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INSECT GROWTH INHIBITOR FROM THE BARK OF *SANTALUM ALBUM*

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Key Word Index—*Santalum album*; Santalaceae; bark; insect growth inhibitor; triterpene; urs-12-en-3β-yl palmitate.

INTRODUCTION

The sandal tree is exploited at present for its scented heartwood which gives the fragrant sandalwood oil. A large quantity of sandal bark, which does not find any use at present, is available in sandal forests. Experiments were undertaken for the first time to explore the possible uses of this waste material. This report deals with one of the constituents of the benzene extract of sandal bark, which exhibits an excellent insect growth inhibiting property and chemosterilant activity.

RESULTS

The isolated triterpenoid (**1**), 115–116°, $[\alpha]_D^{24}+20°$ had the formula $C_{46}H_{80}O_2$ and was identified by MS and ^{1}H NMR as urs-12-en-3β-yl palmitate.

The topical application of **1** in microdoses on freshly formed pupae of the economically important forest insects (viz. *Atteva fabriciella*, *Eligma narcissus*, *Eupterote geminata*, etc.) produced morphologically defective adults with crumpled wings and shorter abdomen, suggesting a growth inhibition activity of the compound [1]. In another experiment, it was found that freshly emerged moths of *Atteva fabriciella*, fed with a glucose solution containing a minute quantity of the compound **1**, did not mate and lay eggs, indicating the possible use of this compound as a 'chemosterilant'. Such compounds, of late, are becoming popular as 'third-generation pesticides' [2] in controlling forest pests without the bad side effects (like toxicity, environmental pollution, etc.) generally possessed by common organic pesticides.

The IR spectrum of **1** showed a prominent band at 1740 cm^{-1} (ester absorption) and a weak band at 850 cm^{-1} (trisubstituted double band). $LiAlH_4$ reduction of **1** gave two alcohols: **i**, mp 49–50°, and **ii**, mp 169–171°. Alcohol **i** was identified by GLC as cetyl alcohol. Alcohol **ii** gave a violet colour with the Liebermann–Burchard test and had an IR spectrum comparable with the reported spectrum of urs-12-en-3β-ol [3,4]. Its MS had an M^+ peak at *m/e* 426, a base peak at 218 and another significant peak at 189, which are characteristic of the retro-Diels–Alder fragmentation of $\Delta^{12(13)}$-unsaturated triterpenes [5–7]. The ^{1}H NMR spectrum of the acetate (mp 262–265°) of alcohol **ii**, had a characteristic doublet ($J = 10$ Hz) at δ 2.23, attributed to the C-18 proton in a Δ^{12}-ursene compound [8], followed by a complex pattern of six tertiary methyls and two secondary methyls, inclusive of one doublet ($J = 8$ Hz) at δ 0.87.

The above data and results were consistent with the identification of urs-12-en-3β-yl palmitate (**1**). However, some discrepancies in mps were observed. We found that the mps of **1**, **ii**, the acetate of **ii** and the ketone of **ii** differed from the corresponding reported mps [9]. The differences in the mps are probably due to the solvent used during the crystallization or to the possible existence of polymorphism or liquid crystal phenomena, which may, perhaps, be of common occurrence among triterpenoids [10, 11].

EXPERIMENTAL

After extraction with petrol (bp 60–80°) air-dried powdered bark was dried and extracted with C_6H_6 under reflux. A highly viscous extract (2–3% yield) was obtained which was chromatographed over basic Al_2O_3 (1:30). The elute with petrol was dissolved in hot Me_2CO and chilled to −5°. The crude solid (mp 96–98°) was filtered off and rechromatographed (×3) over active Al_2O_3 (1:100), the petrol elute being taken up each time for subsequent chromatography. After the third chromatography, the petrol elute was repeatedly crystallized to mp 111° (Me_2CO–MeOH, 3:1) and finally purified on a $AgNO_3$–Si gel to give the triterpenoid **1** with a yield of 0.1–0.3%, mp 115–116°, $[\alpha]_D^{24}+20°$ ($CHCl_3$, *c* 0.5) and IR ν_{max}^{Nujol} cm^{-1}: 1740, 1000, 870. (Found: C, 82.81; H, 11.78. Calc. for $C_{46}H_{80}O_2$: C, 83.13; H, 12.05%.) Reduction of **1** with $LiAlH_4$ gave 2 alcohols: **i**, mp 49–50°, and **ii**, mp 169–171°. The acetate of **i** was identical with authentic cetyl acetate (GLC: 10% Carbowax on celite, 190°). Alcohol **ii** had IR ν_{max}^{Nujol} cm^{-1}: 3400–3300 (OH), 1045, 860; MS (70 eV) *m/e* (rel.int.): 426 (M^+, 43), 257 (7), 218 (100), 207 (27), 189 (73). Acetylation of **ii** with Ac_2O in Py, gave an acetate, mp 262–265°, which had a M^+ peak at *m/e* 468. ^{1}H NMR (100 MHz, $CDCl_3$); δ 4.86 (*br*, vinylic H), 4.47 (CHOAc, *m*), 2.23 (C-18H, *d*, $J = 10$ Hz), 2.00 (3H, *s*, $OCOCH_3$), 1.08 (3H, *s*, *tert.* Me), 1.00 (3H, *s*, *tert.* Me), 0.87 (9H, *d*, $J = 8$ Hz, 2 *sec.* Me's, and one *tert.* Me), 0.84 (6H, *s*, 2 *tert.* Me's) and 0.73 (3H, *s*, *tert.* Me). (Found: C, 82.12; H, 11.45. Calc. for

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$C_{32}H_{52}O_2$: C, 82.05; H, 11.11%.) Oxidation of **ii** with a CrO_3–Py complex [12] gave a ketone, mp 180–182°, IR ν_{max}^{Nujol} cm^{-1}: 1710, 845. (Found: C, 84.86; H, 11.50. Calc. for $C_{30}H_{48}O$: C, 84.9; H, 11.32%.)

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LANOSTEROL, THE FIRST POLYCYCLIC INTERMEDIATE IN STEROL BIOSYNTHESIS BY *UROMYCES PHASEOLI**

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INTRODUCTION

Dichotomy at the point of cyclization of squalene has been well established in sterol biosynthesis; lanosterol is the first polycyclic compound in the biosynthesis of sterols in animals while cycloartenol is found in photosynthetic plants and algae [1, 2]. Fungi have been considered to follow the pathway operating in animals. Support for this conclusion came from the isolation of lanosterol from *Saccharomyces cerevisiae* [3], *Phycomyces blakesleeanus* [4] and *Aspergillus fumigatus* [4] and from the demonstration of 2,3-oxidosqualene-lanosterol cyclase in cell-free preparations of *Saccharomyces cerevisiae* [5] and *Phycomyces blakesleeanus* [6]. Furthermore, other lanostane-type structures have been found in some of the wood-rotting fungi [7] but cycloartenol has not been detected in any fungi whose sterol contents have been determined [7, 8]. The conclusion that lanosterol is the first polycyclic precursor in fungi is based on a generalization drawn from the three species mentioned above which contain lanosterol in detectable amounts.

It has been observed previously that photosynthetic organisms synthesize cycloartenol, yet both lanosterol and cycloartneol are utilized equally well in the synthesis of 4-desmethyl sterols [9]. However, in rat liver, cycloartenol is not metabolized to 4-desmethyl sterols whereas lanosterol is utilized [9]. To our knowledge, lanosterol and cycloartenol utilization studies have not been carried out for any fungal species. Thus the purpose of this work was to determine the first polycyclic product in sterol biosynthesis for *Uromyces phaseoli*, which is an obligately parasitic fungus that differs taxonomically from the fungi mentioned above. Cycloartenol and lanosterol have not been detected among the sterols of this organism [10]. A second

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