NONGLYCERIDE LIPIDS OF THE SEED COATS OF *Artemisia absinthium* AND *Onopordum acanthium*

É. I. Gigienova and A. U. Umarov

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The seed coats of *Artemisia absinthium* and *Onoporum acanthium* have been shown to contain paraffinic hydrocarbons (C_{31}-C_{25} and C_{31}-C_{27}, respectively), wax esters (C_{32}-C_{23} and C_{51}-C_{33}), acetyltriterpenols (six types, five types), and acyltriterpenols with a predominance of palmitoyltriterpenols (esters of higher saturated unbranched $C_{32:0}$-$C_{12:0}$ fatty acids and triterpenols with a molecular weight of 426 belonging to the ursene group).

The total substances have been extracted with hexane from the unground botanically ripe seeds of the plants *Artemisia absinthium* L. and *Onoporum acanthium* L., family Asteraceae, of the 1978 harvest growing on the slopes of the western Tien Shan. The extracts obtained contained 0.12% and 0.1% of substances from the seeds and 5 and 7%, respectively, of moisture. From each total extract, fractions of nonglyceride lipids were extracted with the aid of column chromatography. They consisted of mixtures of homologs which, according to their IR and PMR spectra and migration in a thin layer of adsorbent in solvent systems a-g, corresponded to hydrocarbons, wax esters, and esters of triterpenols with carboxylic acids.

The mass spectra of homogeneous mixtures of substances permitted the detection of the homologous composition of the lipids that are usually found in the oil seeds of the majority of plants [1-5]. In the seed coats of *A. absinthium* we found seven paraffinic hydrocarbons with even and odd numbers of carbon atoms from C_{31} to C_{25}, among which the paraffins of the odd series predominated, with maximum contents of pentacosane and heptacosane; ten C_{32}-C_{23} wax esters of the odd and even series; six types of natural acetyltriterpenols mainly with a molecular weight of 468 and traces with a molecular weight of 482 without a maximum content of one of the types of acetates being observable in a thin layer of argentized silica gel (solvent system h). The maximum fragment in the spectrum of the acetates of the triterpenols with m/e 189 (100%) shows a predominance of acetylated ursenes.

We isolated the nonglyceride components from the seed coats of *O. acanthium* and in them we detected three series of homologs. These were the five C_{31}-C_{27} paraffinic hydrocarbons with a predominance of nonacosane (C_{29}); five types of natural triterpenol acetates with a molecular weight of 468, mainly of the ursene group (TLC/$AgNO_3$; mass spectrum, m/e 189 — 100%); twenty-one esters of the $C_{32:0}$-$C_{12:0}$ fatty acids and of pentacyclic alcohols with a molecular weight of 426; and nineteen homologous C_{51}-C_{33} wax esters. The dominating components of the wax esters of pentacyclic alcohols were palmitoyltriterpenols.

No triterpenol esters were detected in the coats and oil of the seeds of *O. acanthium* of the 1974-1976 harvests [6]. However, in the seed oil we found fatty acid ethyl esters which were not present in the seed coats of the 1978 harvest.

With the aim of a comparative investigation of the composition of the hydrocarbons of the oil and coats of the seeds we performed an additional [7] chromatography of the hydrocarbon zone of the seed oil of *A. absinthium* in a thin layer of silica gel with solvent system *a*. In the slower-moving part of the hydrocarbon zone we detected traces of C_{41}-C_{26} paraffins.

The results of a comparison of the compositions of the lipids of the nonglyceride complex of the seed coats with the composition of the lipids of the nonglyceride fraction of the oil [6, 7], showed that they differed considerably. For example, in *A. absinthium* the

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hydrocarbons of the seed coats consist of the C_{31}–C_{25} paraffins with a maximum at C_{25} and C_{27}, and the hydrocarbons of the seed oil consisted of the C_{41}–C_{20} paraffins with a predominance of C_{29} and C_{27} and traces of four homologous series of olefins, $C_{25:1}$–$C_{20:1}$, $C_{25:2}$–$C_{20:2}$, $C_{25:3}$–$C_{20:3}$, and $C_{25:4}$–$C_{20:4}$, without a pronounced predominance of any of them; triterpenol acetates were found in the coat and were absent from the oil, and the same applies to wax esters.

In *O. acanthium*, the hydrocarbons of the seed coats consist of C_{31}–C_{27} paraffins with a predominance of C_{29}, while the oil contains in addition to C_{33}–C_{25} paraffins (again C_{29} is predominating) C_{18} and C_{17} paraffins and olefins of the monoenic, dienic, and trienic series; triterpenol acetates are found in the coat and are not found in the oil. The same thing has been observed for wax esters and esters of triterpenols with higher fatty acids.

The results obtained indicate, in the first place, a difference in the qualitative and quantitative compositions of the nonglyceride lipids of the coats and oil of the seeds of the plants studied. It follows from this that the evolution of the biosynthesis and/or transport of substances in the coat took place in the direction of a specific differentiation of the compositions of the lipids of the coats and kernels of the seeds. In the second place the nonglyceride lipids of the seed coats have no influence on the composition of the lipids in the seed oils, which can explain the low amounts of these lipids in the coats as compared with their amount in the seeds.

EXPERIMENTAL

The mass spectra were taken on an MKh-1303 instrument at an ionizing voltage of 40 V and a temperature of the inlet tube of 135-150°C. The authenticity of the molecular ions was determined by comparison with mass spectra taken at an ionizing voltage of 17 V.

IR spectra were obtained on a UR-10 instrument and PMR spectra on a JNM-100/100 MHz instrument (δ, ppm) with respect to HMDS in CCl_4.

Extraction of the Lipids. The unground seeds (200 g) were treated with hexane in a Soxhlet apparatus for 3-4 h.

Column chromatography was performed on silica gel L 100/250 μ. The internal diameter of the column was 1 cm and the height of the layer of adsorbent 15 cm. The whole of the sum of the extracted substances was introduced into the column for separation. The eluents used were 50-milliliter volumes of hexane with gradually increasing amounts of diethyl ether of from 0 to 6% by volume. The eluates were collected in 10-drop portions and their compositions were checked on Silufol in the corresponding solvent systems a-g.

Thin-layer chromatography was carried out on 18 × 24 cm glass plates coated with silica gel L 5/40 μ containing 3% of gypsum. In the separation of the triterpenol acetates, 10% of silver nitrate was added to the adsorbent.

Solvent systems: hexane—ether in the following proportions: a) 10:0; b) 9.8:0.2; c) 9.6:0.4; d) 9.4:0.6; e) 9.0:1.0; f) 8.0:2.0; g) 5.0:5.0; and h) chloroform—carbon tetrachloride in a ratio of 1:1 (by volume).

Hydrocarbons of the Seed Coat of *A. absinthium*. Mass spectrum, 135°C m/e (% rel.): M^+ 436 (tr.) – C_{31}, 422 (tr.), 408 (0.7), 394 (0.2), 380 (2.4), 366 (0.6), 352 (4.2) – C_{25}, 421 (tr.), 407 (tr.), 393 (0.1), 379 (tr.), 365 (0.5), 351 (tr.), 337 (1.6), 323 (2.6), 309 (3.4), 295 (4.2), 281 (3.9), 267 (4.1), 253 (4.5), 239 (4.7), 225 (4.8), 211 (6.0), 197 (6.2), 183 (6.6), 169 (7.5), 155 (12.0), 141 (6.3), 127 (4.5), 125 (4.0), 113, 111 (6.0), 99 (20.0) 97 (18.2), 85 (75.0), 83 (42.2), 71 (72.0), 69 (60.0) 57 (100), 55 (50.0), 43 (55.0), 41 (30.0). IR spectrum: ν_{max}^{KBr}, cm^{-1}: 2975 s, 2885 s, 1380 m $-CH_3$, 2945 v. s, 2870 s, 1465 s, doublet 730 m $-(CH_2)_n-$Silufol, solvent system *a*, R_f 0.93.

Wax Esters of the Seed Coats of *A. absinthium*. Mass spectrum, 120°C, m/e (% rel.): M^+ 480 (0.12) – C_{32}, 466 (0.36), 452 (0.6), 438 (0.8), 424 (1.0), 410 (1.7), 396 (1.8), 382 (2.9), 368 (1.6), 354 (1.0), 340 (1.3) – C_{23}: The other peaks corresponded to the fragments $(M-15)^+$, $(M-15-14n)^+$, RCO^+, RO^+, R^+; 43 (100). PMR spectrum: t 0.86 (CH_3—), m 1.23 (—CH_2—), t 2.2 (—RCH_2CO—), and m 4.02 (—OCH_2R). Silufol, solvent system d, R_f 0.60.

Triterpenol Acetates from the Seed Coats of *A. absinthium*. Mass spectrum, 135°C, m/e (% rel.): M^+ 468 (10.0), 482 (0.5), $(M-15)^+$ 453 (1.5), 467 (tr.), $(M-42)^+$ 426 (tr.), 440 (tr.), $(M-60)^+$ 408 (12.0), 422 (9.0), RO^+ 425 (0.7), 439 (0.3), R^+ 409 (4.0), 423 (tr.), 218 (32.0), 203 (25.0), 189 (100). IR spectrum, ν_{max}^{KBr}, cm^{-1}: 1740 s, 1250 s ($-OCOCH_3$). PMR spectrum: s 1.92 ($-OCOCH_3$). Silufol, solvent system d, R_f 0.35.

Hydrocarbons of the Seed Coats of *O. acanthium*. Mass spectrum, 115°C, m/e (% rel.): M^+ 436 (0.3) — C_{31}, 422 (0.1), 408 (1.8), 394 (0.2), 380 (0.4) — C_{27}, 365 (0.4), 351 (0.5), 337 (0.5), 323 (0.5), 309 (0.6), 295 (1.3), 281 (2.5), 267 (3.3), 253 (4.5), 239 (5.3), 225 (6.8), 211 (9.5), 197 (11.0), 183 (11.5), 169 (12.0), 155 (14.0), 141 (14.5), 127 (22.5), 125 (22.0), 113, 111 (32.5), 99 (37.0), 97 (37.5), 85 (67.5), 83 (34.0), 71 (87.5), 69 (17.5), 57 (100), 55 (10.0), 43 (10.0), 41 (5.0).

Acetates of Pentacyclic Alcohols of the Seed Coats of *O. acanthium*. Mass spectrum, 135°C, m/e (% rel.): M^+ 468 (100.0), 453 (81.0), 426 (13.0), 425 (13.0), 408 (25.0), 218 (19.0), 204 (13.0), 189 (35.1).

Acyl Triterpenols of the Seed Coats of *O. acanthium*. Mass spectrum, 150°C, m/e (% rel): fragments of a homologous series of $C_{32:0}$–$C_{12:0}$ fatty acid esters with triterpenols having a molecular weight of 426 — M^+ 888 (tr.) — $C_{32:0}$, 860 (6.8), 832 (1.0), 804 (1.0), 790 (0.8), 776 (1.8), 762 (1.3), 748 (1.2), 734 (3.0), 720 (3.5), 706 (5.0), 692 (12.5), 678 (11.8), 664 (48.0), 650 (10.0), 636 (5.0), 622 (12.0), 608 (2.5), $(M - RCOOH)^+$ 408 (48), $RCOOH^+$ 480 (8.7), 466 (8.7), 452 (2.1), 438 (9.0), 424 (19.0), 410 (28.0), 396 (12.3), 382 (3.0), 368 (13.0), 354 (4.8), 340 (11.0), 326 (7.5), 312 (32.0), 298 (14.0), 284 (11.0), 270 (11.0), 256 (12.5), 242 (5.0), 228 (tr.), 214 (tr.), 200 (tr.), 218 (68), 203 (48), 189 (100). Silufol, solvent system b, R_f 0.75.

Wax Esters of the Seed Coats of *O. acanthium*. Mass spectrum, 120°C, m/e (% rel.): M^+ 746 (tr.) — C_{51}, 732 (5.0), 718 (4.0), 704 (5.0), 690 (12.5), 676 (13.0), 662 (20.0), 648 (22.0), 634 (4.5), 620 (21.0), 606 (4.5), 592 (37.5), 578 (4.5), 564 (52.5), 550 (3.8), 536 (7.5), 522 (3.0), 508 (2.7), 494 (2.7) — C_{33}; the other peaks correspond to the fragmentation of the waxes; m/e 57 was taken as the maximum fragment (100).

SUMMARY

The nonglyceride lipids of the seed coats of the *Artemisia absinthium* and *Onopordum acanthium* have been shown to contain a series of homologs: hydrocarbons (C_{31}–C_{25} and C_{31}–C_{27}, respectively), wax esters (C_{52}–C_{23} and C_{51}–C_{33}), fatty acid esters ($C_{32:0}$–$C_{12:0}$), and triterpenols with a molecular weight of 426 belonging mainly to the ursene group (six types of skeletons and isomers), and acetates of triterpenols with a molecular weight of 426 (five types).

It has been shown that the composition of the nonglyceride lipids of the seed coats of the plants studied does not affect the composition of the nonglyceride components of the seed oils and may change substantially from harvest to harvest.

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