

CHEMISTRY IN THE ANNONACEAE, XXIII.¹
24-METHYLENE-LANOSTA-7,9(11)-DIEN-3 β -OL FROM
ARTABOTRYS ODOROTISSIMUS STEM BARK

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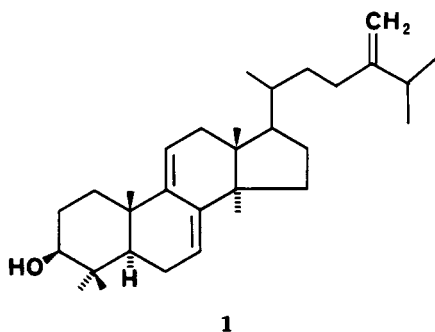
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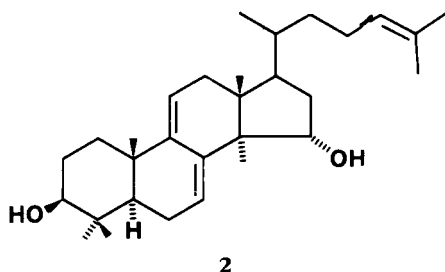
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Artabotrys odoritissimus R. Br. (Annonaceae) is a shrub native to eastern Asia and is cultivated widely in Bangladesh (1). The fruits are recorded as containing fixed and volatile oils, glycosides, and resin; extracts are reported to exhibit hypotensive and spasmogenic effects (2). Decoctions of the leaves are used as a remedy for cholera (1) and have been found to exhibit antifertility effects in rats (3). Other species of *Artabotrys* are reported to contain aporphine alkaloids (4,5), cyanogenic glycosides (6), and sesquiterpenes (6).

Extraction of the stem bark with petroleum ether followed by preparative tlc and then column chromatography gave 24-methylene-lanosta-7,9(11)dien-3 β -ol [**1**] in a yield of 0.003%. The ¹H-nmr spectrum of **1** indicated the presence of two olefinic protons, an exo methylene, three secondary and five tertiary methyls, and an axial oxymethine, and the high resolution eims revealed a molecular ion that analyzed for C₃₁H₅₀O. These data suggested a 24-methylene sterol, and this was substantiated by the loss in the eims of a 9-C unit due to the C-17 side chain. The conjugated 7,9(11)-diene system was indicated by the uv maxima in the region 230-260 nm. The identity of **1** was further confirmed by the co-incidence of ¹³C-nmr (Table 1) and ¹H-nmr data with that reported for the closely related



1



2

ganodermediol (7) and cycloeucaneol (8).

This appears to be the first definite report of the occurrence of **1**, although it was tentatively identified as a minor component of *Euglena gracilis* chloroplasts (9). Few triterpene derivatives have been reported from the Annonaceae, but the most common, polycarpol [**2**], which is also a lanosta-7,9(11)-diene, is regarded as a useful chemotaxonomic marker (6).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—

Melting points are uncorrected. Uv spectra were measured in MeOH and ir spectra as nujol mull.

¹For Part XXII, see J. T. Etse and P. G. Waterman, *J. Nat. Prod.*, **49**, 684 (1986).

TABLE 1. ^{13}C -nmr Spectral Data of **1** and Comparison with Published Data for the Sterol Nucleus of Ganodermediol (7) and 24-Methylene Side Chain of Cycloeucaneol (8)

Carbon No.	Compounds		
	1	Ganodermediol	Cycloeucaneol
1	35.7(t)	35.8(t)	
2	27.8(t)	28.2(t)	
3	78.9(d)	79.0(d)	
4	38.6(s)	38.7(s)	
5	50.3(d)	50.4(d)	
6	22.9(t)	23.1(t)	
7	120.1(d)	120.3(d)	
8	142.7(s)	142.7(s)	
9	145.9(s)	145.9(s)	
10	37.3(s)	37.3(s)	
11	116.2(d)	116.3(d)	
12	37.8(t)	37.9(t)	
13	43.7(s)	43.8(s)	
14	49.1(d)	49.2(d)	
15	27.8(t)	28.0(t)	
16	31.4(t)	31.5(t)	
17	50.9(d)	50.9(d)	52.0(d)
18	15.6(q)	15.7(q)	
19	22.6(q)	22.8(q)	
20	36.2(d)	36.1(d)	36.0(d)
21	18.4(q)	18.4(q)	18.3(q)
22	34.9(t)		35.0(t)
23	31.3(t)		31.3(t)
24	156.8(s)		156.2(s)
25	33.8(d)		33.7(d)
26	21.8(q) ^a		21.8(q)
27	21.9(q) ^a		21.8(q)
28	25.5(q)	25.6(q)	
29	28.1(q)	27.8(q)	
30	15.7(q)	15.8(q)	
31	105.9(t)		105.6(t)

^aInterchangeable.

^1H -nmr spectra were run at 360 MHz and ^{13}C -nmr spectra at a 90.56 MHz in CDCl_3 using TMS as internal standard. High resolution eims were obtained on an AEI MS902 double-focusing instrument by direct probe insert at elevated temperature and 70 eV.

PLANT MATERIAL.—Stem bark was collected from plants growing in the area of Curzon Hall on the campus of Dhaka University. A voucher specimen has been deposited at the Herbarium of the university.

ISOLATION OF 24-METHYLENE-LANOSTA-7, 9(11)-DIEN-3 β -OL [1].—Ground stem bark (500 g) was successively extracted with petroleum

ether (bp 40–60°), CHCl_3 , and then MeOH. The petroleum ether extract was concentrated and subjected to preparative tlc over Si gel eluting with petroleum ether (bp 60–80°)–EtOAc (4:1). A blue fluorescent band (R_f 0.75) was separated and eluted with CHCl_3 to give crude **1** which was then purified by column chromatography over Si gel, eluting with petroleum ether (bp 60–80°)–EtOAc (17:3) to give **1** (15 mg).

24-Methylene-lanosta-7,9(11)-dien-3 β -ol [1].—Needles from $\text{CHCl}_3/\text{EtOAc}$, mp 168–173°, $[\alpha]^{25} + 51.3^\circ$ ($c=0.078$, CHCl_3); uv max 232, 242, 252 nm; ir max 3450 (OH), 1640 (CH_2) cm^{-1} ; ^1H nmr δ 0.56 (s, 3H, 18-H), 0.87 (s, 6H, 28-H, 30-H), 0.90 (d, $J=6.4$ Hz, 3H, 21-H), 0.97 (s, 3H, 29-H), 1.00 (s, 3H, 19-H), 1.01, 1.02 ($2\times d$, $J=6.8$ Hz, $2\times 3\text{H}$, 26-H, 27-H), 3.24 (dd, $J=11.0$, 4.6 Hz, 3-H), 4.65, 4.71 ($2\times$ br. s, $2\times 1\text{H}$, 31-H), 5.30 (d, $J=6.6$ Hz, 1H, 7-H), 5.46 (br. s, 1H, 11-H) ppm; ^{13}C nmr—see Table 1; eims (m/z , rel. int.) 438 (M^+ , 100), 423 (438- CH_3 , 8), 311 (438- C_9H_{17} [side-chain]-2H, 22), 272 (3), 171 (3), 95 (9), 83 (8), 69 (19); Calcd. for $\text{C}_{31}\text{H}_{50}\text{O}$ 438.3861, found (eims) 438.3871.

ACKNOWLEDGMENTS

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