Cardanol in Germ and Seed Oils Extracted from Cashew Nuts Obtained by the Oltremare Process

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ABSTRACT

The presence of cardanol in cashew seed and germ oils was detected by using a combination of the thin layer chromatography (TLC) and gas liquid chromatography (GLC) techniques with infrared spectroscopy (IR) and mass spectrometry (MS). The oils were extracted from cashew nuts obtained by the Oltremare process (heating the nuts in cashew nut shell liquid bath at 180 C for 100-120 sec). The cardanol content was about 40 mg/100 ml of germ oil and 20 mg/100 ml of seed oil. The four cardanol components were found in the following percentages: 3-(pentadecyl)-phenol (II), 3.0%; 3-(8-pentadecenyl)-phenol (III), 55.7%; 3-(8,11-pentadecadienyl)-phenol (IV), 24.2%; and 3-(8,11,14-pentadecatrienyl)-phenol (V), 17.1%, respectively. Because a constant distribution of the four cardanol components was found both in the seed and in the germ oils, it was suggested that cardanol is not a natural component of germ and seed oils, but is derived from the cashew nut-shell liquid during the processing of the nuts.

INTRODUCTION

In earlier research on the chemical composition of cashew seed and germ oils (1), the presence of a compound with an unknown structure was detected in relatively high amounts (40 and 20 mg/100 ml of oil respectively) in the unsaponifiable matter of the respective oils. Initial research directed towards determination of the unknown structure showed that the unknown compound was a mixture of phenolic olefins differing from each other only in the degree of unsaturation of the fifteen carbon side chain.

Similar compounds were previously detected in cashew nut shell liquid (2-8) and collectively named cardanol. Structures II-V, corresponding to 3-(pentadecyl)-phenol, 3-(8-pentadecenyl)-phenol, 3-(8,11-pentadecadienyl)-phenol and 3-(8,11,14-pentadecatrienyl)-phenol, respectively (Scheme 1), previously assigned to these compounds were based on early work (7,8) using, above all, classical "wet chemistry" methods. Therefore, the present research was extended to include characterization of the cardanol components to confirm the proposed structures using modern analytical methods. Also we sought to ascertain whether the cardanol in the seed and germ oils was a natural product or one produced by contamination.

EXPERIMENTAL PROCEDURES

Identification of the Cardanol

The germ and seed oils were extracted with hexane in Soxhlet apparatus for 8 hr from the grounded cashew germ and seed, separately. The cashew germ and seed were obtained by the Oltremare process (9) (heating the nuts in cashew nut shell liquid at 180 C for 60-120 sec.) and delivered to us by the Oltremare S.p.A. Company (Zola Predosa, Bologna). The analytical procedure used to study the unknown compound, indicated as component x, present in the tocopherols fraction of the unsaponifiable matter is shown in Scheme 2.

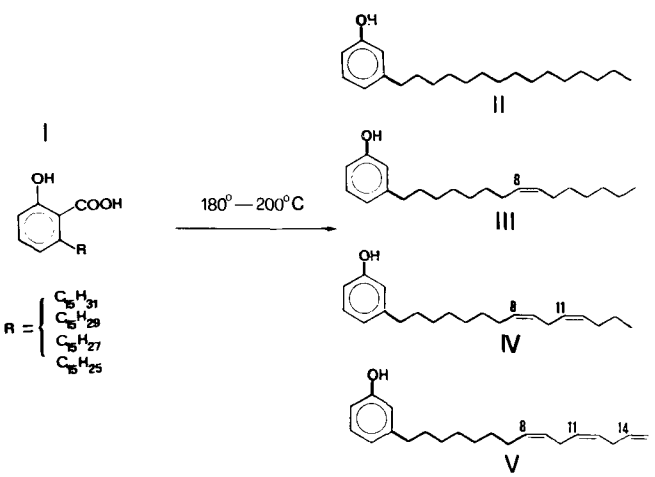
The component x was first isolated from the fatty acids along with the unsaponifiable matter and 50 mg were extracted in two successive stages: (a) column chromatography (LC-SiO_2), to separate the tocopherols fraction; (b) preparative gas chromatography (GLC-SF96) to isolate component x from the tocopherols. The component x was subsequently purified by thin layer chromatography (TLC-SiO_2) in order to eliminate the GLC column bleeding.

The resulting product was analyzed by gas chromatography (GLC-SP1000), mass spectrometry (GLC-MS), and infrared spectroscopy (IR).

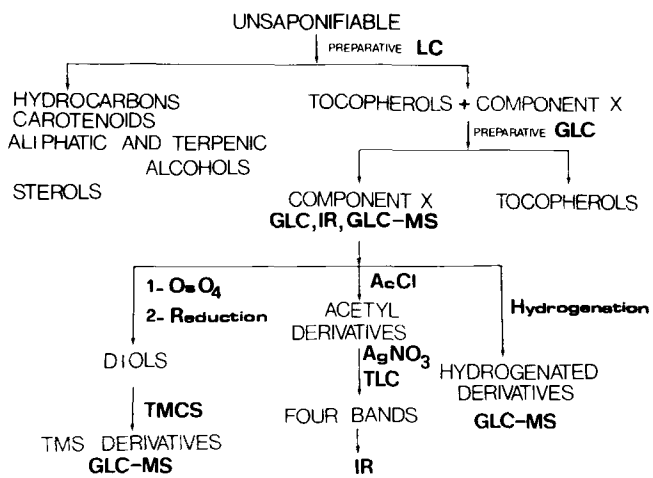
Experimental conditions for the various analytical procedures were as follows:

LC-SiO_2 — A water-jacketed column (2 x 40 cm) containing silicic acid (100 mesh) was used. A 3 g portion of unsaponifiable matter was applied on the column and eluted at atmospheric pressure with hexane/ethyl ether, 100:2 (v/v).

TLC-SiO_2 — Silica gel G plates (0.3 mm) developed in hexane/ethyl ether, 60:40 (v/v) were used. The band of component x was scraped off and extracted with 2 x 25 ml of ethyl ether



SCHEME 1.



SCHEME 2.

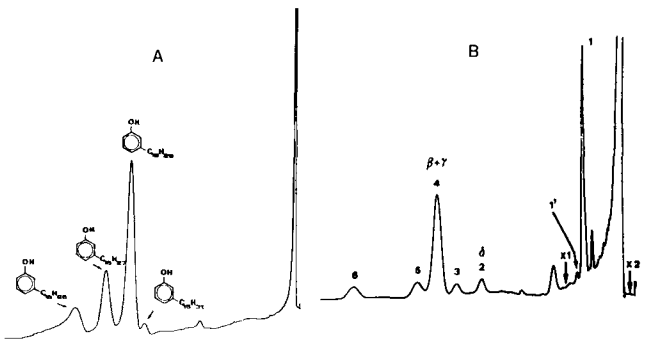


FIG. 1. Gas liquid chromatographic (GLC) profiles of: A. component x (peaks 1 and 1′ of FIG. 1 B) by preparative GLC-SF 96, from tocopherol fraction. Column SP 1000 10%, oven temperature: 270 C. B. tocopherol fraction (as trimethylsilyl ethers) by preparative LC-SiO_2 from unsaponifiable matter.

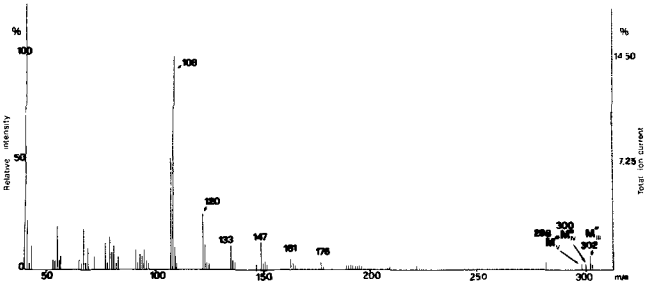


FIG. 2. Mass spectrum of peak 1 of FIG. 1B.

for the recovery (see GLC of Fig. 1 B).

Preparative GLC-SF 96: A 6 ft ¼ in. o.d. 5% SF-96 column was programmed from 200 C to 250 C at 5 C/min. The helium flow rate was 50 ml/min and the thermal conductivity detector temperature was 300 C. The fraction of component x was collected in glass tubes loosely packed with a 5 mm segment of glass wool.

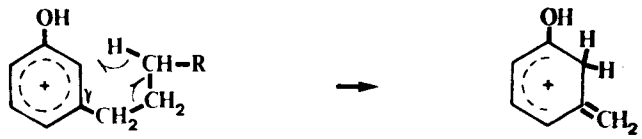
GLC-SP1000: A 6 ft x 1/8 in. o.d. 10% SP 1000 column at 270 C was used. The nitrogen flow rate was 25 ml/min, and the flame ionization detector temperature was 300 C.

GLC-MS: Mass spectra were recorded at the Center for Mass Spectrometry of the University of Bologna on an LKB 9,000 mass spectrometer equipped with a gas chromatographic inlet system (1% SE-30, 200-250 C). The transfer system (including the separators) and the ion source were maintained at 300 C. Ionizing potential was 70 eV. Spectra were recorded in 30 sec to m/e 1000 at the apex of the GC peak.

IR: Infrared spectra were run from 2 to 15, without solvent (neat), on a Perkin Elmer Mod 21 spectrophotometer with KBr disks.

Characterization of Cardanol

Three different analytical procedures were applied on the isolated mixture (Scheme 2): (a) hydrogenation followed by analysis by GLC (SP 1000) and GLC-MS (10); (b) reaction with acetyl chloride (AcCl) followed by separation by silver nitrate-silica gel thin layer chromatography (TLC-$AgNO_3$) and final IR analysis (11); (c) reaction with OsO_4 followed by reduction and transformation of the diols into trimethylsilyl ether derivatives and analysis by GLC (SE 30) and GLC-MS (12).



m/e 302 (300—298) m/e 108

SCHEME 3.

RESULTS AND DISCUSSION

Identification of the Cardanol

Preliminary analyses showed that the unknown compound of the germ and seed oils consisted of four alkyl phenols differing from each other only in the degree of unsaturation of the fifteen carbon side chain. These compounds correspond to those previously detected in heated cashew nut-shell liquid and collectively named cardanol (structures II-V of scheme 1) (7-8). Our identification in the germ and seed oils is supported by the following evidence. GLC-SP 1000 (Fig. 1A) and GLC-SF 96 (Fig. 1B) analyses give four and two peaks (1 and 1′), respectively, with percentage areas 3.0, 55.7, 24.2, 17.1 (Fig. 1A) and 97.0, 3.0 (Fig. 1B). The mass spectra of the peaks 1 of Figure 1B present in the region of high masses three peaks at m/e = 302, 300, 298 (Fig. 2) and one peak at m/e = 304, respectively, which correspond to the molecular weights of the four compounds of cardanol. The base peak at m/e = 108 for both spectra can be rationalized in accordance with the main characteristic of alkyl benzenes (13), as derived from the molecular ions M^+ 304, 302, 300, 298, through the β-cleavage of the aliphatic chain (Scheme 3).

The IR spectrum (Fig. 3A) exhibits absorption bands that are characteristic of structures II-IV. The specific group frequencies are: the O-H stretching vibrations for the bonded state of the phenolic group at 3200-3250 cm^{-1}, ν(OH); the skeletal ring breathing vibrations of an aromatic type structure at 1575 cm^{-1} and 1600 cm^{-1}, ν(C=C); the out-of-plane C-H deformation vibrations of the hydrogen atoms remaining in a 1,3-disubstituted benzene ring, at 870 cm^{-1}, $\gamma(=CH)_{1H}$ and 780 cm^{-1} $\gamma(=CH)_{3H}$; the out-of-plane skeletal vibrations at 690 cm^{-1}, δ′ (ring).

The high absorption intensity of the aromatic bands at 1575-1600 cm^{-1} is also indicative of meta substitution, because with meta substitution the intensity is related to the algebraic sum of the electronic effects of the substituents, both electron donors (14).

All these absorption bands are also present in the IR spectrum of 3-pentyl-phenol, taken as reference (15).

Additionally the absorption band in our spectrum is also present at 910 cm^{-1}, which arises for the out-of-plane deformations of the hydrogens of the vinyl group, $\gamma(=CH_2)$.

Characterization of Cardanol

The molecular weight 304 (m/e 304, M^+) for the hydrogenated cardanol, as determined by GLC-MS analysis and the presence of only one peak in GLC-SP 1000 analysis, clearly indicates that the four compounds are isologues.

On TLC-Ag NO_3 plates the acetylated cardanol shows four bands with Rf values 0.82, 0.55, 0.20, 0.05, very close to those of the fatty acid methyl esters 18:0, 18:1 (9c), 18:2 (9c, 12c), 18:3 (9c, 12c, 15c) in the same operating conditions, 0.93, 0.56, 0.25, 0.10, respectively.

The absorption bands at 870, 780 and 690 cm^{-1} in the IR spectra of the recovered TLC bands (Fig. 3 C, D, E) indicate a 1,3-disubstituted benzene ring for all the components of cardanol.

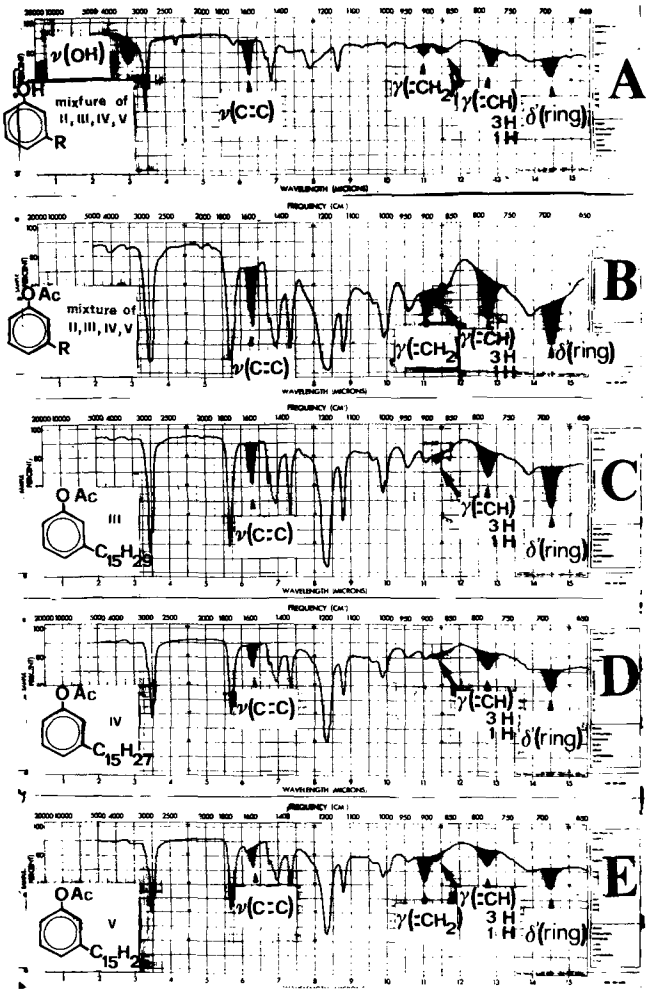


FIG. 3. IR Spectra of: A – cardanol (mixture of II, III, IV and V) B – acetyl derivatives of cardanol; C, D and E – acetyl derivatives of III, IV and V, respectively.

It was not possible to run the IR spectrum of the first TLC band (Rf = 0.93) corresponding to the saturated cardanol component, due to the small amount of material.

The lack of the absorption band at 3200-3250 cm^{-1} in these IR spectra and in that of the acetylated cardanol (Fig. 3B) is due to the transformation of the -OH phenolic group in the corresponding acetyl derivative.

These data indicate that cardanol is a mixture of phenolic olefins differing from each other only in the unsaturation degree of the fifteen carbon side chain.

The mass spectral fragmentation pairs m/e 187-365; 363-365 and 145-583; 365-539 and 321-583 (Scheme 4) determined by GLC-MS of the trimethylsilyl ether derivatives of diols (tri-, penta-, epta-TMS derivatives) (Fig. 4)

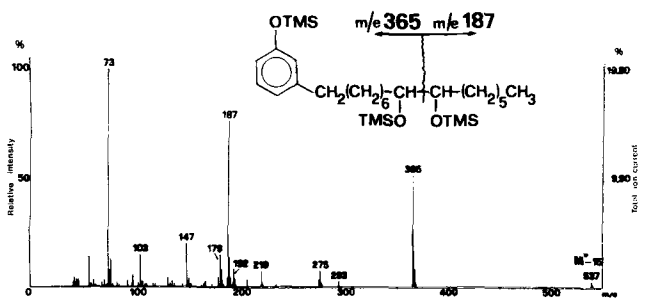
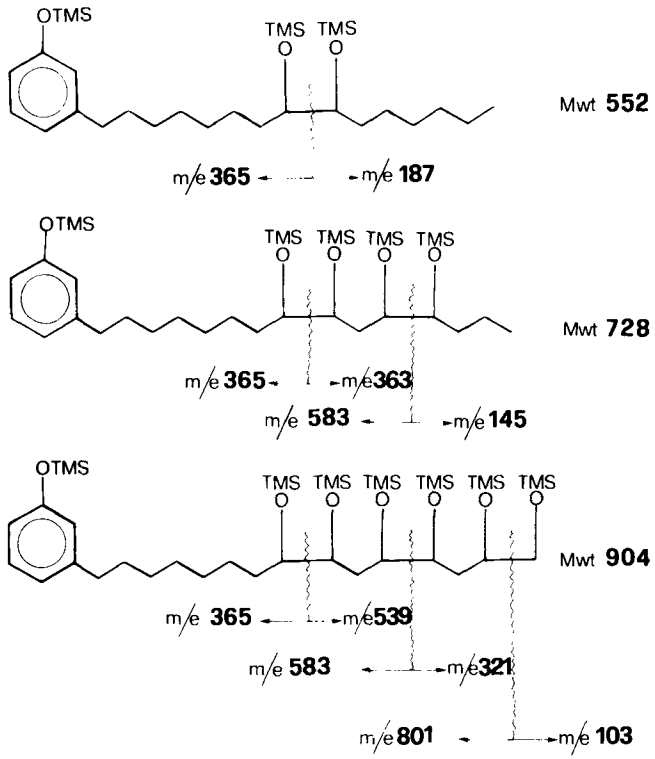


FIG. 4. Mass spectrum of trimethylsilyloxy derivatives of 3-(8-pentadecenyl)-phenol (III).



SCHEME 4.

indicate that the double bonds in the side chain are localized in the position 8-9 (Fig. 2) for the monounsaturated compounds, 8-9, 11-12 for the diunsaturated compound, and 8-9, 11-12 for the triunsaturated compound (Scheme 4).

The position of the third double bond in the unsaturated compound could not be determined by GC-MS because the third fragmentation partner was lacking. However, the IR absorption band at 910 cm^{-1}, $\gamma(=CH_2)$, in the spectrum of triunsaturated acetyl derivative clearly indicates the presence of a vinyl group. Therefore, the third double bond is localized in 14-15. The proposed structures II-V of Scheme 1 for the four components of cardanol are therefore confirmed.

Origin of Cardanol in Cashew Germ and Seed Oils

GLC-SP 1000 analyses of cardanol obtained from three different sources, heated cashew nut shell liquid, seed and germ oils, with the techniques described previously, show that its quantitative composition was almost the same: 3.0, 55.7, 24.3, 17.1% (in order of increasing unsaturation). Hence, it is suggested that the presence of cardanol in the seed and germ oils might be due to a slight contamination by the cashew nut shell liquid.

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