A PHTHALATE AND A DIENOIC ACID FROM THE OIL OF Eremostachys molluceloides

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Continuing a study of the fatty oil of the seeds of Eremostachys molluceloides [1] we have isolated another two compounds rarely found in oils: a fatty acid (I) and an aromatic ester (II).

The acid was obtained from the total fatty acids by a combination of the methods of precipitation with urea [2], low-temperature crystallization from acetone, and preparative TLC (20% of $AgNO_3$, benzene, R_f 0.65) in an amount of 0.5% of the total acids. The retention time of its methyl ester on GLC (17% of PEGS, 198°C) [1] corresponded to $C_{18:2}$ (98% purity). UV spectrum: λ_{max}^{hexane} 232 nm ($E_{1\,cm}^{1\%}$ 1075); IR spectrum: $\nu_{max}^{CCl_4}$ 985 cm^{-1} (trans, trans-conjugated diene).

The destructive oxidation of (I) with periodate-permanganate gave sebacic and caproic acids, which showed the positions of the double bonds at Δ10.12. From its chromatographic behavior and spectral characteristics, compound (I) was identified as octa-trans-10,trans-12-dienoic acid.

The aromatic ester obtained from the total unsaponifiables by TLC on silica gel L 5/40 (Chemapol) in the hexane—diethyl ether—CH_3CCOH (70:30:1) system had R_f 0.76, coinciding with the R_f value of triglycerides in this system. After the chromatogram had been treated with 50% H_2SO_4 and had then been heated at 150°C, the color of the spot of compound (II) was pinkish brown, changing on standing for an hour to lilac. Compound (II) formed a clear faintly yellow oil (0.9% of the total unsaponifiables), mol. wt. 390 (mass spectrum). UV spectrum: λ_{max}^{hexane} 225 nm (ε 8155), 276 nm (ε 1182), 284 nm (ε 1064); IR spectrum: ν_{max} (cm^{-1}) 1720, 1285, 1130 (aromatic ester), 1605, 1585, 1075, 1043, 746 (o-substituted benzene). In the NMR spectrum (60 MHz, CCl_4, τ scale) of (II) there was a multiplet at 2.56 ppm (4H) of an o-substituted benzene; a doublet at 5.94 ppm (4H) ($-CO_2CH_2-CH$); a broad singlet at 8.75 ppm (∿ 18H) ($-CH_2-$, CH); and a triplet at 9.14 ppm (6H) ($-CH_3$). In the mass spectrum (MKh-1303, 40 eV, 130°C), in addition to M^+ 390 (0.9%) there were strong peaks with m/e 167 (100), 149 (89), and 279 (49). From its spectral characteristics, the substance was identified as di(2-ethylhexyl) phthalate. To confirm the spectrometric results, compound (II) was subjected to alkaline hydrolysis. From the reaction products we isolated phthalic acid, the dimethyl ester of which had the same retention time (C_{sp}) as authentic dimethyl phthalate (DMP) under the conditions of GLC (15% of Reoplex 400 on Chromaton N-AW-HDMS, 203° C, C_{sp} DMP/C_{sp} $C_{16:0}$ = 2.8). When the total unsaponifiables were separated by extraction with solvents, part of the phthalate remained in the mixture of fatty acids. On subsequent separation of the methyl esters of the acids on a layer of silica gel impregnated with $AgNO_3$, the phthalate migrated together with the oleic acid.

Biologically active [3] phthalic acid esters have recently been found in various organs of higher plants of the families Balanitaceae [4], Umbelliferae [5], and others [6].

This is the first time that di(2-ethylhexyl) phthalate and octadeca-trans-10,trans-12-dienoic acid have been found in seed oils of the family Labiatae.

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