Chemistry of the Meliacins (Limonoids). The Structure of Melianin A, a new Protomeliacin from *Melia azedarach*

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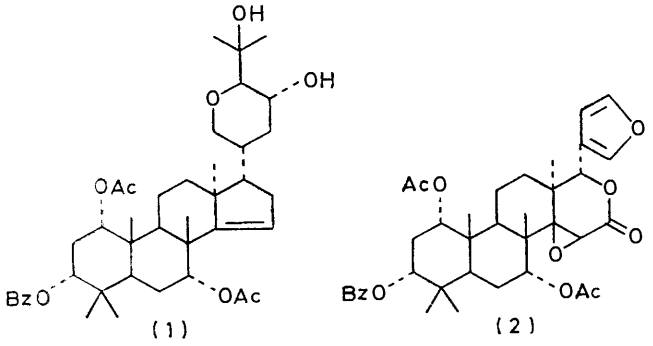
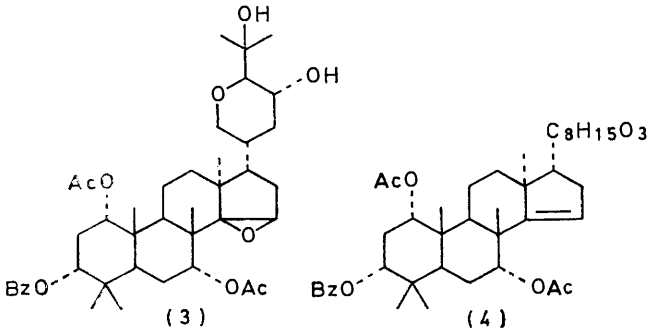
Evidence is presented for the structures of a new protomeliacin (melianin A) and the related melianin B, which co-occur with gedunin (or 7-deacetoxy-7-oxogedunin), nimbolin A, fraxinellone, and cycloeucalenone in the wood extracts of *Melia azedarach*.

In continuation of our studies of the chemistry of the Meliaceae we have examined the constituents of the wood of *Melia azedarach*. The isolation and characterisation of the meliacins gedunin, 7-deacetoxy-7-oxogedunin, fraxinellone, and nimbolin A as well as the triterpene cycloeucalenone were described previously.[1] We now report the isolation of a new protomeliacin, melianin A, for which we propose the structure (1). The chopped wood from a large tree felled in the grounds of the Federal Department of Forest Research in Ibadan was extracted with light petroleum. The extract afforded material which was triturated with light petroleum, to give a precipitate, which was chromatographed. Elution with 75% ether–light petroleum from a silica gel column afforded two closely related non-furanoid compounds which we have named melianins A and B. Analysis of melianin A agreed with the formula $C_{41}H_{58}O_9$ (M 694) and the peak of highest mass in its mass spectrum, m/e 676, was attributed to $M^+ - H_2O$. Its i.r. spectrum indicated the presence of a hydroxy-group (3 500 cm^{-1}), an ester (1730 and 1260 cm^{-1}), and a monosubstituted phenyl group (715 cm^{-1}). N.m.r. signals assigned to seven tertiary methyl groups suggested a triterpene skeleton. Quantitative hydrolysis showed the presence of three hydrolysable groups, two acids (acetic and benzoic) being identified from the n.m.r. spectra of their potassium

[1] D. E. U. Ekong, C. O. Fakunle, A. F. Fasina, and J. I. Okogun, *Chem. Comm.*, 1969, 1166.

salts. The presence of the corresponding acyloxy-groups was confirmed by the n.m.r. spectrum of melianin A itself: τ 1.86—2.62 (5H, aromatic) and 7.97 (s, Ac).





Another acetate group gave an unusually high-field signal at τ 8.34. Three of the low-field n.m.r. peaks, τ 4.80 (m, $W_{\frac{1}{2}}$ 4 Hz), 5.11 (m, $W_{\frac{1}{2}}$ 5 Hz), and 5.30 (m, $W_{\frac{1}{2}}$ 4 Hz) were therefore assigned to C*H*-O-acyl groups, and that at τ 4.64 (m, $W_{\frac{1}{2}}$ 5 Hz) was attributed to an olefinic proton on a trisubstituted double bond. With a view to determining the nature of the double bond, melianin A was hydrogenated over platinum. Unexpectedly a hexahydro-derivative was obtained, from the hydrogenation of the phenyl group (the i.r. and n.m.r. spectra of the product lacked the phenyl signals). Furthermore the acetate signal originally at τ 8.34 had moved downfield to a more usual position (8.07), indicating that the paramagnetic shift was due to the anisotropy of the phenyl group. An analogous paramagnetic shift of acetate protons was observed by Connolly [2] in 3-deacetyl-3-benzoylkhivorin (2) prepared from 3-deacetylkhivorin, lending support to the placement of one acetate and the benzoate at C-1 and C-3 (not necessarily respectively). The shapes and chemical shifts of the ^{1}H n.m.r. signals for C*H*–O-acyl also justify the indicated stereochemistries at C-1, C-3, and C-7 in (1), as in 3-deacetyl-3-benzoylkhivorin (2) and khivorin.[3] The signal at τ 5.11 had moved upfield to τ 5.27 after hydrogenation and was thus assigned to C*H*·OBz. In the hydrogenation product two of the tertiary methyl signals had moved upfield from τ 9.02 to 9.09 and 9.22. By comparison with the methyl signals of khivorin [3] these must be the *gem*-methyl groups at C-4, and models showed that the most probable position for the benzoate was therefore C-3. Decoupling experiments carried out in Glasgow supported the C-1,C-3 arrangement for the acetoxy- and benzoyloxy-groups. On irradiation at τ 7.80 the signals at τ 5.11 and 5.30 became sharp singlets, as would be expected from 1-H and 3-H which are both coupled to the same protons at C-2. The peak at 5.30 was therefore assigned to C(1)*H*·OAc.

The signal at τ 4.64 remained after hydrogenation and is therefore not likely to be due to a proton on a 7,8-double bond. This was confirmed by reaction with mercury(II) acetate. No heteroannular diene [4] was formed and the starting material was recovered. An apoeuphol skeleton therefore appeared likely, with the double bond at C-14 and the second acetoxy-group at C-7. In support of this, treatment of melianin A with *m*-chloroperbenzoic acid gave an epoxide (3) in the n.m.r. spectrum of which the 15-H and 7-H signals had moved upfield from τ 4.64 to 7.05 and from 4.80 to 5.15, respectively. From the above evidence the partial structure (4) could be written for melianin A.

On oxidation with chromium trioxide in pyridine a ketone was obtained whose i.r. spectrum, however, still showed hydroxy-absorption at 3450 cm^{-1} suggesting the presence of a tertiary as well as a secondary hydroxy-group in melianin A. Of the nine oxygen atoms in the moleculae, eight had now been accounted for. The ninth must therefore be in an ether group, since complete hydrolysis of melianin A gave a product without any carbonyl i.r. absorption. Neither hydrobromic acid nor boron trifluoride caused cleavage of the ether, which was therefore not likely to be an epoxide. The region between τ 5.8 and 6.8 in the n.m.r. spectrum of melianin A appears to consist of a doublet of a doublet (2H) with a multiplet (1H) buried under it. On acetylation the multiplet moved downfield to τ 5.14 and was thus assigned to >C*H*·OH. The quartet could then be clearly recognized as the AM portion of an AMX system with J_{AM} 11 Hz and J_{AX} and J_{MX} each less than 2 Hz. The quartet with its two halves centred at τ 6.09 and 6.62 was assigned to one arm (–CH_2–) of the ether. A doublet (1H) at τ 7.15 (J 9 Hz) was assigned to the other arm. On acetylation the doublet moved downfield to τ 6.86 and in the spectrum of the oxidation product it became a singlet at τ 6.42. These observations led to assignment of the partial structure (5) for the side chain.

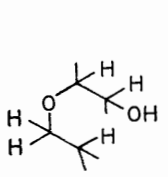
This was confirmed by decoupling experiments. On irradiation at τ 6.14 the doublet at 7.15 became a singlet. Similarly on irradiation of the acetylation product at τ 5.14 the doublet at 6.86 collapsed to a singlet. Treatment of melianin A acetate with thionyl chloride in pyridine afforded a dehydration product whose n.m.r. spectrum showed a vinylic methyl (τ 8.27) and a terminal

[2] J. D. Connolly, D. A. Okorie, and D. A. H. Taylor, *J.C.S. Perkin I*, 1972, 1145.

[3] N. S. Ohochuku, Ph.D. Thesis, Ibadan, 1970, p. 35; J. W. Powell, *J. Chem. Soc.* (*C*), 1966, 1794.

[4] W. V. Ruyle, T. A. Jacob, J. M. Chemerda, E. M. Chamberlin, D. W. Rosenburg, G. E. Sita, R. L. Erickson, L. M. Aliminosa, and M. Tishler, *J. Amer. Chem. Soc.*, 1953, **75**, 2604.

methylene (τ 5.07) in place of two of the tertiary methyl groups. Furthermore the doublet at τ 6.86 had moved to 6.27, a position to be expected for a proton allylic to the newly introduced double bond. The side chain could therefore be written as (6), so that the partial structure of the dehydration product could be written as (6a). Melianin A ketone would then have the structure (6b) and its dehydration product could be written as (6c).



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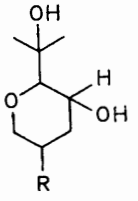

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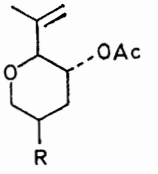
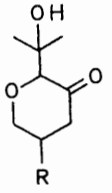


(6a)



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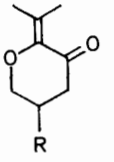

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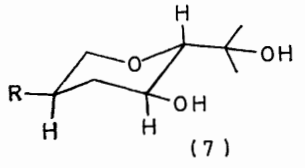

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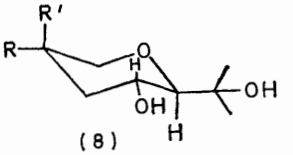

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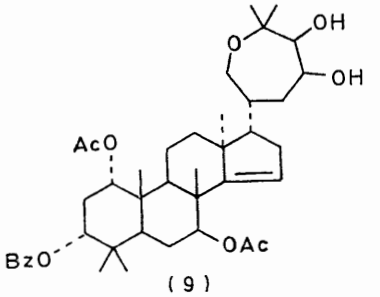

(9)

The configuration of the substituents in the ether ring was assigned from consideration of the coupling constants. H-23 and H-24 are probably each axial in view of their coupling constant (9 Hz). In the absence of factors that might force it into a boat conformation, the ether ring is expected to be in the more stable chair form. Two conformers may then be written, (7) and (8), which are consistent with the observed coupling constant for H-24. For a euphol derivative (20β-H) the molecule would take up the less crowded conformation (8; R = H), which would make H-20 axial. However H-20 has to be equatorial in view of the coupling constant ($J < 2$ Hz) between it and the two C-21 protons. On the other hand for a tirucallol derivative (20α-H) both (7) and (8) (R = H) would be sterically possible, but since H-20 is axial, (7) can be discounted leaving (8; R = H) as the probable configuration and conformation of the side chain. Melianin A is therefore formulated as a tirucallol derivative with the configuration of its substituents as shown in (1).

The side chain of melianin A is identical with that found in the protomeliacins grandifoliolenone,[5] bourjotinolone A,[6] and sapelin A;[7] and the assignments in its n.m.r. spectrum and those of its various derivatives compare well with those reported for these other compounds.

Melianin B was slightly more polar on t.l.c. than melianin A and their spectra were very similar. Its i.r. spectrum however showed the presence of strongly hydrogen bonded hydroxy-group ($\nu_{max.}$ 3400 cm^{-1}). Its ^{1}H n.m.r. spectrum was different from that of melianin A mainly in the region τ 6.0—7.0, indicating that the difference in their structures lay in their side-chains. Although melianin B was not obtained in sufficient quantities to permit detailed studies the evidence available (see Experimental section) suggested that its structure might be (9). This relationship between melianins A and B is analogous to that established[7] between sapelins A and B.

EXPERIMENTAL

M.p.s were taken on a Kofler hot-stage apparatus. I.r. spectra of solids (Nujol mulls) were taken on a Perkin-Elmer 137 instrument, and u.v. spectra were determined for solutions in methanol. Except where otherwise stated n.m.r. spectra were run for solutions in $CDCl_3$ solutions (Me_4Si as internal standard) with a Varian A 56/60 MHz instrument. Mass spectra were obtained with a Perkin-Elmer–Hitachi R.M.U. 6E instrument. Silica gel refers to Merck silica gel (mesh 0.05—0.2 mm). Activated alumina refers to Spence type H. Petroleum refers to the fraction of b.p. 60—80°.

Extraction of Melia azedarach.—The chopped stem wood of *Melia azedarach* (26.5 kg) was extracted as usual for 48 h with light petroleum (b.p. 62—82°). Removal of the solvent gave an oil (100 g) which gave a precipitate (15 g) on trituration with petroleum. The petroleum mother liquor gave an oil on removal of solvent.

Isolation[1] *of Cycloeucalenone, Fraxinellone, and Azedaric Acid.**—The oil from the petroleum mother liquor (100 g) was chromatographed on silica gel (700 g). Elution with petroleum containing an increasing proportion of ether gave cycloeucalenone, fraxinellone (2 g), m.p. 108—110°, and azedaric acid, m.p. 257—259°.

Isolation of Nimbolin A, Gedunin, 7-Deacetyl-7-oxogedunin, and Melianins A and B.—The precipitate (40 g) was chromatographed on silica gel (850 g). Ether–petroleum (1:1) eluted nimbolin A (2.5 g), m.p. 180—185°, ether–petroleum (3:2) eluted gedunin or (in its absence) 7-deacetyl-7-oxogedunin.

Ether–petroleum (3:1) eluted melianin A (0.2 g), closely

* Details of the evidence for the structure of azedaric acid are in the press.

[5] J. D. Connolly and R. McCrindle, *J. Chem. Soc.* (*C*), 1971, 1715.

[6] G. J. W. Breen, E. Ritchie, W. T. L. Sidwell, and W. C. Taylor, *Austral. J. Chem.*, 1966, **19**, 455.

[7] W. R. Chan, D. R. Taylor, and T. Yee, *J. Chem. Soc.* (*C*), 1970, 311.

followed by melianin B (30 mg; after further purification by preparative t.l.c.). It was later found that a better recovery of melianin A resulted from a preliminary purification of the crude extract by chromatography on 5% deactivated * alumina followed by chromatography as above on silica gel.

Melianin A had m.p. 258—259° (from ether–petroleum); $\nu_{max.}$ 3500 (OH), 1730 and 1260 (CO_2R), and 715 cm^{-1} (monosubstituted benzene ring); τ 9.10 (3H, s, CH_3), 9.02 (9H, s, 3 CH_3), 8.84 (3H, s, CH_3), 8.76 (3H, s, CH_3), 8.74 (3H, s, CH_3), 8.34 (3H, s, CH_3CO), 7.94 (3H, s, CH_3CO), 7.72br (1H, s, exchanged with D_2O), 7.15 (1H, d, *J* 9 Hz, H-24), 6.62 and 6.09 (2H, AM part of an AMX system,† J_{AM} 11, $J_{MX} = J_{AX} =$ 1.5 Hz, H_2-21), 5.30 (1H, m, H-1), 5.11 (1H, m, H-3), 4.80 (1H, m, H-7), 4.64 (1H, m, H-15), and 2.55 (3H, m) and 1.95 (2H m) (Ph); *m/e* 694 (M^+) and 676 (intense, $M^+ - H_2O$) (Found: C, 70.45; H, 8.35. $C_{41}H_{58}O_9$ requires C, 70.85; H, 8.4%).

Melianin B had m.p. 198—201°; $\nu_{max.}$ 3400 (OH), 1720 (CO_2R), and 714 cm^{-1} (monosubstituted benzene); τ 9.10 (3H, s, CH_3), 9.00 (9H, s, 3H), 8.86 (6H, s, 2 CH_3), 8.73 (3H, s, CH_3), 8.36 (3H, s, CH_3CO), 7.96 (3H, s, CH_3CO), 5.30 (1H, m, H-1), 5.10 (1H, m, H-3), 4.82 (1H, m, H-7), and 4.67 (1H, m, H-15).

Quantitative Hydrolysis of Melianin A.—Melianin A (106.6 mg) in methanol (5 cm^3) and aqueous sodium hydroxide (0.9912M; 1 cm^3) were heated at reflux for 6 h on a water-bath. The excess of sodium hydroxide was neutralized by titration with dilute hydrochloric acid (0.1007M; 5.50 cm^3). From these quantities the number of hydrolysable groups was calculated to be 2.85, implying the presence of three acyl groups in melianin A.

Isolation of the Volatile Acid Components of Melianin A.—Melianin A (100.6 mg) in methanol (5 cm^3) and dilute sodium hydroxide (2M; 10 cm^3) was heated at reflux for 3 h. The cooled mixture was acidified (pH 5) with dilute sulphuric acid and distilled, more water being added during distillation to avoid charring of the residue. The distillate was neutralized by titration with dilute potassium hydroxide (phenolphthalein). Evaporation of the resulting mixture gave the potassium salts of the acids, τ (D_2O) 8.12 (CH_3CO_2) and 2.06—2.64 ($PhCO_2$).

Hexahydromelianin A. Melianin A (104 mg) in acetic acid (10 cm^3) and platinum oxide (30 mg) were shaken with hydrogen at atmospheric pressure until absorption terminated. The catalyst was removed and the filtrate was diluted considerably with ether. The ethereal extract was washed with dilute aqueous sodium hydroxide then water, dried ($MgSO_4$), and evaporated. The solid was recrystallised from methanol; m.p. 233—235°, $\nu_{max.}$ 3440 (OH), and 1730, 1234, and 1245 cm^{-1} (CO_2R); τ 9.22 (3H, s, CH_3); 9.09 (3H, s, CH_3), 9.06 (3H, s, CH_3), 9.02 (3H, s, CH_3), 8.87 (3H, s, CH_3), 8.76 (3H, s, CH_3), 8.73 (3H, s, CH_3), 8.07 (3H, s, CH_3CO), 7.94 (3H, s, CH_3CO), 7.14 (1H, d, *J* 9 Hz, H-24), 6.60 and 6.05 (2H, AM part of an AMX system, J_{AM} 11 Hz, H_2-21), 5.37 and 5.27 (2H, m, overlapping H-1 and H-3), 4.89 (1H, m, H-7), and 4.55 (1H, m, H-15).

Attempted Oxidation [4] *of Melianin A with Mercury*(II) *Acetate.*—Melianin A (50 mg) and mercury(II) acetate (100 mg) in acetic acid (10 cm^3) were left for 24 h at room temperature. The expected precipitate of mercury(I) acetate was not observed. On work-up the starting material was recovered and did not show any evidence (u.v.) for the presence of a heteroannular diene.

Melianin A Epoxide.—Melianin A (150 mg) in chloroform (2 cm^3) was treated with *m*-chloroperbenzoic acid [8] in chloroform (200 mg, 3 cm^3). The mixture was left overnight at room temperature and then filtered in ether through a short column of silica gel. Removal of solvent gave a reddish brown gum which was chromatographed on silica gel to give *melianin epoxide*, m.p. 283—286° (from ether–petroleum); $\nu_{max.}$ 3400 (OH), 1720 and 1236 (CO_2R), and 714 cm^{-1} (monosubstituted benzene); τ 9.09 (3H, s, CH_3), 9.03 (9H, s, 3 CH_3), 8.94 (3H, s, CH_3), 8.72 (3H, s, CH_3), 7.2 (1H, m, H-15), 7.03 (1H, d, *J* 9 Hz, H-24), 6.37 and 6.17 (2H, m, AM part of AMX system, J_{AM} 12 Hz, H_2-21), and 5.12 (3H, m, H-1, -3, and -7) (Found: C, 69.35; H, 8.65. $C_{41}H_{58}O_{10}$ requires C, 69.25; H, 8.2%).

Sarett Oxidation [9] *of Melianin A.*—Melianin A (150 mg) in pyridine (2 cm^3; dried by refluxing with, and distilling from, BaO) was added with stirring to CrO_3 (150 mg; dried *in vacuo* over P_2O_5) and pyridine (6 cm^3). The mixture was then stoppered and left for 6 h. It was poured into water and extracted with ether (3 × 100 cm^3). The extract was washed with water, dried ($MgSO_4$), and evaporated to give a gum. The gum was purified by chromatography on silica gel. The *ketone* (66) crystallised from carbon tetrachloride–petroleum as a carbon tetrachloride solvate, m.p. 142–145°, $\nu_{max.}$ 3450 (OH), 1720, 1240, and 1260 (CO_2R), 1710 (ketone), and 720 cm^{-1} (monosubstituted benzene); τ 9.09 (3H, s, CH_3), 9.00 (9H, s, 3 CH_3), 8.86 (3H, s, CH_3), 8.80 (6H, s, 2 CH_3), 6.42 (1H, s, H-24), 6.09 (2H, m, $W_{\frac{1}{2}}$ 7 Hz, H_2-21), 5.30 (1H, m, H-1), 5.13 (1H, m, H-3), 4.83 (1H, m, H-7), 4.67 (1H, m, H-15), and 2.65—1.87 (5H, m, Ph) (Found: C, 60.1; H, 6.5; $C_{41}H_{56}O_9,CCl_4$ requires C, 59.6; H, 6.6%).

Complete Hydrolysis of Melianin A.—Sodium (*ca.* 100 mg) was added in bits to a stirred solution of melianin A (100 mg) in methanol (10 cm^3). The mixture was heated at reflux for a few minutes until t.l.c. showed complete reaction. The mixture at pH 8 (with M-H_2SO_4) was extracted with chloroform (3 × 50 cm^3). The extract was washed with water, dried ($MgSO_4$), and evaporated to give a solid *residue* which crystallised from methanol, m.p. 249—252°; $\nu_{max.}$ 3460 and 3200 cm^{-1} (OH) (Found: C, 71.45; H, 10.15. $C_{30}H_{50}O_6$ requires C, 71.1; H, 9.95%).

Melianin A Monoacetate.—Melianin A (150 mg) was added to a mixture of pyridine (2 cm^3) and acetic anhydride (2 cm^3) and left overnight at room temperature. The mixture was poured onto ice chips and cautiously acidified (2M-HCl). The solution was extracted with ether. The extract was washed until neutral with water, dried ($MgSO_4$), and evaporated. The solid *residue*, crystallised from ether, had m.p. 281—280°; $\nu_{max.}$ 1725, 1265, and 1260 (CO_2R), and 714 cm^{-1} (monosubstituted benzene); τ 9.10 (3H, s, CH_3), 9.00 (9H, s, 3 CH_3), 8.83 (9H, s, 3 CH_3), 8.38 (3H, s, CH_3CO), 8.00 (3H, s, CH_3CO), 7.97 (3H, s, CH_3CO), 6.86 (1H, d, *J* 9 Hz, H-24), 6.50 and 6.03 (2H, AM part of AMX system, J_{AM} 11 Hz, H_2-21), 5.31 (1H, m, $W_{\frac{1}{2}}$ 6 Hz, H-1), 5.13 (2H, m, $W_{\frac{1}{2}}$ 6 Hz), 4.64 (1H, m, $W_{\frac{1}{2}}$ 5 Hz, H-15), and 2.61—1.86 (5H, m, Ph); M^+ 736 (Found: C, 70.35; H, 8.4. $C_{43}H_{60}O_{10}$ requires C, 70.1; H, 8.2%). Melianin A monoacetate was

* Deactivated alumina (5%) is obtained from Spence Activated Alumina by thoroughly shaking the alumina (100 g) with aqueous 10% acetic acid (5 cm^3).

† These were determined through decoupling experiments at Glasgow with melianin A and its monoacetate.

[8] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 1956, p. 932; R. N. McDonald, R. N. Stepped, J. E. Dorsey, *Org. Synth.*, 1970, **50**, 15.

[9] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Amer. Chem. Soc.*, 1953, **75**, 422.

also obtained from melianin A as follows. Melianin A (100 mg) in acetic acid (2 cm^3) was treated while stirring with cold hydrogen bromide–acetic acid (5 drops) and stirred for 2 h at room temperature. It was diluted with water and extracted for 2 h at room temperature. It was diluted with water and extracted with ether (3 × 50 cm^3). The extract was washed with saturated aqueous sodium hydrogen carbonate, then water, dried ($MgSO_4$), and evaporated. The gummy residue was purified by chromatography on silica gel and crystallised from ether to give a compound identical with melianin A monoacetate.

Dehydration Products of Melianin A Monoacetate and Melianin A Ketone.—Melianin A monoacetate (150 mg) in pyridine was cooled (ice–salt) and treated while stirring during 1 h with thionyl chloride (30 drops). The mixture was poured onto ice chips, cautiously acidified (6M-HCl), and extracted with ether (3 × 50 cm^3). The extract was washed with water until neutral, dried ($MgSO_4$), and evaporated. The residue was chromatographed on silica gel to give the *dehydration product*, crystals (50 mg) (from chloroform–petroleum), m.p. 286—290°; $\nu_{max.}$ 1725, 1234, 1224, and 1219 (CO_2R), and 717 cm^{-1} (monosubstituted benzene); τ 9.10 (3H, s, CH_3), 9.01 (9H, s, 3 CH_3), 8.87 (3H, s, CH_3), 8.37 (3H, s, CH_3CO), 8.27 (3H, m, vinylic Me), 8.01 (3H, s, CH_3CO), 7.99 (3H, s, CH_3CO), 6.27 (1H, d, J 8 Hz, H-24), 6.37 and 6.27 (2H, m, H-21), 5.30 (1H, m, $W_{\frac{1}{2}}$ 6 Hz, H-1), 5.07 (3H, m, $W_{\frac{1}{2}}$ 3 Hz, H-3 and $C{=}CH_2$), 4.80 (1H, m, $W_{\frac{1}{2}}$ 3 Hz, H-7), 4.63 (1H, m, $W_{\frac{1}{2}}$ 5 Hz, H-15), and 2.62—1.82 (5H, m, Ph) (the H-23 signal was also located as a non-discernible multiplet in the region τ 5.0 by integration of this part of the spectrum) (Found: C, 71.35; H, 8.35. $C_{43}H_{58}O_9$ requires C, 71.85; H, 8.15%). Similar dehydration of melianin A oxidation product gave an impure amorphous solid, which however had [6] $\lambda_{max.}$ 231 and 277 nm; τ 9.07, 8.99, 8.89, 8.84, and 8.73 (each 1H, s, CH_3), 8.21 and 7.93 (each 3H, s, 2 vinylic CH_3), 5.28, 5.09, 4.80, and 4.63 (each 1H, m, H-1, H-3, H-7, and H-15 respectively), and 2.7—1.8 (5H, m, Ph).

Acetylation of Melianin B.—Melianin B (30 mg) in pyridine (2 cm^3) and acetic anhydride (2 cm^3) was left overnight at room temperature. The mixture was worked up in the usual way to give a gum after preparative t.l.c. The n.m.r. spectrum of this product showed the presence of two additional acetate groups: τ 9.09 (3H, s, CH_3), 9.00 (9H, s, 3 CH_3), 8.97 (9H, s, 3 CH_3), 8.37 (3H, s, CH_3CO), 8.00 (3H, s, CH_3CO), 7.96 (6H, s, 2 CH_3CO), 5.29—4.82 (5H, m, 5 × CH·O-acyl), 4.67 (1H, m H-15), and 2.57—1.80 (5H, m, Ph).

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