

CHEMICAL INVESTIGATION OF *CORNUS MACROPHYLLA* WALL.

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ALTHOUGH a number of medicinal plants belonging to the *Coranaceae* family have been chemically investigated and some organic compounds isolated from them, no work has been reported on the plant *Cornus macrophylla* Wall. The latter is an erect tree with horizontal branches and occurs through out the Himalayas¹ at altitudes of 4000–5000'. The plant is known in Hindi as Kandar or Kachur, but no medicinal applications of any of its parts are reported. Its wood is used to make shutters, pulleys, bobbins etc and is particularly useful for making gunpowder charcoal².

The dried roots and bark of C.M. (3 kg) were extracted with *n*-hexane for 4 days at room temperature. Evaporation of the solvent under vacuum left behind a deep brown pasty residue (112g). Usual methods of purification failed to give a pure substance. However, vacuum distillation (oil bath temp. 250°/0.1 mm) afforded a yellow oil (300 mg) which could not be purified further.

The plant material left after the hexane treatment was extracted repeatedly with CH₂Cl₂. Evaporation of the solvent left a green sticky residue (40 g). The latter was boiled in a Soxhlet extractor with hexane to remove traces of an oil. A small amount of the resulting solid (1 g) was slowly sublimed under vacuum (250–60°/10 mm) to get a colourless solid. This was chromatographed over silica gel and elution with benzene gave a colourless solid, m.p. 295–298° (decomp.) (tlc. single spot). It was insoluble in NaHCO₃ but soluble in alcoholic alkali. The mass spectral data (M^+ 456) and elemental analysis agreed with the molecular composition C₃₀H₄₈O₃.

The UV spectrum (alcohol) did not show any absorption whereas in the IR spectrum bands were obtained at 3465 (OH) and 1680 (C=O). No bands were seen in the aromatic region. Further, the compound gave only a slight specific rotation. It gave positive Lieberman-Burchard and Salkowski colour tests indicating its triterpenoid or steroidal nature. Its acetyl derivative (M^+ 498) gave m.p. 278–80° while the benzoyl derivative had m.p. 330–33°. The IR of the acetyl derivative showed bands at 3500 (OH), 2960, 1730 (C=O), 1685 (C=O). From the above data the compound was identified as betulinic acid which is

known to occur frequently in plants. Its identity was confirmed by a comparison with an authentic specimen of the acid (m.m.p., I.R. and to-tlc). It is of interest to note that from about 3 kg of plant material, the amount of crude betulinic acid was approximately 40 g i.e. about 1.2%. No other substance could be isolated from the plant in a pure condition.

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2. *The Wealth of India, Raw Materials*, Vol. II, CSIR, New Delhi, 1950, p. 350.

³⁵Cl NUCLEAR QUADUPOLE RESONANCE (NQR) STUDIES OF SOME CHLOROPYRIDINOLS AND CHLOROPYRIDINE-N-OXIDES

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PYRIDINOLS form an interesting class of heterocyclic compounds, the 2 and 4 pyridinols having been known to exist in the tautomeric pyridone form¹ both in solution and in the solid state. In pyridine *N*-oxides however, substitution at positions 2 and 4, has shown that the hetero-oxygen atom can either release or accept electrons according to the substituent. Further the study of some of the chlorosubstituted pyridine *N*-oxides assumes importance in view of their biological properties, especially strong antifungal and antibacterial activities^{2,3}.

Since the substitution of hydroxyl and the chloro groups at different positions in the heterocyclic pyridine ring results in a different electronic charge distribution round the ³⁵Cl nucleus in each chloropyridinol, it will be appropriate to study the ³⁵Cl NQR frequency shifts in such systems. Such a study can also be extended to include the chlorosubstituted pyridine *N*-oxides. Consequently we have prepared a number of chloropyridinols and chloropyridine *N*-oxides

and subjected them to NQR studies at different temperatures.

The preparation of chloropyridinols involves diazotisation of a corresponding chloro-amino pyridine followed by hydrolysis using dilute H_2SO_4 . Chloropyridine-*N*-oxides⁴ were prepared according to the earlier reported procedure⁵.

A modified Dean-type self-quenched super-regenerative NQR spectrometer has been built in our laboratory. A lock-in amplifier (phase-sensitive detector) has been employed for recording the NQR signals. The frequency of the resonance signal is measured using a BC 221 frequency meter (accuracy of ± 1 kHz).

The frequencies of NQR signals of some of the chloro pyridinols and chloropyridine *N*-oxides is reported here for the first time (table 1). A search for some of the weak signals was made at 77K. The frequency range of the scan was between 32 and 37 MHz.

In order to chart out the motional behaviour and to investigate the phase transitions, if any, in these compounds the temperature variation of ^{35}Cl NQR frequency was carried out in the range 77 to 300K, by means of a low temperature assembly. Temperature is measured using a copper-constantan thermocouple to an accuracy of $\pm 1K$.

Table 1 Summary of ^{35}Cl NQR frequencies for chloropyridinols and chloropyridine *N*-oxides

Name of the compound	Frequency in M.Hz.	
	Room temperature 300 K	77 K
1. 6-chloro 2-pyridinol	34.508 (80)	34.971 (100)
2. 5-chloro 2-pyridinol	35.641 (80)	35.613 to 36.782
3. 5-chloro 3-pyridinol	No signal	35.818 (60) 35.735 35.416 35.236
4. 2-chloro 3-pyridinol	No signal	34.813 to 35.725
5. 4-chloro pyridine <i>N</i> -oxide	34.971 (60)	35.386 (40)
6. 2-chloro pyridine <i>N</i> -oxide	No signal	34.586 (10)

Number in parenthesis is S/N ratio.

All the chloropyridinols except the 6-chloro 2-pyridinol show multiplicity of NQR signals at 77K showing the presence of crystallographically inequivalent ^{35}Cl sites in the unit cell of the compound. Thus there is strong evidence for the existence of phase transitions in the temperature range 77–300K. 5-chloro 2-pyridinol showed number of closely spaced lines in the frequency range 35.61 to 36.782 MHz (table 1). However, after a careful analysis, it is inferred that the unit cell of the compound may contain as many as eight ^{35}Cl in equivalent sites giving rise to eight signals. Similarly for 2-chloro-3-pyridinol, number of closely spaced lines were obtained in the range 34.813 to 35.725 MHz. Chloropyridine *N*-oxides show only a single line throughout the temperature range 77–300K indicating that the site symmetry around the ^{35}Cl nucleus in the unit cell of the molecule does not change. 2-chloropyridine *N*-oxide gives a weak signal, the detection of which becomes difficult above 183K.

Studies on the temperature dependence of the resonance frequency and on phase transitions as well as investigations using techniques like DTA, DSC etc are in progress. Evaluation of the torsional frequencies in these molecules using the modified Bayer theory⁶ is in progress and will be reported later.

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