Table II

Equilibrium constants of pyrrole-dimethyl formamide and pyrrole-diphenyl formamide complexes

Initial molar concentrations in CCl_4 of			Absorbance of				
				Free N-H stretch in the presence of			
Pyrrole	Dimethyl formamide	Diphenyl formamide	Free N–H stretch in CCl_4	Dimethyl formamide	Diphenyl formamide	K_{DMF}	K_{DPF}
0·004	0·0329	0·0345	0·70	0·53	0·59	11·3	6·4
0·00267	0·0329	0·0343	0·47	0·36	0·41	11·5	6·3
0·0020	0·0329	0·0343	0·37	0·28	0·30	11·4	7·4

The free N—H stretching frequency and the bonded N—H stretching frequencies in various complexes are given in Table III.

Table III

Complex	N–H stretching frequency of pyrroie ($cm.^{-1}$)	
	Free N–H s retch	Bonded N–H stretch
Pyrrole-dimethyl acetamide	3500	3328
„ diphenyl „	3500	3362
„ dimethyl formamide	3500	3350
„ diphenyi „	3500	3381

The observations in Tables I, II and III indicate that the frequency difference between the free and bonded N—H stretching frequencies and the value of the equilibrium constants in case of pyrrole-dimethyl amide complexes are higher than the values of the same quantities in case of the corresponding pyrrole-diphenyl amide complexes. These results show that the hydrogen-bonding in the pyrrole-dimethyl amide complexes is stronger than that in the corresponding pyrrole-diphenyl amide complexes. In amides where there are two possible resonance structures, the authors[2] discussed in their earlier work that the dipolar resonance structure makes substantial contribution to the ground state of the molecule. In the LCAO-MO terms, Cannon[3,4] discussed the interaction and the mixing of the π-orbitals of C=O and the lone pair orbital of the N atom from $2P_z$ atomic orbitals in the O=C—N group and concluded that this π-P interaction is responsible for the high polarity of the group. But in diphenyl amides, there is a competitive effect of the phenyl ring for the lone pair of electrons on the nitrogen atom with the result that the contribution of the dipolar resonance structure to the ground state of the molecule is considerably reduced in these molecules. This explains the manifestation of weaker hydrogen-bonding in the pyrrole-diphenyl amide complexes compared to that in the corresponding pyrrole-dimethyl amide complexes.

One of us (V. V. C.) is grateful to the University Grants Commission, Government of India, for the award of a Research Fellowship.

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THE *'IN VIVO'* MECHANISM OF LIPOLYSIS OF PEA-NUT AND COTTON SEED FATS

J. M. S. MATHUR

Division of Botany, Indian Agricultural Research Institute, New Delhi

THE currently accepted hypothesis about lipolysis of triglycerides is a stepwise reaction involving degradation of a triglyceride molecule through 1, 2-/1, 3-diglyceride, 2-monoglyceride and 1-monoglyceride with liberation of one mole of fatty acid at each step. *In vivo* and *in vitro* studies by various authors[1-8] support this theory.

While much literature is available in favour of the stepwise hydrolysis of triglycerides, the same is not true about one-step 'quantum' mechanism of hydrolysis of triglycerides recently put forward by Kartha and Mathur.[9] According to them a triglyceride molecule is directly converted into glycerol and fatty acids without intermediate liberation of di- and monoglycerides, since no appreciable increase in acetyl value of remnant fat, as otherwise expected, at different stages of fat mobilization in germinating gingili and mustard seeds, could be detected.

This is not in agreement with *in vitro*

studies. Therefore, it appears that the pathway of lipolysis of triglycerides differs *in vivo* and *in vitro*. Tris prompted the author to undertake the present investigations.

Pea-nut kernels (*Arachis hypogea*) and dehusked cotton seeds (*Gossypium virnar*) were germinated in Minnesota Seed Germinator maintained at 30° C. At different intervals, a known number of seedlings were taken, washed free of sand, drained and dried, followed by oil extraction by cold percolation[10] using carbon tetrachloride.

Kartha and Mathur's method[11] was adopted for gravimetric determination of acetyl values throughout the course of these studies. The results are summarized in Table I. The acetyl values given by various authors for the original seed oils are indicated in Table II.

TABLE I

Results of studies on germinating Pea-nut and cotton seeds

Stage	Number of seeds/ seedlings	Dry weight (gm.)	Oil %	Oil mobilized %	Acetyl value	Unsaponifiable matter %
Pea-nut						(Rabari *et al.*[16])
Original seeds	2	1·3500	42·9	Nil	7·1	0·3
3 days ..	3	1·5078	35·5	17·3	9·4	0·4
5 „ ..	5	2·0200	24·5	42·9	11·7	0·6
7 „ ..	5	1·9640	16·2	62·3	11·7	0·6
8 „ ..	6	2·0220	8·2	80·9	15·1	0·65
Cotton seed						(Author)
Original seeds	30	1·3096	17·4	Nil	9·9	0·72
3 days ..	28	0·9885	14·6	16·1	9·2	0·76
5 „ ..	37	0·8101	11·0	36·8	8·9	0·76
7 „ ..	52	0·7864	6·3	63·8	10·6	0·77
8 „ ..	87	0·9024	2·8	84·0	10·1	0·78

TABLE II

Acetyl values

Oil	A.O.C.S.[12]	Lewkowitsch[13]	Roberts and Shuette[14]	Helrich and Reiman[15]	Author
Pea-nut oil ..	7·5–12·5	..	5·5	..	7·1
Cotton-seed oil	8·5– 9·5	9·1	..	12·5	9·9

It is observed that in pea-nut the acetyl value gradually increases with increase in fat mobilization and that this increase is proportional to the increase in percentage of unsaponifiable matter. This increase in acetyl value is not sufficient enough to prove presence of any appreciable amounts of di- and monoglycerides at any stage. An almost steady acetyl value in case of cotton seed fat is probably due either to, no increase in percentage of unsaponifiable matter or increase of a component having negligible acetyl value.

The present note provides evidence in support of one-step pathway of *in vivo* lipolysis of triglycerides.

The author is grateful to Dr. A. B. Joshi, Director, and Dr. M. S. Swaminathan, Head, Division of Botany, for kindly providing all facilities.

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