[Jour. Indian Chem. Soc., Vol. 47, No. 8, 1970]

Studies on Insecticidal Plants: Chemical Examination of the Leaves of *Capparis sepiaria**

N. Adityachaudhury and (Miss) D. Ghosh

From the leaves of *Capparis sepiaria*, four pentacyclic triterpene alcohols, *viz.*, α-amyrin, β-amyrin, taraxasterol and erythrodiol, characterised as their crystalline acetates, have been isolated besides a liberal amount of β-Sitosterol. The occurrence of taraxasterol and erythrodiol is reported for the first time in a *Capparis* species.

The plants of the genus *Capparis* belonging to the family *Capparidaceae* are reported to possess insecticidal properties[1]. The three families, *Capparidaceae*, *Cruciferae* and *Residaceae* fall in the N.O. Rhoeadales. Plants of these three families have been found to be the chief sources of thioglucosides.[2]

The distribution of the triterpenoid constituents in different species of the genus *Capparis* (Fam : *Capparidaceae*) is still unknown. We therefore thought it worthwhile to undertake a systematic chemical investigation on the triterpene constituents of some *Capparis* species. We report in this paper our preliminary results on the triterpenoid constituents of the leaves of *Capparis sepiaria*. Four pentacyclic triterpene alcohols, *viz.*, α-amyrin, β-amyrin, taraxasterol and erythrodiol, characterised as their crystalline acetates, have been isolated besides a liberal amount of β-sitosterol. The occurrence of taraxasterol and erythrodiol is reported for the first time in a *Capparis* species.

The concentrated benzene extract of the leaves of *C. sepiaria* was chromatographed over silica gel. The earlier benzene eluates yielding gummy residues (which could not be crystallised) were mixed together to give a fraction (A), which responded to triterpene colour reaction. The latter benzene elunates afforded another crop of solid (B) responding to sterol colour reaction. Further eluation with benzene-ether yielded a fraction (C) which also responded to triterpene colour reaction.

Fraction (A) was acetylated. The acetylated product on chromatography over silica gel and on repeated crystallisation afforded three crystalline solids. All the three solids responded to Liebermann-Burchardt test for triterpenes.

The first crop of crystalline solids obtained on repeated crystallisation from chloroform-methanol furnished glistening needles, m.p. 238°–40°, $(\alpha)_D$ +87° ($CHCl_3$). The I.R. spectrum

* This paper was presented at the "Convention of Chemists—1969" held at Kharagpur, December 27–31, 1969.

1. D. E. H. Frear, *A catalogue of insecticides and fungicides*, Chronica Botanica Co., Waltham, Mass, U.S.A., Vol. II, p. 69, (1947).
2. T. Swain, *Chemical Plant Taxonomy*, Academic Press London, p. 468 (1963).

(KBr) of the compound disclosed the presence of an acetoxy function (5·8μ, 8·02μ) and a trisubstituted double bond (6·0μ, 12·28μ). These data suggested its identity with β-amyrin acetate which was finally confirmed by direct comparison with an authentic sample (m.m.p.)

The third crop of crystalline solids on repeated crystallisation afforded glistening flakes, m.p. 238°–40°, (*lit.*[3] m.p. 245°–48°), $(\alpha)_D$+96° ($CHCl_3$). It analysed for $C_{32}H_{52}O_2$ (M^+ 468). The compound contained an acetoxy group (peaks at 5·81 and 8·01μ) in I.R., a three proton singlet at 2·04 δ in N.M.R., a secondary methyl group (a doublet centered at 1·05 δ, J = 6 c/s) and six more methyl groups (two broad singlets around 0·9–1·18 δ) and two exocyclic vinylic protons (6·18 and 11·3μ) in I.R., a broad band of 2 protons centred at 4·65 δ in N.M.R). The mass spectral fragmentation pattern resembled closely those of the saturated oleanane and ursane series, species '*g*' (m/e 249) and its decomposition product (m/e 189 due to loss of acetic acid) being the most abundant fragments in the spectrum. Besides the above ion species, peaks at m/e 218, 203, 204 and 205 were also discernible in this spectrum. The mass data showed remarkable similarity with that reported for ψ-taraxasterol.[4] The mass spectral fragmentation pattern coupled with the N.M.R., I.R., and optical rotation data of this triterpenoid derivative agree with those reported for taraxasterol acetate.

The third triterpene acetate obtained by repeated crystallisation from chloroform-methanol showed m.p. 220°–24°, $(\alpha)_D$+79° ($CHCl_3$). The I.R. spectrum, optical data, and other behaviour correspond to those of α-amyrin acetate, which was finally confirmed by direct comparison with an authentic sample.

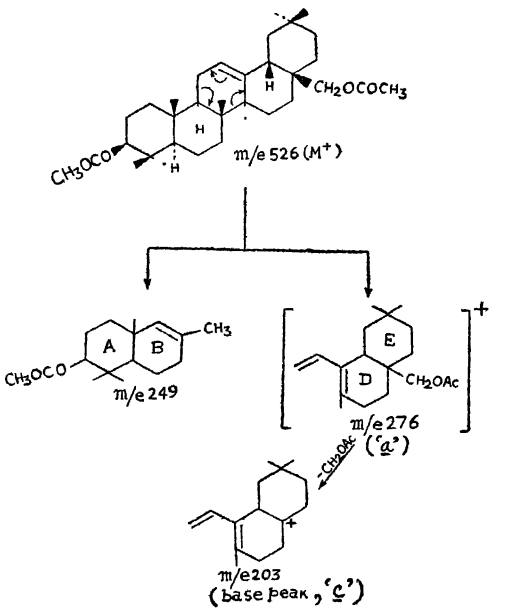
The sterol fraction (B) was identified as β-sitosterol, m.p. 139°. It was confirmed as β-sitosterol by preparing its acetate, m.p. 125–26°, $[\alpha]_D$−39° ($CHCl_3$). The latter showed no depression in m.p. upon admixture with an authentic sample of β-sitosterol acetate.

Fraction (C) was acetylated and the acetylated product on chromatography over silica gel afforded a solid, which on crystallisation from methanol gave needles, m.p. 180°–82°, $[\alpha]_D$+60·2° ($CHCl_3$). It analysed for $C_{34}H_{54}O_4$. The I.R. spectrum showed bands at 5·8μ, 8·01μ (acetoxy function) and 12·28μ (trisubstituted double bond). The N.M.R. spectrum of this triterpene revealed the presence of 6-quat. methyls (0·95 to 1·18δ). The appearance of a methyl singlet at 1·2δ suggested the presence of a C_{17}–CH_2OAc function.[5] In conformity with this, the methylene protons of the $-CH_2OAc$ group absorbed as a quartet at 3·93δ (J = 11 c/s). Other peaks were present at 2·05δ (singlet, 2–$OCOCH_3$), 4·52δ, (triplet, CHOAc) J = 7 c/s and 5·38δ (multiplet, $-CH=C<$). The mass spectrum showed molecular ion peak at m/e 526, together with the ions at m/e 466 and 453 corresponding to loss of CH_3COOH and $-CH_2OAc$. Retro-Diels Alder fragmentation of the molecule (Chaart I) gave the ions at m/e 249 (rings A and B) and m/e 276 (rings D and E)[4]. Elimination of 60 mass units from the former gave a peak at m/e 189 which revealed the attachment of the acetoxy group at C_3. The base peak at m/e 203 (species '*c*')[4] resulted from the expulsion of $-CH_2OAc$ group from the fragment at m/e 276. That the $-CH_2OAc$ group was fixed at C-17 was

3. P. Boiteau, B. Pasich et A. R. Ratsimamanga, *Les Triterpenoids en physiologie vegetale et animale*, Gauthier-Villars, Paris p. 192 (1964).
4. R. Budzikiewicz, J. M. Wilson and C. Djerassi, *J. Amer. Chem. Soc.*, 1963, **85**, 3688.
5. M. Shamma, R. E. Glick and R. O. Mumma, *J. Org. Chem.*, 1962, **27**, 4513.

indicated by the fact that species '*c*' (m/e 203) was several times more intense than '*a*' (m/e 276)[4]. The mass data of the above triterpene diacetate along with other physical properties were found to be identical with those reported for erythrodiol diacetate.

CHART-1



EXPERIMENTAL

All m.p.s are uncorrected. The petroleum ether used had b.p. 60°–80°. Optical rotations were measured in $CHCl_3$.

Investigation on the leaves of Capparis sepiaria : Dried and powdered leaves (1 kg.) was extracted with benzene for 18 hrs. The benzene extract (25 g.) was concentrated and chromatographed over silica gel (250 g.). The chromatogram was eluted successively with solvents and solvent mixtures of increasing polarity. The earlier benzene eluates gave oily residues which exhibited positive test for triterpenes, and were collected together to give the fraction (A). Evaporation of the latter benzene eluates gave gummy residues which showed positive test for sterols and these were mixed to give a fraction (B). Further elution of the chromatogram with benzene : ether (9 : 1) yielded a fraction (C) which also responded to triterpene colour reaction.

Isolation of triterpenoid alcohols as their acetates : Fraction (A) was acetylated with acetic anhydride-pyridine in the usual way. The acetylated product (3 g.) obtained was chromatographed over silica gel (60 g). With petroleum ether : benzene (95·5 : 0·5) as the eluent, white solid appeared upon evaporation of the solvent. The solids in each flask were crystallised from a mixture of chloroform-methanol. The first lot (fractions 24–30) showed m.p. range 205°–228°. The 2nd crop (fractions 31–36) melted at 180°–85° and the third lot (fractions 37–50) melted at 205°–215°.

β-Amyrin acetate : The first crop (*fractions* 24–30) of solids on repeated crystallisation from chloroform methanol furnished crystalline needles (80 mg.), m.p. 238°–40°, $[\alpha]_D$+87°. It was identified as β-amyrin acetate by direct comparison (m.p., m.m.p., I.R.), with an authentic sample of β-amyrin acetate.

Fractions 31–36, m.p. 180°–85°, were proved to be a complicated mixture of triterpene acetates (TLC) and were not further investigated.

Taraxasterol acetate : The third lot (*fractions* 37–50) on repeated crystallisation from chloroform-methanol gave glistening flakes (100 mg.), m.p. 238°–40°, $[\alpha]_D$+96°. (Found C, 81·87; H, 11·35. Calcd. for $C_{32}H_{52}O_2$: C, 82·05; H, 11·11%). This compound was identified as taraxasterol acetate by direct comparison (m.m.p., I.R., TLC) with an authentic sample of taraxasterol acetate.

α-Amyrin acetate : The mother liquor from the above compound upon concentration and crystallisation from chloroform-methanol gave a third triterpene acetate (40 mg.), m.p. 220°–224°, $(\alpha)_D$+79°. It was identified as α-amyrin acetate by direct comparison (m.p., m.m.p., I.R., TLC) with an authentic sample of α-amyrin acetate.

β-Sitosterol : The sterol fraction (B) on repeated crystallisation from chloroform-methanol gave crystals (120 mg.), m.p. 136°–38°. It was converted to its acetate in the usual way. The acetate crystallised from chloroform-methanol, m.p. 125°–26°, $[\alpha]_D$−39°. It was confirmed as β-sitosterol acetate by m.m.p. with an authentic sample.

Erythrodiol diacetate : Fraction (C) was acetylated with acetic anhydride-pyridine in the usual way. The acetate obtained was chromatographed over silica gel. Elution of the chromatogram with petroleum ether : benzene (8 : 2) afforded a solid (60 mg.) which on crystallisation from methanol gave needles, m.p. 180°-81°, $[\alpha]_D$+60·2°. (Found : C, 77·7; H, 10·3. Calcd. for $C_{34}H_{54}O_4$: C, 77·5; H, 10·2%). The compound was identified as erythrodiol diacetate by direct comparison with an authentic sample (m.p., m.m.p., I.R., TLC).

The authors express their sincere thanks to Dr. C. P. Dutta, Fordham University, New York, for I.R. and N.M.R. spectra, to Dr. B. C. Das, Gif-sur-Yvette, France for mass spectra, to Dr. S. K. Talapatra, Department of Chemistry, Calcutta University and to Dr. C. R. Mitra, National Botanic Gardens, Lucknow for kindly supplying authentic samples of taraxasterol acetate and erythrodiol caprylate, respectively. Financial assistance from C.S.I.R., New Delhi is gratefully acknowledged.

Agricultural Chemistry Laboratory,
Faculty of Agriculture,
University of Kalyani,
Kalyani, West Bengal.

Received March 10, 1970