and mass spectra and to Sri. P. S. Sastry to uv spectra. Thanks are due to Prof. E. V. Sundaram, Head of the Department of Chemistry and to Prof. K. Venkata Ramiah, Director, P.G. Centre, for their encouragement.

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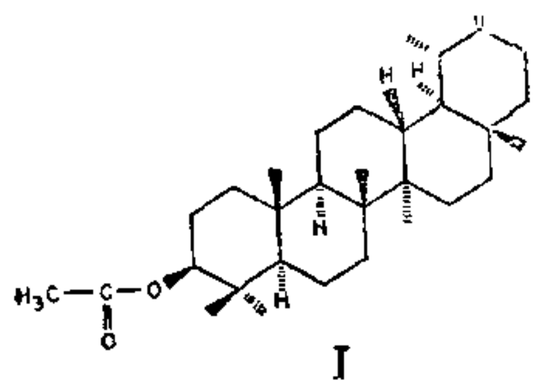
CONVERSION OF TARAXASTERYL ACETATE INTO TARAXASTANE 3β-20 DIOL

EPOXIDATION (PBA) of taraxasteryl acetate[1] (I) gives a mixture of two stereoisomeric epoxides (TLC) (C_{20}-epimers). One of these epoxides (less polar), $C_{32}H_{52}O_3$, M+ 484, m.p. 236–38° (hexane + 10% benzene) has been isolated in the TLC pure state by chromatography. It shows IR absorptions at 1724, 1250 cm^{-1} (acetate) and NMR (CCl_4) signals at τ : 9·17, 9·14, 9·07, 9·04, 8·97, 8·9 (21 H, methyls at C_4, C_8, C_{10}, C_{14}, C_{17} and C_{19}) ; 8·07 (3 H, *s*, acetate methyl at C_3) ; 7·4 (2 H, *s*, CH_2 protons at C_{28}) and 5·6 (1 H, *t*, C_3-proton).

LAH reduction of the epoxide gives a diol (II), $C_{30}H_{52}O_2$, M+ 444, m.p. 266–68°, $(\alpha)_D$ — 9° (*c*, 1·5). It shows IR absorptions at 3344 (OH) and NMR ($CHCl_3$) signals at τ : 9·2, 9·14, 9·0, 8·93, 8·9 (21 H, methyls at C_4, C_8, C_{10}, C_{14}, C_{17} and C_{19}) ; 8·8 (3 H, *s*, methyl at C_{20}) and a triplet at 6·8 (1 H, C_3-proton). Acetylation of (II) (Ac_2 O/Py) affords a monoacetate (III), $C_{34}H_{54}O_3$, M+ 486, m.p. 276–80° (hexane), $(\alpha)_D \pm 0°$. It shows IR absorptions at 3448 (OH), 1718, 1266 cm^{-1} (acetate) and NMR (CCl_4) signals at τ : 9·18, 9·15, 9·0, 8·9 (21 H, methyls at C_4, C_8, C_{10}, C_{14}, C_{17} and C_{19}) ; 8·86 (3 H, *s*, methyl at C_{20}) ; 8·0 (3 H, *s*, acetate methyl at C_3) and a triplet centred at 5·57 (1 H, C_3-proton).

Two taraxastane 3 β-20 diols which are epimeric at C_{20} have been described in literature[2,3]. A comparison of the IR spectrum of diol (II) with that of 20-epi-ψ-taraxastane, 3 β-20 diol[3], isolated from black dammar resin, suggests a close relationship between the two compounds. However, some differences were observed in the NMR spectra of their monoacetates[3] especially in the methyl region signals. In addition, the physical constants especially, the optical rotation of the two diols and their monoacetates are found to be different [Lit.[3] records for 20-epi-ψ-taraxastane-3 β-20 diol, m.p. 261–63°, $(\alpha)_D \pm 0°$; monoacetate, m.p. 266–67°, $(\alpha)_D$ + 23°].



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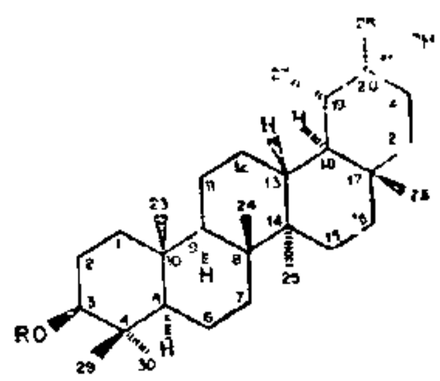

II. R = —H
III. R = —COCH$_3$

However, the physical constants of both (II) and (III) are in close agreement with those reported for ψ-taraxastane 3 β-20 diol[2] and its monoacetate. [Lit.[2] records for ψ-taraxastane 3 β-20 diol, m.p. 270–72°, $(\alpha)_D$ — 10·9°, monoacetate, m.p. 281–84°, $(\alpha)_D$ — 1·5°].

It therefore appears that diol (II) is identical with ψ-taraxastane 3 β-20 diol, isolated from manila elemi resin. A direct comparison between the two, however, could not be made due to the non-availability of the sample of ψ-taraxastane 3 β-20 diol.

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STUDIES ON PESTICIDES

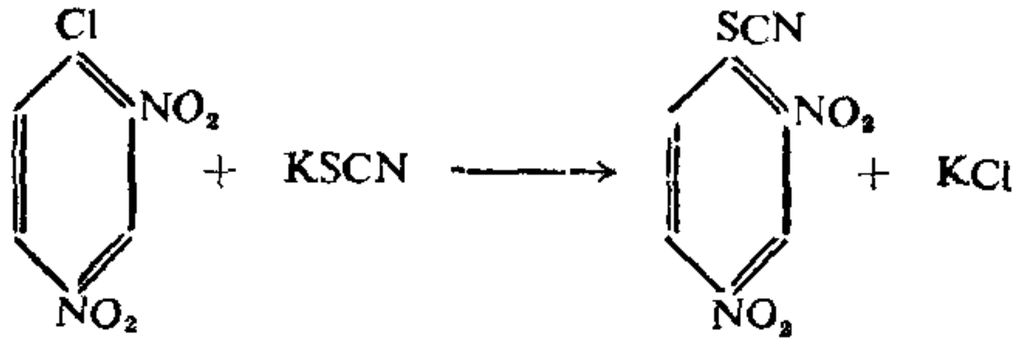
Part I. Some Halogeno-polynitro Phenyl, Tolyl and Naphthyl Thiocyanates

NITRO phenyl, thiocyanates have been claimed to be toxicants for fungi[1,2], bacteria, moulds and other pests[3,4]. The pesticides also show some tuberculostatic and acaricidal activity[5]. Incorporation of one or more substituents of electrophilic character in the ortho or para positions to the thiocyanate group results in an increase of both bacteriostatic and fungistatic activity[5]. It has been suggested that these compounds exert their anti-microbial

activity by an intra-cellular interaction of —SH enzymes.

In view of the known pesticidal activity of nitro phenyl thiocyanates, the synthesis of some analogues of these compounds containing methyl, halogens and other substituents at various positions in the ring and their pesticidal activity have been undertaken.

These compounds have been prepared[6] by heating halogenonitrobenzene, toluene or naphthalene (0·01 M) with potassium thiocyanate (0·01 m) in methanolic solutions (20–40 ml) till the product separated. The compound so obtained has been crystallised from anhydrous ethanol. These are yellow crystalline compounds insoluble in water but soluble in organic solvents. Their melting points, yield, etc., are given Table I. The compounds have been analysed for C, N, H and S and the analytical results agreed with the calculated within the experimental errors.



Microbial activity.—The compounds have been tested for their fungicidal activity against *Alternaria solani* and *Aspergillus niger* by poisoned food technique. The fungus is grown on potato-dextrose agar-agar media containing various concentrations of the test compound. A concentration at zero served as check. After seven days of the inocula-

TABLE I

$R-S-C\equiv N$

Halogeno nitro benzene used	R	M.P.* °C	Yield %	*Aspergillus niger* Concentration in ppm 100	50	25	10	0	*Alternaria solani* Concentration in ppm 100	50	25	10	0
				Radial growth of the fungus colony in millimeters									
1-Chloro-2:4-DN	2:4-DNP	138	70	nil	14	14	22	64	nil	nil	32	52	56
1-Chloro-2:6-DN	2:6-DNP	71	50	nil	55	70	81	85	nil	nil	nil	20	50
1-Chloro-2:4:6-TN	2:4:6-TNP	100*d*	80	70	83	86	88	90	36	41	46	52	52
1:2-Dichloro-4:6-DN	6-Chloro-2:4-DNP	143	40	..	..	..	..	..	..	..	..	..	..
1:3-Dichloro-4:6-DN	5-Chloro-2:4-DNP	193	50	56	60	62	66	80	45	56	58	60	72
1:4-Dichloro-2:6-DN	4-Chloro-2:6-DNP	102	55	nil	nil	70	75	80	nil	nil	nl	27	46
1-Chloro-4:6-DN-3-methyl	5-methyl-2:4-DNP	70	65	nil	nil	30	44	66	nil	nil	10	42	58
1-Chloro-2:4:6-TN-5-methyl	3-methyl-2:4:6-TNP	139	65	tuil	n.l	nil	nil	80	nil	nil	nil	nil	46
1:4-Dibromo-2:6-DN	4-Bromo-2:6-DNP	105	50	nil	nil	nil	44	61	nil	60	40	48	58
1-Chloro-2:4-DN-naphthalene	2:4-dinitro-naphthyl	150*d*	50	..	..	..	..	..	..	..	..	..	..

*All melting points are uncorrected.

N.B.—DN, TN, DNP and TNP refer respectively to dinitro, trinitro, dinitro phenyl and trinitro phenyl.

tion of the fungus the radial growth is measured. The temperature is kept between 24–28° during the whole period. The radial growth of the fungi at various concentrations of the thiocyanates and in the absence of the compound are given in Table I.

It is interesting to note that a methyl group at meta position and nitro group at ortho and para position to the thiocyanato group increases fungicidal activity of the thiocyanate. The 3-methyl 2 : 4 : 6 trinitro-phenyl thiocyanate is found to be the most active towards both the test fungi.

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TANNINS OF *CAESALPINIA PULCHERRIMA* BARK

The seeds[1,2] of *Caesalpinia pulcherrima* have been reported to contain a galactomannan. The stem bark of this plant is highly astringent and is widely used as an abortifacient and as an emmenagogue. It has now been investigated and found to contain gallic acid, ellagic acid, leucodelphinidin and a new tannin, which has been studied in detail.

Extraction

Following a general procedure for the extraction of polyphenols the bark was extracted with ethanol. The ether soluble fraction from the concentrated ethanolic extract was found to contain gallic acid, ethyl gallate and traces of ellagic acid. Ethyl acetate extracted a leucoanthocyanidin along with a tannin (A). The mother liquor was further concentrated to a viscous residue and macerated with acetone, which extracted some more of the tannin (A). From the residue free ellagic acid could be extracted out with ethanol containing traces of pyridine. The leucoanthocyanidin could be characterised as leucodelphinidin by its characteristic colour reactions and spectral studies. On acid treatment, it could be converted to its corresponding anthocyanidin delphinidin, which was found to be identical with an authentic sample isolated from *Solanum melongena* fruits, in its colour reactions, paper chromatography and λ_{max} (560 mμ, ethanolic HCl).

The isolation of ethyl gallate, which is usually isolated as an artefact formed as a result of alcoholysis of depside links present in tannins, during the extraction with ethanol, led us to modify the method of extraction. The bark was extracted with water at room temperature. The combined extract was demineralised over a mixed bed of cation and anion exchange resins to constant conductance and then concentrated under diminished pressure to a syrupy mass. Maceration with ether of the viscous residue gave some gallic acid and further extraction with ethyl acetate gave a mixture of gallic acid, leucodelphinidin and another tannin (B). Maceration with acetone of the remaining sticky residue gave some more amount of tannin (B). The acetone concentrate was charged over a silica gel (deactivated) column and eluted with benzene-acetone mixture. Final crystallisation of the last fractions from acetone-ether mixture gave a colourless semi-crystalline compound, which was found to be a homogeneous entity by paper chromatography and TLC.

Tannins (A) and (B)

Both these tannins gave positive Molisch test and blue-black precipitate with ferric chloride, suggesting these to be polyphenolic glycoside, but positive colour reaction with aniline hydrogen phthalate reagent[3], confirmed their non-glycosidic nature. Tannin (A) on alkali hydrolysis gave D (+)-glucose, gallic acid and ellagic acid, suggesting thereby that these acids are possibly esterified with the glucose moiety.

Tannin (B) on acid as well as alkali hydrolysis gave glucose, gallic acid and ellagic acid. The quantitative estimation of glucose shows the presence of 19% glucose. Ellagic acid precipitated out almost quantitatively during hydrolysis and could be directly weighed and found to be 30%. Gallic acid was found to be 55% by potentiometric titration. This calculates to 3 moles of gallic acid and one mole of ellagic acid per mole of glucose. The acetate of this tannin analysed for 15 acetyl groups ($-COCH_3$, 40·5%) per mole of acetate. Methylation was done with diazomethane. IR spectrum of the methyl ether confirmed the absence of any free hydroxyl group. The methyl ether on acid as well as alkaline hydrolysis gave three acids, which were identified as trimethyl gallic acid, 3 ; 4 dimethyl gallic acid and