Anal. Calcd. for $C_{22}H_{36}O_3$ (360.51): C, 76.62; H, 10.07. Found: C, 76.35, 76.10; H, 10.27, 10.41.

6α-16α-Dimethylprogesterone (VII). A solution containing 150 mg. of 5α-hydroxy-6β,16α-dimethylpregnan-3,20-dione (VI) and 0.5 ml. of 5% sodium hydroxide in 10 ml. of methanol was heated to reflux for 1 hr. under nitrogen. The mixture was acidified with a few drops of acetic acid and concentrated to a colorless viscous oil *in vacuo* on a steam bath. The crude product was dissolved in *ca.* 30 ml. of ether, and ether solution was washed with 5% sodium hydroxide, water, and saturated sodium chloride solution. The extract was concentrated to a viscous oil, and the latter was crystallized from aqueous methanol to give 123 mg. (87%) of fine colorless needles, m.p. 109.5–113.5° (Kofler). A sample for analysis melted at 113–116.5° (Kofler); $[\alpha]_D$ +145°; λ_{max} 242 mμ (ε = 16,100); ν_{max}^{KBr} 1705, 1678 and 1610 cm.$^{-1}$

Anal. Calcd. for $C_{23}H_{34}O_2$ (342.50): C, 80.65; H, 10.01. Found: C, 80.41; H, 10.32.

3β-Acetoxy-20-ethylenedioxy-16α-methyl-5-pregnene (VIII). To a solution containing 1.88 g. of 16α-methylpregnenolone acetate (I) and 49 mg. of *p*-toluenesulfonic acid (monohydrate) in 63 ml. of benzene was added 1.90 ml. of ethylene glycol. The resulting mixture was heated to reflux for 16 hr., and the water formed during the reaction was collected in a Dean-Stark apparatus. Pyridine (0.3 ml.) was added, and the solution was washed successively with ice-cold 5% sodium hydroxide, water, and saturated sodium chloride solutions. On evaporation *in vacuo* of the benzene solution, a semicrystalline solid was obtained which crystallized from methanol (containing a few drops of pyridine) to give 1.33 g. (63%) of fine, colorless needles, m.p. 134.5–140.5°. A sample for analysis melted at 144.5–146°; $[\alpha]_D$ −62.5°; ν_{max}^{KBr} 1740, 1255, 1238, and 1037 cm.$^{-1}$

Anal. Calcd. for $C_{26}H_{40}O_4$ (416.58): C, 74.96; H, 9.68. Found: C, 75.02; H, 9.83.

3β-Acetoxy-5α,6α-epoxy-20-ethylenedioxy-16α-methylpregnane (IX). To a solution containing 913 mg. of 3β-acetoxy-20-ethylenedioxy-16α-methyl-5-pregnene (VIII) in 20 ml. of benzene–methylene chloride (1:1) cooled to −10° was added 7.45 ml. of a 0.37*M* solution of perbenzoic acid in benzene dropwise with stirring over 17 min. The mixture was let stand at −5° for 23 hr. and washed successively with ice cold 5% sodium hydroxide, water, and saturated sodium chloride solutions. On evaporation *in vacuo* a semicrystalline solid was obtained. The latter on crystallization from methylene chloride–petroleum ether afforded 533 mg. of colorless needles, m.p. 169–171.5°. A sample for analysis melted at 171.5–172.5°; $[\alpha]_D$ −61°; ν_{max}^{KBr} 1730, 1243, 1218, 1100, 1047, and 1033 cm.$^{-1}$

Anal. Calcd. for $C_{26}H_{40}O_5$: C, 72.19; H, 9.32. Found: C, 72.09; H, 9.56.

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The Triterpenes of *Befaria racemosa* (Vent.)[1]

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Befaria racemosa (Vent.), a striking shrub found in the pinelands of the Coastal Plain of Florida and Georgia, gave a negative test for andromedotoxin in a recent survey of *Ericaceae*,[4] but seems not to have been investigated in other respects. This note describes the isolation and identification of ursolic acid, taraxerol, β-amyrin, lupeol, and β-sitosterol. In addition there was isolated what appears to be crude α-amyrin and a poor yield (0.07%) of an alkaloid mixture which was reserved for future investigation.

The major triterpene constituents were ursolic acid (0.5%), of common occurrence in *Ericaceae* species,[5,6] and taraxerol (0.2%), which has recently been found in *Pieris japonica* (D. Don.)[7] The former was identified through preparation of acetylursolic acid, methyl ursolate, methyl ursolate acetate, and methyl ursolate benzoate. The latter was identified through the acetate and benzoate and by conversion to taraxerone. The other triterpenes were isolated in small amounts only and were identified by comparison with authentic samples of β-sitosterol, β-amyrin acetate, lupeol benzoate, and α-amyrin acetate.

EXPERIMENTAL

Dried *Befaria racemosa* (Vent.) leaves, collected near Tallahassee in summer 1959, 4.1 kg., were extracted continuously with 20 l. of 95% ethanol for 48 hr. The solution was concentrated to a small volume and filtered from crystalline material (precipitate A). The filtrate was concentrated almost to dryness, stirred with several portions of 3% phosphoric acid, the acid extract made basic with concd. ammonia, and extracted with chloroform until exhausted of alkaloids. The chloroform solution was concentrated to dryness at reduced pressure, the residue taken up in 50 ml. of fresh chloroform and diluted with ether to the point where an insoluble precipitate began to form. The solution was extracted repeatedly with 3% phosphoric acid, the acid extracts were made basic with ammonia and the alkaloids extracted with chloroform. Removal of chloroform left 3 g. of gummy residue (positive to Mayer's reagent) which paper chromatography showed to be a mixture of alkaloids.

Precipitate A was taken up in hot chloroform-ethanol, filtered and allowed to stand. There precipitated crude taraxerol which was recrystallized five times from chloroform-methanol, yield 2.5 g., m.p. 268–272° (Hershberg), 280–281° (Kofler), $(\alpha)_D^{25}$ +2.0 (*c*, 1.5, chloroform).[8]

The acetate, prepared by refluxing with acetic anhydride, crystallized from methanol as colorless scales, m.p. 302°

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(Kofler), $(\alpha)_D^{23}$ +9.3 (*c*, 0.75, chloroform). The benzoate, prepared by the benzoyl chloride–pyridine method, crystallized from benzene as colorless needles, m.p. 292–293° (Kofler), $(\alpha)_D^{23}$ +35.7° (*c*, 0.7, chloroform). Oxidation in benzene with chromic acid–acetic acid at room temperature furnished taraxerone, colorless plates from chloroform-methanol, m.p. 240–201°, $(\alpha)_D^{25}$ +11.7° (*c*, 0.59, chloroform).

The filtrate from the taraxerol isolation was evaporated to dryness at reduced pressure, 64 g. (precipitate B). Precipitate B was worked up by two methods: (1) alkaline hydrolysis of 20 g. of B with 250 ml. of ethanol, 200 ml. of benzene, and 25 g. of potassium hydroxide followed by evaporation, dilution with water, and chloroform extraction gave chloroform-insoluble material which was filtered (precipitate C). The chloroform extract was evaporated, the residue was stirred with benzene, and the benzene-insoluble material (crude taraxerol) recrystallized repeatedly from ethanol-chloroform, yield of taraxerol 1.2 g., m.p. 280°. The benzene extract was evaporated and the residue chromatographed over 40 g. of neutral alumina (activity II, solvent and eluent petroleum ether–benzene). The first fractions gave 0.23 g. of paraffin-like material melting near 60° which gave a negative Liebermann-Burchard test and was discarded. Further elution gave a crystalline triterpene mixture of m.p. 95–160°, which gave a positive Liebermann-Burchard test and was separated through the acetates as described in Section 2.

Precipitate C, obviously a potassium salt, was neutralized upon dilution with water. Here separated 6.1 g. of amorphous material (precipitate D) giving a positive Liebermann-Burchard test. Crystallization from ethanol gave colorless needles of ursolic acid, m.p. 277°, which were converted to the acetate by refluxing with acetic anhydride. The product crystallized from methanol as colorless needles, m.p. 289–291°, $(\alpha)_D^{23}$ +67.5° (*c*, 1.23, chloroform).[9] Another portion of precipitate D, 1.7 g., was converted to the methyl ester by treatment with diazomethane. A solution of the crude ester, 1.4 g., in 170 ml. of benzene was chromatographed over 70 g. of neutral alumina (activity III). Elution with benzene–chloroform (3:1) furnished 1.2 g. of methyl ursolate, m.p. 160–167°, which after several crystallizations from methanol-water melted at 165–168°. The acetate crystallized from methanol as needles, m.p. 239–242°, $(\alpha)_D^{23}$ +63.1° (*c*, 1.49, chloroform). The benzoate was recrystallized from methanol, m.p. 234° (softening at 209–210°).

(2) Precipitate B, 24 g., was extracted thoroughly with 1500 ml. of ether. The ether extract was shaken repeatedly with 1*N* sodium hydroxide solution. There separated 9.5 g. of sodium urosolate which was filtered. The ether extract was washed, dried, concentrated to small volume, filtered from crude taraxerol (0.4 g.), passed through 80 g. of alumina, and eluted with 100 ml. portions of ether. Fractions 1–3 gave crystalline material, fractions 4–7 (ether) and 8–12 (ether-ethanol) gave only small amounts of gums.

Fractions 1–3 were combined and extracted with petroleum ether. The insoluble material was taraxerol, 0.8 g. The petroleum ether extract was chromatographed over 35 g. of alumina (activity III). Petroleum ether (b.p. 30–60°) (ten 30 ml. fractions) eluted 2.1 g. of a triterpene mixture, m.p. 130–160°. Elution with petroleum ether–benzene (1:1) eluted triterpene mixtures together with 58 mg. of taraxerol which was isolated by fractional crystallization from chloroform-methanol. Elution with benzene furnished 20 mg. of β-sitosterol, m.p. (from acetone) 133–136°, characteristic Liebermann-Burchard test. The acetate, prepared by the acetic anhydride–pyridine method, was purified by chromatography and recrystallization from methanol, m.p. 118–121°, $(\alpha)_D^{24}$ −39° (*c*, 0.59, chloroform), m.p. undepressed on admixture of an authentic sample. The infrared spectra were identical.

The triterpene mixture, 2.1 g., was refluxed with acetic anhydride for 2 hr. Fractional crystallization of the acetate mixture from methanol-chloroform furnished 43 mg. of β-amyrin acetate, m.p. 240–241°, $(\alpha)_D^{23}$ +80.9 (*c*, 2.2, chloroform), melting point undepressed on admixture of an authentic sample. The mother liquors from the recrystallization were combined, evaporated, dissolved in petroleum ether-benzene (2:1), and chromatographed over 50 g. of alumina (activity II). Elution with petroleum ether-benzene (2:1) gave a fraction which on crystallization from acetone gave an additional 7 mg. of β-amyrin acetate. The mother liquor was combined with the other eluates, the solvents removed and the residue, 1.8 g., saponified. The neutral product, 1.1 g., was converted to the benzoate. Crystallization of the crude benzoate from ethanol-chloroform, ethyl acetate, and petroleum ether gave colorless plates of lupeol benzoate, 28 mg., m.p. 265–268° $(\alpha)_D^{23}$ +60.6° (*c*, 2.08, chloroform), melting point undepressed on admixture of authentic lupeol benzoate. The infrared spectra were superimposable.

The mother liquors from the recrystallization of lupeol benzoate were combined and evaporated. The residue, m.p. 190–220°, 0.7 g. was chromatographed over alumina (activity III). Fractions 9–11 (20-ml. portions of petroleum ether) yielded 90 mg., m.p. 165–175°, fractions 12–16 (petroleum ether–benzene 9:1) 420 mg., m.p. 190–230° fractions 17–20 140 mg., m.p. 225–250°. Fractions 12–16 were rechromatographed over 20 g. of alumina. This chromatogram yielded fractions 6–9 (petroleum ether), 55 mg., 170–180°, fractions 10–15 (petroleum ether) 95 mg., m.p. 160–210°, fractions 16–20 (petroleum ether–benzene 4:1) 240 mg., m.p. 210–245°.

Fractions 9–11 of the first and 6–9 of the second chromatogram were combined and rechromatographed. Elution with petroleum ether–benzene (9:1) gave a fraction which after recrystallization from chloroform-methanol melted at 179–182°, $(\alpha)_D^{22}$ +89° (*c*, 1.3, chloroform). Hydrolysis gave crude α-amyrin, m.p. 155–177°, acetate m.p. 200°, $(\alpha)_D^{23}$ +74° (*c*, 0.58, chloroform). The rotations and infrared spectra were those of α-amyrin acetate (m.p. 226°, $(\alpha)_D$ +76°) and benzoate (m.p. 194°, (α) +94.6°) but the melting points remained low.

Fractions 17–20 of the original chromatogram and 16–20 of the second chromatogram exhibited the typical 1640 and 890 cm.$^{-1}$ bands of lupeol. They were combined, rechromatographed, and recrystallized m.p. 255–263°, yield 180 mg. Although the melting point was low, the infrared spectrum and rotation was identical with the infrared spectrum and rotation of lupeol benzoate. Hydrolysis furnished crude lupeol, m.p. 200°, $(\alpha)_D^{23}$ +23.4° (*c*, 1.37, chloroform) which was converted to the acetate 200–204°, $(\alpha)_D^{25}$ +37° (*c*, 1.6, chloroform). The infrared spectrum and rotation were similar to those of authentic lupeol acetate.

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(9) For physical constants of ursolic acid and its derivatives, see ref. 5, p. 118 or ref. 8, Vol. 5, p. 114.