Natural Product Sciences
6(2) : 102~105 (2000)

Triterpenoids of *Gordonia dassanayakei*

H. M. T. B. Herath* and P. S. Athukoralage

Natural Products Programme, Institute of Fundamental Studies, Kandy, Sri Lanka.

Abstract – Chemical investigation of the hot hexane extract of the stem bark of *Gordonia dassanayakei* afforded a new oleanane triterpenoid, 11α,13β-dihydroxyolean-3,12-dione (**1**) and two other oleanane triterpenoids, 3β-acetoxy-11α,13β-dihydroxyolean-12-one (**2**) and 3β,11α-diacetoxy-13β-hydroxyolean-12-one (**3**) and a hopane 6α,22-diol (**4**), which are new to the plant.
Key words – *Gordonia dassanayakei,* Theaceae, triterpenoids, oleanane, hopane.

Introduction

Gordonia dassanayakei (Theaceae) has been identified in the recent past, as a new *Gordonia* species endemic to Sri Lanka (Dassanayake *et al.*, 1996). It is a medium sized tree with beautiful reddish-pink flowers. Twelve Theaceae species, under five different genera, are found in Sri Lanka. Among them all four species of genera *Gordonia*, *G. ceylanica*, *G. dassanayakei, G. speciosa* and *G. elliptica* are endemic to the country. "Mihiriya" is the local name for all *Gordonia* species and the colour of the flower is used as an adjective to differentiate some of the species (Dassanayake *et al.*, 1996). Theaceae family have shown a wide range of activity, including anti-tumor, anti-HIV, antibacterial and antifungal (Hatano *et al.*, 1994, Jin *et al.*, 1993 & Hamaya *et al.*, 1986). In addition, various plants of this family are used as remedies for rheumatism, swelling, traumatic bleeding, tropical ulcers and sores (Khan *et al.*, 1992, Inada *et al.*, 1989 & Chang *et al.*, 1994). Although all the *Gordonia* species are being used in traditional medicine in Sri Lanka, no previous chemical investigations have been reported on any of these endemic species. Therefore, the chemical and biological investigations of Sri Lankan *Gordonia* species are of great interest. In our previous work we have reported the isolation and characterization of six oleanane triterpenoids from *G. ceylanica* (Herath *et al.*, 1998, Herath *et al., in press*) and four oleanane triterpenoids and two steroids from *G. dassanayakei* (Herath *et al.*, 1999). This work reports the isolation and characterization of a new oleanan triterpenoid (**1**) and another two structurally related oleanane triterpenoids, 3β-acetoxy-11α,13β-dihydroxyolean-12-one (**2**) and 3β,11α-diacetoxy-13β-hydroxyolean-12-one (**3**) and a hopane type triterpenoid, hopane 6α,22-diol (**4**), which is new to the species. Compounds **2** and **3** have recently been isolated from *G. ceylanica* for the first time (Herath *et al., in press*).

*Author for correspondence.

Experimental

General – Melting points were determined on a Gallenkamp apparatus and are uncorrected. ^{1}H and ^{13}C-NMR (1D) spectra were recorded on either a Varian Unity 300 spectrometer at the Department of Chemistry, University of Wollongong, HMQC and HMBC spectra were recorded on a Varian Unity 400 spectrometer at the Department of Chemistry, University of Wollongong, Australia. IR spectra were recorded on a Shimadzu IR-460 instrument in KBr discs and mass spectra were recorded on a Shimadzu QP-1000A spectrometer at the Institute of Fundamental Studies, Kandy, Sri Lanka. Prep. TLC was carried out on Merck Kieselgel 60 F_{254}. Flash and medium pressure column chromatography were carried out on Merck Kieselgel 60 (230-400 mesh ASTM).

Plant material – The stem bark of *G. dassanayakei* was collected from Nuwara Eliya district in the Central Province of Sri Lanka and the voucher specimen was authenticated by comparison with the herbarium specimen (No. 133) at the National herbarium Royal Botanic Gardens, Peradeniya, Sri Lanka.

Extraction and isolation – Air dried and powdered stem bark (3.2 kg) of *G. dassanayakei* was extracted with hot hexane using a soxhlet apparatus. The con-

centrated hexane extract (8.3 g) was chromatographed on a medium pressure silica gel column and eluted with hexane, dichloromethane and methanol by gradually increasing the polarity gradient. Further purification of the column fractions using small-scale column chromatography followed by prep. TLC and recrystallization etc. afforded compound **1** (27.9 mg). **2** (120.7 mg), **3** (16.7 mg) and **4** (23.8 mg).

11α,13β-Dihydroxyolean-3,12-dione (1): Crystalline needles, mp 219-220°; IR ν_{max} (KBr) cm^{-1}: 3440.0, 2928.0, 1696.0, 1683.2, 1645.0, 1462.4, 1388.8; ^{1}H NMR(300MHz, $CDCl_3$) δ: 4.92(1H, *dd*, *J* = 12.3 & 3.0 Hz, H-11), 3.62(1H, *d*, *J* = 2.9 Hz, 11-OH), 2.70(1H, *m*, H-1a), 2.41(2H, *m*, H-2a & H-2b), 2.10(1H, *ddd*, *J* = 13.5, 13.2 & 3.9 Hz, H-15a), 1.96 (1H, *br.d*, *J* = 12.9 Hz, H-19a), 1.80(1H, *ddd*, *J* = 13.8, 13.2 & 3.9 Hz, H-21a), 1.56(1H, *d*, *J* = 12.3 Hz, H-9), 1.48(1H, *br.d*, *J* = 12.9 Hz, H-18), 1.39 (3H, *s*, C_{26}-Me), 1.22(3H, *s*, C_{29}-Me), 1.17(3H, *s*, C_{25}-Me), 1.08(3H, *s*, C_{23}-Me), 1.06(3H, *s*, C_{24}-Me), 0.93(3H, *s*, C_{30}-Me), 0.92(3H, *s*, C_{27}-Me), 0.87(3H, *s*, C_{28}-Me); ^{13}C NMR(75 MHz, $CDCl_3$) δ: 217.9(C-3), 210.9(C-12), 82.4(C-13), 72.2(C-11), 56.2(C-9), 55.1(C-5), 49.2(C-18), 47.8(C-4), 45.4(C-14), 43.2 (C-8), 41.1(C-1), 39.0(C-22), 38.8(C-10), 38.6(C-19), 34.2(C-2), 33.9(C-7), 33.6(C-20), 33.1(C-16), 31.8(C-29), 31.3(C-28), 30.7(C-21), 25.2(C-30), 29.7 (C-17), 26.9(C-23), 25.2(C-30), 22.6(C-15), 21.0(C-24), 19.8(C-26), 19.1(C-6), 18.2(C-27), 15.9(C-25); EIMS (70 eV) *m/z*(rel.int.%): 472(M^+ ,22), 458(2), 455(82), 438(9), 397(3), 343(3), 287(100), 197(18), 179(16), 153(40), 81(40).

3β-acetoxy-11,13-dihydroxyolean-12-one (2): Colourless needles, mp 286-287°; IR ν_{max} (KBr) cm^{-1}: 3498.0, 2925.0, 1710.0, 1230.0; ^{1}H-NMR (200 MHz, $CDCl_3/CD_3OD$) δ 4.86(1H, *d*, *J* = 12.1 Hz, H-11), 4.40(1H, *dd*, *J* = 10.2 & 7.4 Hz, H-3), 3.05(1H, *s*, -OH), 2.46(1H, *ddd*, *J* = 14.0, 3.6 & 3.6 Hz, H-18), 1.98(3H, *s*, $-OCOCH_3$), 1.31, 1.15, 1.07, 0.87, 0.84(each 3H, *s*, 5 x CH_3), 0.82(6H, *br. s*, 2 x CH_3), 0.79 (3H, *s*, CH_3); ^{13}C-NMR (50 MHz, $CDCl_3$/ CD_3OD) δ 201.2(C-12), 171.5($O\underline{C}OCH_3$), 81.5(C-13), 80.8(C-3), 71.9(C-11), 56.7(C-9), 55.2(C-5), 44.9(C-18), 44.9(C-14), 43.1(C-8), 39.6(C-10), 39.1 (C-16), 38.4(C-4), 38.1(C-1), 37.9(C-19), 33.7(C-21), 33.2(C-7), 31.4(C-17), 31.0(C-30), 30.4(C-22), 29.3(C-28), 29.3(C-29), 27.7(C-20), 27.7(C-23), 24.7(C-2), 23.4(C-27), 22.3($OCO\underline{C}H_3$), 20.7(C-15), 20.2(C-26), 17.9(C-6), 17.2(C-25), 15.9(C-24); MS (70 eV) *m/z* = 516 (M^+, 0.5), 498(1), 483(5), 219 (20), 208(22), 109(18), 95(38), 43(100).

3β,11-diacetoxy-13-hydroxyolean-12-one (3): Colourless needles, mp 340°; IR ν_{max} (KBr) cm^{-1}: 3456.0, 2960.0, 1737.8, 1708.8, 1628.0, 1456.0, 1366.4, 1267.2, 1241.6, 1024.0; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.11 (1H, *d*, *J* = 12.3 Hz, H-11), 4.45 (1H, *dd*, *J* = 9.9 & 7.5 Hz, H-3), 2.14 (3H, *s*, $OCOCH_3$), 2.04 (3H, *s*, $OCOCH_3$), 1.41, 1.20, 1.02, 0.96, 0.91, 0.87, 0.87, 0.86 (each 3H, *s*, 8 x CH_3); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 202.4(C-12), 170.9($O\underline{C}OCH_3$), 170.1 ($O\underline{C}OCH_3$), 82.8(C-13), 80.0(C-3), 74.2(C-11), 55.0(C-5), 53.8(C-9), 48.8(C-18), 44.6(C-14), 43.8 (C-8), 39.7(C-10), 39.2(C-16), 39.0(C-19), 38.4(C-1), 38.3(C-4), 34.3(C-21), 33.9(C-7), 33.5(C-17), 33.4(C-20), 32.0(C-29), 31.3(C-28), 30.3(C-22), 28.1 (C-23), 24.7(C-30), 23.8(C-2), 22.7(C-15), 21.4 ($OCO\underline{C}H_3$), 21.3($OCO\underline{C}H_3$), 20.7(C-26), 18.6(C-27), 17.6(C-6), 16.4(C-24), 16.2(C-25); MS (70 eV) *m/z* = 558 (M^+, 1), 541(95), 499(20), 481(100), 439 (80), 421(35), 263(20), 203(22).

Hopane 6α,22-diol (4): Crystalline needles mp 226-227° {Lit. Elix *et al.*, (mp 223-227°)}; IR ν_{max} (KBr)cm^{-1}: 3428.0, 2928.0, 1522.0, 1470.0, 1420.8; ^{1}H NMR(300 MHz, $CDCl_3$) δ : 3.93(1H, *ddd*, *J* = 12.0, 10.3 & 4.2 Hz, H-6), 2.18(1H, *m*), 1.18, 1.16, 1.13, 1.02, 0.99, 0.95, 0.84, 0.74(each 3H, *s*, 8 x CH_3); ^{13}C NMR(75 MHz, $CDCl_3$) δ: 73.9(C-22), 69.3 (C-6), 61.1(C-5), 54.0(C-17), 51.5(C-21), 49.8(C-13), 49.4(C-9), 45.5(C-7), 43.9(C-18), 43.8(C-3), 42.9 (C-8), 41.9(C-14), 41.2(C-19), 40.3(C-1), 39.3(C-10), 36.8(C-23), 34.3(C-15), 33.6(C-4), 30.9(C-30), 28.7 (C-29), 26.6(C-20), 24.0(C-12), 22.1(C-24), 21.9(C-16), 21.1(C-11), 18.5(C-2), 18.3(C-26), 17.1(C-25), 17.1(C-27), 16.1(C-28); EIMS (70 eV) m/z(rel. int %): 444(M^+, 12), 427(50), 409(100), 369(20), 219 (95), 207(35), 191(80), 189(40), 149(85), 109(32), 81(42).

Results and Discussion

The molecular ion peak appeared at *m/z* 472 in the mass spectrum suggested that the molecular formula $C_{30}H_{48}O_4$ for compound **1**. The thirty well-resolved signals appeared in the ^{13}C-NMR spectrum was strongly supported to confirm that the proposed molecular formula for compound **1**. Two down field signals at δ 217.9 and 210.9 in ^{13}C-NMR of **1** indicated the presence of two carbonyl groups (C-3 and C-12) in the molecule. Furthermore, the eight characteristic methyl signals, nine methylene carbons,

Table 1. Correlations indicated in the HMQC and HMBC spectra of compound **1**

Atom No	^{13}C NMR	^{1}H NMR	HMBC
C-9	56.2	1.56	15.9(C-25), 19.7(C-26)
C-11	72.2	4.92	56.1(C-9), 210.9(C-12)
11-OH	–	3.62	56.1(C-9), 210.9(C-12)
C-23	26.9	1.08	217.9(C-3), 47.8(C-4), 55.1(C-5), 21.0(C-24)
C-24	21.0	1.06	217.9(C-3), 47.8(C-4), 55.1(C-5), 26.9(C-23)
C-25	15.9	1.17	41.1(C-1), 55.1(C-5), 56.1(C-9), 38.8(C-10)
C-26	19.8	1.39	33.9(C-7), 43.2(C-8), 56.1(C-9), 45.4(C-14)
C-27	18.2	0.92	43.2(C-8), 82.2(C-13), 45.4(C-14), 22.6(C-15)
C-28	31.3	0.87	33.1(C-16), 29.7(C-17), 49.2(C-18), 39.0(C-22)
C-29	31.8	1.22	38.6(C-19), 33.6(C-20), 30.7(C-21), 25.2(C-30)
C-30	25.2	0.93	38.6(C-19), 33.6(C-20), 30.7(C-21), 31.8(C-29)

four methaine carbons and seven quaternary carbons appeared in the DEPT spectrum of **1** was in concurred with the typical signals induced by the oleanane triterpenoid skeleton. In addition to the two carbonyl groups the occurrence of two other oxygen bearing carbon atoms in the molecule was indicated by the two signals at δ 72.2 and 82.2 in the ^{13}C-NMR spectrum of **1**. According to the DEPT spectrum, carbon represented by δ 72.2 should be a methaine carbon and the carbon at 82.2 should be a tertiary carbon. Therefore, these two signals were assigned to C-11 and C-13 respectively. Proton attach to C-11 was appeared as a double doublet at δ 4.92 in the ^{1}H-NMR spectrum of **1** due to the coupling of 9-H proton (J = 12.3 Hz) and the hydroxyl proton attach to C-11 (J = 3 Hz). The above *trans* diaxial coupling constant between H-9 and H-11 and the chelation of the 11-hydroxyl group with C-12 carbonyl suggested the α configuration of the hydroxyl group attach to C-11. The configuration of the C-13 hydroxyl should be β to have the stable triterpenoid skeleton. Further, the strong correlation of eight methyl groups with their respective carbons indicated in the HMBC spectrum of **1** (table-1), the correlation of 9-H, 11-H and the hydroxyl proton with their neighboring carbons also provided concrete evidence to confirmed the structure, 11α,13β-dihydroxyolean-3,12-dione for compound **1**, which was suggested by ^{1}H, ^{13}C and the other spectral data.

The comparison of the spectral data, mp and co-tlc studies were confirmed the structures of compounds **2** and **3** as 3β-acetoxy-11α,13β-dihydroxyolean-12-one and 3β,11α-diacetoxy-13β-hydroxyolean-12-one, which have been isolated very recently from *G. ceylanica* (Herath *et al.*, *in press*).

The ^{1}H and ^{13}C-NMR spectral data of compound **4** illustrated the presence of eight characteristic methyl signals analogous to the triterpene skeleton. Additional information provided by the HMQC and HMBC spectra suggested that the compound **4** should be a hopane type triterpenoid. Two down field signals appeared at δ 69.3 and 73.9 in the ^{13}C-NMR of **4** indicated the two carbons bearing hydroxyl groups, while the DEPT spectrum of **4** showed that the above signals are denoting the methaine and quaternary carbons respectively. Therefore with the additional support of the other spectral data these two signals were assigned to C-6 and C-22 carbons. Hence the structure of **4** was suggested as hopane 6,22-diol. Further the mp and the ^{1}H and ^{13}C-NMR spectral data of compound **4** were identical with the values reported for hopane 6α,22-diol (Zeorin) (Elix *et al.*, 1982).

Acknowledgements

Authors wish to thank Mr. Aruna Weerasooriya of the Department of Botany, University of Peradeniya, Sri Lanka for collection and identification of the plant materials, Dr. Joanne Jamie of the Department of Chemistry, University of Wollongong, NSW 2522, Australia for some of the NMR spectral data and Technical staff of the Natural Products programme at the Institute of Fundamental Studies, Kandy, Sri Lanka.

References

Chang, C. W., Yang, L. L., Yen, K. Y., Hatano, T., Yoshida, T. and Okudia, T. (1994). New γ-Pyrone Glucoside, and Dimeric Ellagitannins from *Gordonia axillaris*. *Chem. Pharm. Bull.* **42**(9), 1922.

Dassanayake, M. D., Clayton, W. D. A. (1996). *Revised Handbook of the flora of Ceylon*, Volume **10**,

Oxford IBH Publishing Co. Ltd. New Delhi:, 336-396.

Elix, J. A., Whitton, A. A. and Jones A. L. (1982). Triterpenes from the Lichen Genus *Physcia*. *Aust. J. Chem.*, **35**, 641.

Hamaya, E., Manabe, S. and Enoki, N. (1986). Triterpene Saponins from *Camellia* leaves as microbicides. *Jpn. Kokai* Takkyo Koho JP 61 07, 290 (8607, 290) CCl.C07H15/256), 5pp; *Chem. Abst.* 1986, **105**, 110508 r.

Hatano, T., Han, L., Taniguchi, S., Chou, T., Shingu, T., Sakagami, H., Takeda, M., Nakashima, H. and Murayama, T. (1992). AntiHIV tannins from *Camellia japonica* and related species. *Tennen Yuki Kagobutsu Toronkai Koen Yoshishu*, **34**, 510; *Chem. Abst.* (1994). **120**, 253139 s.

Herath, H.M.T.B. and Athukoralage, P. S. (1998). Oleanane triterpenoids from *Gordonia ceylanica*. *Nat. Prod. Sci.* **4**(4), 253.

Herath, H.M.T.B., Athukoralage, P. S. and Jamie, J. F., (1999). Triterpenoids and Steroids from *Gordonia dassanayakei*. *ACGC Chem. Res. Comm.* **9**, 3.

Herath, H.M.T.B., Athukoralage, P. S. and Jamie, J. F., (*in press*). Two new oleanane triterpenoids from *Gordonia cylanica* and their conversions to taraxarane triterpenoids. *Phytochemistry.*

Inada, A., Fujiwara, M., Kakimoto, L., Kitamura, F., Toya, H., Konishi, M., Nakanishi, T. and Murata, H. (1989). Structure of a New Acetylated Flavonoid Glycoside, Euryanoside from the Flowers of *Eurya japonica* THUNB. *Chem. Pharm. Bull.* **37**, 2819.

Jin, J., Du, S. and Zhong, M. (1993). Studies on antifungal active constituents in the oil

cakes of *Camellia oleifera*. *Tianran Chanwu Yanjiu Yu Kaifa*, **5**(2), 48; *Chem. Abst.* (1994). **121**, 53897 w.

Khan, I. A., Erdelmeier, C. A. J. and Sticher, O. (1992). New Phenolic Glucosides from the Leaves of *Eurya tigang*. *J. Nat. Prod.* **55**(9), 1270.

(Accepted June 3, 2000)