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11,12-DEHYDROURSOLIC ACID LACTONE FROM LEAVES OF Eucalyptus viminalis

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We have continued a study of the triterpenoids of the leaves of the ribbon eucalyptus [1]. In addition to ursolic and maslinic acids, according to TLC the chloroform extract contained a less polar triterpenoid with R_f 0.8 (Silufol; chloroform–methanol (9:1)). Liquid-phase extraction of the chloroform extract with 2% sodium hydroxide solution gave the combined acid components, which were partially freed from phenolic components by treatment of a 2% chloroform solution with a 2% solution of sodium bicarbonate (5:3).

The residue was chromatographed successively on OU-A alkaline carbon (1:4), silica gel 40/100 (1:100), alumina (activity grade II, 1:100), and silica gel 40/100 (1:50). The eluents were ethanol, chloroform, chloroform–methanol (9:1), and chloroform, respectively. The presence of a desired substance in the fractions was monitored by TLC in comparison with the extract. Crystallization from petroleum ether gave the compound $C_{30}H_{46}O_3$, mp 270-272°C.

The nature of the coloration on a Silufol plate on visualization with an ethanolic solution of tungstophosphoric acid was typical for 11,12-dehydro derivatives of oleanolic and ursolic acids: a bright orange coloration changing to crimson, and then to greyish green [2]. The IR spectrum contained the absorption band of a γ-lactone (1745 cm^{-1}). The PMR spectrum showed a doublet of doublets at 3.21 ppm, J_1 = 10.1 Hz, J_2 = 5 Hz (H-3). In the weak-field region there were doublets of doublets of a –CH=CH– group at 5.95 ppm, J_1 = 10.25 Hz, J_2 = 1.95 Hz, and at 5.52 ppm, J_1 = 10.25 Hz, J_2 = 3.17 Hz.

The weaker-field signal was due to a proton experiencing additional descreening through the closeness of an oxygen function. Its splitting with a SSCC of 1.95 Hz is characteristic for allyl interaction [3]. Thus, the parameters of the signals mentioned were characteristic for olefinic protons at C-11 and C-12 where a gamma-lactone was present in the 28-13 position. Doublets of two methyl groups of the seven signals of CH_3 groups showed that the compound was an ursolic acid derivative.

The mass spectrum also agreed with the structure of 11,12-dehydroursolic acid lactone. Thus, a peak with m/z 410 (11.22%) corresponded to the ion formed as the result of the elimination of CO_2 from the molecular ion, and peaks with m/z 241 (2.52%) and 169 (14.82%) to the ions formed by the successive cleavage of the C9-C10 and C7-C8 bonds and the migration of a proton (fragments from rings D, E, and A, B, respectively).

The spectral features mentioned, and also the melting point of the acetyl derivative (262°C, decomp.) correspond to the 11,12-dehydroursolic acid lactone isolated previously from the leaves of some eucalypt species other than the ribbon eucalyptus in the form of the acetate [2]. In the PMR spectrum of 11,12-dehydroursolic acid lactone, a doublet of one of the secondary CH_3 groups at 0.97 ppm had components of equal intensitsy, while the ratio of the intensities of the weak-field and the strong-field components of the doublet of another secondary CH_3 group at 0.92 ppm was 1:3. On this basis, it may be concluded that the signal of the methine proton interacting with this CH_3 group was located to the right of its signal, in the stronger field at ~0.85-0.9 ppm, i.e., the methine proton experienced additional screening. This condition would correspond to a proton at C-19 present below the plane of the D ring because of the rigid fixation of ring E due to the γ-lactone grouping. This proton is screened by four simple carbon-carbon bonds: C13-C18, C17-C18, C20-C21, and C20-C30. The signal of H-5 was located in an even stronger field (dd at 0.74 ppm, J_1 = 11 Hz, J_2 = 3 Hz), being screened by seven simple bonds: C3-C4, C6-C7, C1-C10, C10-C9, C4-C23, C4-C24, and C10-C-25. The assignment of the H-5 signal agrees with the literature [4]. The spectrum of the substance was obtained on a Bruker WM-500 instrument.

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INFLUENCE OF INDUSTRIAL OPERATIONS ON THE ISOMERIC COMPOSITION OF THE TOCOPHEROLS IN PRODUCTION OF COTTONSEED OIL

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A special place in the group of biologically active substances participating in the regulation of a number of the most important vital functions belongs to the tocopherols (vitamins of the E group).

One of the promising sources of tocopherols are the wastes from the oils and fats industry. The tar obtained in the distillation of the fatty acids of cottonseed soapstock contains an average of 400-500 mg-% of tocopherols [1]. The amount and, in particular, the isomeric composition of the tocopherols in the tar, may, in the final account, be affected by all the preceeding industrial operations.

The aim of the present work was to study the influence of industrial operations on the isomeric composition of cottonseed tocopherols. The oils and the products of processing the seeds were investigated, the raw material having the following characteristics: contamination – 3.55%; moisture – 8.32%; kernel – 52.60%; husk – 47.40%.

The oils from the seeds, crushed seeds, flakes, meal, and husks were extracted with petroleum ether in a Soxhlet apparatus for 10-12 h. The amounts of tocopherols were determined by thin-layer chromatography followed by colorimetry [2].

Information on the change in the total amount and the isomeric composition of the tocopherols is given in Table 1. In none of the technological stages up to the neutralization of the cottonseed oil is there an appreciable change in the isomeric composition of the tocopherols: the amount of α-tocopherol is 46-47% and that of β- + γ-tocopherols 53-54%. This is explained by the fact that up to the neutralization of the cottonseed oil it undergoes no chemical or prolonged temperature treatment.

In the neutralization stage, the total amount of tocopherols decreases, which is due to their passage into the soapstock and partial oxidation. The amount of α-tocopherol also

TABLE 1. Change in the Amounts of Tocopherols in the Production of Cottonseed Oil

Sample	Oil, % on the abs. dry matter	Unsaponifiable substances, % in the oil	Total amount of tocopherols, mg-%	Individual isomers, % on the total amount of tocopherols	
				α	β+γ
Cotton seeds	18,2	2,8	120,0	46,0	54,0
Crushed seeds	20,0	1,8	122,0	46,3	53,7
Husks	1,5	4,1	34,2	45,0	55,0
Flakes	24,1	2,3	140,0	45,1	54,9
Roasted flake	26,9	2,3	153,0	47,7	52,3
Forepressed oil		2,4	140,0	46,2	53,8
Extraction oil		2,4	144,0	46,7	53,3
Neutralized oil		0,9	115,8	38,0	62,0
Meal	1,1	1,6	73,5	46,7	53,3
Soapstock		4,7	158,5	36,8	63,2
Fatty acids		3,3	—	—	—
Cottonseed tar.		20.0	500.0	33.3	66.7

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