NOTES

A Chemical Examination of *Euphorbia hirta Linn.*

By D. R. GUPTA and S. K. GARG

Department of Chemistry, University of Roorkee, Roorkee, India

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Euphorbia hirta Linn. (Fam: Euphorbiaceae; Hindi, Dudhi) is a small herb which grows throughout the hotter parts of India. This plant has been medicinally used in the teratment of bowel complaints, coughs, dysentery, colic pains, bronchial affections, and asthma.[1] Some varieties of *Euphorbia hirta,* viz., procumbens, pedilantus calcaratus and pedilantus tehuacanus, have been chemically examined by earlier workers.[2] We have now undertaken a systematic chemical examination of *Euphorbia hirta Linn.,* which has not yet been worked up. In a previous communication,[3] the free organic acids of the stems and leaves of this plant were reported. The present work will concern the chemical examination of the petroleum ether and ethanol extracts of the stems and the ethanol extract of the flowers of *Euphorbia hitra Linn.*

Experimental

Air-dried, powdered stems (2 kg.) were successively soxhletted with petroleum ether (b. p. 60—80°C) and ethanol for 30 hr.

The Examination of the Petroleum Ether Extract of the Stems.—The petroleum ether extract was concentrated and left in a refrigerator overnight; the white solid (7.2 g.) which thereupon separated, was filtered and dissolved in petroleum ether, and then chromatographed over Brockmann alumina (64×4 cm.) using petroleum ether, benzene, chloroform and their mixtures as eluants, as is shown in Table I. Eluants were collected in fractions of 30—40 ml. each and evaporated to dryness.

Fractions 1—14 gave a waxy material which, on repeated crystallisation from ethanol, afforded silky needles (1.2 g.), m. p. 84°C.

Found: C, 82.14; H, 14.12. Calcd. for $C_{30}H_{62}O$: C, 82.19; H, 14.15%.

The compound was soluble in benzene, chloroform, ethyl ether and petroleum ether, but was insoluble in water. It was identified as myricyl alcohol by a mixed m. p. determination with an authentic sample and by the preparation of its acetyl derivative,[4] m. p. 71.5°C, and a chloro derivative,[4] m. p. 64°C.

Found: Cl, 7.50. Calcd. for $C_{31}H_{63}Cl$: Cl, 7.54%.

TABLE I

Fraction No.	Eluant	Residue left on the evaporation of the solvents
1—14	Petroleum ether (b. p. 60—80°C)	Waxy material
15—24	Petroleum ether+Benzene (5:1 v/v)	Colourless solid
25—32	Petroleum ether+Benzene (3:2 v/v)	Colourless solid
33—40	Petroleum ether+Benzene (1:1 v/v)	Nil
41—49	Benzene	Short needles
50—58	Benzene+Chloroform (3:2 v/v)	Shining flakes
59—66	Benzene+Chloroform (1:1 v/v)	Shining flakes
67—72	Chloroform	Nil

Fractions 15—32 gave a colourless solid which, when crystallised from a methanol-chloroform mixture, afforded needle-shaped crystals (1.1 g.), m. p. 281°C.

Found: C, 84.46; H, 11.71. Calcd. for $C_{30}H_{50}O$: C, 84.51; H, 11.74%.

This product gave colour reactions characteristic of triterpenes, including Noller's test. A sequence of colour (yellow→orange→red→purple) was developed when the compound was treated with thionyl chloride in the presence of tin. The compound was identified as taraxerol by a mixed m. p. determination and by the preparation of its acetate,[5] m. p. 304°C, and a benzoate,[5] m. p. 292°C.

Fractions 41—49, on crystallisation from benzene, gave colourless needles (2.4 g.), m. p. 260—261°C.

Found: C, 84.44; H, 11.82. Calcd. for $C_{30}H_{50}O$: C, 84.51; H, 11.74%.

The compound, which gave no colour reaction in Salkowski or Liebermann-Burchard reaction or with tetranitromethane reagent was identified as friedelin

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2) H. Estrada, *Bol. Inst. Quim. Univ. Nacl. Auton. Mex.*, **11**, 15 (1959).

3) D. R. Gupta and S. K. Garg, *Indian J. Appl. Chem.*, **28**, 113 (1965).

4) M. C. Sheth and C. M. Desai, Science and Culture, **20**, 243 (1954).

5) S. Burrows and J. C. E. Simpson, *J. Chem. Soc.*, **1938**, 2042.

by a mixed m. p. determination and by preparing its derivatives, i. e., friedelinol,[6] m. p. 299°C; oxime acetate,[7] m. p. 239°C, and friedelin-2, 4-dinitrophenyl hydrazone,[7] m. p. 297—298°C.

Fractions 50—66 gave shining flakes which, on repeated crystallisation from a methanol - ethyl acetate mixture, yielded coloruless flakes (1.4 g.), m. p. 136—137°C.

Found: C, 84.15; H, 12.16. Calcd. for $C_{29}H_{50}O$: C, 84.05; H, 12.08%.

The compound was fairly soluble in benzene, methanol ethanol, and was readily soluble in chloroform, ethyl ether and ethyl acetate. The compound gave a positive Salkowskii-Hesse reaction and developed a green colour in the Liebermann-Burchard reaction. It formed an acetate,[8] m. p. 126°C; a benzoate,[8] m. p. 144°C, and a digitonide,[9] m. p. 230°C. The compound was identified as β-sitosterol by a mixed m. p. determination and by the formation of a mixed chromatogram of the compound with an authentic sample of β-sitosterol.

The Examination of the Ethanol Extract of the Stems.—The ethanol extract was concentrated under reduced pressure and then kept overnight in a refrigerator; it thereupon left a greenish, waxy material (4.1 g.), which was then dissolved in petroleum ether and then chromatographed over Brockmann alumina (32×2 cm.) using petroleum ether, benzene, chloroform and their mixtures as eluants, as is shown in Table II. Eluants were collected in fractions of 30—40 ml. each and evaporated to dryness.

Table II

Fraction No.	Eluant	Residue left on the evaporation of the solvents
1—10	Petroleum ether (b. p. 60—80°C)	Way material
11—17	Petroleum ether+Benzene (3: 2 v/v)	White solid
18—25	Petroleum ether+Benzene (1: 1 v/v)	White solid
26—30	Benzene	Nil
31—35	Benzene+Chloroform (3: 2 v/v)	Nil
36—40	Benzene+Chloroform (1: 1 v/v)	Nil
41—44	Chloroform	Nil

Fractions 1—10 gave a waxy material which, on repeated crystallisation from a mixture of methanol-acetone-benzene (1 : 1 : 1 v/v), gave a colourless solid (2.2 g.), m. p. 68°C.

Found: C, 85.44; H, 14.71. Calcd. for $C_{31}H_{64}$: C, 85.32; H, 14.67%.

Its infrared absorption spectrum did not indicate the presence of any functional groups. It did not absorb bromine and, on oxidation with air in the presence of potassium permanganate and boric acid at 200°C, gave an alcohol,[10] m. p. 58°C. The compound was identified as hentriacontane.[11]

Fractions 11—25 gave a white solid which, on crystallisation from a chloroform-methanol mixture, afforded colourless needles (1.3 g.), m. p. 199°C.

Found: C, 84.46; H, 11.78. Calcd. for $C_{30}H_{50}O$: C, 84.51; H, 11.74%.

The substance gave a positive Liebermann-Burchard reaction for a triterpene. It formed an acetate,[12] m. p. 237°C, which produced a yellow colouration with tetranitromethane; a benzoate,[12] m. p. 232°C, and a *p*-nitrobenzoate,[12] m. p. 258°C. The compound was identified as β-amyrin by a mixed m. p. determination with an authentic sample.

The Examination of the Flowers of *Euphorbia hirta Linn.*—Fresh flowers of *Euphorbia hirta Linn.* (2 kg.) were soxhletted with ethanol for 30 hr. Ethanol was distilled off from the extract under reduced pressure, and the sticky mass left was taken up in water (100 ml.). The aqueous solution was extracted with petroleum ether to remove the fatty material and chlorophyll, and then extracted with ethyl ether in a liquid-liquid extractor. The ether was removed, and the residue left was taken up in methanol and filtered. Distilling off the methanol afforded a yellow solid which, on crystallisation from pyridine, gave yellow needles (4.2 g), m. p. 360°C.

Found: C, 55.64; H, 2.02. Calcd. for $C_{14}H_6O_8$: C, 55.62; H, 1.98%.

The compound gave a green colour with ferric chloride, dissolved in aqueous sodium hydroxide with a bright yellow colour, and gave a positive Griessmeyer reaction. The compound was identified as ellagic acid by a mixed m. p. determination with an authentic sample and by the preparation of its tetraacetate,[13] m. p. 342—343°C, and an ellagorubin,[14] m. p. 218—219°C. It was further confirmed by paper chromatography,[15] using Whatman filter paper No. 1, and an aqueous solution of 60% formamide buffered at pH 3.5 with formic acid as the developer. The chromatogram was exposed to ammonia vapours in order to locate ellagic acid as yellow spot. The co-chromatography of the compound with an authentic sample of ellagic acid gave a single yellow spot with a R_f value of 0.58.

Summary

Petroleum ether and ethanol extracts of the stems of *Euphorbia hirta Linn.* were submitted to chromatography over Brockmann alumina using petroleum ether, benzene, chloroform and their mixtures as eluants, myricyl alcohol, taraxerol, friedelin, β-sitosterol, hentriacontane and β-amyrin were isolated, while the ethanol extract of the flowers

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15) A. Singh and V. N. Sharma, *Indian J. Chem.*, **2**, 253 (1964).

of *Euphorbia hirta Linn.* gave only ellagic acid. The above compounds were characterized by their physical and chemical properties and by the preparation of their derivatives.

It is interesting to observe that *Euphorbia hirta Linn.* contains myricyl alcohol, taraxerol and ellagic acid, besides friedelin, β-amyrin, hentriacontane and β-sitosterol already reported[20] in some varieties of *Euphorbia hirta.*

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