

New Constituents of *Euphorbia resinifera* Berg

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During an investigation of phorbic acid¹ it became evident that the crude drug *Euphorbium*, which is the dried latex of *Euphorbium resinifera* Berg, still contained several unknown constituents.

Evidence will now be presented that these constituents were (–)-quinic acid, D(+)- α -hydroxyglutaric acid, myoinositol, L(–)-inositol and probably vanillic acid. Quinic acid 1,3-lactone, isolated in one experiment, was most likely an artefact from the working-up procedure.

Experimental. (–)-Quinic acid-1,3-lactone. A high-boiling fraction (190–204°C, 10^{–2} mm) of the methyl ester mixture from the isolation of phorbic acid¹ was diluted with ethanol and stored at –20°C for 2 months when a white substance separated. Recrystallized from methanol, m.p. 170–180°. [α]_D¹⁹ = –17.7° (*c* = 0.0060; water). (Found: C 48.6; H 5.8. Calc. for C₇H₁₀O₅: C 48.3; H 5.8.) Infra-red spectrum identical with that of synthetic quinic acid-1,3-lactone.

(–)-Quinic acid. *Euphorbium* powder was treated with water (20°C) and the extract precipitated with basic lead acetate. The filtrate was treated with hydrogen sulphide and concentrated *in vacuo* until a yellowish substance separated. This was deionized with Dowex 50 and gave a crystalline acid (yield 3%), m.p. 164°C. (Found: C 43.8; H 6.2. Calc. for C₇H₁₂O₆: C 43.7; H 6.3.) [α]_D²⁰ = –43.7° (*c* = 2.0; water). Infra-red spectrum identical with that of authentic quinic acid. In the mass-spectrum small peaks for M+1 (*m/e* = 193) and M+1–H₂O (*m/e* = 175) and a large peak of M–2 H₂O (*m/e* = 156) were observed. The mother liquor from quinic acid was shown by TLC to contain three additional acids, which so far remain unidentified.

D(+)- α -Hydroxyglutaric and veratric acids. An aqueous extract of *Euphorbium* was exhaustively precipitated with lead acetate (Precipitate I) and the filtrate precipitated in the same way with basic lead acetate (Precipitate II). Precipitate II was decomposed with hydrogen sulphide and the filtrate concentrated under reduced pressure to a brown syrup. The acetone-soluble part of this

was esterified with diazomethane and the ester mixture fractionated *in vacuo*. One fraction (b.p. 125–130°C, 0.1 mm) was shown by GLC to contain the methyl ester of phorbic acid dilactone as well as esters of two unknown acids. Preparative GLC separated these esters (A and B). Ester A was converted by conventional methods into a benzylamide and a hydrazide. Bis-benzylamide, m.p. 131–132°C. (Found: C 69.9; H 6.8; N 8.8; M (cryoscopic) 329. Calc. for C₁₉H₂₂O₃N₂: C 69.9; H 6.8; N 8.6; M 326.) Dihydrazide, m.p. 146–148°C, undepressed in mixture with an authentic sample of D(+)- α -hydroxyglutaric acid dihydrazide. [α]_D¹⁹ = +33.8 (*c* = 0.0067; H₂O). IR-spectrum identical with that of the authentic substance.

Ester B crystallized in part; recrystallized from ethanol m.p. 57–59°C. (Found: C 61.1; H 7.0; OCH₃ 46.7. Calc. for C₇H₃O(OCH₃)₃: C 61.2; H 6.2; OCH₃ 47.4.) Veratric acid methyl ester has the above m.p. and identical IR- and NMR-spectrum with ester B.

When the beforementioned acetone-soluble matter was esterified with methanol/sulphuric acid, no veratric ester could be detected by GLC. However, a peak appeared which corresponded to vanillic acid methyl ester. This supports the notion that vanillic acid is present in *Euphorbium*, while methyl veratroate is produced in the diazomethane treatment.

Myoinositol. The acetone-insoluble part of the syrup from Precipitate II was dissolved in water, deionized with Dowex 50 and concentrated under reduced pressure to a syrup. On treatment with methanol and refrigeration for some days this yielded white crystals. Recrystallized from methanol (60%), dried over P₂O₅, m.p. 220–223°C. Optically inactive. (Found: C 39.9; H 7.0. Calc. for C₆H₁₂O₆: C 40.0; H 6.7.) The IR-spectrum of this compound was identical with that of myoinositol.

L(–)-Inositol. The filtrate from Precipitate II was treated with hydrogen sulphide, the filtrate concentrated under reduced pressure, deionized with Dowex 50 and stored at –20°C. In a few weeks a white substance separated. Recrystallized from ethanol (70%) and dried over P₂O₅, m.p. 228–234°C. (Found: C 39.5; H 7.0. Calc. for C₆H₁₂O₆: C 40.0; H 6.7.) [α]_D²² = –61.6° (*c* = 0.044; water.) The IR-spectrum was identical with that of L(–)-inositol.

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