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Antifeedant Activity of Some Pentacyclic Triterpene Acids and Their Fatty Acid Ester Analogues

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The 3-*O*-fatty acid ester derivatives (C_{12}−C_{18}) of two pentacyclic triterpenic acids, ursolic acid and oleanolic acid, were synthesized under mild esterification conditions in excellent yields (80−85%) and screened for their antifeedant activity, together with the parent acids, against the agricultural pest tobacco caterpillar larvae (*Spodoptera litura* F) in a no-choice laboratory study. The Urs-12-ene-28-carboxy-3β-octadecanoate and olean-12-ene-28-carboxy-3β-hexadecanoate were found to exhibit exceptionally potent antifeedant activities at 50 μg/cm^2 concentration, even after 48 h.

KEYWORDS: Antifeedant activity; ursolic acid; oleanolic acid; fatty acid esters; tobacco caterpillar; *Spodoptera litura*

INTRODUCTION

The search for natural-product-based agrochemicals has intensified recently, as they are biodegradable, eco-friendly, and safe to the environment (*1a*). To survive in a competitive ecosystem consisting of insects, mites, microbes, and fungi, certain plant species develop highly sophisticated chemical defense mechanisms and produce secondary metabolites such as terpenoids, alkaloids, flavonoids, and polyacetylenes (*1b*). Among these classes, the terpenoids, in particular pentacyclic triterpenoids, are extremely useful for the development of potent agrochemicals in view of their high natural abundance and relatively nontoxic nature. A literature search reveals that urs-12-ene-3β-palmitate, isolated from the bark of *Santalum album*, showed excellent insect growth-inhibiting properties and chemosterilant activity (*2*), and ursolic acid, isolated from *Duboisia myoporoides* leaves, showed antifeedant activity (*3*). Recently, Jagdeesh et al. (*4*) synthesized some 3-*O*-allyl and cinnamyl esters of the lupane class of pentacyclic triterpene acid, specifically betulinic acid, and these compounds were found to exhibit antifeedant activity. It was reported in the literature that the acid moiety at C_{17} and the ester functionality at C_3 are essential for enhanced biological activities of pentacyclic triterpenes (*5*, *6*). The representative pentacyclic triterpene acids of ursane and oleanane skeletons, i.e., ursolic acid and oleanolic acid, with high natural abundance and favorable structural features, form useful models for the development of potent antifeedants. Further more, structure−activity studies suggest that the defined substituents on the lipophilic 5-ring backbone can increase the selectivity and potency of a desired action, and pentacyclic triterpenes might provide a rich natural source of lead compounds for the development of bioactive molecules (*7*). The C_3 hydroxy functionality of these acids can be exploited to synthesize long-chain fatty acid esters as potent antifeedants.

In connection with our investigation of *Diospyros melanoxylon* (kendu) leaves for value-added products (*8*), we have isolated large quantities of ursolic acid (0.56%) and oleanolic acid (0.1%), which prompted us to synthesize some of their long fatty acid ester chains and screen for antifeedant activity.

MATERIALS AND METHODS

General. IR spectra were obtained on a Jasco FT-IR 5300 spectrometer. NMR spectra were obtained with Gemini 200 MHz (^{1}H) and Bruker 100 MHz (^{13}C) instruments in $CDCl_3$ with TMS as an internal standard. TLC was performed with Acme grade silica gel G and column chromatography with Acme grade silica gel (100−200 mesh).

Extraction and Isolation. The coppiced *D. melanoxylon* (Family Ebenaceae) leaves were collected during April−May 1994 from Beltigiri (20°35′ N, 85°56′ E) in the Dhenkanal area and were supplied by the Forest Department, Government of Orissa. A voucher specimen (No. 940401) has been deposited in the Herbarium of the Forest and Marine Products Division, Regional Research laboratory, Bhubaneswar, India. The leaf material was powdered in a pulverizer and extracted successively with hot *n*-hexane and ethyl acetate solvents, followed by concentration under reduced pressure. The resulting *n*-hexane and ethyl acetate extracts were subjected to independent column chromatography, which yielded oleanolic acid (**2**, 0.1%, mp 272 °C, M^+ 456.3590) and ursolic acid (**1**, 0.56%, mp 259 °C, M^+ 456.3629), respectively (*9*).

General Procedure for Synthesis of Fatty Acid Esters. The 3-*O*-fatty acid ester derivatives (**7**−**12**) were synthesized in excellent yields

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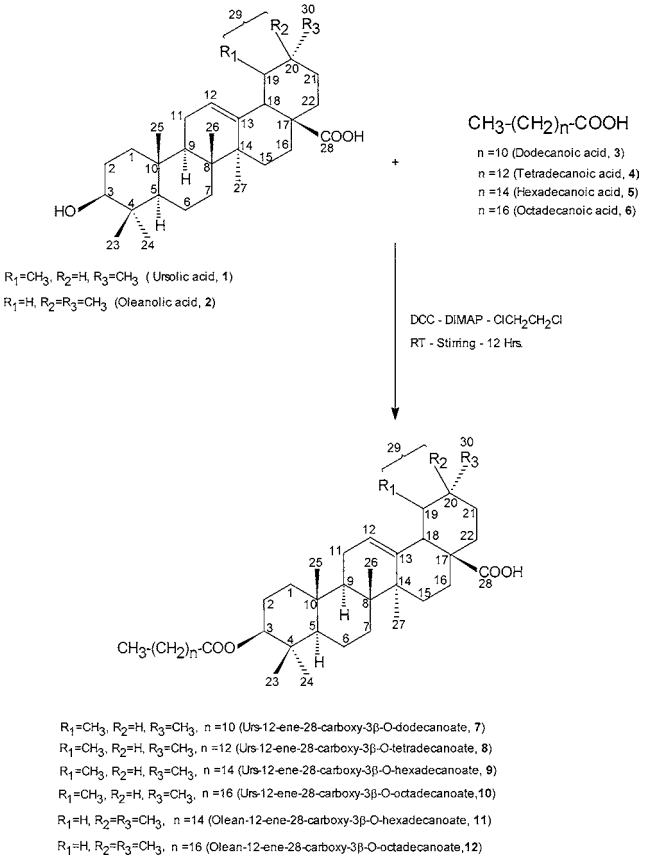

Figure 1. Synthesis of ursolic acid and oleanolic acid esters with different chain lengths at C-3.

(80−85%) by employing a modified Hassner reaction (*10*) under essentially neutral conditions. In a typical experiment, a mixture of triterpene acid (0.5 g, 0.109 mmol, 1 equiv), long-chain fatty acid (2 equiv), *N*,*N*′-dicyclohexylcarbodiimide (5 equiv), and 4-(dimethylamino)pyridine (5 equiv) in 1,2-dichloroethane (15 mL) was stirred at room temperature for 12 h. The reaction mixture was filtered to remove the precipitated dicyclohexyl urea. The filtrate was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography with *n*-hexane as an eluent to afford the corresponding fatty acid esters **7**−**12** (Figure 1).

Bioassay. The antifeedant activity of the compounds was assessed on tobacco caterpillar (*Spodoptera litura* F). The tobacco caterpillars were reared on fresh castor leaves (*Ricinus communis*) grown on the Osmania University campus, Hyderabad, at 27 ± 1 °C, relative humidity 65 ± 5%, and 14:10 light:dark photoperiod. Freshly molted fourth-instar larvae were used in the assays. The assays were conducted as described by Ascher and Rones (*11*). To study the antifeedant activity of the test compound, a large circular leaf disk of 10 cm diameter was cut from fresh castor leaf and dipped in acetone solution of the test compound containing 5% Triton-X-100 as sticker. The leaf disk was dried and placed on a moist filter paper in a Petri dish of 15 cm diameter (*12*).

A circular leaf disk of 10 cm diameter from fresh castor leaf was cut and dipped in acetone containing 5% Triton-X-100 as sticker. The leaf disk was placed in another Petri dish of 15 cm diameter, and this setup was used as control. In each Petri dish, a prestarved fourth-instar larva of *S. litura* F was introduced for assessing the antifeedant activity. Progress of the consumption of the leaf area by the insect after 6, 12, 24, and 48 h was recorded in both treated and control leaf disks; the time period of the experiment was 48 h. The leaf area consumed (damaged) was measured with the help of a planimeter, and the percentage of protection, which is the antifeedant activity, was calculated.

For each concentration, 10 experimental sets were assayed. Each test was replicated three times. The mean of the 10 sets was taken for each compound, and the percent antifeedant activity with standard deviation was calculated.:

leaf area protected =
initial leaf area introduced into the Petri dish − leaf area consumed by the insect (in both the control leaf disk and the treated leaf disk)

The percent leaf area protected, which is the percent antifeedant activity, was calculated by the method of Singh and Panth (*13*):

$$\text{percent protection due to treatment, i.e., \% antifeedant activity} = \left(\frac{\text{\% protection in treated} - \text{\% protection in control}}{100 - \text{\% protection in control}}\right) \times 100$$

The treatment/control consumption was calculated for each compound at each dosage level. Variation within the controls was between 0.42 and 0.6%, and variation in the treated samples was between 1.5 and 4%.

RESULTS AND DISCUSSION

The two pentacyclic triterpene acids, ursolic acid (**1**) and oleanolic acid (**2**), were isolated from the ethyl acetate and *n*-hexane extracts of *D. melanoxylon* (kendu) leaves in 0.56 and 0.1% yields, respectively. In view of their high natural abundance, interesting structural features, and relatively nontoxic nature, these compounds have now been exploited to synthesize the 3-*O*-fatty acid ester derivatives (**7**−**12**) in excellent yields as potent antifeedants. The synthesized esters were thoroughly characterized by their diagnostic spectral features (*14*−*16*), specifically IR signals at 1732 (−OCOCH$_2$−) and 1697 (−COOH) cm^{-1}, ^{1}H NMR resonance at δ 4.55 (3α-H), and ^{13}C NMR resonances at δ 173.63 (−*O*C*O*CH$_2$−) and 172.53 (−*C*OOH).

Urs-12-ene-28-carboxy-3β-dodecanoate (7): colorless oil (0.573 g, 82%); TLC R_f 0.82 (hexane/ethyl acetate, 95:5); IR (neat, cm^{-1}) 1732, 1699, 1649, 1458, 987, 721; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 5.31 (1H, s, 12-H), 4.5 (1H, t, J = 8 Hz, 3α-H), 2.29 (2H, t, J = 8 Hz, 2-H), 2.17 (1H, d, J = 11 Hz, 18-H), 1.25 (20H, br s, −CH$_2$), 1.09 (3H, s, 27-H), 0.9 (3H, s, 23-H), 0.86 (12H, s, 24,25,26-H), 0.82 (6H, s, 29,30-H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 173.63 (−OCO−), 172.53 (C-28), 137.92 (C-13), 126.17 (C-12), 80.61 (C-3), 56.39 (C-5), 52.65 (C-18), 49.82 (C-17), 47.98 (C-9), 42.21 (C-14), 39.74 (C-8, C-19), 39.02 (C-20), 37.77 (C-4, C-1), 36.93 (C-10), 34.87 (C-22), 31.92 (C-7), 29.59 (C-21), 29.20 (C-15), 28.16(C-23), 27.80 (C-2), 25.21 (C-27), 23.54 (C-16), 22.67 (C-11), 21.09 (C-30), 18.30 (C-6), 17.39 (C-29), 16.82 (C-26), 15.48 (C-24), 14.08 (C-25), 29.59−29.26 (−CH$_2$ of fatty chain), 17.06 (−CH$_3$ of fatty chain). Anal. Calcd for C$_{42}$H$_{70}$O$_4$: C, 78.94; H, 11.07. Found: C, 78.62; H, 11.12.

Urs-12-ene-28-carboxy-3β-tetradecanoate (8): colorless oil (0.620 g, 85%); TLC R_f 0.83 (hexane/ethyl acetate, 95:5); IR (neat, cm^{-1}) 1732, 1697, 1647, 1464, 987, 758 ; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 5.31(1H, s, 12-H), 4.5(1H, t, J = 8 Hz, 3α-H), 2.29 (2H, t, J = 8 Hz, 2-H), 2.17 (1H, d, J = 11 Hz, 18-H), 1.25 (24H, br s, −CH$_2$), 1.09 (3H, s, 27-H) 0.9 (3H, s, 23-H), 0.86 (12H, s, 24,25,26-H), 0.82 (6H, s, 29,30-H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 173.64 (−OCO−), 172.53 (C-28), 137.92 (C-13), 126.17 (C-12), 80.61 (C-3), 55.43 (C-5), 52.82 (C-18), 49.82 (C-17), 47.58 (C-9), 42.21 (C-14), 39.74 (C-8, C-19), 39.08 (C-20), 38.45 (C-4), 37.80 (C-1), 36.93 (C-10), 34.87 (C-22), 31.92 (C-7), 30.70 (C-21), 29.20 (C-15), 28.16 (C-23), 25.18 (C-2), 25.00 (C-27), 23.54 (C-16), 22.70 (C-11), 21.09 (C-30), 18.31 (C-6), 17.39 (C-29), 16.85 (C-26), 15.48 (C-24), 14.08 (C-25), 29.65−29.26 (−CH$_2$ of fatty chain), 17.06

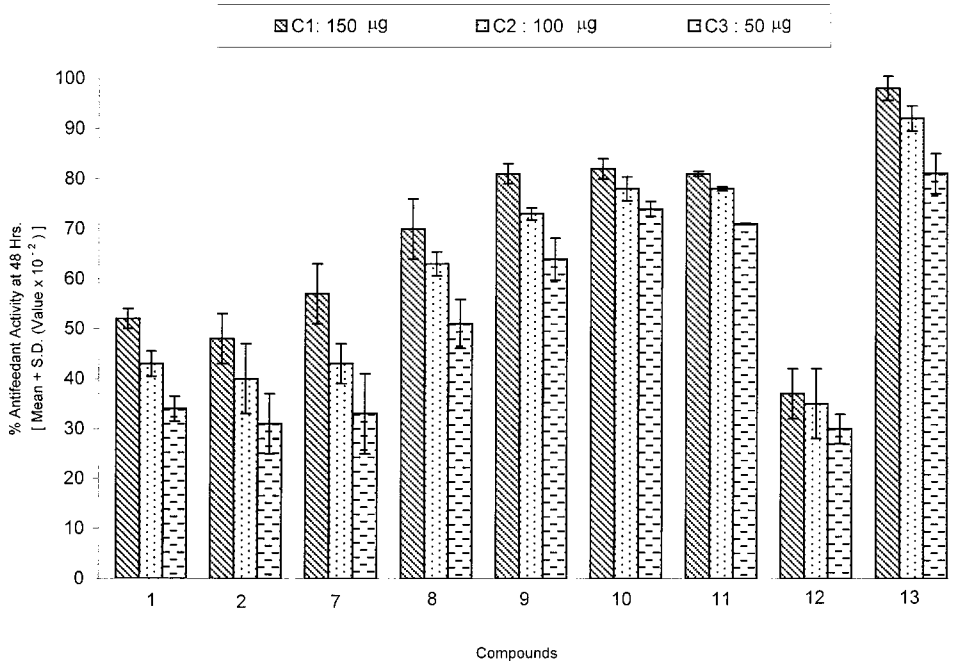

Figure 2. Antifeedant activity of ursolic acid, oleanolic acid, and their analogues.

(−CH_3 of fatty chain). Anal. Calcd for $C_{44}H_{74}O_4$: C, 79.22; H, 11.18. Found: C, 79.31; H, 11.05.

Urs-12-ene-28-carboxy-3β-hexadecanoate (9): colorless oil (0.624 g, 82%); TLC R_f 0.82 (hexane/ethyl acetate, 95:5); IR (neat, cm^{-1}) 1732, 1697, 1642, 1464, 987, 758; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.31 (1H, s, 12-H), 4.5 (1H, t, J = 8 Hz, 3α-H), 2.29 (2H, t, J = 8 Hz, 2-H), 2.17 (1H, d, J = 11 Hz, 18-H), 1.25 (28H, br s, −CH_2), 1.09 (3H, s, 27-H), 0.9 (3H, s, 23-H), 0.86 (12H, s, 24,25,26-H), 0.82 (6H, s, 29,30-H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.64 (−OCO−), 172.51 (C-28), 137.83 (C-13), 126.11 (C-12), 80.52 (C-3), 55.33 (C-5), 52.57 (C-18), 49.74 (C-17), 47.48 (C-9), 42.14 (C-14), 39.64 (C-8), 39.05 (C-19), 38.97 (C-20), 38.32 (C-4), 37.71 (C-1), 36.86 (C-10), 34.82 (C-22), 31.89 (C-7), 30.50 (C-21), 29.15 (C-15), 28.08 (C-23), 27.81 (C-2), 25.14 (C-27), 23.46 (C-16), 22.65 (C-11), 21.06 (C-30), 18.18 (C-6), 17.31 (C-29), 16.80 (C-26), 15.43 (C-24), 14.08 (C-25), 29.64−29.16 (−CH_2 of fatty chain), 17.02 (−CH_3 of fatty chain). Anal. Calcd for $C_{46}H_{78}O_4$: C, 79.47; H, 11.23. Found: C, 79.12; H, 11.42.

Urs-12-ene-28-carboxy-3β-octadecanoate (10): colorless oil (0.633 g, 80%); TLC R_f 0.84 (hexane/ethyl acetate, 95:5); IR (neat, cm^{-1}) 1732, 1698, 1645, 1464, 987, 738; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.31 (1H, s, 12-H), 4.50 (1H, t, J = 8 Hz, 3α-H), 2.29 (2H, t, J = 8 Hz, 2-H), 2.17 (1H, d, J = 11 Hz, 18-H), 1.25 (32H, br s, −CH_2), 1.09 (3H, s, 27-H), 0.9 (3H, s, 23-H), 0.86 (12H, s, 24,25,26-H), 0.82 (6H, s, 29,30-H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 173.60 (−OCO−), 172.49 (C-28), 137.85 (C-13), 126.11 (C-12), 80.53 (C-3), 55.36 (C-5), 52.60 (C-18), 49.76 (C-17), 47.51 (C-9), 42.16 (C-14), 39.66 (C-8), 39.07 (C-19), 38.98 (C-20), 38.34 (C-4), 37.72 (C-1), 36.87 (C-10), 34.83 (C-22), 31.91 (C-7), 30.54 (C-21), 29.17 (C-15), 28.10 (C-23), 27.83 (C-2), 25.15 (C-27), 23.49 (C-16), 22.67 (C-11), 21.07 (C-30), 18.20 (C-6), 17.33 (C-29), 16.81 (C-26), 15.45 (C-24), 14.09 (C-25), 29.66−29.17 (−CH_2 of fatty chain), 17.03 (−CH_3 of fatty chain). Anal. Calcd for $C_{48}H_{82}O_4$: C, 79.72; H, 11.43. Found: C, 79.41; H, 11.56.

Olean-12-ene-28-carboxy-3β-hexadecanoate (11): colorless oil (0.632 g, 83%); TLC R_f 0.82 (hexane/ethyl acetate, 95:5); IR (neat, cm^{-1}) 1732, 1697, 1642, 1520, 1464, 987, 758; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.32 (1H, s, 12-H), 4.5 (1H, t, J = 8 Hz, 3α-H), 2.85 (1H, m, 19-H), 2.29 (2H, t, J = 8 Hz, 2-H), 1.25 (28H, br s, −CH_2), 1.14 (3H, s, 27-H), 0.93 (3H, s, 23-H), 0.93 (3H, s, 24-H), 0.88 (3H, s, 25-H), 0.86 (6H, s, 26,29-H), 0.82 (3H, s, 30-H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.64 (−OCO−), 172.51 (C-28), 143.33 (C-13), 122.86 (C-12), 80.52 (C-3), 55.33 (C-5), 52.57 (C-18), 49.74 (C-17), 47.48 (C-9), 42.14 (C-14), 39.64 (C-8), 39.05 (C-19), 38.97 (C-20), 38.32 (C-4), 37.71 (C-1), 36.86 (C-10), 34.82 (C-22), 31.89 (C-7), 30.50 (C-21), 29.15 (C-15), 28.08 (C-23), 27.81 (C-2), 25.14 (C-27), 23.46 (C-16), 22.65 (C-11), 21.06 (C-30), 18.18 (C-6), 17.31 (C-29), 16.80 (C-26), 15.43 (C-24), 14.08 (C-25), 29.64−29.16 (−CH_2 of fatty chain), 17.02 (−CH_3 of fatty chain). Anal. Calcd for $C_{46}H_{78}O_4$: C, 79.47; H, 11.23. Found: C, 79.28; H, 11.31.

Olean-12-ene-28-carboxy-3β-octadecanoate (12): colorless oil (0.664 g, 84%); TLC R_f 0.84 (hexane/ethyl acetate, 95:5); IR (neat, cm^{-1}) 1732, 1698, 1645, 1464, 987, 738; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.32 (1H, s, 12-H), 4.51 (1H, t, J = 8 Hz, 3α-H), 2.85 (1H, m, 19-H), 2.31 (2H, t, J = 8 Hz, 2-H), 1.27 (32H, br s, −CH_2), 1.16 (3H, s, 27-H), 0.94 (3H, s, 23-H), 0.93 (3H, s, 24-H), 0.89 (3H, s, 25-H), 0.88 (6H, s, 26,29-H), 0.84 (3H, s, 30-H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.69 (−OCO−), 172.89 (C-28), 143.17 (C-13), 122.93 (C-12), 80.50 (C-3), 55.28 (C-5), 52.49 (C-18), 49.79 (C-17), 47.49 (C-9), 42.09 (C-14), 39.59 (C-8), 39.39 (C-19), 39.00 (C-20), 38.20 (C-4), 37.69 (C-1), 36.87 (C-10), 34.83 (C-22), 31.90 (C-7), 30.62 (C-21), 29.15 (C-15), 28.03 (C-23), 27.42 (C-2), 25.15 (C-27), 23.52 (C-16), 22.67 (C-11), 21.03 (C-30), 18.16 (C-6), 17.27 (C-29), 16.74 (C-26), 15.30 (C-24), 14.12 (C-25), 29.67−29.24 (−CH_2 of fatty chain), 17.12 (−CH_3 of fatty chain). Anal. Calcd for $C_{48}H_{82}O_4$: C, 79.72; H, 11.43. Found: C, 79.81; H, 11.24.

The two parent acids, ursolic acid (**1**) and oleanolic acid (**2**), and their 3-*O*-fatty acid ester analogues (**7**−**12**), along with standard azardirachtin (**13**), were screened for antifeedant activity against the agricultural pest tobacco caterpillar *S. litura* larvae, in a no-choice laboratory study at the dosages of 150, 100, and 50 μg/cm^2. The antifeedant activities were determined after 6, 12, 24, and 48 h. In general, all of the compounds showed antifeedant activity. It is very interesting to note that significant activity was retained even after 48 h (**Figure 2**).

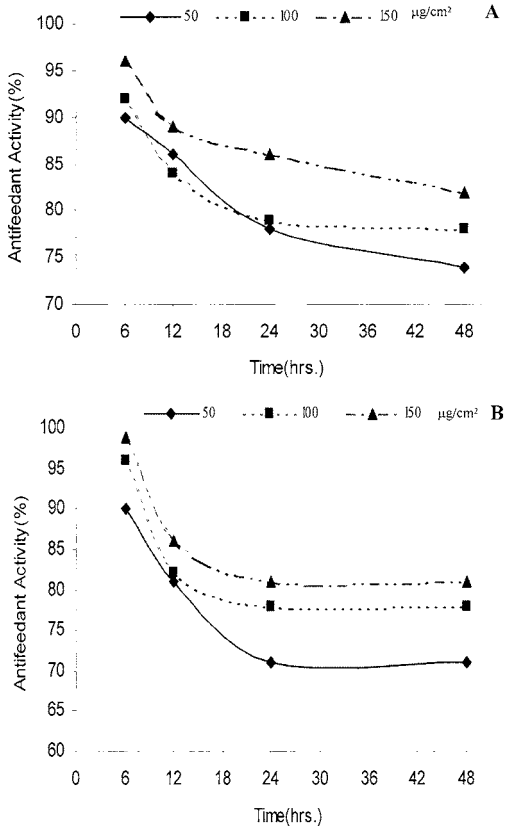

Figure 3. (A) Antifeedant activity vs time of compound **10**. (B) Antifeedant activity vs time of compound **11**.

Detailed analysis of the data revealed that, at 150 μg/cm^2 dose, all the tested compounds showed more than 50% activity, except compounds **2** and **12**. At 100 μg/cm^2 dose, the compounds showed 40−78% activity, while compound **12** again showed the lowest activity. Even at 50 μg/cm^2, the four compounds **8**−**11** exhibited more than 50% activity. The exceptionally potent antifeedants were found to be urs-12-ene-28-carboxy-3β-octadecanoate (**10**) and olean-12-ene-28-carboxy-3β-hexadecanoate (**11**), which showed 74% and 71% activity, respectively, at 50 μg/cm^2 concentration. Correlation studies have been made for these two compounds with respect to antifeedant activity versus time, and the data are presented in **Figure 3**. It is noteworthy to mention here that the synthesized analogues were found to exhibit activity comparable with that of standard azardirachtin, which showed 81% activity under identical bioassay conditions.

In conclusion, we have synthesized some fatty acid ester chains (C_{12}−C_{18}) of ursolic acid and oleanolic acid under mild esterification conditions in excellent yields and screened for antifeedant activity along with the parent acids and standard azardirachtin. The compounds **10** and **11** were found to exhibit exceptionally potent activity, while compounds **8** and **9** showed fairly good activity.

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