

STUDIES ON EUPHORBIA HELIOSCOPIA LINN

AZIZ AHMAD DURRANI, M. RAFIULLAH AND M. IKRAM

North Regional Laboratories, Pakistan Council of Scientific and Industrial Research, Peshawar

(Received July 6, 1966)

One steroid with molecular formula $C_{29}H_{50}O$, one triterpenoid with molecular formula $C_{32}H_{52}O_2$ and a saturated aliphatic alcohol with molecular formula $C_{21}H_{44}O$ have been isolated from *E. helioscopia*. The plant was also examined for the sugars present.

Introduction

Euphorbia helioscopia Linn., locally known as Gandi Buti, is a very common plant available throughout the plains of West Pakistan. The roots are reported to be anthelmintic, whole plant cathartic, milky juice applied to eruptions, seeds with roasted pepper given in cholera, and oil from seeds used as a purgative.¹

Though other species of the plant have been studied by various workers very little work²⁻¹³ has been done on *E. helioscopia* and only the isolation of a saponin has been reported.¹

Our investigations gave three crystalline compounds: compound A, saturated aliphatic alcohol melting at $75-6^\circ$; compound B, a steroid melting at $133-4^\circ$; compound C, a triterpenoid melting at $183-4^\circ$.

The IR spectra of compound A gave peak at 3450 cm^{-1} showing hydroxyl group. A saturated, straight chain alcohol with molecular formula $C_{21}H_{44}O$ has been reported from the flowers of *Forsythia intermedia*¹⁴ which also formed acetate having the same m.p. as that of compound A. The compound was neither named by the previous workers nor detailed structure given. We propose the name "helioscopiol" for this alcohol. Due to non-availability of an authentic sample, of the alcohol from *F. intermedia* direct proof of its identity with the compound could not be confirmed. Since it does not form an adduct with urea, it is in isoform¹⁵. Further work is in progress to determine the structure of the alcohol.

The IR spectra of compound B showed a peak at 3450 cm^{-1} . The secondary nature of the group is indicated by the IR peak at 1360 cm^{-1} . Its acetate gave IR peak at 1240 cm^{-1} . This steroid may be β -dihydrofucosterol which has identical molecular formula, solubility, crystalline shape and m.p. The m.p. of acetates are also identical.¹⁶ In the absence of an authentic sample of β -dihydrofucosterol, the identity of the compound could not be directly confirmed.

The IR spectra of compound C gave a peak at 1720 cm^{-1} showing the presence of carbonyl group, probably due to an ester. It could not, however, be hydrolysed. Further work is in progress to identify the compound.

Experimental

All the melting points were recorded by Gallenkamp electrothermal micro-melting point apparatus. Molecular weights and microanalyses were done by Dr. A. Bernhardt, 433, Mulheim Ruhr, West Germany. IR spectra were taken on Beckmann Spectrophotometer model IR-5.

Isolation of Compound A.—The plant was collected in the beginning of March from the Peshawar Valley and used fresh and also after air drying. The whole plant (1.25 kg) was percolated with 95% ethanol (5 l.) four times and the extract reserved for further processing. The residue was Soxhleted with petroleum ether ($50-70^\circ$) for 6 hr. The resulting extract was charcoaled, and the solvent removed completely. The residue was extracted with methanol and the extract concentrated. On standing a solid deposited, m.p. $50-60^\circ$. Recrystallisation from methanol gave a semi-crystalline product, m.p. $75-6^\circ$ (0.74% yield on dry basis). (The alcohol from *Forsythia intermedia* is reported to melt at $75-6^\circ$.¹⁴) Found C, 80.60; H, 14.23; O, 5.17%. $C_{21}H_{44}O$ requires C, 80.69; H, 14.19; O, 5.12%.

The compound is soluble in hot petroleum ether, benzene, ether, chloroform, carbon tetrachloride, amyl alcohol, ethanol, methanol and ethyl acetate. It neither reduced Fehling's solution nor decolorised bromine in carbon tetrachloride.

The compound was acetylated by heating with acetic anhydride and fused sodium acetate. The acetate was crystallised from methanol as a semi-crystalline powder, m.p. $56-57^\circ$. The acetate of the alcohol from *Forsythia intermedia* is reported to melt at m.p. $56-7^\circ$.¹⁴

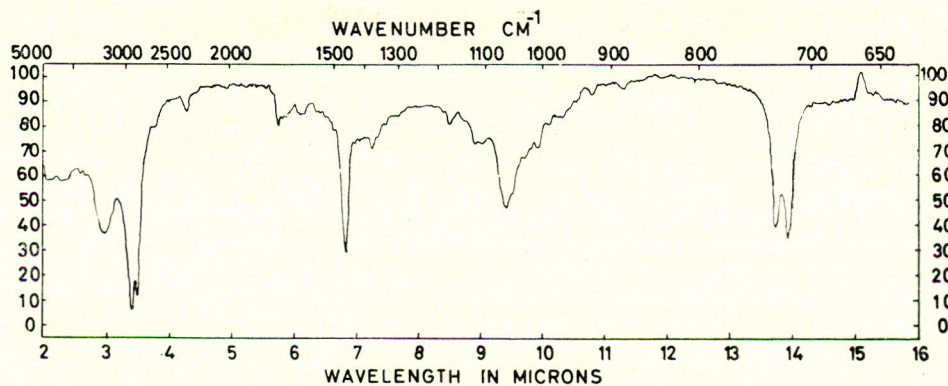


Fig. 1.—I R spectra of compound A in (KBr pellet).

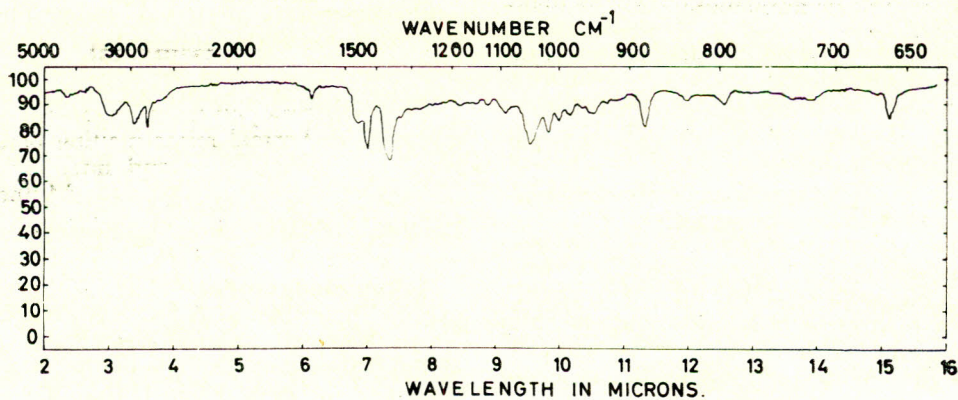


Fig. 2.—I R spectra of compound B (in nujol).

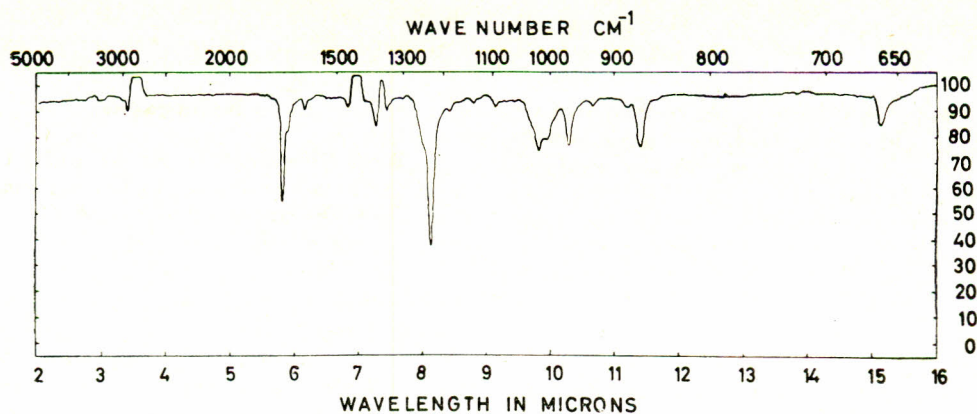


Fig. 3.—I R spectra of compound C (in nujol).

On benzoylation with benzoyl chloride in pyridine and crystallisation from methanol a semi-crystalline powder, m.p. 54-6°, was obtained.

Isolation of Compounds B and C.—The alcoholic percolate of the plant was first concentrated in a

cyclone evaporator and finally the solvent was removed completely under vacuum. The residue (62.0 g) thus obtained was extracted with petroleum ether (50-70°) and charcoaled. The solvent was partially distilled off and the concentrated liquid passed through a column of alumina (24

cm × 4 cm, Alumina for chromatography from May and Baker, 300 g). The column was first eluted with petroleum ether and then with ethyl acetate.

Petroleum Ether Eluate (Compound C).—Two fractions (100 ml each) were collected which were separately charcoaled, and the solvent distilled off. The oily residue was extracted repeatedly with methanol. On concentrating the extract and keeping in the cold both the fractions deposited a white powder, m.p. 139–61°, which was combined and recrystallised from methanol, m.p. 183–4° (yield 0.03% on dry basis). Found: C, 81.94; H, 11.08; O, 6.92%. $C_{32}H_{52}O_2$ requires: C, 81.99; H, 11.18; O, 6.83%. Mol. wt., 442.

The compound is soluble in petroleum ether, benzene, ether, chloroform, carbon tetrachloride, amyl alcohol and ethyl acetate, in hot methanol and ethanol. It does not reduce Fehling's solution but decolorises bromine in carbon tetrachloride.

Ethyl Acetate Eluate (Compound B).—Two fractions (100 ml each) were collected from which the solvent was distilled off. The residue was dissolved separately in ethanol and the solutions concentrated. On allowing the solutions to stand overnight, colorless shining needles appeared in both the fractions, m.p. 121–25°, which were combined and on recrystallisation from the same solvent, it melted at 133–4° (yield 0.07% on dry basis). Found: C, 83.42; H, 12.22; O, 3.99. $C_{29}H_{50}O$ requires: C, 83.99; H, 12.15; O, 3.86%.

The compound is soluble in benzene, petroleum ether, ether, chloroform, carbon tetrachloride, amyl alcohol and ethyl acetate, in hot methanol and ethanol. It does not reduce Fehling's solution but decolorises bromine in carbon tetrachloride. It gives positive Liebermann–Burchard test. β -Dihydrofucosterol melts, as reported in literature at 133–4°. ¹⁶

The compound was acetylated with acetic anhydride and fused sodium acetate, and the product crystallised from ethanol, m.p. 122–3° as needle shape, colorless crystals. The acetate of β -dihydrofucosterol melts as reported in literature, at 12–12°. ¹⁶

The acetates of compounds A and B were hydrolysed with 5% ethanolic sulphuric acid and refluxed on a microflame for $\frac{1}{2}$ hr. Water was

added to precipitate the product and the precipitate was crystallised from the solvents originally used for them.

Identification of Sugars.—The plant was also examined for the presence of sugars by paper chromatography and by preparing osazones. The alcoholic extract of the plant after removal of the steroidal compounds was used for paper chromatography using Whatman No. 1 chromatographic paper and n-butanol: acetone: water (4:5:1) as irrigating solvent (descending chromatography). Nine spots appeared out of which three could be identified as glucose, fructose and maltose by comparing the R_f values with the authentic samples.

Osazones were prepared using phenylhydrazine hydrochloride and sodium acetate. Only four osazones melting at 206°, 207°, 122° and 215° were obtained after an interval of 5, 8, 12 and 20 min, respectively. Out of these only the first two osazones melting at 206° and 207° could be identified as those of fructose and glucose respectively by comparing their m.ps and crystalline shape reported in the literature.

Acknowledgement.—The authors wish to express their thanks to Dr. S.A. Warsi, Director, North Regional Laboratories, Peshawar, for the facilities provided throughout the progress of this work and to Dr. S. Fazal Hussain for giving helpful suggestions. Thanks are also due to Dr. G.W. McCrea, Visiting Professor, Department of Chemistry, University of Peshawar for taking the IR Spectra and also to Mr. Gharibullah for assistance in the initial extraction experiments.

References

1. R.N. Chopra, S.L. Nayar and I.C. Chopra, *Glossary of Indian Medicinal Plants* (Council of Scientific and Industrial Research, New Delhi, 1956), p. 113.
2. M. Nazir, Naeemuddin, Iftikhar Ahmed, S.A. Khan, M.K. Bhatti and Karimullah, *Pakistan J. Sci. Ind. Res.*, **8**, 80 (1965).
3. R.C. Sharma, A. Zaman and A.R. Kidwai, *Indian J. Chem.*, **2**, 254 (1964).
4. N.M. Khanna, *Indian J. Pharm.*, **16**, 110 (1954).
5. H. Ueda and Chiao-Mu Hsu, *J. Taiwan Assoc.*, **1**, 40 (1949).
6. Victor Plouvier, *Compt. rend.*, **236**, 317 (1953).
7. A.G. Gonzalez, J.L. Breton and C. Breton, *Chem. Ind.*, 416 (1955).

8. Mme. S. Chapon and S. David, Bull. Soc. Chim., 456 (1962).
9. A.G. Gonzalez and A. Carlero, Anales Real Soc. espan fisy' quim., **48B**, 269 (1949).
10. A.G. Gonzalez and A.H. Toste, Anales real Soc. espan fisy' quim. **48B**, 495 (1952).
11. Mohammad Nazir, Iftikhar Ahmed, M.K. Bhatti and Karimullah, Pakistan J. Sci. Ind. Res., 9, 38-40 (1966).
12. Ch. Montant, Comp. Rend Soc. Biol, 1950, 44^o-4 (1956).
13. Michel Kilkas, Ann. Chim, 6, 325-66 (1951).
14. Victor Plouvier and Antoine Sosa, Bull. Soc. Chim. Biol., 35, 477-89 (1953); of. Chem. Abstr., **48**, 10760a, (1954).
15. Raymond E. Kirk and Donald F. Othmer (Editors), Encyclopedia of Chemical Technology (The Interscience Encyclopedia, Inc. New York 1952), Vol. 14, p. 465.
16. E. Josephy and F. Radt (Editors), Elseviers Encyclopedia of Org. Chemistry, Series III (Tetracyclic and Higher Cyclic Compounds), (Elseviers Publishing Co. Inc. New York-Amsterdam, 1940), p. 90.