ein Erdenion zu binden, damit einen „zweierdigen" Komplex zu bilden.

Sofern man eine mehr oder weniger ungestörte oktaedrische Symmetrie der 4 O- und 2 N-Atome beider endständiger Gruppen um ein Nd-Ion im 1:1-Komplex annimmt, läßt sich die komplexe SE-Molekel entsprechend Fig. 4 modellmäßig darstellen.

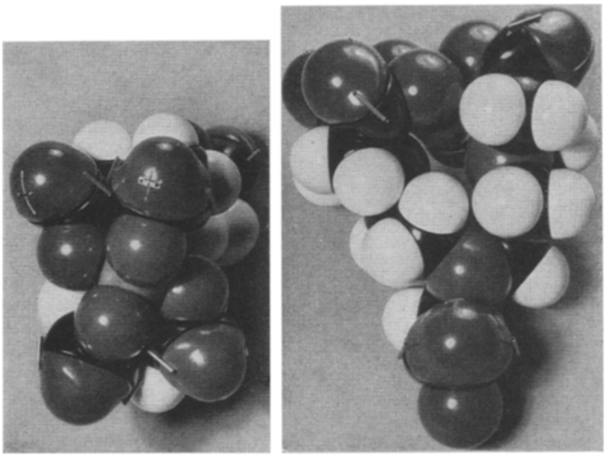

Fig. 4. Der 1:1-Komplex Nd „J". Links in Aufsicht; rechts in Seitenansicht

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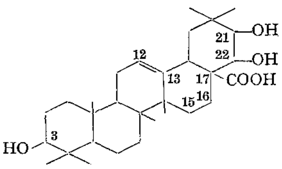
Triterpenoids III: The Constitution of Entagenic Acid

In the previous communication[1] the isolation of entagenic acid, a new triterpene acid from the seeds of the plant *Entada phaseoloides Merrill* has been reported. Entagenic acid has the molecular formula, $C_{30}H_{48}O_5$, m.p. 310 to 315° (dec.). With diazomethane it gives a mono-methyl ester $C_{31}H_{50}O_5$, m.p. 243 to 245°. Methyl entagenate on hydrolysis with alcoholic KOH for several hours gives back the original acid in poor yield. Similar hindrance has been noticed in α-amyrin and β-amyrin type triterpene acid e.g., methylechinocystate, methyl oleanolate[2] etc. With pyridine and acetic anhydride, entagenic acid gives a tri-acetyl derivative, $C_{36}H_{54}O_8$, m.p. 188 to 189°. Methyl entagenate forms a mono-tosyl derivative, $C_{38}H_{56}SO_7$, m.p. 151 to 152°. Entagenic acid has got a hindered double bond. It forms a mono-bromo-lactone, $C_{30}H_{47}O_5Br$, m.p. 263 to 264°, with bromine in acetic acid. I.R. spectrum studied in Nujol mull shows characteristic γ-lactone band at 1770 cm⁻¹, closely comparable with that found by BARTON for mono-bromo-lactone of oleanolic acid[2] (1779 cm⁻¹). The formation of the mono-bromo-lactone proves that entagenic acid is similar to oleanolic acid and other triterpene acids of the α- and β-amyrin groups, having a carboxyl group at C-17 and a double bond at 12:13 position[2]. Since methyl entagenate in chloroform consumes nearly one mole of perbenzoic acid, entagenic acid appears to be a member of the β-amyrin group, as members of the α-amyrin group are inert to this reagent[3]. One of the hydroxyl groups in entagenic acid may be assumed to be at C-3 in ring A, as it is almost ubiquitous. Methyl entagenate forms an acetonide, $C_{34}H_{54}O_5$, m.p. 200 to 201°. Methyl entagenate in methanol consumes one mole of periodic acid proving the presence of a single α-glycol system. The periodic acid oxidation product, $C_{31}H_{48}O_5$, m.p. 195°, could not be cyclised to give an αβ-unsaturated aldehyde. This indicates that the α-glycol system is not in ring A. Methyl entagenate on oxidation with CrO_3 in acetic acid gives a neutral triketone, methyl entagentrione, $C_{31}H_{44}O_5$, m.p. 212°. It does not give any colouration with ferric chloride and is deep yellow in colour which suggests it to be a true α-diketone. It gives a mono-2:4-dinitrophenyl hydrazone, m.p. 225 to 226°. Methyl entagentrione on hydrolysis with alcoholic KOH gives a decarboxylated product.

Nor-entagentrione, $C_{29}H_{42}O_3$, m.p. 209 to 210°. The above decarboxylation suggests that there is one ketonic group in methyl entagentrione, which is β to the carboxyl group. Nor-entagentrione gives colouration with ferric chloride which indicates it to be a diosphenol. (U.V. spectrum: λ_{max} 283 mμ; ε, 12,060). From the above experiments it appears that most probably the α-glycol system is either in ring D or E and entagenic acid may be represented either as I or II.



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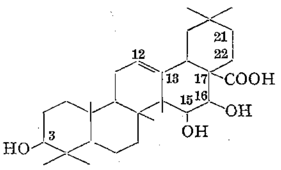

II

Further work is in progress.

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Analytical Use of Some Azo Dyes of Chromotropic Acids: Volumetric, Gravimetric and Spectrophotometric Determinations

Chromotropic acid (1,8-Di-hydroxy naphthalene 3,6 disulphonic acid) finds considerable importance in the analytical field as a colorimetric reagent for a number of elements like chromium, iron, titanium and uranium. This substance has also been used for the production of a large number of patent azo-dyes. KULBERG[1] demonstrated the colour changes for magnesium, calcium, cadmium, copper and bismuth with 0·1% solution of the dye: 3,4,5,2,7-(p-nitro-phenyl azo) dihydroxy naphthalene disulphonic acid in 10 p.c. alkali solution.

Recently methods have been developed by BANERJEE for the spectrophotometric determination of microgram amounts of thorium and zirconium with a dye "SPADNS" prepared from chromotopic acid and sulphanilic acid[2]. This dye has also been used by him for the volumetric determination of thorium, zirconium and fluorine. A number of azo dyes have been prepared by the present author by diazotising various aromatic amino sulphonic and carboxylic acids and coupling them with chromotropic acid under suitable conditions. Three of the dyes "SNADNS", "di-SNADNS" and „nitroso-SNADNS", prepared from diazotised naphthionic acid and chromotropic acid have already been utilised in the volumetric determination of thorium and fluorine[3a]. Di-SNADNS [2-7 di-(4-sulpho naphthyl azo)-1,8 dihydroxy-naphthalene 3,6 disulphonic acid] has been successfully used for the spectrophotometric determination of thorium at a wave length of 640 mμ[3b]. The azo dye prepared by MAGIDSON and RUBTSON[4] from sulphanilamide and chromotropic acid as a chemotherapeutic agent for streptocide series, has now been used by the author in the gravimetric determination of thorium and zirconium. The analytical properties of such azo dyes prepared from chromotropic acid have been studied by the author and a number of them was found to exhibit useful colour reactions with thorium, a metal which does not form coloured ion (Table 1).

Test analysis and spectrophotometric determination of thorium and zirconium with these dyes have been carried out, where ever possible. Volumetric determination of these metals with the dyes, involving the use of versene and fluoride have also been made; the details of these works will be published elsewhere.

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