

ANTIFEEDANT ACTIVITY OF INDIGENOUS PLANTS AGAINST *DIACRISIA OBLIQUA* WALKER

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AS synthetic insecticides are known to have wide spread toxicity, a world-wide task has been started to look for useful, non-hazardous natural products. Antifeedants of plant origin have the additional advantage of quick biodegradability and safety to non-target organisms¹. Extensive literature has appeared on antifeedant activity of numerous compounds. Apart from crude extracts, different oils have been reported to possess feeding deterrency². Active constituents of a number of plants, which possess strong antifeedant activity at low dosages³⁻⁵ have been isolated.

This communication deals with the study of anti-feedant property of some plant extracts against Bihary Hairy Caterpillar, *Diacrisia obliqua* Walker.

The shoot portions from plants listed in table 1 were shade-dried, powdered and extracted in a soxhlet

apparatus using different solvents⁶. The solvent extracts were evaporated to dryness. Two per cent solutions of the different plant extracts in acetone were employed at 18°C with a relative humidity of 78% ($\pm 2\%$). Third instar larvae of laboratory bred *D. obliqua* were used for bioassay. Castor leaves were cut into small bits of uniform size, its leaf area was measured by leaf area meter. These leaf bits were dipped in the plant extracts for 2 seconds and air dried. Two treated leaf bits were kept on a moist blotting paper. Each treatment was replicated thrice. Two larvae starved for 6 hr were released on the treated leaf material. Observations were recorded after 48 hr and area of left over leaf bits was measured. Leaves treated with acetone was used as control. Percentage feeding and leaf area protected over control were calculated⁷, and the data were analysed statistically.

The results indicate that all extracts inhibited feeding of the larvae, and the crude extract of *Ailanthus excelsa* gave 89.67% protection followed by the extracts of other plants (table 1). The extracts of *Juniperus recurva* have also been reported having insecticidal property⁸. Similarly the extracts of *Clerodendron infortunatum* and *Hibiscus syriacus* have been reported for their antifeedant activity^{9, 10}.

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Table 1 Antifeedant activity of plant extracts against *D. Obliqua* (Walker)

Plant Material	Family	Extract	Mean per cent Feeding	Mean per cent protection
<i>Ailanthus excelsa</i> Roxb.	Simarubaceae	Acetone	10.33 (17.19)	89.67
<i>Bursera delpechiana</i> Poiss.	Burseraceae	do	12.33 (20.33)	87.67
<i>Albizia lebbeck</i> Benth.	Leguminosae	do	15.33 (23.02)	84.67
<i>Rauwolfia canescens</i> Linn.	Apocynaceae	do	17.33 (24.31)	82.67
<i>Sesbania aegyptiaca</i> Poir.	Leguminosae	do	22.00 (27.25)	78.00
<i>Terminalia belerica</i> Roxb.	Combretaceae	do	23.00 (28.54)	77.00
<i>Terminalia chebula</i> Retz.	Combretaceae	do	25.00 (29.09)	75.00
<i>Erythrina variegata</i> Linn.	Leguminosae	do	26.00 (30.56)	74.00
<i>Juniperus pseudosabina</i> Hook.	Pinaceae	do	31.00 (33.03)	69.00
<i>Hibiscus sabdariffa</i> Linn.	Malvaceae	do	33.00 (35.04)	67.00
<i>Artemisia sacrorum</i> Ledeb.	Compositae	do	33.67 (35.13)	66.33
<i>Clerodendron inerme</i> Prod.	Verbenaceae	do	35.00 (36.09)	65.00
<i>Martynia</i> sp.	Pedalaceae	do	40.00 (40.86)	57.00
<i>Vitex negundo</i> Linn.	Verbenaceae	do	50.00 (45.23)	50.00
<i>Trigonella foenum-graecum</i> Linn.	Papilionaceae	Butanol	65.67 (54.23)	34.33
<i>Solanum verbascifolium</i> Linn.	Solanaceae	Hexane	78.33 (66.83)	21.67
<i>Trigonella foenum-graecum</i> Linn.	Papilionaceae	do	79.00 (67.26)	21.00
<i>Trigonella foenum-graecum</i> Linn.	Papilionaceae	Chloroform	91.00 (79.56)	9.00
Control			99.98 (89.38)	—
C. D. at 5% level			19.56	
S. E. at 5% level			9.58	

Figures in parantheses are angular values.

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of the column with petroleum ether-benzene (1:1) gave two syrupy fractions A and B. TLC of fraction A on AgNO₃ (15%)/silica gel plate, revealed its complex nature. Fraction A when subjected² to IDCC over silica gel (same as above); solvent chloroform: benzene: dichloromethane: : 1:5:4 afforded only one crystalline compound (II, 3 α -epimer of α -amyrin) m.p. 108–110° (Lit³ m.p. 110–111°). IR and MS of this compound were similar to those of α -amyrin. Its PMR displayed the signals at 0.8 . . . 1.1 (24H, 8 Mes); 5.12 (1H, m, olefinic proton of a trisubstituted double bond); 3.4 (1H, t, J = 3Hz, which is characteristic of an equatorial proton⁴). Therefore it can be concluded that hydroxyl group is in 3 α position. Hence the compound is characterised as a 3 α -epimer of α -amyrin. This was further confirmed by converting (II) into its acetate m.p. 133–134° (Lit⁵ m.p. 130–131°). In addition, compounds (I) and (II) have the same ketone (m.m.p. and superimposable IR). Fraction B could not be purified as such. Hence it was acetylated. The acetate when subjected to IDCC (solvent petroleum ether: benzene: dichloromethane: : 2:2:1) afforded three crystalline acetates (R_f 0.65, 0.47 and 0.19). The acetate (R_f 0.65) m.p. 208–210° was identified as α -amyrin acetate by direct comparison with the authentic sample (IR, PM, MS, m.m.p.). Another acetate (R_f 0.47) m.p. 145–146° (Lit⁶ 145–146°) was characterised as butyrospermol acetate.

THE CONSTITUENTS OF THE EXUDATE OF *GARUGA PINNATA*

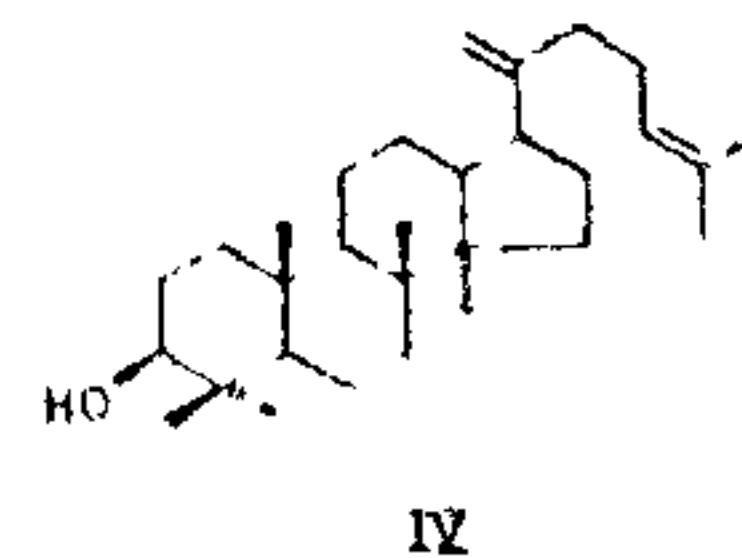
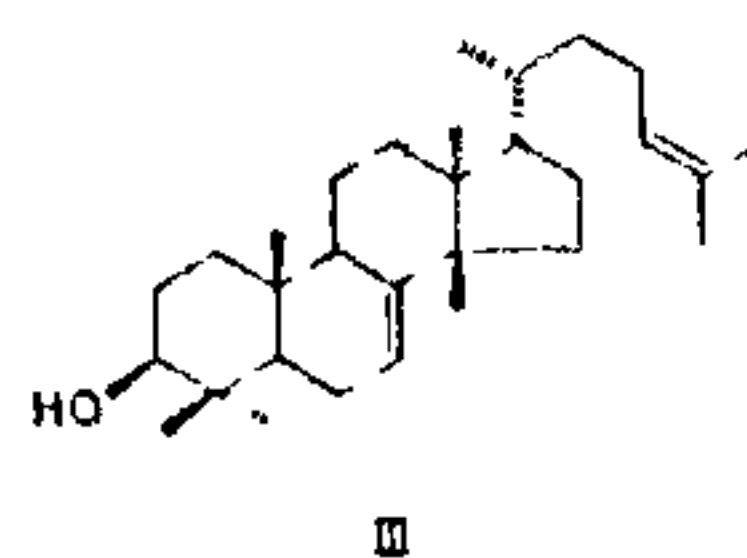
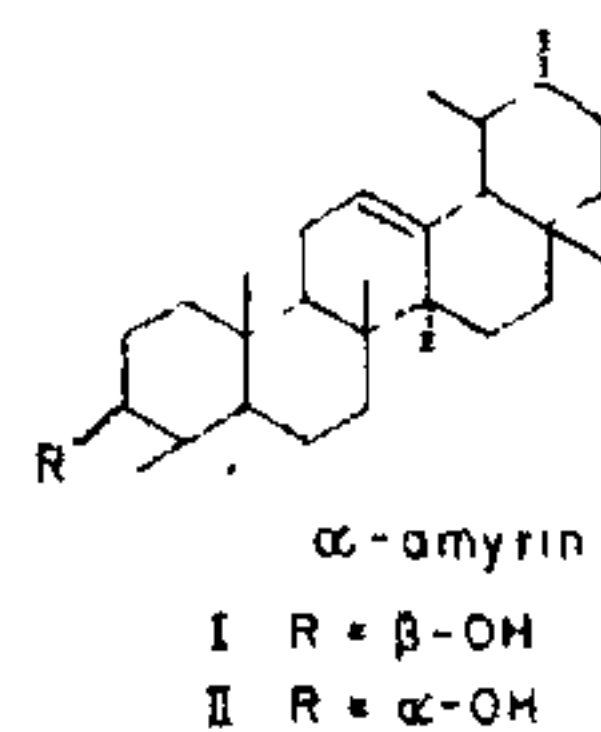
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GARUGA PINNATA (N. O. Burseraceae) is an important plant of medicinal value. Rehman *et al*¹ have reported amentoflavone from the acetone extract of the leaves. However, the resinous exudate of this plant has not been studied so far. In this note we report the isolation of α -amyrin (I); its 3 α -epimer (II); butyrospermol (III) and dammaradienol (IV) from the resinous exudate.

The characterisation of these compounds is based on spectral data (IR, PMR, MS) and chemical evidence.

The resinous exudate of the plant collected from Chandrapur area was extracted with benzene at room temperature (23–25°). The benzene insoluble material was analysed by Emission spectrophotometry. The presence of Ca, Mg, Si, Al, Ti, Sr, Cu and Na was detected. The benzene extract on removal of the solvent was chromatographed over alumina. Elution



Butyrospermol acetate was converted^{6,7} to dihydroeuphyl acetate. The comparison of final product with an authentic sample of dihydroeuphyl acetate⁸ confirmed its identity. The last compound had R_f 0.19 and m.p. 155 (Lit⁹ m.p. 155) and was characterised as dammaradienyl acetate (IR, PMR, MS)¹⁰.

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ROTATIONAL ISOMERISM IN BENZIL

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THE molecular configuration of benzil has been a subject of considerable interest and was investigated by several workers, by different methods, *viz* dipole-moment¹, x-ray diffraction², IR³⁻⁵, UV⁶, NMR⁷, molar refractivities and Kerr constants⁸. It was established that the molecule is not planar and has a skew configuration with the two carbonyl groups making an angle of 90°–100° and that the two benzene rings are twisted by 5.1° from the carbonyl planes. But from the study of IR spectra in nujol and decalin, Sterk⁴ had shown that at higher temperatures two different conformations exist with quasi-cis-trans character. As nothing has been reported about the existence of more than one conformer in solution at room temperature and the influence of solvents on the relative stabilities of the conformations, it was considered useful to carry out the work on these aspects and the results of the investigations are reported in this communication.

IR spectra of equimolar solutions of different protic

and non-protic solvents of different dielectric constants were recorded at slow speed on Perkin Elmer 337 grating spectrophotometer at 28°C using NaCl matched cells of 0.5 mm path length. The spectra g & h (figure 1) were recorded as binary solvent mixtures (Phenol/Pyrrole + CCl₄) on Perkin Elmer 283 grating spectrophotometer. In carbontetrachloride benzil exhibited two carbonyl bands at 1672, 1682 cm⁻¹. Similar observation was also made by Bernal⁵ who attributed the splitting of the band to C₂ symmetry of the molecule. If this is true, similar splittings are expected in anisil and furil which also have the same symmetry. They however exhibit sharp singlets⁹.

In carbontetrachloride the intensity of the lower frequency band is greater than that of the higher frequency band. The relative intensities did not suffer any change with change in concentration of benzil. The splitting of the carbonyl band, therefore, is not due to the intermolecular interactions. However, the relative intensities of the bands changed with change in polarities of the solvents (figure 1). This pattern of intensity variation of the doublet is quite analogous to that observed in the case of chloroacetone¹⁰ and *o*-bromo acetophenone¹¹ which are known to exhibit rotational isomerism. The two carbonyl bands of benzil are therefore due to two rotational isomers of the molecule. The rotamer stabilized in more polar solvent (acetonitrile) should have a large dipole-moment. This may be the cis form in which the two carbonyl groups of benzil are in eclipsed position. The carbonyl frequency of such a rotamer is expected to be higher due to field inductive effect. The rotamer with preferential stability in carbontetrachloride should obviously have smaller dipolemoment. This could be the skew form which has lower carbonyl frequency. The higher frequency band is therefore assigned to the cis form and the lower frequency to the skew form. Thus, in all the solvents used, benzil at room temperature exists as an equilibrium mixture of two rotamers, *viz* the skew and the cis, with the cis form predominating in solvents of larger polarities as is evident from the cis/skew ratio (table 1).

The influence of protic solvents like phenol and pyrrole on the relative stabilities of the two rotamers is examined as binary solvent mixtures. In the presence of a small quantity of phenol (or pyrrole) in carbontetrachloride the intensity ratio of cis/skew increased showing the relative stabilization of the cis rotamer. The stabilization of the cis form in phenol/pyrrole is attributed, besides dielectric effect, to the formation of bifurcated H-bonds between phenolic OH (or NH of pyrrole) and the two carbonyl groups (figure 2).