Technical

Studies on Leguminous Seeds

A.R. CHOWDHURY, R. BANERJI, G. MISRA and S.K. NIGAM, National Botanical Research Institute, Lucknow-226 001, India

ABSTRACT

The seeds of 8 plant species of Mimosaceae were studied for their fat and protein contents and fatty acid and mineral compositions. The oil from *Entada phaseoloides* contained 14 newly identified acids in addition to 8 previously reported. Six seed oils were rich in oleic and linoleic acid as the sum of 18:1 and 18:2 ranged from 64.4-78.5%.

INTRODUCTION

The leguminous trees are well known for their rapid growth, nitrogen fixation properties and adaptability to a wide range of soils. They produce copious amounts of seed at an early age and withstand frequent pollarding (1). Because of such properties, these trees have promise for forestation and biomass production.

The seed fats of Mimosaceae have arachidic, behenic and lignoceric as major saturated acid(s), e.g., *Adenanthera, Pentaclethra, Parkia* and *Xylia* species (2). In contrast, the saturated acids of *Acacia* and *Albizzia* species consist largely of palmitic, with insignificant quantities of arachidic, behenic and lignoceric (2). Such variations in the fatty acid composition of the seed fats of Mimosaceae need fruther investigation.

During our investigation to explore new sources of fat and protein, the results of our studies on the seeds of the genera *Acacia* and *Bauhinia* have already been reported (3,4). This communication deals with the chemical composition of the seeds of 8 plant species of Mimosaceae.

EXPERIMENTAL

Most of the seed samples were collected locally, except *Entada phaseoloides*, which were obtained from Andaman and Nicobar Islands. The oil was extracted with petroleum ether and the methyl ester of the fatty acid mixtures were analyzed by gas chromatography (GC) using a stainless-steel column packed with 10% DEGS on chomosorb W (80-100 mesh) as described earlier (3). All the oil samples were subjected to tests for epoxy function and cyclopropenoid moiety (5,6). The defatted and detoxified seed meals were analyzed for total nitrogen content and mineral constituents (3).

RESULTS AND DISCUSSION

Of the 8 species, *Albizzia lucida, Parkia biglandulosa* and *Pithecolobium dulce* yielded more than 10% by weight of oil compared to others that gave only 0.7-8.0%. The oil content of *P. biglandulosa* (19.8%) was the highest among the species studied (Table I).

The GLC analyses (Table I) showed that octadecenoic (18:1) and octadecadienoic (18:2) acids were predominant in 6 oil samples. The sum of the concentrations of 18:1 and 18:2 acids ranged from 29.3% of total area in *Parkia biglandulosa* to as high as 78.5% in *Albizzia lebbek*. The variation in the ratio of unsaturated (18:1 and 18:2) acids in the same genus, viz. *Albizzia* (1:2 in *A. lebbek* and 1:4 in *A. lucida*) and *Pithecolobium* (1:1 in *P. bigemina* and 4:1 in *P. dulce*) is noteworthy and could be attributed to 2 common causes, biological and climatic, as suggested in case of *Bauhinia* (7) and *Helianthus* (8). These observations, however, agree with the contention that leguminous seed oils are invariably rich in oleic and linoleic acid (2-4).

The major saturated acid in all the oil samples was hexadecanoic acid (12.0-30.4%) except *Parkia biglandulosa*, which showed a higher percentage of 18:0 (32.7%). The oil from *P. biglandulosa* was rich in linoleic (38.1%) acid (9,10) whereas we observed the oil was rich in stearic acid followed by 18:1 and 16:0 (Table I). The oil is also notable for the high content of 16:1 (7.0%).

Twenty-two fatty acids were identified in the oil from the *Entada phaseoloides* kernel. In addition to confirming the 8 previously reported (11), 14 more acids were characterized. The newly identified acids were octanoic, nonanoic, decanoic, hendecanoic, dodecanoic, dodecenoic, tridecanoic, tridecenoic, tetradecenoic, pentadecenoic, hexadec-

TABLE I

Chemical Composition of the Seeds

Name of seeds	Oil[a] (%)	Protein[a] (%)	Fatty acid composition[b]								
			14:0	16:0	16:1	18:0	18:1	18:2	20:0	22:0	24:0
Albizzia lebbek Benth.	5.3	29.5	–	12.0	0.5	2.7	21.4	57.1	2.5	2.9	0.9
A. lucida Benth.	12.7	30.2	0.5	20.6	0.3	4.4	20.3	49.0	2.9	1.4	–
A. richardiana King & Prain	2.8	28.4	–	15.0	–	13.7	30.9	36.2	3.7	0.5	–[c]
Entada phaseoloides Merrill SYN. *E. scandens* Benth.	8.0	27.7	Tr.	12.5	0.5	8.8	57.5	12.5	0.4	1.1	0.6[d]
Leucaena leucocephala (Lamk.) Wit.	7.5	24.5	0.1	15.8	0.2	6.2	15.9	56.8	2.7	2.1	–
Parkia biglandulosa W. & A.	19.8	28.4	0.2	25.6	7.0	32.7	26.8	2.9	3.9	Tr.	–[e]
Pithecolobium bigemina (L) Mart. SYN. *Inga bigemina* Hook & Arn.	0.7	21.3	0.5	39.5	–	7.3	24.9	23.6	4.0	–	–
P. dulce Benth.	13.0	37.5	Tr.	12.3	0.3	3.3	51.1	13.3	2.5	10.0	5.3[f]

[a]Percentage by weight.
[b]Percentage by area.
[c]Also contains 17:0, 0.2%.
[d]Also contains 8:0, 0.9; 9:0, 0.2; 10:0, 0.2; 11:0, 0.1; 12:0, 0.2; 12:1, 0.1; 13:0, 0.3; 13:1, Tr.; 14:1, 0.1; 15:1, 1.6; 17:0, Tr.; 18:3, 1.6 and 20:1, 0.7%.
[e]Also contains 15:1, 0.8%.
[f]Also contains 17:0, 0.1 and 20:1, 1.9%.

enoic, heptadecanoic, eicosenoic and tetracosanoic acids; all but pentadecenoic acid (1.6% by area) were less than 1%. The fatty acids with an odd number of carbon atoms, viz. 9:0, 11:0, 13:0, 13:1, 15:1 and 17:0, were found in small quantities amounting to 2.2% in total.

The protein content of all the defatted seed meals ranged from 21.3-37.5% by weight (Table I), which is lower than that of usual oilseed meals, but adequate enough to be useful as a cattle and poultry feed. The protein from leucaena is of high nutritional value and compares well with the nutritive value of alfalfa (12). However, leucaena is toxic to nonruminants when the levels of mimosine reach ca. 10% in the diet. New, low mimosine varieties are now in an advanced stage of development (12).

The mineral composition of the defatted meals were comparable with our earlier reports on *Acacia* (3) and *Bauhinia* (4).

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Oxidative Cyclization of 1-Octadecanol and Hydroxy Fatty Esters with Lead Tetraacetate

M. HASHMI, M. KHAN, M.S. AHMAD, JR., F. AHMAD and **S.M. OSMAN,*** Section of Oils and Fats, Department of Chemistry, Aligarh Muslim University, Aligarh-202001, India

ABSTRACT

Oxidative cyclization of methyl 2-hydroxyoctadecanoate, methyl 10-hydroxyundecanoate and 1-octadecanol produced a good yield of the corresponding tetrahydrofuran (THF) derivatives characterized successively as methyl 2,5-epoxyoctadecanoate, methyl 7,10-epoxyundecanoate and 1,4-epoxyoctadecane. The structure of these cyclic derivatives have been established by elemental analyses and spectral studies.

INTRODUCTION

Lead tetraacetate (LTA) oxidation of monohydric alcohols bearing a carbon hydrogen bond in the γ-position represents a valuable synthetic route to tetrahydrofuran derivatives. The fact that cyclization proceeds via hydrogen abstraction at an unactivated position (γ-carbon hydrogen bond) places this transformation among a class of highly useful reactions for controlled functionalization of remote intramolecular position. This reaction has received attention primarily in short-chain alcohols. Abbot and Gunstone (1) have reported the formation of 1,4- and 1,5-epoxides from long-chain hydroxy esters with LTA and with silver oxide/bromine and mercuric oxide/iodine. Continuing our work (2) on the synthesis of fatty acid derivatives with LTA, an attempt has been made to prepare long-chain heterocyclic derivatives of potential physiological interest. The present paper describes the synthesis of THF derivatives from 1-octadecanol and the fatty esters containing a hydroxy group at the penultimate carbon and in close proximity to the ester function, using benzene, dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) to study the solvent effect.

*To whom correspondence should be addressed.

EXPERIMENTAL PROCEDURES

Infrared (IR) spectra were obtained with a Perkin-Elmer 621 Spectrophotometer (liquid films). Nuclear magnetic resonance (NMR) spectra were obtained on a Varian A60 spectrometer. Chemical shifts were observed in ppm with tetramethylsilane as the internal standard. The abbreviations s, t, m and br denote singlet, triplet, multiplet and broad. Mass spectra were recorded on a JEOL JMS-D300 spectrometer at 70 eV. Column and thin layer chromatography (TLC) were carried out by standard procedures using light petroleum and diethyl ether as the developing solvent.

MATERIALS AND METHODS

2-Hydroxyoctadecanoic acid was prepared from α-brominated product (3) by hydrolysis, as described by Sweet and Estes (4). 10-Hydroxyundecanoic acid was obtained by solvomercuration demercuration (5) of 10-undecenoic acid. 1-Octadecanol was prepared by a lithium aluminium hydride reduction of stearic acid by the procedure of Gunstone and Inglis (6).

Acids were converted to methyl esters using methanolic sulphuric acid (0.25 M) and LTA was freshly prepared (7).

Reaction of Methyl 2-Hydroxyoctadecanoate (*1a*) with LTA

The hydroxy ester (1 g, 3.1 mmol) in benzene (20 mL) and LTA (1.37 g, 3.1 mmol + 10% excess) were refluxed for 3 hr. When a starch iodide test showed complete consumption of tetravalent lead, dry ether (20 mL) was added to the reaction mixture. After keeping the mixtures for 1-2 hr at 5 C, lead diacetate was removed by filtration and was subsequently washed twice with benzene to extract the