functions of the ammonium ion concentrations. Therefore, a number of measurements were made in which the alkylammonium ion concentration was constant, and the hydrogen ion concentration varied from 10^{-3} to 10^{-5} *M*.

The exchange reactions considered in this study are the ones given by Grunwald, Loewenstein, and Meiboom[1]. The two major mechanisms for protolysis of aqueous alkylammonium ions are reactions 3 and 4. The simplest mechanisms for reaction 4, are as follows : (a) Proton transfer from R-NH_3^+ to H_2O, followed rapidly by proton transfer to R-NH_2 ; (b) Concerted transfer of both protons ; and (c) Proton transfer from H_2O to R-NH_2, followed rapidly by release of a proton from R-NH_3^+. Mechanism (a) can be ruled out because the rate is not expected to be much faster than that of reaction (1), and hence much slower than the observed rate (K_4). In mechanism (b), the rate determining step is either the reorientation of the water molecule between the alkylammonium ion and alkylamine so as to permit the concerted proton transfer or it is the proton transfer itself. In the former, the rate should depend on the extent of reorientation. In mechanism (c), the electrostatic field of the ion is expected to increase the acid strength of the adjacent water molecules by, at least, a few orders of magnitude[5]. The increase of the acid strength of the water facilitates the proton transfer to the alkylamine and the the observed magnitude of K_4 is reasonably relative to the values of K_{-2} listed in Table 3. Since, the field produced by the ion at the nearest water molecules is the same for NH_4^+ and $CH_3CH_2NH_3^+$, the rate should parallel the base strength of the proton-accepting amine as is observed. Thus mechanism (c) is most consistent with the experimental facts.

It is interesting to compare the trend of the rate constants with the pK_a values, because the latter give some measure of the proton donating capacity of the ion. Table 4, shows that K_1 increases as pK_a decreases (i.e.), as the ion becomes a stronger acid, and is more capable of donating its exchangeable protons to water. In the series, ethyl, diethyl-, and triethylammonium ions, ethylammonium ion has the smallest pK_a value, and it has a lower K_3 than di-, and triethylammonium ion. Triethylammonium ion has a higher K_6 than diethylammonium ion, as would be expected from the small-value of pK_a for the former. The value of K_4 has no correlation with pK_a. In the above series of the three ammonium ions, ethylammonium ion has a much lower K_4 than would be expected from its low pK_a.

It is interesting to compare the basicity of ethyl and isopropylamines in which we have introduced another methyl group at the α-carbon atom. If the inductive effect alone was the only important factor in determining the basicity of alkylamines, isopropylamine would be the stronger base. In fact, it is a weaker base than ethylamine, and this suggests that other factors such as hydrogen bonding with water molecules and electrostatic interactions[6,7,8] are very important in determining the basicity of alkylamines.

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Chemical Constituents of the Leaves of *Callicarpa macrophylla* Vahl.

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CALLICARPA macrophylla (Verbenaceae) grows in the Himalayan region. It is used in the treatment of stomach disorder[1,2] and biological transformation to gibberellins[3]. The recent report[4-6] on the isolation of calliterpenone and its monoacetate[4-6], β-sitosterol, ursolic acid and 7-*o*-glucuronides of luteolin and apigenin[6] from the same plant prompted us to publish our work on the chemical examination of the leaves of the plant. We have encountered the ethyl ester of C_{23}-fatty acid, free C_{22}, C_{23} and C_{24}-fatty acids, β-sitosterol, β-sitosterol-β-D-glucoside, calliterpenone, calliterpenone monoacetate, ursolic acid, 2α-hydroxyursolic acid and crategolic acid. Dried and powdered leaves of *C. macrophylla* were percolated with rectified spirit and the extract was separated into neutral and acidic fractions.

Neutral fraction :

Ethyl ester of $C_{22}H_{45}COOH$: The neutral fraction was chromatographed over silica gel. Elution with petroleum ether-benzene (4 : 1) afforded a clear oil, $C_{25}H_{50}O_2$, b. p. 135°–137°/0.5 mm of Hg, which is found to be the Ethyl ester of $C_{22}H_{45}COOH$. I.R. 1740 and 1240 cm^{-1}. NMR. Signals at 4.14 (2H, dd, J=6 Hz, -O.CH_2. CH_3), 2.29 (2H, t, -CO. CH_2. CH_2-), 1.25 (40H, s) and 0.90 (6H, t, J=6 Hz, two terminal CH_3). (Found : C, 78.60 ; H, 12.95. Calc. for $C_{25}H_{50}O_2$: C, 78.47 , H, 13.17%).

β-Sitosterol : Further elution of the column with petroleum ether-benzene (2 : 3) furnished β-sitosterol, m. p. 136°-138°, acetate, m. p. 126–128°, $(\alpha)_D$-38° ($CHCl_3$).

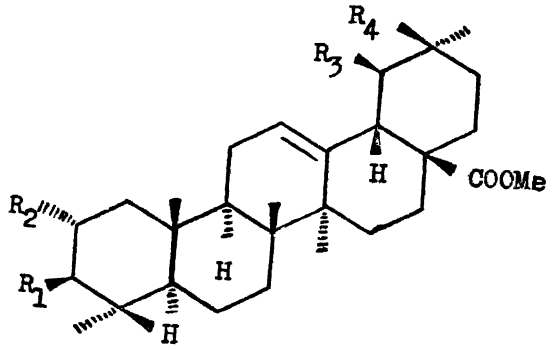
Calliterpenone Monoacetate and Calliterpenone[4-6] : Elution of the column with benzene-ethyl acetate (9 : 1) yielded calliterpenone monoacetate[4-6], m. p. 122°-124°, $(\alpha)_D$ + 25° ($CHCl_3$) and with benzene-ethyl acetate (7 : 3) yielded calliterpenone[4-6], m. p. 154°-156°, $(\alpha)_D$ + 35° ($CHCl_3$).

Calliterpenone Diacetate : Calliterpenone on acetylation at 100° with acetic anhydride and pyridine gave two acetates which were separated by chromatography on silica gel. One of these was calliterpenone monoacetate, while the other one was the hitherto unknown calliterpenone diacetate, m. p. 141°-142°, $(\alpha)_D$ + 8.9° ($CHCl_3$), **I.R.** 1720 (cyclohexanone), 1750 and 1240 (-COOMe) cm^{-1}. **NMR.** Signals at 1.03 (6H, s, 2t-CH_3), 1.09 (3H, s, t-CH_3), 4.43 and 4.97 (J_{gem}=13 Hz, -CH_2.OAC). **MS.** m/e 344 (M^+-AcOH), 302, 289. 284 and 244. (Found : C, 71.92 ; H, 8.97. $C_{24}H_{36}O_5$ requires : C, 71.25 ; H, 8.97%). The diacetate on alkaline hydrolysis furnished calliterpenone.

β-Sitosterol-β-D-glucoside[7] : Further elution of the original column with benzene-ethyl acetate (1 : 1) afforded β-sitosterol-β-D-glucoside[7]. m. p. 288°-290°, $(\alpha)_D$-35° (pyridine), tetraacetate, m. p. 170°-173°, $(\alpha)_D$-25° ($CHCl_3$). The glucoside on hydrolysis with ethanolic hydrochloric acid furnished β-sitosterol.

Acidic fraction : The acidic fraction of the alcoholic extract of leaves mentioned above was esterified with an ethereal solution of diazomethane and the crude mixture of methyl esters was chromatographed over deactivated alumina.

Methyl esters of C_{22}, C_{23} and C_{24} fatty acids : Elution of the above column with petroleum ether yielded a clear oil, which gave a single spot on TLC but GLC showed it to be a mixture of three components. **I.R.** 1725 and 1240 (-COOMe) cm^{-1}. **NMR.** Signals at 3.68 (3H, s, -COOCH_3), 2.32 (2H, t, -CO.CH_2.CH_2-), 1.30 (s, -CH_2-groups) and 0.92 (3H, br. d, terminal CH_3). MS and GLC showed the mixture to consist of three esters, $C_{21}H_{43}$.$COOCH_3$ (M^+ 354 ; 56%), $C_{22}H_{45}$.$COOCH_3$ (M^+ 368 ; 24%) and $C_{23}H_{47}$.$COOCH_3$ (M^+ 382 ; 20%).



I a) R_1=OH, R_2=R_4=H, R_3=Me
b) R_1=OAc, R_2=R_4=H, R_3=Me
c) R_1=R_2=OH, R_3=Me, R_4=H
d) R_1=R_2=OH, R_3=H, R_4=Me
e) R_1=R_2=OBz, R_3=Me, R_4=H
f) R_1=R_2=OBz, R_3=H, R_4=Me

Methyl ursolate (1a) : Elution of the column with petroleum ether-benzene (3 : 7) provided methyl ursolate (1a), m. p. 169°-170°, $(\alpha)_D$ + 68.5° ($CHCl_3$) identical (mmp, TLC and IR) with an authentic specimen. On acetylation it gave methyl ursolate acetate (1b), m. p. 238-240°, $(\alpha)_D$ + 59.5° ($CHCl_3$).

Methyl 2α-hydroxyursolate (1c) and Methyl crategolate (1d) : Further elution of the column with benzene ethyl acetate (4 : 1) yielded a solid, m. p. 218°-220°, $(\alpha)_D$ + 63.5° ($CHCl_3$). **I.R.** 3300, 1720, 1245 and 830 cm^{-1}. **NMR.** Signals at 3.64 (s, -COOCH_3), 3.62 (s, -COOCH_3), 5.24 (1H, m, CH=C), 0.98 and 0.93 (3H each, d, CH-CH_3), 0.85, 1.01, 1.05, 1.10 and 1.15 (3H each, s, t-CH_3). **MS** m/e 486 (M^+), 471, 468, 453, 450, 262, 203, 189 and 133. All these data suggested this ester to be a mixture of two closely related esters of triterpenic acids. The ester could not be resolved into its components by crystallisation or by chromatography. So it was converted into a benzoate mixture by benzoylation with benzoyl chloride and pyridine. This mixture on fractional crystallisation however could be resolved into the dibenzoate ester (1e). m. p. 215°-217°, **I.R.** 1725 and 1250 cm^{-1} and a gummy dibenzoate ester (1f). The ester (1e) on hydrolysis with methanolic KOH (5%) furnished methyl 2α-hydroxyursolate (1c), m. p. 211°-213°, $(\alpha)_D$+55° ($CHCl_3$) identical with an authentic specimen[8]. The gummy benzoate ester (1f) on similar hydrolysis yielded methyl crategolate (1d), m. p. 220°-222°, $(\alpha)_D$ + 55.5° ($CHCl_3$) identical with an authentic specimen[9].

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