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SHORT COMMUNICATION

CONSTITUENTS OF LOCAL PLANTS—XI.

THE TRITERPENOID ACIDS OF *SALVIA LANIGERA* POIR. AND *S. TRILOBA* L.

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Abstract—The reportedly "new" constituents of *Salvia lanigera* Poir. have been shown to contain oleanolic and ursolic acids and those of *S. triloba* L. to contain the same acids and betulic acid. Convenient thin-layer chromatographic conditions are described for the effective resolution and identification of these acids.

SEVERAL reports[1–3] indicate that *Salvia* species (Labiatae) contain monohydroxylic pentacyclic triterpenoid acids. However, the difficulties encountered in the isolation of these intimately related acids seem to be responsible for the description of such indefinite products as ursolic acids I and II[2, 3] in both *S. officinalis* L. and *S. triloba* L., and "new" compounds in *S. lanigera* Poir.[4] and *S. triloba* L.[5]

The leaves, stems and flowers of *S. lanigera* Poir. were reported by Saleh *et al.*[4] to contain two new aromatic constituents named "lanigerin" ($C_{24}H_{40}O_3$), m.p. 256°, and "lanigerein" ($C_{24}H_{40}O_3$), m.p. 230°. Investigation of the light petroleum extract of this source, as described by these authors,[4] afforded "lanigerin" which was shown by TLC to be a complex mixture and from which oleanolic acid was isolated. The ethereal extract (source of "lanigerein") of the marc of plant material gave ursolic acid.

It is known that mixtures of ursolic, oleanolic and betulic acids, the commonest natural triterpenoids which frequently occur together, are extremely difficult to resolve on chromatoplates or paper chromatograms. However, we have recently reported[6] on a number of solvent systems, and now describe further two (Experimental) which effectively and completely resolve these acids on kieselguhr thin layers. Their use, which revealed the heterogeneity of both "lanigerin" and "lanigerein" and the nature of their principal triterpenoid constituents, was helpful in a re-examination of *S. triloba* L., known for its use in popular medicine.[5] From the leaves and stems of this plant, Haddad *et al.*[5] reported the isolation of two crystalline principles, "trilobin" ($C_{24}H_{39}O_3$) and "trilobein" ($C_{27}H_{42}O_3$) from the light petroleum and ether extracts respectively. Inspection of fractions corresponding to these preparations by TLC revealed that the principal component was ursolic acid and that small amounts of

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oleanolic and betulic acids were also present. Ursolic acid was isolated from a fraction corresponding to "trilobin" and β-sitosterol from the unsaponifiable fraction of the fat.

EXPERIMENTAL

Thin-Layer Chromatography

Kieselguhr plates were prepared as usual and impregnation with undecane was made by spraying with a 10 per cent solution in *n*-hexane. After development, the spots were revealed by spraying with a chlorosulphonic acid–acetic acid (1:2) mixture followed by a brief heating (110°) and the colours[6] viewed by day and short-wave u.v. light.

The use of an ethylene dichloride–hexane–acetic acid (5:10:0·01) solvent system for ursolic, oleanolic and betulic acids on kieselguhr gave R_f values 0·19, 0·74, and 0·79 and the same solvent mixture (11:4:0·01) on kieselguhr impregnated with undecane gave R_f 0·21, 0·38 and 0·44, respectively.

The Triterpenoid Acids of Salvia lanigera *Poir.*

The residue from a light petroleum extract was digested with boiling EtOH and after cooling, filtration and evaporation, the resulting residue again extracted with light petroleum then dissolved in hot EtOH. Upon cooling, a product (corresponding to "lanigerin",[4] 0·05 per cent of dry plant weight) deposited which was crystallized (EtOH; m.p. 228–230°) and shown by TLC[6] to be a complex mixture comprising oleanolic acid and traces of ursolic acid. Column chromatography on alumina afforded (by elution with 3% MeOH in benzene) oleanolic acid (0·0086 per cent of dry plant weight) as needles (MeOH), m.p. and mixed m.p. 310–315°, $[\alpha]_D$ +85·3° (reported[7] m.p. 306–309°, $[\alpha]_D$ +76°; identical i.r. spectra), which gave an acetate, m.p. and mixed m.p. 265–267°, $[\alpha]_D$ +76° (reported[7] m.p. 264–267°, $[\alpha]_D$ +70°; identical i.r. spectra).

The residue from an ethereal extract of the marc of plant material was dissolved in hot MeOH and after cooling, filtration and concentration, a solid material (corresponding to "lanigerein",[4] 0·085 per cent of dry plant weight) resulted. It was shown by TLC[6] to be a complex mixture comprising ursolic acid. The latter was isolated (0·01 per cent of dry plant weight) by column chromatography (alumina, 1% MeOH in benzene) as needles (aq. EtOH), m.p. and mixed m.p. 287–289°, $[\alpha]_D$ +75·3° (reported[8] m.p. 284–285°, $[\alpha]_D$ +72·2°; identical i.r. spectra) and gave an acetate, m.p. 289–290°, $[\alpha]_D$ +65·2° (reported[9] m.p. 289–290°, $[\alpha]_D$ +61·5°) and a methyl ester acetate, m.p. 248–250° (reported[10] m.p. 246–247°).

The Triterpenoid Acids of Salvia triloba *L.*

Concentration of a benzene extract to a small volume gave a deposit (5·3 per cent of dry plant weight) which was filtered off and chromatographed on alumina to give (by elution with 5% MeOH in benzene) a crude product (2·37 per cent of dry plant weight). This, after crystallization (EtOH), was shown to be ursolic acid, m.p. and mixed m.p. 280–283°, $[\alpha]_D$ +62·4°, giving an acetate, m.p. 289°, $[\alpha]_D$ +57·3°, a methyl ester, m.p. 170–171·5°, $[\alpha]_D$ +69·5°, and a methyl ester acetate, m.p. 235–238°, $[\alpha]_D$ +70·3° (reported[11] $[\alpha]_D$ +66°). Inspection of the 10% EtOH in benzene eluate by TLC[6] showed the presence of small amounts of ursolic and oleanolic acids. Alkali hydrolysis of the benzene extract filtrate (above) gave an unsaponifiable fraction (0·16 per cent of dry plant weight) which by column chromatography (alumina, 1% EtOH in benzene) gave β-sitosterol (0·005 per cent of dry plant weight), m.p. and mixed m.p. 136–138°, $[\alpha]_D$ −35°; acetate, m.p. and mixed m.p. 123–125°, $[\alpha]_D$ −44°.

Column chromatography (alumina) of the EtOAc extract (17·7 per cent of dry plant weight) of the marc of plant material failed to afford crystallizable products. However, inspection of the fractions on silica gel plates[6] revealed the presence of a monohydroxylic acid which, after transfer to a kieselguhr plate, was shown to be betulic acid.

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