EPOXYTRIGLYCERIDE OILS OF THE SEEDS OF *Onopordum acanthium*

N. T. Ul'chenko, É. I. Gigienova,
and A. U. Umarov

UDC 547.915+665.31

From the seed oil of *Onopordum acanthium* L. we have isolated about 4% of mono(epoxyocta· decenoyl)diacyl triglycerides (TGs) by CC on silica gel L 100/250 μ with hexane—ether (8:2), these triglycerides having R_f on Silufol plates (same system). IR spectrum, (ν_{max} in a film cm^{-1}): 3020 m, 1635 w (—CH=CH—), 2970 s, 2880 s, 1380 m (—CH_3); 2940 s, 2865 s, 1465 m, 730 m (—CH_2—); 1745 s, 1420 m, 1245 s, 1170 s (—OCOR); and 845 and 830 m (ethoxy group). NMR spectrum (20% solution in carbon tetrachloride, hexamethyldisiloxane as standard, δ scale): unsymmetrical t, CH_3—, 0.86 ppm; m, —(CH_2)—, 1.22 ppm; m, —$\underline{CH_2}CH_2COO^-$, 1.55 ppm; coincident m's, —$\underline{CH_2}CH_2$= and —$\underline{CH_2}CH_2CH$=, 2.0 ppm; m, —CH_2COO^-, 2.24 ppm; coincident m's =$CHCH_2CH$= and the protons of an epoxide ring, 2.70 ppm; m, —CH_2OC—, 4.13 ppm; m, $-\underset{|}{C}HOC-$, 5.1 ppm; m, —CH=CH—, 5.24 ppm.

The products of mild alkaline hydrolysis (0.1 M KOH, 37°C, 40 min): glycerol [TLC/KSK, solvent systems: 2% ammonia—methanol (2:3); chloroform—methanol (85:15); revealing reagents silver nitrate, iodine; in the NMR spectrum two singlets in the 3.51 and 4.78 ppm regions, δ scale]; fatty acids [methylation with diazomethane, GLC (%): $C_{14:0}$, 0.1; $C_{16:0}$, 5.9; $C_{18:}$ 0.3; $C_{18:1}$, 23.4; $C_{18:2}$, 70.3]; epoxyoctadecenoic acids (the NMR, IR, and mass spectra correspond to the structure of methylesters of epoxyoctadecenoic acids) [1]. The weight ratio of the fatty and epoxy acids was 2:1. Hence, the fatty-acid composition of the epoxytriglycerides (%) is: $C_{14:0}$, 0.1; $C_{16:0}$, 4.0; $C_{18:0}$, 0.2; $C_{18:1}$, 15.6; $C_{18:2}$, 46.8; epoxy-$C_{18:1}$, 33.3.

The products of enzymatic hydrolysis with the lipase of porcine pancreatic gland [2] were: traces of epoxytriglycerides, fatty acids, epoxyoctadecenoic acids, traces of diglycerides, an acyl monoglyceride, an epoxyacyl monoglyceride [TLC/Silufol; solvent system: diethyl ether—hexane (9:1); revealing reagents: picric acid, and sulfuric acid followed by heating; for identification according to mobility we used markers of triglycerides, diglycerides, and epoxy acids].

The weight ratio between the acyl monoglycerides and the epoxyacyl monoglycerides [TLC/silica gel L 5/40 μ; ether—hexane (9:1) system] was 1.8:1.

Products of the mild alkaline hydrolysis of the acyl monoglycerides were: glycerol (TLC/KSK etc., see above) and fatty acids [methylation with diazomethane; GLC (%): $C_{16:0}$, 0.2; $C_{18:1}$, 19.9; $C_{18:2}$, 79.9]. On the basis of the weight ratio of the two monoglycerides, the calculated fatty-acid composition of the total monoglycerides (%) was: $C_{16:0}$, 0.1; $C_{18:}$ 12.8; $C_{18:2}$, 51.4; epoxy-$C_{18:1}$, 35.7.

Below we give the typical triglyceride composition calculated from the four types of fatty acids — palmitic (P), oleic (O), linoleic (L), and epoxyoctadecenoic (E) found by Coleman's method:

α-epoxy-TGs (63.1%)			β-epoxy-TGs (36.9%)	
POE, 1.2	OPE, 0.1	LPE, 0.1	PEP, 0.3	OEO, 2.3
PLE, 4.7	OOE, 3.1	LOE, 8.2	PEO, 1.7	OEL, 12.1
	OLE, 12.6	LLE, 33.1	PEL, 4.5	LEL, 16.0

The results obtained showed that 63% of the epoxyoctadecenoyl residues in the triglycerides isolated are in the α position.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 514-515, July-August, 1978. Original article submitted March 3, 1978.

0009-3130/78/1404-0438$07.50

LITERATURE CITED

1. N. T. Ul'chenko, E. I. Gigienova, and A. U. Umarov, Khim. Prirodn. Soedin., 705 (1976).
2. T. V. Markman, T. V. Chernenko, and A. U. Umarov, Prikl. Biokhim. Mikrobiol., 616 (1969).

QUINONES OF *Salvia sclarea*

A. S. Romanova, A. V. Patudin,
L. N. Pervykh, and L. P. Zobenko

UDC 547.99

We have previously made a qualitative estimate of the presence of quinones in the roots of all species of sage growing in the Soviet Union, finding a definite connection between the presence of quinones of the type of royleanone or tanshinone in the plants and the systematic positions of the corresponding species [1-3]. On comparing the tanshinone-containing species with the aid of thin-layer chromatography it was found that many species differ in the set of substances they obtain.

The comminuted roots of *Salvia sclarea* L. were covered with petroleum ether (1:6), stirred for 15 min and steeped for 12 h. The extract was evaporated in vacuum and a resinous residue was obtained. This operation was repeated three times.

To isolate individual substances, approximately 10 mg of the resinous residue from the petroleum ether fraction was dissolved in 0.5 ml of chloroform and was deposited on a silica gel plate in the form of a number of spots. After chromatography in chloroform, the corresponding bands were removed, the substances were eluted with chloroform, and, after the solvent had been distilled off in vacuum, reddish or orange residues were obtained which were crystallized from chloroform or benzene. The operation was repeated several times. The following substances were isolated from the roots of wild clary sage and were identified:

Isotanshinone (I), $C_{18}H_{12}O_3$ — orange-red crystals, mp 217-219°C, melting point of a mixture with an authentic sample 218-219°C; R_f 0.72 (chloroform, pinkish-orange spot). IR spectrum (paraffin oil, cm^{-1}): 3150, 1660, 1585; UV spectrum (ethanol, nm): 234, 293, 346, 450.

Tanshinone (II), $C_{19}H_{18}O_3$ — red crystals, mp 198-200°C; melting point of a mixture with an authentic sample 198-200°C. R_f 0.53 (chloroform, pink spot). IR spectrum (paraffin oil, cm^{-1}): 3150, 1690, 1670, 1580: UV spectrum (ethanol, nm): 224, 252, 269, 350, 460.

Methyl tanshinonate, $C_{20}H_{18}O_5$ — red crystals with mp 174-176°C, melting point of a mixture with an authentic sample 175-178°C R_f 0.32 (chloroform, pink spot). IR spectrum (paraffin oil, cm^{-1}): 3150, 1725, 1690, 1580; UV spectrum (ethanol, nm): 223, 252, 269, 352, 465.

Hydroxytanshinone, $C_{19}H_{18}O_4$ — red crystals, mp 185-187°C; melting point of a mixture with an authentic sample 185-187°C; R_f 0.13 (chloroform, cherry-red spot); IR spectrum (paraffin oil, cm^{-1}): 3525, 3150, 1685, 1670, 1580; UV spectrum (ethanol, nm): 222, 252, 273, 348, 462.

All these substances have been obtained earlier by Japanese workers from the roots of *Salvia milthiorhiza* Bunge [4].

In addition we isolated another substance consisting, after crystallization from ethanol, of orange-red crystals, $C_{19}H_{18}O_4$, R_f 0.8 (chloroform, pink spot). IR spectrum (paraffin oil, cm^{-1}): 3345, 3070, 1645, 1570; UV spectrum (ethanol, nm): 203, 252 infl., 258.5, 283, 293 infl., 360. Molecular weight 310. The facts given permit the assumption that the substance is new and of the isotanshinone type. We have obtained this substance previously from the roots of Drobov's sage.

LITERATURE CITED

1. A. S. Romanova, A. V. Patudin, G. F. Vlasova, and A. I. Ban'kovskii, Rast. Res., 9, No. 2, 218 (1973).

All-Union Scientific-Research Institute of Medicinal Plants, Moscow. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 515-516, July-August, 1978. Original article submitted March 1, 1978.

0009-3130/78/1404-0439$07.50