

**Triterpenoid and Related Compounds, Part-
XXIII : Triterpenoid Constituents of**

Alnus nepalensis* D. Don

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ALNUS nepalensis (Fam. Betulaceae) is a moderate sized tree available throughout the Himalayas from Kashmir eastwards to the Khasia Hills and is said to be of considerable medicinal value¹. A survey of literature revealed that no chemical work has been reported on it.

Petroleum ether extract of the bark of *Alnus nepalensis* collected from the Darjeeling district afforded β -sitosterol (0.05%) and 5 triterpenoids identified as lupeol (0.26%), betulin (0.23%), betulinic acid (0.21%), taraxerone (0.03%) and taraxerol (0.005%).

Experimental

Powdered trunk bark of *A. nepalensis* (1.7 kg) was exhaustively extracted with petroleum ether (60-80°). The extract concentrate (32 g) was chromatographed over silica-gel (60-100 mesh), elution being carried out with petroleum ether and petroleum ether-ethyl acetate mixtures of increasing polarity, when the compounds described below were obtained in order of the elution. The identity of the compounds has been established from their physical properties (m.p., optical rotation, etc.) and in some cases through the preparation of derivatives.

Taraxerone (from petroleum ether eluate): $C_{30}H_{48}O$ (M^+ 424) m.p. 236° (petroleum ether-chloroform) (lit² m.p. 240°), $[\alpha]_D + 10^\circ$ ($CHCl_3$, c 0.0974), $LiAlH_4$ reduction afforded taraxerol, m.p. 276°, $[\alpha]_D + 1^\circ$ ($CHCl_3$, c 0.105°).

Lupeol (from petroleum ether eluate): $C_{30}H_{48}O$ (M^+ 424), m.p. 213° (chloroform-methanol) (lit² m.p. 215°), $[\alpha]_D + 24^\circ$ ($CHCl_3$, c 0.0918), acetate, m.p. 217°-218°, $[\alpha]_D = +45^\circ$ ($CHCl_3$, c 0.103°).

Taraxerol (from 1% ethyl acetate in petroleum ether): $C_{30}H_{50}O$ (M^+ 426), m.p. 276° (petroleum ether chloroform) (lit² m.p. 280°), $[\alpha]_D + 1^\circ$ ($CHCl_3$, c 0.1), acetate, m.p. 296° $[\alpha]_D + 7.2^\circ$ ($CHCl_3$, c 0.105°).

Betulin (from 5% ethyl acetate in petroleum ether): $C_{30}H_{50}O_2$ (M^+ 442), m.p. 252° (absolute alcohol) (lit² m.p. 255°), $[\alpha]_D + 17^\circ$ ($CHCl_3$, c 0.1), diacetate, m.p. 215°, $[\alpha]_D + 20^\circ$ ($CHCl_3$, c 0.092°).

Betulinic acid (from 5% ethyl acetate in petroleum ether and more polar fractions): $C_{30}H_{48}O_3$ (M^+ 456), amorphous, $[\alpha]_D + 9^\circ$ (C_6H_5OH , c 0.10) (lit² m.p. 320°), methyl ester, m.p. 222°, $[\alpha]_D + 7.5^\circ$ ($CHCl_3$, c 0.099°).

β -*Sitosterol* (from 2% ethyl acetate in petroleum ether): white needles, m.p. 136°-137° (chloroform-methanol), (lit² m.p. 136°-137°), acetate, m.p. 126°.

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**Liquid-Liquid Extractive Separation of
Cobalt(II) with 2'-Hydroxy-4-Methoxy-5'-
Methylchalkone Oxime¹ (HMMCO)**

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2'-Hydroxy-4-methoxy-5'-methylchalkone oxime (HMMCO) has been used for extraction and spectrophotometric determination of palladium(II)¹ and copper(II)². The stability constants and partition coefficients of extractable chelates have also been evaluated^{2,3}. It has been employed as indicator for titration of iron with EDTA and NTA^{4,5}. The quantitative separation of palladium(II), copper(II) and nickel(II) as oximates is also reported⁶.

The purpose of this paper is to establish the scope of application of 2'-hydroxy-4-methoxy-5'-methylchalkone oxime (HMMCO) to solvent extraction of cobalt(II). The method proposed here is rapid, simple and affords separation and determination of cobalt at trace level.

Experimental

Reagents and Solutions: 2'-Hydroxy-4-methoxy-5'-methylchalkone oxime (HMMCO) was synthesized and purified as reported earlier⁶. 0.001 M HMMCO in distilled benzene was used. The reagent was always stored in a refrigerator.

A stock solution of 0.01 M cobaltous sulphate was prepared in distilled water and standardised by known method⁷. The dilute solution of cobalt of desired concentration was prepared by appropriate dilution of stock solution.

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Apparatus : A Beckman model DU-2 spectrophotometer, with 10 mm quartz cells, an ELICO pH-meter, model LI-10T with saturated calomel and glass electrodes and a Ganson flask shaker with to and fro action were used in the present studies.

General procedure : To an aliquot of solution containing 58.9 μg cobalt, enough acetic acid (0.2 M) and sodium acetate (0.2 M) are added to get pH 6.0 to 7.2 in 25 ml volume. The solution is shaken with 10 ml of 0.001 M HMMCO in benzene for 15 min. The organic layer is separated and its absorption is measured at 390 nm against reagent solution as a blank. The extracted cobalt is computed from calibration curve.

Results and Discussion

Absorption spectra : The absorption spectra of the cobalt complex in benzene show a maximum at 390 nm. The molar absorptivity of the complex at 390 nm is 2.28×10^4 litre mole⁻¹ cm⁻¹. The sensitivity of the method as defined by Sandell is 0.0026 $\mu\text{g}/\text{cm}^2$ at 390 nm. The system obeys Beer's law over the range of 0.6-17.7 μg cobalt per ml of benzene. The complex is stable up to 24 hr.

Effect of pH and HMMCO concentration : It is observed that the extraction is quantitative in the pH range 6.0-7.2. Below pH 6.0 extraction is incomplete and above pH 7.2 it decreases. There is no extraction below pH 3.0 and above pH 9.5. 10 ml of 0.001 M HMMCO in benzene at pH 6.5 suffice for quantitative extraction of cobalt.

Effect of solvent : To have a proper choice of non-aqueous solvent for the extraction of cobalt(II) from aqueous phase, several solvents like benzene, toluene, *p*-xylene, hexane, cyclohexane, chloroform, carbon tetrachloride, *iso*-amyl alcohol, *n*-butanol, *iso*-butanol, cyclohexanol, *iso*-butylmethylketone, cyclohexanone, etc. were tried. It is revealed that benzene is the most suitable solvent for the present system. It is further noted that the extraction is quantitative in 10-15 min of agitation; a time of 15 min is therefore recommended.

Effect of diverse ions : Various ions were tested for possible interferences. The tolerance limit is set at the amount of foreign ion required to cause $\pm 2\%$ error in the recovery of cobalt. Ions such as alkali and alkaline earth metals, beryllium, aluminium, selenite, arsenite, halide anions, sulphite, thiosulphate, nitrate, nitrite are tolerated in the ratio of 1 : 200. Silver, cadmium, zinc, mercury, manganese, chromium, ruthenium, rhodium, gold, platinum and osmium(VIII) can be tolerated in twenty fold excess. Two fold excess of nickel does not interfere, while copper, palladium, iron(III), uranyl, vanadyl, thorium and EDTA interfere seriously.

Precision : The average absorbance found for 58.9 μg of cobalt is 0.230 ± 0.005 for 20 determinations. The relative standard deviation is $\pm 1.1\%$.

The method proposed here is simple, rapid, sensitive and applicable at trace concentration of cobalt. It is possible to separate and determine cobalt from various ions.

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Spectrophotometric Studies on Palladium(II) with 2-Thiopyrogallol and β -Mercapto-resorcylic Acid

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SULPHUR bearing ligands are long being used for photometric determination of palladium. Some of the most important ligands are dithio-oxamide¹, N, N'-bis-(3-dimethyl-aminopropyl) dithio-oxamide², 3-phenyl-3H-5-mercapto-1,3,4-thiadiazole-2-thion³, diethyldithiophosphate⁴, α -ethyl thio-isonicotinamide⁵ and 2-mercaptopyridine-1-oxide⁶.

In the present investigation attempts have been made to find some new chromogenic reagents for palladium with sulphur as donor atom. Effects on sensitivity with change of functional groups were also investigated. The stepwise formation constants k_1 and k_2 of the complexes PdL₁⁺ and PdL₂, respectively have been evaluated following the graphical extrapolation methods of Leden⁷ and Yatsimirskii⁸⁻¹⁰. The overall formation constants of the palladium complexes have also been evaluated by Harvey-Manning method¹¹.

Experimental

Equipment : A Hilger Uvispek spectrophotometer and a Spektromom 204 with 1 cm quartz cells