Reprint No. 1

Chemical Investigation of the Stem-bark of
Jatropha Gossypifolia Linn.
Chemical Investigation of the Stem-bark of Jatropha Gossypifolia Linn.

P. Sengupta and P. B. Das

Jatropha gossypifolia Linn. (Family: Euphorbiaceae), originally a native of Brazil, is a shrub naturalised in Bengal. Villalba examined the bark of the plant and reported the isolation of an alkaloid, jatrophone \((C_{14}H_{25}O_2N)\), and an 'isophytosterol' \((C_{27}H_{45}OH)\), m.p. 124°, \([\alpha]_D -49° (\text{CHCl}_3)\).

In this investigation the present workers failed to isolate the above 'isophytosterol', but instead isolated from the neutral fraction of the benzene extract of the stem-bark, \(\beta\)-sitosterol, characterised as its acetate.

Isolation of Neutral Fraction.—Dried and powdered bark of Jatropha gossypifolia Linn. (800 g.) was extracted with benzene in a Soxhlet apparatus for 6 hr. The dark green residue was taken up in ether, successively washed with cold 10% aq. NaOH solution and water, dried (Na\(_2\)SO\(_4\)), and evaporated to furnish the partially crystalline neutral fraction (5 g.).

\(\beta\)-Sitosterol.—The above neutral fraction (5 g.) was chromatographed over a column of activated alumina (150 g.). On elution with a mixture of benzene and ether (2:3), a greyish yellow crystalline fraction (1.14 g.) was obtained. It was rechromatographed over activated alumina (70 g.). Elution with a mixture of benzene and ether (2:3) furnished a white crystalline solid (0.57 g.) which on several crystallisations from methanol furnished a pure sample of \(\beta\)-sitosterol, m.p. 136-37°, \([\alpha]_D -37° (\text{CHCl}_3)\) (lit.\(^4\) m.p. 140°, \([\alpha]_D -36°)\).

\(\beta\) Sitosterol Acetate.—The above \(\beta\)-sitosterol (0.57 g.) was acetylated with acetic anhydride (2 ml) and pyridine (2 ml) in the usual manner. The acetate on crystallisation from acetone furnished \(\beta\)-sitosterol acetate (0.12 g.), m.p. 128°, \([\alpha]_D -38° (\text{CHCl}_3)\), identical (mixed m.p.) with an authentic sample of \(\beta\)-sitosterol acetate (Found. C, 81.21; H, 11.32. Calc. for \(C_{39}H_{38}O_2\): C, 81.52; H, 11.48%).

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Reprint No. 2

Terpenoids and Related Compounds. Part IV.

Triterpenoids from the Stem-bark of Eugenia jambolana Lam.
Terpenoids and Related Compounds. Part IV. Triterpenoids from the Stem-bark of Eugenia Jambolana Lam

Pasupati Sengupta and Prasanta Bikram Das

Betulinic acid, friedelin, epi-friedelanol, β-sitosterol, and a new ester of epi-friedelanol (eugenin) have been isolated from the stem-bark of Eugenia jambolana Lam.

Eugenia jambolana Lam, Syn Syzygium cumini Linn, (Fam Myrtaceae) is a large evergreen tree, found all over India. The bark, seeds, leaves, and fruits of the tree have been used in the indigenous system of medicine. The seeds have been shown to contain ellagic acid, essential oil, and oleanolic acid. Recently Nair and Subramanian have reported the isolation of three triterpenoids Eugenia terpenoid A, Eugenia terpenoid B, and acetyloleanolic acid, besides possibly ellagic acid from the yellowish white, fragrant flowers of E. jambolana. These workers, however, failed to isolate any triterpenoid from the stem-bark of the tree.

The present communication deals with the chemical investigation of the stem-bark of E. jambolana. Benzene extract of the stem-bark was separated into ether-soluble and ether-insoluble fractions. The latter fraction was amorphous and resisted all attempts at crystallisation. The former fraction was separated into acidic and neutral fractions. The acidic material has been shown to be betulinic acid by its conversion to methyl betulinate, m.p. 219-20°, [α]D +8° (CHCl3), and comparison of its IR spectrum with that of an authentic specimen of methyl betulinate.

The neutral fraction on chromatography over alumina first provided a very small amount of a new substance, m.p 169-72°, [α]D—42° (CHCl3). This substance has been named eugenin (vide infra). It was followed by friedelin, m.p 256-60°, [α]D—26° (CHCl3), identical (mixed m.p and IR) with an authentic sample. The third solid to come out of the column was epi-friedelanol, m.p. 279-83°, [α]D +30° (CHCl3), which was oxidised with chromium trioxide-pyridine complex to friedelin, m.p. 256-58°, identical (mixed m.p and IR) with an authentic sample. The last crystalline solid from the chromatogram was identified as β-sitosterol.


The authors are highly indebted to Prof Carl Djerassi of Stanford University, Stanford, California, U.S.A. for comparing the IR spectra of their methyl betulinate with his authentic sample.
Eugenin, the new neutral compound mentioned above, has the molecular formula \( C_{29}H_{50}O_{10} \) and shows an IR peak at 1718 cm\(^{-1} \) due to an ester carbonyl. The compound was resistant to alkali even under drastic conditions. With sodium methoxide in anhydrous methanol, eugenin did, however, undergo ester exchange and epi-friedelanol, identical (mixed m.p. and IR) with an authentic specimen, was obtained. This experiment establishes that eugenin is an ester of epi-friedelanol (\( C_{30}H_{51}OH \)) with a fatty acid (\( C_{27}H_{55}COOH \)). Due to a very poor yield of eugenin, we have so far not been able to identify the fatty acid part. Further, on treatment with lithium aluminium hydride, eugenin furnished epi-friedelanol, identified as its acetate.

**EXPERIMENTAL**

Extraction of the Bark of E. Jambolana — Dried and powdered bark (1 kg) of *E. jambolana* was extracted with benzene for 8 hr. The resinous mass (12 g) after removal of the benzene was taken in ether and filtered from some amorphous solid which resisted all attempts at crystallisation. The ether solution was shaken with a cold 10% solution of NaOH when a white precipitate appeared in the aqueous layer which was separated and filtered. The ether solution was washed with water, dried (\( Na_2SO_4 \)), and evaporated to furnish a partially crystalline material (6 g).

Betulmic Acid — The above solid sodium salt was suspended in water and after addition of HCl (cone.) was extracted with chloroform. The chloroform layer was washed with water, dried (\( Na_2SO_4 \)), and evaporated to yield a crystalline solid (1.7 g), m.p. 225-60\(^{\circ} \), which on crystallisation from a mixture of chloroform and acetone furnished betulmic acid (1.1 g), m.p. 306-310\(^{\circ} \).

Methyl Betulnate — An ethereal solution of the preceding acid (1 g) was esterified with ethereal solution of diazomethane (from 1 g of nitrosomethylurea) and after usual working up, the crude methyl betulnate was chromatographed over alumina (10 g, deactivated with 0.3 ml of 10% aqueous acetic acid). Elution with petroleum-benzene mixture (3:2) furnished a solid (0.5 g), m.p. 203-209\(^{\circ} \), which on crystallisation from acetone furnished pure methyl betulnate, m.p. 219-20\(^{\circ} \), [\( \alpha \)]\(_D^0^+\)8\(^{\circ} \) (CHCl\(_3\)), identical (IR) with an authentic sample of methyl betulnate of Djerassi (Found C, 79.31, H, 10.72 Calc. for \( C_{31}H_{50}O_3 \) C, 79, H, 10.71%)

Investigation of the Partially Crystalline Neutral Material, Eugenin — The above partially crystalline neutral material (6 g) was chromatographed over activated alumina (120 g). After a forerun of a gummy material (1.3 g), elution with a mixture of petroleum and benzene (4:1) furnished a partially crystalline material (0.2 g), which on several crystallisations from a mixture of benzene and methanol yielded colorless crystals of eugenin (0.02 g), m.p. 169-72\(^{\circ} \), [\( \alpha \)]\(_D^0 -42\(^{\circ} \) (CHCl\(_3\))]. It did not show any colour with tetrantromethane. [Found C, 83.53, H, 12.74 \( MW \) (Rast)], 788 \( C_{29}H_{51}O_{10} \) requires C, 83.45, H, 12.71%, \( MW \), 834]. IR peak at 1718 cm\(^{-1} \) (ester carbonyl).

Friedel — Elution with a mixture of petroleum and benzene (3:2) in the above chromatogram furnished a solid (0.8 g), m.p. 240-46\(^{\circ} \), which on crystallisation from a mix-
ture of chloroform and methanol afforded a solid, m.p. 256-60°, [$\alpha$]$_D$ $-26^\circ$ (CHCl$_3$). It showed negative test with tetrantromethane and an IR peak at 1710 cm$^{-1}$ (six-membered ring ketone). Finally it was identified as friedelin by comparison (mixed m.p. and IR) with an authentic specimen (Found: C, 84.26; H, 11.72; Calc for C$_{30}$H$_{50}$O: C, 84.44; H, 11.81%).

**Friedelin Oxime** — Friedelin was converted into its oxime according to the procedure of Drake and Shrader. The oxime, m.p. 290-94°, did not depress the m.p. of an authentic specimen.

**epi-Friedelanol** — Elution with a mixture of benzene and ether (4:1) in the above chromatogram furnished a crude solid (0.6 g), m.p. 270-74°, which on repeated crystallisation from a mixture of chloroform and methanol provided pure epi-friedelanol, m.p. 279-83°, [$\alpha$]$_D$ +30° (CHCl$_3$) (lit. m.p. 279-83°, [$\alpha$]$_D$ +24°).

**epi-Friedelanyl Acetate** — epi-Friedelanol (0.2 g) was acetylated in the usual manner with acetic anhydride (5 ml) and pyridine (5 ml). The crude acetate on crystallisation from a mixture of chloroform and methanol furnished epi-friedelanyl acetate, m.p. 290-94°, [$\alpha$]$_D$ +38° (CHCl$_3$) (lit. m.p. 290-94°, [$\alpha$]$_D$ +45°) (Found: C, 81.53; H, 11.36; Calc for C$_{32}$H$_{54}$O$_2$: C, 81.64; H, 11.56%).

**epi-Friedelanyl Benzoate** — epi-Friedelanol (0.13 g) was benzoylated in the usual manner with benzoyl chloride (2 ml) and pyridine (10 ml). The crude benzoate on crystallisation from a mixture of chloroform and methanol furnished epi-friedelanyl benzoate, m.p. 250-54°, [$\alpha$]$_D$ +44° (CHCl$_3$) (lit. m.p. 254-57°, [$\alpha$]$_D$ +40°).

**Friedelin from epi-Friedelanol** — A cold solution of epi-friedelanol (0.15 g) in pyridine (4 ml) was added to a complex, prepared from chromium trioxide (0.15 g) in pyridine (1.5 ml), and cooled to 15°. After usual working up, the crude solid, m.p. 252-56°, on crystallisation from a mixture of chloroform and methanol furnished friedelin, m.p. 256-58°, identical (mixed m.p. and IR) with an authentic specimen of friedelin.

**$\beta$-Sitosterol** — Elution with a mixture of benzene and ether (1:4) in the above chromatogram furnished a solid (0.6 g), m.p. 124-36°, which on several crystallisations from a mixture of chloroform and methanol yielded $\beta$-sitosterol, m.p. 134-36°, [$\alpha$]$_D$ $-38^\circ$ (CHCl$_3$) (Found: C, 84.05; H, 12.40; Calc for C$_{29}$H$_{50}$O: C, 83.99; H, 12.15%).

**$\beta$-Sitosterol Acetate** — $\beta$-Sitosterol (0.43 g) was acetylated in the usual manner with acetic anhydride (5 ml) and pyridine (5 ml). The crude acetate on crystallisation from acetone furnished $\beta$-sitosterol acetate, m.p. 124-26°, [$\alpha$]$_D$ $-39^\circ$ (CHCl$_3$), identical (mixed m.p.) with an authentic specimen of $\beta$-sitosterol acetate (Found: C, 81.67; H, 11.30; Calc for C$_{31}$H$_{54}$O$_2$: C, 81.52; H, 11.48%).

**Attempted Hydrolysis of Eugenin** — (a) Eugenin (0.09 g) was refluxed for 30 hr. with KOH (0.5 g), methanol (25 ml), and benzene (10 ml). After working up as usual, unchanged eugenin (0.08 g), m.p. and mixed m.p. 169-70°, was obtained.

(b). Eugenin (0.06 g) was refluxed for 8 hr. with KOH (0.4 g.), water (0.1 ml), and tetrahydrofuran (5 ml). After working up as usual, unchanged eugenin (0.05 g), m.p., and mixed m.p. 168-70°, was obtained.

(c). Eugenin (0.07 g) was refluxed for 5 hr. with KOH (1 g.) in ethylene glycol (10 ml). After working up as usual, unchanged eugenin (0.06 g), m.p. and mixed m.p. 167-70°, was recovered.

**Methanolyis of Eugenin** — Eugenin (0.068 g) was refluxed for 5 hr. with a solution of sodium methoxide (from 0.5 g. Na and 5 ml of methanol) in benzene (7 ml). The reaction mixture was treated with cold water and the neutral material was extracted with chloroform. The chloroform solution was washed with water, dried (Na₂SO₄), and evaporated to furnish a crystalline solid (0.03 g), m.p. 250-65°. It was chromatographed over alumina (10 g.) and the solid eluted with benzene on crystallisation from a mixture of chloroform and methanol afforded epi-friedelanol, m.p. 271-75°, identical (mixed m.p. and IR) with an authentic specimen.

The above aqueous alkaline layer on acidification provided only a trace of a gummy material which could not be examined further.

**Treatment of Eugenin with LiAlH₄** — A solution of eugenin (0.05 g) in THF (5 ml) was added to a suspension of LiAlH₄ (0.05 g) in THF (5 ml) and the mixture was refluxed for 5 hr. After working up as usual, a crystalline material, m.p. 226-252°, was obtained. The solid after chromatography on alumina, followed by crystallisation from chloroform-methanol, as above, furnished epi-friedelanol, m.p. 270-74°, identical (mixed m.p. and IR) with an authentic specimen.

A small fraction of this epi-friedelanol was acetylated as usual and the acetate, m.p. 286-90°, was identical (mixed m.p. and IR) with authentic epi-friedelanyl acetate.

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Reprint No. 3

Terpenoids and Related Compounds. Part V.

Triterpenoids from the Flowers of Eugenia jambolana Lam.
Terpenoids and Related Compounds. Part V. Triterpenoids from the Flowers of Eugenia Jambolana Lam.

Pasupati Sengupta and Prasanta Bikram Das

Two triterpene acids, oleanolic acid and orategolic acid (maslinic acid), have been isolated from the flowers of Eugenia jambolana Lam. as their respective methyl ester.

In a previous communication, we reported the isolation of betulinic acid, friedelanol, epi-friedelanol, β-sitosterol, and eugenol, a new ester of epi-friedelinol from the stem-bark of Eugenia jambolana Lam. Nair and Subramanian reported isolation from the flowers of Eugenia jambolana of two new triterpenoids, Eugenia terpenoid A' and Eugenia terpenoid B' besides acetyloleanolic acid. In view of this and the reported medicinal uses of the different parts of the plant in the indigenous system of medicine, we thought it relevant to undertake a chemical investigation of the flowers.

By following a different extraction procedure, using benzene instead of ethanol, we obtained a crude semicrystalline product from the flowers of Eugenia jambolana. The product was separated into ether-soluble and ether-insoluble fractions. The former fraction on extraction by cold aqueous alkali, followed by acidification of the alkaline extract, afforded a crystalline mixture of triterpene carboxylic acids, which was esterified with diazomethane, and the mixture of the methyl esters was chromatographed on deactivated alumina. The first ester, eluted from the column, on acetylation and crystallisation from acetone furnished methyl oleanolate acetate, mp. 218-20°, [α]D +65° (CHCl₃), identical (mixed m.p. and IR) with an authentic specimen. Further, the acetate ester was hydrolysed to yield methyl oleanolate, mp. 194-96°, [α]D + 70° (CHCl₃), identical (mixed m.p.) with an authentic specimen.

The second methyl ester, mp 227-28°, [α]D +36° (CHCl₃), eluted from the column in the above chromatogram, had the molecular formula C₅₈H₈₀O₆ and was found to be identical (IR) with methyl orategolate (methyl maslinate). The structure of orategolate (maslinic) is C₅₈H₈₀O₆, but it was wrongly printed as C₅₈H₈₀O₆ in Part IV.

1. This Journal, 1965, 42, 255.
4. (a) Tschesche and Fugmann, Chem. Ber., 1951, 84, 810.
   (b) Tschesche et al., ibid., 1953, 86, 629.
acid has recently been established as 2α,3β-dihydroxyolean-12-en-28-oic acid (I. R=Me, R1=R2=H). Further, our methyl crategolate (I. R=Me; R1=R2=H) was converted into methyl crategolate diacetate (I. R=Me; R1=R2=COMe) which was found to be identical (IR) with an authentic specimen.

\[ \text{(I)} \]

The above mentioned ether-insoluble part was separated into acetone-soluble and acetone-insoluble fractions. Each of the fractions was esterified with diazomethane and chromatographed when only methyl oleanolate and methyl crategolate could be isolated from each. We, however, failed to isolate any acetyloleanolic acid and Eugenia terpenoids A and B from the flowers of *E. jambolana*.

**EXPERIMENTAL**

*Extraction of the Flowers of E Jambolana.*—The dried flowers (1 kg), collected during the summer of 1964, were extracted with benzene in a Soxhlet apparatus for 8 hr. The crude, semicrystalline solid (60 g.), left after removal of benzene, was digested with ether, the ether-soluble material was separated by filtration from the ether-insoluble matter (18 g). The ether solution was extracted with cold aqueous 5% NaOH solution and the alkaline aqueous layer acidified with cold HCl (dil.) and filtered when a crystalline acidic material (22 g) was obtained.

**Crude Methyl Oleanolate**—The above ether-soluble acidic matter (22 g) in ether (1 litre) was treated with an ethereal solution of diazomethane (prepared from 20 g. of nitrosomethylurea) and allowed to stand overnight. After working up as usual, the ester mixture (16 g) was chromatographed over alumina (300 g, deactivated with 9 ml of 10% acetic acid). Elution with benzene afforded the crude solvated methyl oleanolate (5 g.), m. p. 110-14°.

**Methyl Oleanolate Acetate**—The above crude methyl oleanolate (15 g.) was acetylated with acetic anhydride (15 ml) and pyridine (15 ml) in the usual manner. The crude acetate on crystallization from acetone afforded methyl oleanolate acetate (0.4 g.), m. p. 218-20°, [\(\alpha\)]D +65° (CHCl₃), identical (mixed m. p. and IR) with an authentic specimen. (Found: C, 77.29; H, 10.22%).

*All melting points are uncorrected. The petroleum used had b. p. 60-80°.

5. (a) Caghoti et al., *Gazzetta*, 1963, 92, 308.
**Methyl Oleanolate from Methyl Oleanolate Acetate** — Methyl oleanolate acetate (0.22 g.) was deacetylated by refluxing in benzene (2 ml) with a solution of methanolic NaOH, prepared from NaOH (0.5 g.), water (0.5 ml), and methanol (4.5 ml). After working up as usual, the crude hydroxy-ester (0.2 g.) on crystallisation from a mixture of acetone and methanol furnished methyl oleanolate, m.p. 194-96°, [α]D +70° (CHCl₃), identical (mixed m.p.) with an authentic specimen. (Found C, 79.59; H, 10.68 Calc for C₃₈H₅₀O₃ C, 79.10, H, 10.71%)

**Methyl Crategolate (Maslinate).** — Elution with ether in the above chromatogram furnished a crude solid (2 g.), m.p. 212-16°, which on crystallisation from a mixture of benzene and petroleum yielded methyl crategolate (0.65 g.), m.p. 227-28°, [α]D +36° (CHCl₃), identical (IR) with an authentic sample of methyl crategolate. It developed a yellow colour with tetranitromethane (Found C, 76.24; H, 10.23, M.W. (East), 473 Calc. for C₃₅H₅₄O₄ C, 76.60, H, 10.36%, M.W., 486).

**Methyl Crategolate Diacetate.** — The acetate of methyl crategolate was prepared by treating methyl crategolate (0.52 g.) with pyridine (5 ml) and acetic anhydride (5 ml) at the room temperature for 4 days. The crude glassy mass (0.5 g.), obtained after working up as usual, was chromatographed over alumina (50 g., deactivated with 1.5 ml of 10% acetic acid). Elution with benzene provided the crude acetate, m.p. 138-58°, which on crystallisation from dilute methanol furnished pure methyl crategolate diacetate (0.11 g.), m.p. 166-68°, [α]D –24° (CHCl₃), identical (IR) with an authentic specimen of methyl crategolate diacetate. (Found C, 73.68, H, 9.29 Calc. for C₃₃H₅₀O₄ C, 73.40, H, 9.54%)

**Treatment of Ether-insoluble Fraction** (a) Acetone-soluble Part — The other-insoluble matter (18 g.) was digested with acetone and filtered from acetone insoluble matter (10 g.). Evaporation of the solvent afforded a solid (6.8 g.) which on esterification with ethereal diazomethane, chromatography over alumina (150 g., deactivated with 4.5 ml of 10% acetic acid), and elution with benzene afforded a solid (2.6 g.) This on acetylation with acetic anhydride (25 ml) and pyridine (25 ml) in the usual manner and crystallisation from acetone furnished methyl oleanolate acetate, m.p. 214-18°, identical (mixed m.p. and IR) with an authentic sample. Elution with ether in the above chromatogram provided a crude solid (1.28 g.), m.p. 214-18°, which on crystallisation from a mixture of acetone and methanol afforded pure methyl crategolate (0.32 g.), m.p. 225-27°, [α]D +36° (CHCl₃), identical (mixed m.p. and IR) with an authentic specimen. (Found C, 76.14; H, 10.47, M.W. (Rast), 402. Calc. for C₃₃H₅₀O₄ C, 76.50, H, 10.36%, M.W., 486)

(b) Acetone-insoluble Part — The above acetone-insoluble solid (10 g.) was extracted with methanol and filtered. Evaporation of the solvent afforded a semicrystalline solid (7.8 g.) which was esterified with ethereal diazomethane. The ester mixture, thus obtained, was chromatographed over alumina (150 g., deactivated with 4.5 ml of 10% acetic acid). Elution with benzene afforded a solid (1.2 g.) which on acetylation with acetic anhydride (12 ml) and pyridine (12 ml) in the usual manner furnished methyl oleanolate acetate (0.31 g.), m.p. 218-20°, identical with an authentic specimen.

Elution with ether in the above chromatogram furnished a crystalline solid (2.3 g.) which on crystallisation from acetone afforded methyl crategolate (0.4 g.), m.p. 216-18°.
identical with an authentic sample (Found. C, 76.30; H, 10.47; M.W. (Rast), 465. Calc.
for C_{36}H_{50}O_{4}: C, 76.50; H, 10.36%, M.W., 466).

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ford, U. S. A., for comparing the IR spectra of methyl oleanolate acetate with that of an
authentic specimen, to Prof. Rudolf Tchesche of Hamburg University, Hamburg, W.
Germany, for comparing the IR spectra of methyl crategolate and its acetate with those
of his respective authentic specimens, and to the University of Kalyani for the award of a
fellowship to one of them (P. B. D.).

We have now been able to isolate methyl ursolate acetate, m.p. 238-42°, [α]_{D} + 65°, identical with an
authentic specimen, from the mother liquor of methyl oleanolate acetate, described above (added
on proofs).
Reprint No. 4

Terpenoids and Related Compounds-XII:

Synthesis of Oleana-2,12-Diene (β-Amyrilene-II)
Terpenoids and Related Compounds-XII:
Synthesis of Oleana-2, 12-Diene (β-Amyrilen-II)

P. Sengupta and P. B. Das

Methyl oleanolate (I) has been converted to oleana-2,12-diene (II) through oleana-2,12-diene-28-oic acid methyl ester (III), oleana-2,12-diene-28-ol (IV) and oleana-2,12-diene-28-aldehyde (V).

In a previous communication2, we reported the isolation of oleanolic, ursolic and crategolic acids from the flowers of Eugenia jambolana Lam. In connection with a scheme for the synthesis of stereoisomeric olean-12-ene-23-diols, we required oleana-2,12-diene, the so-called β-amyrilen II. Oleanolic acid being available in plenty from the flowers of E. jambolana, we attempted to prepare oleana-2,12-diene from it. The present communication describes the successful conversion of methyl oleanolate (I) to oleana-2,12-diene (II).

Methyl oleanolate (I) was treated with phosphorus oxychloride and pyridine to furnish oleana-2,12-diene-28-oic acid methyl ester (III), m.p 180–182° (Lit 4 m.p 180–186°), which on reduction with lithium aluminium hydride gave oleana-2,12-diene-28-ol (IV), m.p 150–152°, [α]D+118°.

It failed to give a crystalline acetate or a p-toluenesulphonate. However, the infra-red spectra of the alcohol (IV) showed a band at 3400 cm\(^{-1}\) (hydroxyl).

The diene-alcohol (IV) could not be oxidised satisfactorily by chromium trioxide-pyridine complex, the product being a gummy substance from which isolation of the desired aldehyde by chromatography was difficult. However, oxidation with Jones chromic acid

1 Part XI P. Sengupta and J Mukherjee, Tetrahedron, in press
2 This Journal, 1965, 42, 639.
4 R. Tschesehe, E Henokel and G Snatzke, Ann., 1964, 676, 175
reagent proceeded smoothly and the product after chromatography over silica gel gave in good yield oleana-2,12-diene-28-aldehyde (V), m.p. 164–170°, [α]D +128°, which showed peaks in the infra-red at 2710 and 1720 cm⁻¹ (aldehyde).

The diene aldehyde (V) on Huang-Minlon reduction furnished oleana-2,12-diene (II), m.p. 148–150° (Lit m.p. 150–153°). The infra-red spectra showed no bands in the carbonyl and hydroxyl regions, but showed peaks at 820 (trisubstituted ethylene) and 725 cm⁻¹ (cis-disubstituted ethylene).

**EXPERIMENTAL**

Oleana-2,12-diene-28-oic acid methyl ester (III), m.p. 180–182°, [α]D +110° was prepared according to the method of Tschesche et al by the treatment of methyl oleanolate (I) with phosphorus oxychloride and pyridine.

Oleana-2,12-diene-28-ol (IV). The dienoic acid methyl ester (III, 1 g) was refluxed with lithium aluminium hydride (1 g) and anhydrous tetrahydrofuran (100 ml) for 8 hr. After cooling, the excess of lithium aluminium hydride was decomposed with crushed ice and the mixture was extracted thoroughly with chloroform. The organic layer was filtered, washed with water, dried (Na₂SO₄) and evaporated to furnish a crude product (0.9 g), which was chromatographed over a column of basic alumina (45 g). Elution with benzene afforded a glass (0.82 g), which on crystallisation from dil methanol gave crystals of oleana-2,12-diene-28-ol (IV, 0.66 g), m.p. 150–152°, [α]D +118° (CH₂OH). (Found: C, 85.05; H, 11.51. C₃₀H₄₈O requires C, 84.84; H, 11.39%).

**Attempted Acetylation of Oleana-2,12-diene-28-ol** (III). The diene alcohol (0.1 g) was heated on the water-bath with acetic anhydride (1 ml) and pyridine (1 ml) for 1 hr and the mixture was allowed to stand overnight. Usual working up furnished a glass, which could not be crystallised even after filtration through a column of silica gel (2 g). A waxy solid, m.p. 60–80° could be obtained on keeping a solution of the product in methanol in a refrigerator for 24 hr. However all attempts at recrystallisation failed.

**Attempted Tosylation of Oleana-2,12-diene-28-ol** (IV). A solution of the diene alcohol (IV, 0.1 g) and p-toluene sulphonyl chloride (0.1 g) in pyridine (1 ml) was allowed to stand at room temperature for 48 hr. The reaction mixture was worked up as usual, when a non-crystallisable glass was obtained.

**Chromic Acid Pyridine Oxidation** of (IV). Oleana-2,12-diene-28-aldehyde (V). The diene-alcohol (IV, 0.34 g) dissolved in pyridine (3.4 ml) was added at 15° to a complex prepared from chromium trioxide (0.34 g) and pyridine (3.4 ml) and the mixture was allowed to stand at room temperature for 18 hr. After working up as usual a crude coloured gum (0.34 g) was obtained, which was chromatographed over alumina (20 g, deactivated with 0.6 ml of 10% aqueous acetic acid). Elution with petroleum afforded a crystalline material (0.08 g) which on crystallisation from a mixture of acetone and methanol furnished flowery crystals of the diene aldehyde (V, 0.04 g), m.p. 164–170°, [α]D +128° (Found: C, 85.24, H, 10.80. C₃₀H₄₆O requires C, 85.24, H, 10.97%).

6 K Bowden, L.M. Heilbron, F.R. H Jones and B C L. Weedon, J Chem Soc, 1946, 39

* All melting points are uncorrected The petroleum used had b.p. 60–80°
Jones Oxidation\(^6\) of (IV). Oleana-2,12-diene-28-aldehyde (V) To a solution of the diene alcohol (IV, 0.2 g) in acetone (8 ml) was added Jones reagent drop by drop through a micro-pipette at room temperature, the mixture being vigorously shaken all the time till the green precipitate no longer formed and the colour of the reagent persisted. After stirring the reaction mixture for further 2 min, cold water was poured into it and the reaction mixture was extracted with CHCl\(_3\). The organic layer was washed with water, dried (Na\(_2\)SO\(_4\)) and evaporated to furnish a glassy solid (0.15 g), which was chromatographed over silica gel (10 g). Elution with petroleum afforded crystals (0.1 g), which after crystallisation from a mixture of acetone and methanol furnished the diene aldehyde (V, 0.07 g), m.p. 164-170°, identical with the above Sarett-oxidation product (mixed m.p.).

Huang-Minlon reduction of (V) Oleana-2,12-diene (II) The diene aldehyde (V, 0.21 g), in ethanol (10 ml) and diethylene glycol (40 ml) was heated under reflux for 1 hr with 80\% hydrazine hydrate (3 ml). KOH (0.25 g) was then added and the mixture refluxed for 1 hr. The condenser was removed and the solution boiled until the inner temperature reached 190°. The condenser was then replaced by a dry one and the solution was heated under reflux for 3 hr. After cooling, water was added to the mixture and the precipitated gum was extracted with ether. The ether solution was washed with water, dried (Na\(_2\)SO\(_4\)) and evaporated to furnish a crude solid (0.2 g), which was chromatographed over activated alumina (5 g). Elution with petroleum furnished a solid, m.p. 144-148° (0.16 g), which on two crystallisations from acetone gave oleana-2,12-diene (II), m.p. 148-150° (Lit\(^3\) m.p. 152-153°) (Found C, 87-96; H, 11-74; Calc for C\(_{30}\)H\(_{48}\) C, 88-16; H, 11-84\%\). Positive tetranitromethane test.

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