Pergamon 0031-9422(94)00619-9 *Phytochemistry*, Vol. 38, No. 1, pp. 205–207, 1995

0031-9422/95 $9.50 + 0.00

PENTACYCLIC TRITERPENOIDS FROM *MIMUSOPS ELENGI*

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(*Received* 31 *May* 1994)

Key Word Index—*Mimusops elengi*; Sapotaceae; mimusopgenone; mimugenone; triterpenoids.

Abstract—Two new pentacyclic triterpenes, mimusopgenone and mimugenone, were isolated from the seeds of *Mimusops elengi* and characterized as 2β,3β,23-trihydroxy-28-noroleana-5,12-dien-16-one and 3β, 23-dihydroxyoleana-5,12-dien-16-one, respectively, based on their spectroscopic properties.

INTRODUCTION

Triterpenoids have attracted considerable interest in recent years due to the widespread reports on their useful biological activities [1, 2] and practical applications [3–5]. The plant *Mimusops elengi* is widely distributed in India and is held in high repute in Indian traditional medicine [6]. Two new pentacyclic triterpene acids, mimusopic (2β,3β,23-trihydroxy-5,10-friedooleana-9,12-dien-28-oic acid) and mimusopsic [2β, 3β-dihydroxy (23→10) oxido-5,10-friedooleana-9(11),12-dien-28-oic acid] acids, possessing the novel mimusopane (5, 10-friedooleanane) skeleton were isolated form the acidic fraction of the MeOH extract of the seeds of the plant [7]. This paper reports on the isolation and structure elucidation of these two new triterpenoids.

RESULTS AND DISCUSSION

Mimusopgenone (**1**), $C_{29}H_{44}O_4$ ($M^+ = m/z$ 456), appeared to be a nor-triterpene. Its IR spectrum showed absorption bands attributable to hydroxyl groups and a non-conjugated 6-ring ketone. The ^{1}H NMR spectrum showed the presence of two trisubstituted double bonds which was also supported by the ^{13}C NMR spectrum which contained the signals for two sp^2 methine and two sp^2 quaternary carbons. That these two trisubstituted double bonds were at the 5:6 and 12:13 positions was evident from comparison of the ^{13}C values with those of bassic acid [8, 9]. The presence of the 5:6 and 12:13 double bonds was also supported by the fragment ions at m/z 238, 218, 198 and 258 whose formations could be rationalized as shown in the Scheme. Thus the presence of the three hydroxyl groups in the A/B rings and the ketone in the C/D rings was also indicated. Comparison of the ^{13}C values of the carbinyl carbons of **1** with those of bassic acid [9] revealed the presence of the 2β, 3β, 23-trihydroxy functions. Moreover, the presence of mass fragment ions at m/z 258 and 218 and the ^{13}C NMR data of ring D/E carbons suggested the presence of a 16-ketone function. The CD curve of **1** showed a negative Cotton effect and application of the octant rule [10] suggested a *cis* D/E ring system. Thus the structure of mimusopgenone was defined as 2β, 3β, 23-trihydroxy-28-norolean-5,12-dien-16-one (**1**).

Mimugenone (**2**), $C_{30}H_{46}O_3$ ($M^+ = m/z$ 454), showed in its IR spectrum absorption bands indicative of the presence of hydroxyl groups and a saturated 6-ring ketone. The ^{1}H NMR spectrum displayed signals ascribed to seven quaternary methyls, one hydroxymethine, one hydroxymethylene and two trisubstituted double bonds. The nature and positions of the olefinic proton signals were comparable to those of mimusopgenone indicating the presence of 5:6 and 12:13-enes in **2**. The mass spectrum showed fragment ions at m/z 182, 272, 222 and 232 whose formations were rationalized as shown in the Scheme. Thus the formation of these ions also supported the presence of the 5:6 and 12:13 double bonds. The ^{13}C NMR spectrum displayed signals at δ77.5 (*d*) and 67.2 (*t*) assigned to a hydroxyl-bearing methine and a hydroxymethylene, respectively. These data along with the highly shielded methyl signal at δ14.2 assigned to C-24 indicated the presence of 3β,23-dihydroxy functions. The olefinic carbon signals appeared at δ121.1, 142.7, 146.5 and 115.2, and were ascribed to C-11, C-12, C-5 and C-6, respectively (Table 1). The carbonyl carbon signal appeared at δ214.0 and its position at C-16 was inferred from the compatibility of the chemical shift values assigned to D/E ring carbons taking into consideration the effects of 16-ketone. Thus the structure of mimugenone was elucidated as 3β,23-dihydroxyoleana-5,12-dien-16-one (**2**).

EXPERIMENTAL

Mps: uncorr.; TLC: silica gel G (BDH), $CHCl_3$–MeOH–EtOAc (10:1:12); ^{1}H and ^{13}C NMR: 99.6 and

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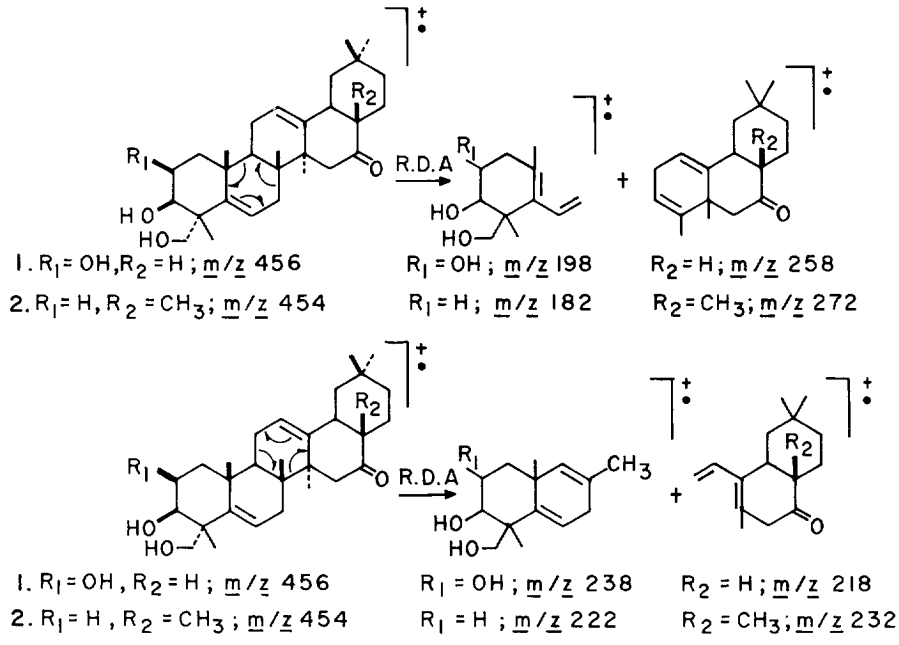

Table 1. ^{13}C Chemical shifts ($\delta_C \pm 0.1$) of mimusopgenone (1) and mimugenone (2) in C_5D_5N

C	1	2
1	43.2[a]	38.2
2	70.8	28.9[a]
3	73.8	77.5
4	45.5	43.3
5	147.1	146.5
6	118.1	115.2
7	34.3	34.5
8	38.3	39.5
9	45.3	40.8
10	37.2	31.9
11	24.1	23.4
12	119.8	121.1
13	143.3	142.7
14	43.2	49.1
15	43.8[a]	42.8
16	213.4	214.0
17	50.2	50.1
18	37.4	37.3
19	44.2	41.9
20	30.7	30.9
21	39.0	29.3[a]
22	23.9	25.0
23	70.2	67.2
24	21.9	14.2
25	23.5	21.6
26	24.9	22.7
27	19.5	19.4
28	—	18.4
29	33.5	32.9
30	24.9	24.7

[a]Assignments may be interchanged in each vertical column.

25.05 or 100 MHz in $CDCl_3$ and C_5D_5N, respectively, with TMS as int. standard; EIMS: direct inlet, 70 eV; IR: KBr discs.

Extraction and isolation. The air dried, powdered seeds of *M. elengi* (1 kg) was first defatted with petrol (60–80°) and then exhaustively extracted with MeOH. The MeOH extract on removal of the solvent under red. pres. yielded a viscous dark brown mass (105 g). The extract was partitioned between *n*-BuOH and H_2O. The *n*-BuOH-soluble part of the MeOH extract (75 g) was hydrolysed with aq. MeOH–HCl (5%) under reflux for 4 hr. The hydrolysate was sepd into acidic and neutral frs by treatment with a satd soln of $NaHCO_3$. The neutral fr. was chromatographed over silica gel and eluted successively with hexane, hexane–$CHCl_3$ (1:1), $CHCl_3$ and $CHCl_3$–MeOH (99:1, 97:3, 19:1, 41:4, 9:1, 17:3).

Isolation of mimusopgenone (1). The $CHCl_3$–MeOH (19:1) fr. was further purified by rechromatography to give a TLC homogeneous fr. This was crystallized from MeOH to yield microneedles (150 mg), mp 268–270°, $[\alpha]_D -4.83°$ (MeOH, *c* 0.24). IR ν_{max}^{KBr} cm^{-1}: 3392, 2936, 1708, 1667, 1626, 1450, 1378, 1288, 1268, 1132, 1048, 815; ^1H NMR (99.6 MHz, $CDCl_3$): δ 0.88 (3H, *s*, Me), 0.90 (3H, *s*, Me), 0.96 (6H, *s*, 2 × Me), 1.34 (3H, *s*, Me), 1.5 (3H, *s*, Me), 3.48 (1H, *d*, $J = 8$ Hz, H-3), 3.78 (2H, *br s*, H-23), 4.1 (1H, *d*, $J = 4$ Hz, H-2), 5.38 and 5.48 (each 1H, each *t*-like, H-12 and H-6); CD (MeOH; *c* 0.001); $[\theta]_{275} -13680°$; ^{13}C NMR (25.05 MHz, C_5D_5N): Table 1; EIMS *m/z* (rel. int.): 456 $[M]^+$ (22), 438$[M-H_2O]^+$ (30), 423$[M-H_2O-Me]^+$ (15), 407$[M-H_2O-CH_2OH]^+$ (20), 393$[M-H_2O-2CH_2OH]^+$ (10), 258 (20), 238 (100), 218 (99.0), 203 (35) and 198 (25). (Found: C, 76.23; H, 9.6; $C_{29}H_{44}O_4$ requires: C, 76.27; H, 9.71%).

Isolation of mimugenone (2). The $CHCl_3$–MeOH (97:3) fr. was purified by rechromatography and the TLC

homogeneous fr. obtained was crystallized from MeOH to yield microneedles, mp 186–188°, $[\alpha]_D$ −3.52 (MeOH, *c* 0.30). IR ν_{max}^{KBr} cm^{-1}: 3392, 2936, 1710, 1670, 1620, 1456, 1380, 1280, 1050, 818; ^1H NMR (99.6 MHz, $CDCl_3$): δ0.92, 0.99, 1.01, 1.08, 1.15, 1.18, 1.27, (each 1H, each *s*, 7 X − Me), 3.04 (2H, *brd*, J = 10 Hz), 3.45 (2H, *brs*, H-23), 3.71 (1H, *t*, H-3), 4.12 (1H, *m*, H-2), 5.71 (1H) and 6.12 (1H) (each *t*-like) (H-12, H-6); CD (MeOH; *c* 0.001): $[\theta]_{275}$ −64857.14°; ^{13}C NMR (100 MHz, C_5D_5N): Table 1; EIMS *m/z* (rel. int.) 454$[M]^+$ (52), 436$[M - H_2O]^+$ (18), 405$[M - H_2O - CH_2OH]^+$ (15), 365 (18), 272 (55), 232 (15), 222 (38) and 182 (20). (Found: C, 79.3; H, 10.1; $C_{30}H_{46}O_3$ requires: C, 79.24; H, 10.20%).

Acknowledgements—We thank Prof. K. Yamasaki, Hiroshima University, School of Medicine, Japan for the ^{13}C NMR spectrum of mimugenone. One of us (S.S.) is thankful to CSIR for financial assistance.

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