seed from a feed to a food. As the panel also increases the concentration of gossypol from cottonseed unders, the process may be suitable as an improved source of gossypol, which is becoming useful in several new areas of research.

Water content, often important in mechanical processing, is also an important factor in electrical processing. The moisture regained in these samples after drying indicates that hulls from sunflower seed and grain have the greatest water-absorbing ability. Agreeing with the known deleterious effect of moisture on electric fields, their translational speeds during separation seem to be the slowest. In contrast, the low moisture regain of the reference lycopodium is reflected in its vigorous action over the panel. The effect of moisture is opposite to and probably less than that of the charge-to-mass ratio. The reduced vigor of pigmented gossypol, however, must be attributed to another property, perhaps its different dielectric characteristics or the high negative value of its specific charge.

Interpretations

As to how and why separation occurs, consider some details of this process. The undulating traveling wave is composed of electric field lines emanating from each conductor of the grid. These lines of potential are stronger nearer the panel than they are at a distance. The electric forces grow from a complex, near-field mode to a simpler, far-field mode. In the process of separating particles, each component comes to equilibrium against gravity at a different mean height above the panel, depending primarily on its charge-to-mass ratio. All components enriched in protein rise to a greater height than the ejected components. The protein components couple with the far-field mode of the wave and ride in the surfing direction. Sunflower seed and wheat hulls, along with the component enriched in pigmented gossypol, reach equilibrium near to and sometimes on the panel. These particles couple with the more complex mode of the wave, are caught in the undertow and move in the opposite direction. Hence, particles are equilibrated according to the properties that affect their charge-to-mass ratio. The particles then couple with the mode of the traveling wave that dominates at that height and are moved accordingly.

ACKNOWLEDGMENTS

Albert Baril, Jr. provided the electric panel; Mary E. Carter suggested the sunflower-seed problem; Robert J. Hron, Sr. supplied sunflower-seed samples; Janice P. Evans assisted with the image analyses.

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[Received June 29, 1983]

Ximenynic Acid in *Santalum obtusifolium* Seed Oil

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ABSTRACT

Analyzing *Santalum obtusifolium* seed oil led to the identification of 12 fatty acids; only ximenynic (71.5%) and oleic (14.3%) acids were present in substantial amounts. Data on the mass spectrum and ^{1}H- and ^{13}C-NMR (nuclear magnetic resonance) spectra of methyl ximenynate are given.

INTRODUCTION

Santalum obtusifolium R. Br. (family Santalaceae) is an erect glaucous shrub 1-2 m high that grows in the Hawkesbury sandstone region of eastern New South Wales (N.S.W.), Australia. The fruits are drupaceous and the average mass of the dry seeds is ca. 200 mg.

Ximenynic (santalbic) acid, *trans*-11-octadecen-9-ynoic acid, is an important constituent of the seed oils of *Ximenia, Santalum* and *Exocarpos* genera of Santalaceae and has been described by Ligthelm et al. (1,2), Gunstone and Russell (3) and Hatt and Szumer (4).

The purpose of the study was to determine whether this acid occurred in the seed oil of *S. obtusifolium* and to substantiate chemical studies with data on its nuclear magnetic resonance (NMR) spectra.

EXPERIMENTAL PROCEDURES

Material

Seeds were collected by L. V. Langley, Robertson, N.S.W.

General Procedures

The methods used for extracting the oil, preparing methyl esters, the Halphen color test and gas chromatography (GC) were similar to those described in 2 previous papers (5).

The methyl esters were hydrogenated by dissolving 5 mg in 5 mL hexane, adding Adams' catalyst and bubbling hydrogen through the solution for 15 min at 20 C.

Separation and Identification of Methyl Ximenynate

The methyl ester of the fatty acid was isolated by argentation thin layer chromatography (TLC) at −20 C, using 90/10 v/v toluene-hexane as the developing solvent. The ester, 95% purity by gas liquid chromatography (GLC), appeared under short-wave ultraviolet (UV) light as a medium-dark band near the top of the plate before the dichlorofluorescein spray solution was applied. Samples of the ester for spectroscopic examination were further purified by GLC by methods previously described by Whitfield et al. (6), using a stainless-steel capillary column (150 m long, 0.75 mm i.d.); the walls coated with silicone OV-101. The UV spectrum of the ester (in hexane) was recorded on a Gilford 2600 spectrophotometer, the infrared (IR) spectrum (as a thin film) on a Perkin Elmer 521 spectrometer and the ^{1}H- and ^{13}C-NMR spectra (as C_6D_6 solutions) on a Bruker CXP100 spectrometer. The low-resolution and high-resolution mass spectra were recorded using a Varian MAT-311A mass spectrometer. The products obtained from the

reduction of the ester with Lindlar catalyst and with hydrazine (7) were isolated by argentation TLC at −20 C (8) and were identified by GLC and mass spectrometry. Products obtained from the oxidative cleavage (9) of the ester and its partial reduction products were identified by GLC using a glass column (4 m long, 2 mm i.d.) packed with 10% Silar 10C on Gas-Chrom Q. The dimethyl dicarboxylates were identified by comparing their GLC retention times with those of a standard ester mixture.

RESULTS AND DISCUSSION

The results for the Halphen test, oil content of seeds and the assay for fatty acids are as follows: Halphen test, negative; oil content, 17.8%; esters (mass percent)—14:0, 0.3%; 16:0, 0.6%; 18:0, 1.2%; dihydrosterculic—0.1%; 16:1, 0.4%; 18:1, 14.3%; 18:2, 0.7%; 18:3, 3.2%; 20:1, 0.3%; 20:2, 2.5%; 20:3, 0.2%; 20:5, 4.3%; ximenynic, 71.5%.

Only oleic and ximenynic acids were present in substantial amounts (total 85.8%). These data give further evidence of the widespread occurrence of the latter acid in the seed oils of Santalaceae species, particularly in the *Santalum* genus. Previous work (4,10,11) shows that the average content of ximenynic acid in the seed oils of 13 Santalaceae species is 47%, with values ranging from 9-84%. The seed oil of *S. obtusifolium* is therefore one of the richest sources of this acid. The presence of ximenynic acid may be an aid in classifying Santalaceae species, although it does also occur less frequently in medium concentrations in Olacaceae species.

Identification of Ximenynic Acid

The structure of the methyl ester was established by a combination of physical and chemical techniques. The GLC-purified ester gave a low-resolution mass spectrum with prominent and diagnostic ions as follows: m/z 292 M^+(8), 150(100), 94(30), 93(51), 91(31), 81(41), 80(92), 79(94), 78(30), 69(23), 67(38). The high-resolution mass spectral examination gave a molecular weight of 292.2404, which was consistent only with the molecular formula $C_{19}H_{32}O_2$ (calc. 292.2402). The UV spectrum showed an absorption at 226-229 nm characteristic of a conjugated system (3) and the IR spectrum had a strong absorption at 950 cm^{-1}, typical of a *trans*-olefin conjugated to an acetylenic group (3). The ^{1}H-NMR spectrum showed a doublet at δ 5.54, J15Hz (1H) and a doublet-triplet at δ 6.11, J15Hz, 7Hz (Fig. 1), assigned to the *trans*-olefinic protons of a conjugated enyne system (12). The ^{13}C-NMR spectrum had signals at δ 80.01 and 88.83 (singlets in the off-resonance decoupled spectrum) assigned to the acetylenic carbon atoms and at δ 110.94 and 143.01 (doublets in the off-resonance decoupled spectrum) assigned to the olefinic carbon atoms (13). The allocation of signals to individual acetylenic and olefinic carbon atoms is based on information already available for other C18 alkenynates (14). Oxidative fragmentation of the ester gave azelaic acid and heptanoic acid as the major dicarboxylic and monocarboxylic acids, indicating the presence of unsaturated linkages at C9 and C11. Hydrogenation with Lindlar catalyst gave a mixture of 3 isomeric 18:1 methyl esters. Two of these were methyl *trans*-11- and methyl *cis*-9-octadecenoates. Oxidative fragmentation of the monoenoate mixture gave mainly the C9 (43%), C10 (25%) and C11 (26%) dicarboxylic acid fragments. The C10 fragment is probably derived from methyl 10-octadecenoate, a product of 1-4 hydrogenation. Partial reduction using hydrazine gave methyl *cis*-9, *trans*-11-octadecadienoate. The parent ester was therefore methyl *trans*-11-octadecen-9-ynoate (methyl ximenynate).

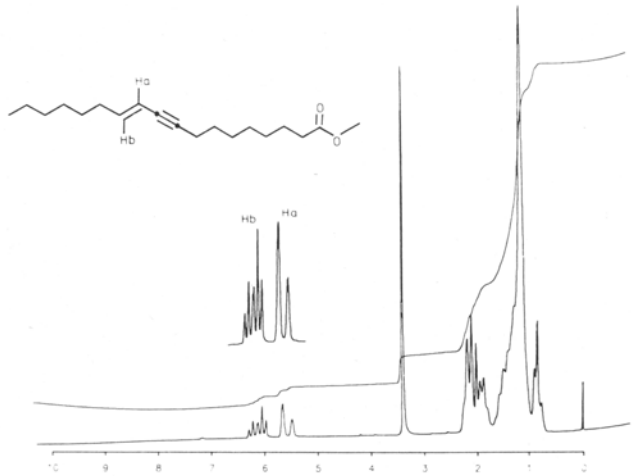

FIG. 1. 90 MHz ^{1}H-NMR spectrum of methyl ximenynate. Sample size was 1 mg in 35 μL C_6D_6. Sample tube was 2.5 mm o.d. Microprobe was 12,000 scans. Inset is a 3× expansion of δ 5.4-6.3 region.

ACKNOWLEDGMENT

K. J. Shaw measured the mass spectra of the methyl esters.

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[Received August 8, 1983]