ_{ppm}, J_{Hz})

Position	δ_C	δ_H	coupling in HMBC
1	210.8		H-2α, H-2β, H-3, H-25
2	40.7	2.97(t, 11.5, H-2β)	
		2.46(dd, 4.7, 11.5, H-2α)	
3	78.6	4.73(dd, 4.7, 11.5)	H-2α, H-2β, H-5, H-23, H-24
4	38.2		H-2α, H-2β, H-3,H-23, H-24
5	53.9	1.03	H-3, H-6β, H-7β, H-23, H-24, H-25
6	18.5	1.45(H-6β)	H-5, H-7β
7	39.8	1.96(H-7β), 1.25(H-7α)	H-5
8	38.9		H-7β, H-9, H-26
9	41.9	2.01	H-7α, H-7β, H-25, H-26
10	53.5		H-2α, H-9, H-5, H-25
11	18.4	1.71(H-11β), 1.64(H-11α)	H-9, H-12α
12	33.5	1.73(H-12β), 1.61(H-12α)	H-27
13	37.5		H-12β, H-12α, H-15, H-18, H-27
14	160.2		H-12α, H-16α, H-16β, H-26
15	116.8	5.51(dd, 3.3, 7.8)	H-16β
16	31.5	2.47(H-16β), 1.97(H-16α)	
17	51.3		H-16α, H-16β, H-18, H-19β, H-19α
18	41.6	2.29(dd, 2.2, 14.7)	H-12α, H-16α, H-16β, H-19α, H-27
19	35.4	1.28(H-19α), 1.16(H-19β)	H-29, H-30
20	29.3		H-19α, H-29, H-30
21	33.7	1.19(H-21β), 1.09(H-21α)	H-19β, H-22β, H-29, H-30
22	30.8	1.68(H-22β), 1.41(H-22α)	H-12α, H-21β
23	28.5	0.94(s)	H-3, H-5, H-24
24	17.4	1.06(s)	H-3, H-5, H-23
25	15.3	1.34(s)	H-5, H-9
26	26.0	0.99(s)	H-7β, H-9
27	22.7	0.99(s)	H-12α, H-12β
28	183.6		H-16α, H-16β, H-18, H-22α
29	31.9[a]	0.94(s)[c]	H-19α, H-21α, H-30
30	28.7[b]	0.91(s)[d]	H-19α, H-21α,H-29
$\underline{CO}CH_3$	169.9		H-3
$CO\underline{CH_3}$	21.0	2.05(s)	

a and b, c and d: assignments may be exchanged.

Acknowledgment

This research was supported by the Teaching and Research Award Program for Outstanding Young Teachers in Higher Education Institutions of MOE, China.

References and Notes

1. E. H. Seip, H. H. Ott, *Planta Medica*, **1983**, *49*, 119.
2. B. P. Pradhan, D. Sibabrat, A. Nath, J. N. Shoolery, *Phytochemistry*, **1984**, *23*, 2593.
3. B. P. Pradhan, H. N. Khastgir, *Ind. J. Chem.* , **1973**, *11*, 1217.
4. W. G. Liu, M. S. Wang, *Nanjing Yaoxueyuan Xuebao*, **1985**, *16*, 69.
5. S. McLean, M. P.-Dumont, W. F. Reynold, H. Jacobs, S. S. Lachmansing, *Can. J. Chem.*, **1987**,*65*,*2519.*
6. Spectrum data of compound **2**: ^{1}HNMR(400MHz, $CDCl_3$) δ 6.31(d, 1H, J=10.1Hz, H-3), 5.66(d, 1H, J=10.1Hz, H-2), 5.53(dd, 1H, J=3.2, 7.8Hz, H-15), 1.28(s, 3H, H-25), 1.25(s, 3H, H-24), 1.13(s, 3H, H-23), 1.07(s, 3H, H-26), 1.02(s, 3H, H-27), 0.95 (s, 3H, H-29), 0.92(s, 3H,

H-30). ^{13}CNMR(100MHz, $CDCl_3$) δ 206.5(C-1), 183.9(C-28), 160.3(C-14), 154.5(C-3), 124.5 (C-2), 116.6(C-15), 51.5(C-5), 51.3(C-9), 49.2(C-17), 41.6(C-10), 41.1(C-18), 39.3(C-7), 39.1 (C-8), 37.4(C-13), 36.2(C-4), 35.4(C-9), 33.8(C-21), 32.0(C-12), 31.5(C-16), 30.8(C-22), 29.7 (C-24), 29.3(C-20), 28.7(C-30), 25.4(C-26), 22.9(C-23), 22.2(C-27), 19.5(C-6), 18.9(C-11), 15.6(C-25).

Received 22 February, 2002