Wrightial, a New Terpene from Wrightia tinctoria

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WRIGHTIAL, A NEW TERPENE FROM *WRIGHTIA TINCTORIA*

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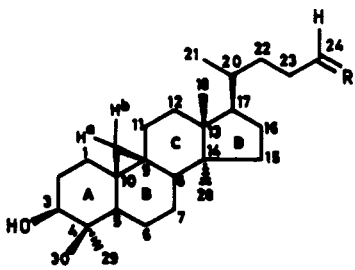
ABSTRACT.—Wrightial [**1**], a new terpene, cycloartenone, cycloeucalenol, β-amyrin, and β-sitosterol were isolated from the MeOH extract of the immature seed pods of *Wrightia tinctoria*. The structure of **1** was established from spectral analysis and by chemical correlation.

Wrightia tinctoria (Roxb.) R.Br. (Apocynaceae) (1) is extensively used in the Indian system of medicine (2). The oil emulsion of the pods, "777 Oil," is used to treat psoriasis [Clinical and Experimental Studies on the Efficacy of 777 Oil, A Sidda Preparation in the Treatment of Kalanjagapadia (Psoriasis), Symposia conducted by the Central Council for Research in Ayurveda and Sidda (Ministry of Health and Family Welfare), Govt. of India, New Delhi (1987)]. The bark and seeds are antidysenteric and also used for stomach pain and toothache. Earlier chemical examination of leaves and pods of *W. tinctoria* led to the isolation of α-amyrin, β-amyrin, β-sitosterol, oleanolic acid, ursolic acid (3,4) and indigo (5). We now report the chemical constituents of immature seed pods.

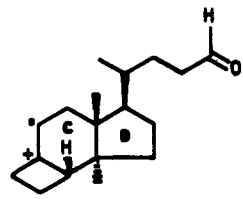
RESULTS AND DISCUSSION

Column chromatography of the MeOH extract of the immature seed pods gave five colorless compounds. Four of these compounds were identified as cycloartenone, β-amyrin, cycloeucalenol, and β-sitosterol from spectral data and by direct comparison with authentic samples.

Wrightial [**1**], mp 99°, $[\alpha]^{20}D$ +18.33 (c=1.01, MeOH), $C_{27}H_{44}O_2$ $[M]^+$ at m/z 400. Ms of **1** showed intense ions at m/z 260 and 175 (Scheme 1) that are characteristic of cycloartanes indicating that **1** has the same ABCD ring system as that of cycloartenol (6). The ^{1}H-nmr spectrum of **1** (200 MHz) showed a two-proton AB quartet at δ 0.32 (J_{AB}=4.0 Hz) and δ 0.52 (J_{AB}=4 Hz), characteristic of C-19 cyclopropane methylene protons. The triplet at δ 9.77 (J=1.0 Hz) is assignable to an aldehydic proton and suggests a CH_2-CHO group. The ir absorption at 1715 cm^{-1} and 2780 cm^{-1} are also characteristic of an aldehydic function. The uv spectrum showed an absorption maximized at 280 nm (log ε 1.5). The ^{13}C-nmr (75 MHz) spectrum showed the aldehydic carbon at 203 ppm. Further, the ^{13}C resonances of the ABCD ring carbons of wrightial [**1**] are the same as those reported for cycloartanol (7). Compound **1**, on Wittig synthesis using 2-bromopropane, afforded cycloartenol [**2**].



1 R=O
2 R=C(Me)(Me)



m/z 260
↓ −side chain
m/z 175

3

SCHEME 1

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp's are uncorrected. The ir and uv spectra were recorded on a Shimadzu instrument in KBr and MeOH. ^{1}H-nmr spectra were taken on Varian Gemini 200 MHz and ^{13}C-nmr spectra on Bruker (75 MHz) spectrometer in $CDCl_3$ with TMS as internal standard. Mass spectra were recorded on CEC-21-110B double focussing mass spectrometer operated at 70 eV. Si gel (200 mesh Acme) was used for cc.

EXTRACTION AND ISOLATION.—The immature seed pods of *W. tinctoria* (1.00 kg) were collected from Mannanoor forest, Andhra Pradesh, India, during April–July (flowering and fruiting) 1990, and a specimen (No. STR 498) of the plant is kept in the Botany Department, Osmania University. Pods were dried, powdered, and extracted with MeOH in a Soxhlet extractor and concentrated to yield a dark brown gum (70.0 g). It was then column chromatographed over Si gel eluting with petroleum ether, C_6H_6, and $CHCl_3$. Compounds were obtained in the following order.

Cycloartenone.—The petroleum ether (60–80°)-C_6H_6 (1:1) eluate gave a colorless compound that was recrystallized from C_6H_6/MeOH, mp 102–103° [lit. (8) mp 109°] (200 mg). The compound was identified by comparison of spectral data reported for cycloartenone (6,8). ^{1}H nmr δ 5.10 (1H, m), 1.60–1.65 (Me×2), 0.9–1.20 (Me×4) 0.40 and 0.60 (H-19, ABq, 4.0 Hz).

β-*Amyrin.*—The petroleum ether-C_6H_6 (1:1) eluate also gave a white solid that crystallized from $CHCl_3$, mp 196° [lit. (3) mp 197.5°] (1.5 g) which was identified by direct comparison with an authentic sample.

Wrightial [**1**].—The $CHCl_3$ eluate gave a colorless white solid, mp 99° (100 mg). Analysis C 80.92, H 10.86; $C_{27}H_{44}O_2$ requires C 81.00, H 11.00. $[\alpha]^{20}D$ +18.33 (c=1.01, MeOH); ir ν max 3420, 2920, 2780, 1715, 1440, 1370, 1040 cm^{-1}; uv λ max (MeOH) 280 nm (log ε 1.5); ^{1}H nmr (200 MHz) ($CDCl_3$) δ ppm 9.77 (t, 1.0 Hz), CHO 3.25 (m, H-3), 0.80–1.00 (Me×4), 0.32 and 0.52 (2H, ABq, 4.0 Hz, H-19); ^{13}C nmr (75 MHz) ($CDCl_3$) 31.97 (t, C-1), 30.38 (t, C-2), 78.83 (d, C-3), 40.48 (s, C-4), 47.11 (d, C-5), 21.1 (t, C-6), 28.08 (t, C-7), 47.98 (d, C-8), 19.97 (s, C-9), 26.12 (s, C-10), 25.99 (t, C-11), 35.53 (t, C-12), 45.37 (s, C-13), 48.83 (s, C-14), 32.90 (t, C-15), 26.44 (t, C-16), 52.17 (d, C-17), 18.03 (q, C-18), 29.85 (t, C-19), 35.67 (d, C-20), 28.08 (q, C-21), 28.27 (t, C-22), 29.68 (t, C-23), 203.11 (d, C-24), 19.31 (q, C-28), 25.43 (q, C-29), 13.98 (q, C-30); ms *m/z* (rel. int. %) $[M]^+$ 400 (5), 383 (10), 339 (12), 325 (5), 313 (7), 260 (20), 175 (30), 149 (40), 43 (100).

CONVERSION OF **1** TO **2**.—Isopropyl triphenyl phosphonium bromide (1.2 equiv.) was stirred in dry THF (5 ml) and cooled in a dry ice/Me_2CO bath, and *n*-butyl lithium (1.2 equiv.) was slowly added. The reaction mixture was stirred for 0.5 h and allowed to settle. Wrightial (10 mg) in dry THF (5 ml) was cooled in ice/salt bath, and to this was added the supernatant solution of ylide. The reaction mixture was stirred for 0.5 h at the same temperature. MeOH (1 ml) was added and the solvent was evaporated. The product was purified by SiO_2 cc using petroleum ether-$CHCl_3$ (1:1) as the eluent, which yielded cycloartenol [**2**] (5 mg).

Cycloeucalenol.—Mp 140° [lit. (9) mp 138–139°] (300 mg) identified by comparison of its ir, ^{1}H-nmr, and mass spectral data with spectral data reported for cycloeucalenol (9).

β-*Sitosterol.*—The $CHCl_3$ eluate gave a colorless white solid (2.0 g) that crystallized from $CHCl_3$, mp 136° [lit. (4) mp 137°], and was identified by direct comparison with an authentic sample.

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