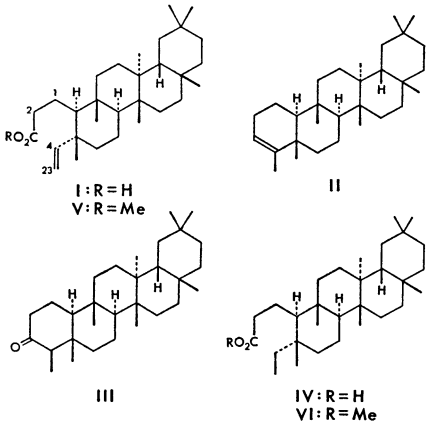
BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 692 (1973)

One-step Synthesis of Putranjivic Acid from Friedelin

Reiko AOYAGI, Takahiko TSUYUKI, and Takeyoshi TAKAHASHI
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

(Received September 11, 1972)

A triterpene, putranjivic acid, isolated from leaves of *Putranjiva roxburghii* (Euphorbiacea) has been characterized by spectral and chemical methods to be 10β-(2-carboxy)ethyl-5α-vinyl-des-A-friedelane (3,4-seco-friedel-4(23)-en-3-oic acid) (I) by Seshadri *et al.*[1-3] Very recently Sengupta and Dey[4] have described the synthesis and stereostructure of putranjivic acid (I). These authors have synthesized this acid from friedel-3-ene (II) through seven steps and established the configuration of all asymmetric centers in the acid.



We now wish to report a one-step synthesis of putranjivic acid (I) from friedelin (III) by photochemical oxidation reaction. It is well-known that cyclohexanone derivatives are irradiated in the presence of oxygen to afford an unsaturated seco-acid and that this reaction was applied to syntheses of nyctanthic and roburic acids.[5]

Irradiation of friedelin (III) in benzene under oxygen atmosphere gave a complex mixture, which was subjected to column chromatographic separation. Acidic fractions were treated with diazomethane. The methyl esters were further separated by silver nitrate-impregnated silica gel tlc into unsaturated and saturated esters. The latter was shown to be methyl 3,4-seco-friedelan-3-oate (VI) by comparison with the authentic sample which was prepared by methylation of 3,4-seco-friedelan-3-oic acid (IV).[6] The former was hydrolyzed to an unsaturated acid. The olefinic acid and its methyl ester were identical with putranjivic acid (I) and its methyl ester (V), respectively, in respects to mp, IR, and MS.

The methyl ester (V) was catalytically hydrogenated to give a saturated ester, which was identical with methyl 3,4-seco-friedelan-3-oate (VI) in every respect. Thus the structure of the synthesized putranjivic acid (I) was confirmed.

Experimental

All melting points were determined on a hot block and uncorrected. IR and mass spectra were measured using Hitachi EPI-G2 and Hitachi RMU-6 mass spectrometers. NMR spectra were recorded in $CDCl_3$ on Hitachi Model R-24 NMR spectrometer at 60 MHz, using TMS as an internal standard.

Photo-oxidation of Friedelin (III). Friedelin (500 mg) was dissolved in benzene (700 ml) and irradiated with a high pressure mercury lamp for 11 hr with introduction of oxygen at room temperature. The concentrated solution was passed through a column (SiO_2, 95 g) and elution was continued with benzene (2.6 l) to give acidic fractions, which were combined and treated with diazomethane. After evaporation, the residue was separated by thin layer chromatography using 10% $AgNO_3$-impregnated silica gel, developed with a 3 : 1 mixture of petroleum ether and benzene. The unsaturated ester (V, R_f=0.23) was extracted with ether and recrystallized from methanol to yield 21 mg of V, mp 136.0—136.5°C; ν_{max}(Nujol) 1737, 1630, and 905 cm^{-1}; NMR: δ 3.65(s, -COOC$\underline{H}_3$) and 4.75—6.0(-C$\underline{H}$=C$\underline{H}_2$); M^+ 456 ($C_{31}H_{52}O_2$) [lit,[1] mp 133—135°C, ν_{max}1754 cm^{-1}, $[\alpha]_D$ −8.3° (*c* 1.2, $CHCl_3$)].

V (13 mg) was heated under reflux with potassium hydroxide (10 mg) in methanol (7 ml) for 4 hr and then treated as usual. The unsaturated acid (I) was obtained (12 mg), mp 173.0—173.5°C; ν_{max}(Nujol) 1705, 1660, 990, and 905 cm^{-1}; $[\alpha]_D$ −12° (*c* 0.24, $CHCl_3$); NMR: δ 4.75—5.90(-C$\underline{H}$=C$\underline{H}_2$) and 2.30(m, -C$\underline{H}_2$-COOH); Found: C, 81.45; H, 11.26%. Calcd for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38%. M^+ 442 [lit,[1] mp 177—179°C, ν_{max} 1730 cm^{-1}, $[\alpha]_D$ −15° (*c* 0.4, $CHCl_3$)].

The saturated ester (VI, R_f=0.8) was extracted with ether from the $AgNO_3$-impregnated silica gel and recrystallized from methanol to give 18 mg of VI, whose spectral data [ν_{max}(Nujol) 1740 and 1163 cm^{-1}; NMR: δ 3.66(s, -CO-OC$\underline{H}_3$), M^+ 458 ($C_{31}H_{54}O_2$)] were identical with those of the authentic methyl 3,4-seco-friedelan-3-oate (VI), prepared by methylation of 3,4-seco-friedelan-3-oic acid (IV)[6] with diazomethane in ether.

The saturated methyl ester (VI) was hydrolyzed with potassium hydroxide in ethanol and recrystallized from methanol to afford 3,4-seco-acid (IV), mp 210.5—211.5°C. Mp, IR, NMR, MS, and tlc were identical with those of the authentic 3,4-seco-friedelan-3-oic acid (IV).[6]

Hydrogenation of Methyl Purtanjivate (V). The unsaturated methyl ester (V, 7 mg) was dissolved in ethanol (7 ml) and hydrogenated in the presence of 10% Pd-C. Recrystallization from methanol gave methyl 3,4-seco-friedelan-3-oate (VI), which was identical with the authentic sample, described above.

1) G. R. Chopra, A. C. Jain, and T. R. Seshadri, *Curr. Sci.*, **37**, 301 (1968); *Chem. Abstr.*, **69**, 93685q (1968).
2) G. R. Chopra, A. C. Jain, T. R. Seshadri, and G. R. Sood, *Indian J. Chem.*, **8**, 776 (1970); *Chem. Abstr.*, **74**, 1024a (1971).
3) G. R. Chopra, A. C. Jain, and T. R. Seshadri, *ibid.*, **7**, 1179 (1969); *Chem. Abstr.*, **72**, 67139g (1970).
4) P. Sengupta and A. K. Dey, *Tetrahedron*, **28**, 1307 (1972).
5) G. Quinkert and H.-G. Heine, *Tetrahedron Lett.*, **1963**, 1659.
6) T. Tsuyuki, S. Yamada and T. Takahashi, This Bulletin, **41**, 511 (1968); F. Kohen, A. S. Samson, and R. Stevenson, *J. Org. Chem.*, **34**, 1355 (1969).