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CHEMICAL INVESTIGATION OF *CAPPARIS DECIDUA* FRUITS

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ABSTRACT

Fruits of *Capparis deciduas* have afforded 14-hydroxytetradec-12-enylbutanoate and stigmastan-4-one. The ester is a hitherto unknown compound.

Key words: Stigmastan-4-one, 14-Hydroxytetradec-12-enylbutanoate, Methanol extract, *Capparis deciduas*, Capparidaceae.

INTRODUCTION

Capparis, a genus famous for the large number of physiologically active constituents and edible quality of fruit, belongs to the family Capparidaceae. *Capparis decidua* is a densely, branched, spinous shrub or tree distributed in arid and semi arid regions of the country. The tree usually grows in dry exposed habitat often on foothills and, grows in wild states in arid and semi arid regions of the country and, it is mainly distributed in western Rajasthan, Punjab, Gujarat, central area and deccan and grows in all types of waste land. It is locally referred as *Kair* in Rajasthan, *Karil* in Uttar Pradesh, *Ker* in Gujarat, *Teent* in Haryana, *Della* in Delhi and Punjab, *Nepti* in western Maharashtra[1]. The plant contains berry-shaped unripe fruits having golden yellow pulp and white seeds. All the parts of the fruit are edible. The unripe fruit, generally consumed as vegetable and pickles, form an integral part of the diet of people in the desert and semi-desert areas of the country[2].

All parts of the plant are used in traditional medicine for a variety of purposes in the regions where it grows. The fruits of the plant are astringent and useful in cardiac troubles and biliousness. The blanched fruits have a significant hypocholesteraemic effect on the serum and liver cholesterol. The root bark is alexiteric, anthelmintic and useful in cough,

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asthma and inflammations. Its aqueous extract possesses purgative activity. This genus is also known to be a rich source of flavonoids, alkaloids, glucosinolates[3].

Some of the flavonoids isolated *Capparis decidua* display diverse biological activities such as antitumor activity. Isothiocynate glucoside, glucocapparin, has also been isolated from this pant, and its aglycone shows high antibacterial activity (25 ug/mL) against *Vibrio cholerae* and several other pathogenic microorganisms. It also possesses anthelmintic activity[4].

Fruits of *Capparis moonii* contain L-stachydrine, rutin and β-sitosterol. The aqueous extract of the rind of the immature fruits contains a chestnut-red pigment, hajiacyn, which is used as an anti-trachoma drug. The fruits are also used in weakness and cough[5].

C. spinosa contains α- and β-amyrin, taraxasterol, erythrodiol, betulin and β-sitosterol. The presence of amino acids and phenolic acids has also been reported in this specie. The plant is credited with antipyretic and antiseptic property, and is useful in skin-diseases. The juice of inner bark of the root is used in scabies and eczema[6].

The ripe fruits of *C. micracantha* have a sweet aromatic flavour and are edible. Roots are diuretic and a uterine tonic; their decoction is given after child birth. Leaves are applied as a poultice to swellings. The roasted seeds are used in India and China for treating cough[5].

Roots of *C. grandis* contain 4, 5, 6, 7-tetrahydroxydecyl isothiocynate along with its glucosinolate and three other unidentified glucosinolates. The presence of quercetin, rhamnetin and phenolic acids has also been reported. Due to this, the plant is used as an ingredient of the ayurvedic drugs "varisthata Hareetahi" and "dhadhika grilha". An infusion of bark and leaves is used internally for swelling and eruption[7].

Leaves of *C. baducca* contain alkaloids mainly a quaternary ammonium alkaloid ($C_{19}H_{18}O_2N$). Its extract exhibited hypotensive, anticonvulsant and anti-inflammatory action on experimental animals[8].

The root bark of *C. zelylanica* is bitter, stomatic, sedative, antithyroidic and is useful in fever. The root bark is reported to contain an alkaloid, a phytosterol, a water soluble acid, and the paste is used for body ache. Leaves contain β-carotene. They are applied as poultice to piles, bowels and swellings. The plant is useful in fever and contains a saponin, p-hydroxybenzoic acid, syringic, vanilic, ferulic and p-coumaric acid[9].

A survey of literature reveals that very little work has been done on chemical constituents of *Capparis decidua* fruit. Therefore, the present study was aimed at isolating and identifying various chemical components present in the fruit of this plant.

EXPERIMENTAL

Methodology

Materials and methods

Benzene (LR), hexane (LR), ethyl acetate (LR), methanol (GR), petroleum ether (LR), pyridine (GR), sulphuric acid (GR), ferric chloride (LR), perchloric acid (LR), acetic anhydride (AR), potassium hydroxide (LR), sodium hydroxide (AR), sodium acetate, glacial acetic acid (AR) were used without further purification. The adsorbents used were silica gel (60-120 mesh) and silica gel (G). Alcoholic ferric chloride, sulphuric acid (10%) and perchloric acid (10%) were used as spray reagents for developing the spots on TLC plates.

Extraction

Fruits of *C. decidua* were procured from village Dhamana, District Hisar (Haryana). These were crushed and the powdered material was refluxed in methanol on a water bath. The methanol extract was concentrated at atmospheric pressure which yielded a dark yellow viscous liquid. It was mixed with silica gel and subjected to column chromatography which yielded two compounds. These were further purified by preparatory TLC and crystallization. The purified compounds obtained in the present investigation were labelled as A and B.

Physical measurements

Infrared spectra

Infrared spectra were recorded on (BIORAD FTS-7) infrared spectrophotometer. The spectra of the compounds were obtained by preparing potassium bromide pellets. **^{1}H NMR Spectra:** The ^{1}H NMR spectra of the compounds were recorded in $CDCl_3$ on a Bruker–300 (300-MHz) nuclear magnetic resonance spectrometer using tetramethylsilane (TMS) as internal standard at Sophisticated Analytical Instrumentation Facility (SAIF), Panjab University, Chandigarh. The chemical shifts are in δ ppm scale. **Mass spectra:** The mass spectra of the compounds were recorded on a SHIMADZU QP-5000 spectrometer at National Institute of Pharmaceutical Education and Research (NIPER), Mohali.

RESULTS AND DISCUSSION

Compound A (14-hydroxytetradec-12-enylbutanoate, 1)

It was obtained on elution with benzene-hexane (1 : 10) purified by preparatory TLC and crystallized from petroleum ether (40 mg), its melting point was 80°C. The R_f value of the compound was found to be 0.62 in benzene-hexane (1 : 1) It showed yellow coloured spot on spraying the TLC plate with 10% H_2SO_4 followed by heating to 110°C. **IR** $\nu_{max.}$ (cm^{-1}): 3318, 1746, 1463, 1377, 1163 ; **MS** (m/z) M^+ 298, 87; **^{1}H NMR (δ, $CDCL_3$):** 5.35 (m, 1H, olefinic proton); 5.23 (m, 1H, olefinic proton); 4.19 (t, 2H, J = 11 Hz, -C-O-CH_2-); 4.0 (d, 2H, *J* = 9 Hz.; = CH-CH_2-OH) 3.63 (s, 1H, -OH proton); 2.30 (t, *J* = 7 Hz, 2H, -CH_2-C-O-); 2.01 (m, 2H, allylic protons -CH_2-CH_1 = CH–); 1.61 (m, 2H-CH_2-CH_2-C-O-) 1.2-1.4 (m, 21H, methylene and methyl protons).

Compound B (Stigmastan-4-one, 2)

It was obtained on elution with benzene-hexane (1 : 1) purified by preparatory TLC and crystallized from petroleum ether (45 mg), its melting point was 154-156°C. The R_f value of the compound was found to be 0.57 in the solvent system hexane–benzene (1 : 2). **IR** $\nu_{max.}$ (cm^{-1}): 2919, 2850, 2362, 1706; **MS** (m/z) M^+ 414 ; **^{1}HNMR (δ, $CDCl_3$):** 0.679 (s, 3H, 18-Me); 0.759 (d, 3H, J = 6.4 Hz, 26-Me); 0.854 (d, 3H, *J* = 6.4 Hz, 27-Me); 0.877 (t, 3H, *J* = 6.5 Hz, 29-Me); 0.901 (d, 3 H, *J* = 6.5 Hz, 21-Me); 1.003 (s, 3H, 19-Me); 2.33 (t, 2H, *J* = 6.5 Hz, C_3-H); 2.28 (dd, 1H, J_1 = 8 Hz and J_2 = 3Hz, C_5-H) 1.93 (2H, m, C_6-H); 1.6 (m, 2H, C_2–H); 1.1-1.4 (m, 9 × CH_2 and 7CH).

Compound A (14-hydroxytetradec-12-enylbutanoate, 1)

It was crystallized from petroleum ether. The TLC plate on spraying with 10% H_2SO_4 followed by heating to 110°C exhibited yellow spot. The IR spectrum of the compound showed peaks at 3318 cm^{-1} and 1746 cm^{-1} indicating the presence of -OH group and ester linkage.

The ^{1}H NMR spectrum of the compound A in $CDCl_3$ exhibited multiplet at δ 5.35 and δ 5.23 for two olefinic protons. One triplet (J = 7 Hz) was observed at δ 4.19 was attributed to the two protons of -C-O-CH_2- group. A singlet of one hydrogen at δ 3.63 was assigned to -OH group. The triplet of two hydrogens at δ 2.30 with J value of 7 Hz may be assigned to -CH_2-C-O- group. The multiplet of two hydrogen at δ 2.01 was assigned as allylic protons and a multiplet of two hydrogens at δ 1.61 may be attributed to the methylene protons -CH_2-CH_2-C-O-. A multiplet integrated for twenty one methylene and methyl protons was observed in the range δ 1.2-1.4. A prominent peak in the mass spectrum at m/z

87 confirmed the butanoate moiety. On the basis of ^{1}H NMR and IR and mass spectral data following structure is assigned to the compound 14-hydroxytetradec-12-enylbutanoate. It is a hitherto unknown compound.

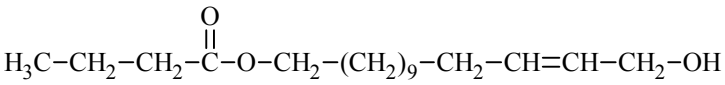

Fig. 1: Compound A: 14–hydroxytetradec–12–enylbutanoate

Compound B (Stigmastan-4-one, 2)

It was obtained on elution with benzene-hexane (1 : 1) and crystallized from petroleum ether. The compound gave green colour with Liberman-Burchard reagent indicating it to be a steroid. The IR spectra of the compound showed peak at 1706 cm^{-1} indicating 6 membered ring ketone. The mass spectrum of this compound showed a molecular ion peak at m/z 414 which suggested the molecular formula $C_{29}H_{50}O$.

The ^{1}H NMR of the compound B in $CDCl_3$ exhibited a triplet at δ 2.33 (J = 6.5 Hz) integrating for two protons and assigned to C-3 protons. Two singlets for two methyl (C-18 and C-19) were observed at δ 0.679 and δ 1.003, respectively. The three doublets for 3 methyl groups (C-26, C-27 and C-21) were observed at δ 0.759, δ 0.854 and δ 0.901, respectively. A triplet at δ 0.877 integrating for 3 protons was due to C-29 methyl. The position of the keto group at C_4 was assigned on the basis of the fact that a triplet of only two protons was observed at δ 2.33 indicting the keto group at C_1 or C_4 position. However, the position of keto at C_1 is ruled out as there is no downfield shift of C-19 methyl signal[10].

The position of keto group at C_4 is further supported by a multiplet at δ 1.93 for 2 H at C-6, which is in the downfield from its normal range δ 1.11 – δ 1.4 and one doublet of doublet at δ 2.28 (J = 8 Hz and 3 Hz) for 1H at C-5. Thus, the following structure has been proposed for the compound Stigmastan–4–one.

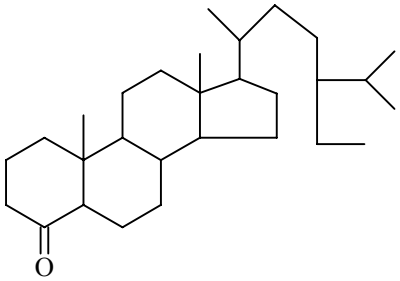

Fig. 2: Compound B: Stigmastan-4-one

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