lysed and catalysed reactions, respectively. A plot of k_3 *versus* the molar concentration of A was found to be linear in each case. From the slopes and intercepts of these lines k and k, respectively, were calculated. The values thus obtained are given in Table II.

TABLE II

Relative reactivity of the added salts in the bromination of acetanilide

Added salt	Added salt conc. range $\times 10^4$ (M)	$k \times 10^{-2}$ (lit^2/mole^2/min)	$k_c \times 10^{-4}$ (lit^3/mole^3/min)	Relative reactivity
Nil	..	3·5	..	..
$FeCl_3$	3·6–54·0	3·7	2·5	1·0
$ZnCl_2$	2·6–16·6	3·5	11·2	4·5
IBr	0·8–4·8	3·5	35·2	14·1

From the last column of Table II it is seen that the order of reactivity of the three halogen carriers is $IBr > ZnCl_2 > FeCl_3$. The role[9] of these catalysts is to polarise the bromine molecule and to remove Br^- as ABr^- in the rate-determining step. Their relative reactivity may be attributed to the following order of stability of ABr^- :

$$IBr_2^- > ZnCl_2Br^- > FeCl_3Br^-.$$

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CHROMATOGRAPHIC IDENTIFICATION OF CERTAIN SULFOXIDES OF CYSTEINE PRESENT IN ONION (*ALLIUM CEPA* LINN.) EXTRACT

Introduction

VIRTANEN AND MATIKKALA[1,2] isolated three sulfoxide amino acids, *viz.*, cycloalliin, S-methyl cysteine sulfoxide and S-propyl cysteine sulfoxide from methanolic extracts of onions (*Allium cepa* Linn.). Bandyopadhyay *et al.*[3] reported that some of the sulphur compounds of the etherial extracts of onion possess carbonyl and hydroxyl groups, but they did not identify them. The therapeutic effects of these extracts[4] created some interest in their chemistry. In a preliminary study the diethyl ether extract of onion showed the presence of amino acids. This posed the question whether the suspected carbonyl compounds reported to be present in the etherial extract of onion[3] really belonged to some of the sulfoxide amino acids of onion. In order to study this question the sulfoxide amino acids were separated from etherial and ethanolic extracts of onion, identified and compared by paper chromatography.

Experimental

Diethyl ether extract of fresh onion was prepared[3] and petroleum ether (B.P. 40–60) soluble fraction[4] was removed from it as reported previously. The insoluble fraction was further extracted with 20 ml of 1 NHCl and centrifuged. This process was repeated thrice. The combined solution was neutralised to litmus with 1 N NaOH and acetone was added to make it 50% acetone. The crystals separated on cooling were recrystallised from 50% acetone-water[1]. The crystals were analysed for amino acids by paper chromatography using butanol : acetic acid : water system. A concentrated ethanolic extract of onion was prepared and the sulfoxide amino acids were separated by column chromatography according to the method of Carson and Wong[5] with certain modifications that IR–120 (H^+ form)[1] and IRA–93 (OH) were used in place of Dowex $50 - X_4$ (H^+ form) and Duolite A–4 (amino form) respectively. To study the total amino acid pattern a sample of crystals obtained from the effluent from IR–120 were analysed by both one and two dimensional chromatography. The amino acids absorbed finally on IRA–93 (OH) were eluted with 0·1 N formic acid and one litre fractions were evaporated, acidified and further concentrated *in vacuo*[4]. Crystals separated were analysed by two-dimensional paper chromatography using butanol : acetic acid : water system first (12 : 3 : 5) and phenol ammonia : water system second[6]. Ninhydrin was used as the colour developing reagent. Each fraction was further recrystallised

from 2 N HCl and analysed again by descending chromatography (Bu : Ac : H_2O). Standard S-methyl and S-propyl cysteine sulfoxides and cycloallin were used as reference compounds.

Results and Discussion

The amino acids obtained from the ether extract (yield 0·1 g/Kg onion) on descending chromatography gave spots corresponding to S-methyl cysteine sulfoxide (R_f = 0·17) and S-propyl cysteine sulfoxide (R_f = 0·35). A third spot also appeared (R_f = 0·63) which may be S-propyl cysteine[1]. The amino acids obtained from the ethanolic extract (yield 0·65 g/Kg onion) on chromatography gave spots corresponding to the above two sulfoxide amino acids and also cycloallin (R_f = 0·24). The identity of the three sulfoxide amino acids in the above preparation was further proved by two-dimensional chromatography. About twelve unidentified amino acids also appeared on the same chromatogram. They may be the other onion amino acids reported in a similar study[7]. By recrystallisation a mixture of the above three sulfoxide amino acids was obtained from fraction 1 [eluent from IRA–93 (OH) yield 0·3 g/Kg onion] and pure cycloalliin from fractions 2 and 3. yield 0·2 g/Kg onion.

Some of the onion sulfur compounds which, Bandyopadhyay *et al.*[3] separated from the ether extract may therefore belong to S-methyl and S-propyl cysteine sulfoxides and their degradation products reported elsewhere[8]. The therapeutic effects of the ether extract of onion and its sulphur compounds[4,9-11] and also the importance of its sulfoxide amino acids with relation to sulphur metabolism[12] warrant further investigation on this vegetable.

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CHEMISTRY OF *TERMINALIA* SPECIES

Part XV*. Chemical Examination of *T. procera* Roxb.

In the course of our studies on the heartwoods of *Terminalia* species[1-4], a sample of heartwood of *T. procera* Roxb. was secured from Andaman islands. Preliminary examination showed the presence of tannins asd phenolic compounds, but no triterpenes.

The hexane extract contained β-sitosterol (m.p. 136–37°, acetate m.p. 125–26°), identified by comparison with an authentic specimen. The chloroform solubles contained three components which could be separated by column chromatography on silica gel. From the analysis and by comparison with the authentic samples, they were identified as (*i*) ellagic acid [m.p. 360°, blood red colouration with Greismeyes's reagent[5], ν_{max}^{Nujol} : 3570(m), 3490, 1730–1705 (br), 1625, 1585, 1540 cm^{-1}, λ_{max}^{EtOH} : 255, 366, with NaOAc 256, 278, 355[6]] (*ii*) 3, 3'-di-O-methyl ellagic acid [yield 0·03%, m p. 325–27°, blood red colouration with Greismeyer's reagent[5], ν_{max}^{Nujol} : 3460 (br), 1715, 1580, 1550 cm^{-1}, λ_{max}^{EtOH} : 248 (log ε 4·75), 372 (log ε 4·15) unaffected with NaOAc or $AlCl_3$[6]] and (*iii*) 3, 3', 4-tri-O-methyl ellagic acid [yield 0·035%, m.p. 285–87°, green-brown-yellow colouration with Greismeyer's reagent[5], ν_{max}^{Nujol} : 3440 (br), 1720, 1580, 1550 cm^{-1}, λ_{max}^{EtOH} : 249 (log ε 4·65), 370 (log ε 4·05) unaffected with NaOAc or $AlCl_3$[6]]. Their identification was further confirmed by the preparation of tetra-O-methyl ellagic acid (m.p. 340–42°) using K_2CO_3 and dimethyl sulphate in acetone. Ellagic acid was obtained (yield 0·5%) from the acetone extracts of the heartwood.

Ellagic acid is a common constituent of a number of species of *Terminalia*. The 3,3'-di-O-methyl ellagic acid was obtained from *Euphorbia formosanum* Hey[7] and it occurs as a glucoside in the