

Chemical Examination of *Euphorbia myrsinitis* Linn.

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Abstract □ The whole plant of *Euphorbia myrsinitis* Linn. was extracted with petroleum ether, and the extract was treated by TLC. Waxlike nonacosane, octacosanol, β -amyirin, and taraxerol were isolated and identified.

Keyphrases □ *Euphorbia myrsinitis*—chemical examination, isolation, identification of nonacosane, octacosanol, β -amyirin, and taraxerol □ Nonacosane—TLC isolation, IR identification from *Euphorbia myrsinitis* □ Octacosanol—TLC isolation, IR identification from *Euphorbia myrsinitis* □ β -Amyirin—TLC isolation, IR identification from *Euphorbia myrsinitis* □ Taraxerol—TLC isolation, IR identification from *Euphorbia myrsinitis*

Euphorbia myrsinitis Linn. (family Euphorbiaceae) is a small herb which grows in the north and central parts of Iran. Its milky juice causes dermatitis and is injurious to the eyes. It has been used by the natives as a purgative.

Previous examination of *E. myrsinitis* indicated the presence of vitamin B₁ (1), a new amino acid *m*-tyrosine (2, 3), 1-methyl-6-hydroxy-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid (4), and, very recently, several flavonoid glycosides (5).

The present work is concerned with the chemical examination of the petroleum ether extract of the whole plant of *E. myrsinitis* Linn. Fractionation of the crude petroleum ether extract by column chromatography using silica gel G indicated the presence of: *n*-nonacosane, m.p. 64–66°; octacosanol, m.p. 81–83°; β -amyirin, m.p. 196–198°; and taraxerol, m.p. 281–283°.

EXPERIMENTAL¹

Extraction Procedure—Whole flowering plants were uprooted, air dried, and milled to a coarse powder. A total of 2.0 kg. of plant material was extracted continuously with petroleum ether for 72 hr. in a Soxhlet extractor. Concentration of this extract *in vacuo* yielded 65 g. of a residue.

Fractionation of Crude Extract—TLC of the petroleum ether fraction on silica gel G, using a developing solvent composed of petroleum ether–benzene (25:75), revealed that the fraction consisted of several spots with different *R_f* values. The residue (25.0 g.) was dissolved in petroleum ether and chromatographed on a column (60 × 4 cm.) containing 800 g. of silica gel G (30–70 mesh). It was eluted sequentially with petroleum ether, mixtures of petroleum ether and benzene, benzene, and a mixture of benzene and chloroform as shown in Table I.

Identification of Eluted Compounds—Fraction I was a waxlike substance (0.65 g.) which, upon repeated crystallization from mixtures of methanol and petroleum ether (25:75), afforded wax-

like shiny plates (0.50 g.), m.p. 64–66°. The compound exhibited no UV absorption spectrum. An IR absorption spectrum in KBr indicated a typical *n*-alkane. It was identified as nonacosane (6, 7). The IR spectrum of the compound was identical with that of an authentic sample of nonacosane, and the mixed melting point of material with the authentic sample of nonacosane was not depressed.

Anal.—Calc. for C₂₀H₄₀: C, 85.20; H, 14.80. Found: C, 84.90; H, 14.60.

Fraction II was a white solid material (0.95 g.) which, upon recrystallization from a mixture of methanol and acetone (80:20), gave fine crystalline needles (0.80 g.), m.p. 81–83°. This compound was identified as octacosanol (8); IR spectrum: $\nu_{\text{max}}^{\text{KBr}}$ 3.02 (OH), 3.65, 6.90, 9.60, and 14.0 μ . The IR spectrum of this compound was identical with the IR spectrum of octacosanol.

Anal.—Calc. for C₂₈H₅₈O: C, 81.67; H, 14.23. Found: C, 81.56; H, 14.08.

Acetylation of the compound with acetic anhydride in pyridine gave an acetate, m.p. 64–65°; IR spectrum: $\nu_{\text{max}}^{\text{KBr}}$ 5.70 and 8.20 (OAc) μ .

Anal.—Calc. for C₃₀H₆₀O₂: C, 79.57; H, 13.36. Found: C, 79.11; H, 13.29.

The benzoate derivative had m.p. 62–64°; IR spectrum: $\nu_{\text{max}}^{\text{KBr}}$ 5.95, 6.80, and 7.95 μ .

Fraction IV was a white powder (1.05 g.) which crystallized from methanol, giving short needles, m.p. 144–146°; $[\alpha]_{\text{D}}^{25}$ +27.3°. It gave a positive Liebermann–Burchardt test. Further work for identification of this compound is under progress.

Fraction V was a white solid powder (2.02 g.). When crystallized from methanol, it afforded fine needles, m.p. 196–198°; $[\alpha]_{\text{D}}^{25}$ +81°. It gave a positive Liebermann–Burchardt test and was identified as β -amyirin (9); IR spectrum: $\nu_{\text{max}}^{\text{KBr}}$ 3.10 (OH), 3.50, 6.90, and 7.30 μ .

Anal.—Calc. for C₃₀H₅₀O: C, 84.44; H, 11.81. Found: C, 84.12; H, 11.71.

The acetate derivative had m.p. 237–239°; $[\alpha]_{\text{D}}^{25}$ +80.0°; IR spectrum: $\nu_{\text{max}}^{\text{KBr}}$ 3.50, 5.87, and 8.0 (OAc) μ .

Anal.—Calc. for C₃₂H₅₂O₂: C, 81.99; H, 11.18. Found: C, 82.08; H, 11.15.

The benzoate derivative had m.p. 226–228°; $[\alpha]_{\text{D}}^{25}$ +98.2°; IR spectrum: $\nu_{\text{max}}^{\text{KBr}}$ 5.90 and 7.97 (OBz) μ .

Fraction VI was a white solid (1.20 g.) which, after recrystallization from methanol, gave small needles, m.p. 281–283°; $[\alpha]_{\text{D}}^{25}$ +7.20°. The compound gave a positive Liebermann–Burchardt test, and it was identified as taraxerol (10, 11); IR spectrum: $\nu_{\text{max}}^{\text{KBr}}$ 2.95 and 9.75 (OH), 6.10, and 12.20 (>C=CH) μ .

Anal.—Calc. for C₃₀H₅₀O: C, 84.44; H, 11.81. Found: C, 84.00; H, 11.57.

The acetate derivative had m.p. 289–291°; $[\alpha]_{\text{D}}^{25}$ +9.10°; IR spectrum: $\nu_{\text{max}}^{\text{KBr}}$ 5.75 and 8.0 (OAc), 6.0 and 12.35 (>C=CH) μ .

Table I—Column Chromatographic Separation of Petroleum Ether Extract of *E. myrsinitis* Linn.

Fraction	Solvent	Milliliters	Eluate
I	Petroleum ether	600	White solid
II	Petroleum ether–benzene (80:20)	800	White powder
III	Petroleum ether–benzene (70:30)	1000	Trace
IV	Petroleum ether–benzene (50:50)	2000	White powder
V	Petroleum ether–benzene (30:70)	1500	White solid
VI	Benzene	2000	White powder
VII	Benzene–chloroform (90:10)	1000	Colored material

¹ Melting points were determined on a Litz micromelting-point microscope and corrected. IR spectra were taken in KBr on a Litz IR spectrophotometer. TLC was carried out on silica gel G (E. Merck), and the chromatograms were sprayed with a Ce(SO₄)₂–H₂SO₄ solution followed by heating until brown spots appeared. Petroleum ether was used, b.p. 40–60°. Evaporation was carried out at less than 45°. Microanalyses of samples were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. The plant material used in this investigation was collected in Gachsar (75 km. north of Tehran) during July 1969. Voucher specimens were prepared and authenticated as *E. myrsinitis* Linn. Specimens representing the collections were deposited in the herbaria of the Department of Pharmacognosy, University of Tehran, Iran.

Anal.—Calc. for $C_{12}H_{12}O_2$: C, 81.99; H, 11.18. Found: C, 81.90; H, 11.10.

The benzoate derivative had m.p. 292–294°; $[\alpha]_D^{25} +35.7^\circ$; IR spectrum: ν_{max}^{KBr} 5.97 and 7.95 (OBz), 6.10 and 12.40 ($>C=CH$) μ .

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Conductimetric Studies of Interactions of Optically Active Ions I: Interactions of Amphetamine with Mandelic and Tartaric Acids

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Abstract □ The conductances of 0.006 *M* aqueous solutions of *d*- and *l*-amphetamine were measured in equimolar aqueous solutions of *d*- and *l*-mandelic acid and *d*- and *l*-tartaric acid. Conductivity changes were recorded, and the results were interpreted in terms of ionic associations.

Keyphrases □ Amphetamine-mandelic acid interaction—conductimetric study of optically active ions □ Amphetamine-tartaric acid interaction—conductimetric study of optically active ions □ Optically active ions—amphetamine with mandelic or tartaric acid, conductivity changes □ Conductivity changes—optically active ions, amphetamine with mandelic and tartaric acids, ionic associations

The observed phenomena that optically active compounds such as bases may be used to resolve racemic acids (and vice versa) suggested that even under aqueous conditions a *d*-acid associates with an optically active base differently than does the corresponding *l*-acid. Conductimetric studies (1) of the association of *d*- and *l*-tris(ethylenediamine)-cobalt (III) iodide in a 0.003 *M* solution of both *d*- and *l*-sodium tartrate in water showed significant differences in mobility between the two cobalt isomers in the solutions of optically active tartrates.

Conductivity was used also to examine molecular associations of some organic salts at different concentrations (2). This method was chosen because association of the cations and anions would be expected to lead to a definite change in the conductivity of the solutions. Similar studies for isotopic lithium chlorides at various concentrations showed a 0.35% greater mobility for the ^6Li than for the ^7Li ions (3).

The purpose of the present report is to present the results of a series of measurements of the conductance of 0.006 *M* amphetamine solutions in equimolar solutions of optically active mandelic and tartaric acids.

EXPERIMENTAL

Materials—The following were used: *d*-mandelic acid¹, m.p. 133.5° [lit. (4) m.p. 133.8°] and specific rotation +156° [lit. (4) +156° in H_2O]; and *l*-mandelic acid¹, m.p. 132.5° [lit. (4) m.p. 132.8°] and specific rotation -156.2° [lit. (4) -156.2° in H_2O]. Mandelic acids were recrystallized from ethyl alcohol, filtered through sintered-glass funnels, and dried before melting points and optical rotations were taken. Also used were: *d*-tartaric acid², m.p. 169.5° [lit. (5) m.p. 168–170°] and specific rotation +12° [lit. (5) +12° in H_2O]; and *l*-tartaric acid², m.p. 169.5° [lit. (5) m.p. 168–170°] and specific rotation -12° [lit. (5) -12° in H_2O]. Tartaric acids were recrystallized from absolute alcohol, filtered, and dried in a desiccator before melting points and optical rotations were taken. *d*-Amphetamine, puriss.³, b.p. 204° [lit. (4) b.p. 203–204°] and n_D^{20} 1.517 [lit. (4) 1.517]; and *l*-amphetamine, puriss.³, b.p. 204° [lit. (4) b.p. 203–204°] and n_D^{20} 1.5172 [lit. (4) 1.517] were also used. The conductivity water of low CO_2 content was prepared by boiling distilled water for about 5 min. and cooling rapidly.

Apparatus and Methods³—Aqueous solutions of the bases and of the acids at exactly 0.006 *M* concentrations were prepared, and the individual resistances were measured at constant temperatures. Then 20 ml. of each base solution was added to exactly 20 ml. of each acid solution in beakers and were mixed well using magnetic stirrers. After temperature equilibrium, the resistances were taken.

¹ Eastman Organic Chemicals.

² Aldrich.

³ A Conductoscop E 365 B (Metrohm A. G.) was used with a Jones cell, model EA-655 (cell constant $c = 7.4 \text{ cm}^{-1}$).