

Chemical Constituents of *Berberis coriaria* Royle

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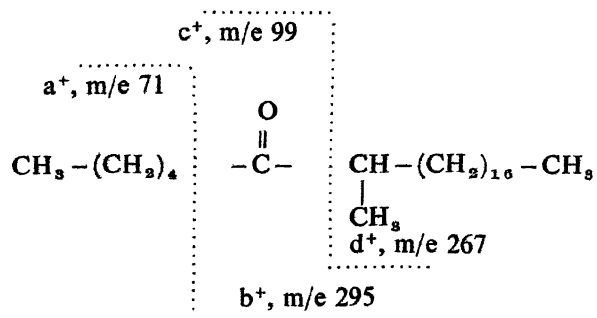
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Berberine and a new ketone, 7-methyl tetracosan-6-one have been isolated from the stem bark of *Berberis coriaria*.

PREVIOUS studies¹⁻¹¹ of the genus *Berberis* have shown it to be a rich source of alkaloids of phytochemical interest. Berberine, the principal alkaloid of the drug has been shown to possess antibiotic activity¹². Keeping in view the medicinal importance of *Berberis*, the chemical examination of the stem bark of *B. coriaria* Royle was undertaken.

The ethanolic extract of the stem bark of *Berberis coriaria* yielded a new ketone, 7-methyl tetracosan-6-one and an alkaloid berberine.

The ketone, $C_{25}H_{50}O$, m. p. 72° , 2:4 dinitrophenylhydrazone, m. p. 94° , on sodium borohydride reduction gave an alcohol, $C_{25}H_{52}O$, m. p. 70° , indicating the presence of a carbonyl group. The IR spectrum of the compound showed peaks at 1738 cm^{-1} (carbonyl group). In its PMR ($CDCl_3$) spectrum peaks were obtained at δ 0.89, s (9H, $3CH_3$ groups), δ 1.27, broad singlet (34H, $17CH_2$ groups), δ 1.78, s (4H, $2CH_2$ groups β to carbonyl group), δ 2.33, s (3H, $1CH_3$ and $1CH$ adjacent to carbonyl group). The compound on potassium permanganate oxidation¹³ yielded n-pentanoic acid and n-hexanoic acid.



M⁺, m/e 366, 7-methyltetracosan-6-one.

Scheme 1

The foregoing evidences indicated the straight chain nature of the smaller alkyl group having C_5 or C_6 methylene groups and branched larger alkyl

group. The size of alkyl groups, position of ketonic function and the position of the side chain was evident from the mass fragmentation pattern of the ketone¹⁴⁻¹⁶ (Scheme 1). The molecular ion peak appeared at m/e 366 (M^+ , 14). The peaks obtained at m/e 310 (86), 238 (29), 128 (84), 72 (65), 56 (74) are due to McLafferty rearrangement on both the sides of carbonyl group. Other significant peaks appeared at m/e 348 ($M^+ - H_2O$, 27), 295 (b^+ , 48), 267 (d^+ , 63), 99 (c^+ , 100), 71 (a^+ , 78), 57 ($a^+ - CH_3$, 76), 43 ($a^+ - 2CH_3$, 78), 29 ($a^+ - 3CH_3$, 70).

Characterisation of Alkaloid (Berberine)

The yellow alkaloid, $C_{20}H_{19}NO_5 \cdot 3H_2O$ (M^+ , m/e 351), m. p. $206-7^\circ$ (d) has been characterised as berberine by colour tests, preparation of derivatives, spectral studies, Co-tlc and m. m. p. with the authentic sample.

Experimental

Isolation of 7-methyltetracosan-6-one and Berberine from *B. coriaria* :

The air dried powdered stem bark (500 g) of *Berberis coriaria* Royle was exhaustively extracted with ethanol (3 lit.) for several days. The hot ethanolic extract when kept in a refrigerator yielded a white deposit which was separated by filtration. On repeated crystallisation from ethanol, the pure ketone was obtained, m. p. 72° , ν_{max}^{KB} 2920, 2855 ($-CH_3$), 1738 ($>C=O$), 1470, 1270, 1170, 730 and 716 cm^{-1} ($>CH_3$). The filtrate was then concentrated to about 400 ml under reduced pressure. The concentrate was defatted by extracting with petroleum ether. The defatted extract was kept in a refrigerator for two days when an yellow deposit settled at the bottom of the flask. It was filtered and washed with a little of cold ethanol. It showed a single spot on TLC plate (adsorbent-alumina; solvent-cyclohexane : chloroform : acetic acid; 45 : 45 : 10, v/v, $R_f=0.55$) and was purified by preparing its acetate by the usual method¹⁷ followed by recrystallisation from chloroform :

absolute alcohol (1 : 10) mixture whereupon an yellow crystalline compound B, $C_{20}H_{19}NO_5 \cdot 3H_2O$, m. p. 206-7° (d) was obtained which showed identical spectral data already reported in the literature^{18,19} for berberine.

Sodium borohydride reduction of 7-methyltetracosan-6-one :

The ketone (100 mg) in methanol (50 ml), $NaBH_4$ (200 mg) was mixed with constant stirring and the mixture was kept at room temperature for 4 hours when the whole of the ketone was converted to alcohol (TLC). Working up in the usual way the alcohol m.p. 70°, IR 3300 (broad hump for hydroxyl group), 729, 718 cm^{-1} (CH_2 groups), was obtained.

Potassium permanganate oxidation of 7-methyltetracosan-6-one :

The ketone (500 mg) in 25 ml acetone, 10 ml of 10% aqueous sodium hydroxide solution and 20 ml of 5% aqueous $KMnO_4$ solution was refluxed on a water bath for 10 hours. The reaction mixture was cooled, acidified with hydrochloric acid and the excess MnO_2 was destroyed by adding a solution of sodium bisulphite and then filtered. The filtrate was again acidified with dilute hydrochloric acid and acetone was removed by distillation. The resulting aqueous solution was washed well with water and evaporated to give a mixture of fatty acids. The descending paper chromatography on Whatman paper using ethanol : ammonia : water (80 : 4 : 16 v/v) solvent system and then spraying the chromatogram with BDH Universal indicator furnished six greenish spots. Two of them were identified by co-chromatography with the authentic samples, as n-pentanoic acid ($R_f=0.62$) and n-hexanoic acid ($R_f=0.69$).

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