LACTONES FROM LAVENDER OIL PRODUCTION WASTES

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Lavender is one of the main industrially important essential-oil crops. The yield of the essential oil amounts to 1-1.5%, and the remainder of the raw material is regarded as waste.

In the All-Union Scientific-Research Institute of Essential-oil Crops, a technology has been developed for isolating from lavender wastes by the action of volatile solvents, mainly petroleum ether, an extract which is subjected to repeated treatment with ethanol at low temperatures (—15 to —18°C) [1]. After the distillation of the ethanol, the residue forms a product of greasy consistency with a pleasant smell ($d_{20} = 1.02$, $n_{20} = 1.5034$, acid No. 24.3, ester No. 69.65, after acetylation 139.6, unsaponifiables content 26.98% ash content 0.24-0.32%).

In the extraction of lavender wastes with petroleum ether, from the miscella a precipitate forms of substances sparingly soluble in petroleum ether which amounts to 15.20% of the yield of extract and has a melting point of 185-190°C, and an acid number of 62.15, an ester number of 52.15, an iodine number of 33.99, an unsaponifiables content of 13.75%, and an ash content of 2.64% [2]. This precipitate has also been a subject of investigation. It was treated with 0.1 N solutions of NaOH and Na_2CO_3. The aqueous alkaline extracts of the organic substances were saturated with carbon dioxide and extracted with diethyl ether.

The ethereal extract was washed with distilled water, dried with anhydrous sodium sulfate, filtered, and concentrated. The further separation of the concentrate was performed by partition chromatography in a column filled with neutral activated alumina. The separate fractions were isolated by successive elution with various solvents (ethanol, benzene, ethyl acetate, toluene, petroleum ether, diethyl ether). The course of the isolation of the individual fractions was checked by the refractive index. The first two fractions were subjected to reseparation on a column filled with alumina.

The substances isolated were recrystallized from the solvent with which they were isolated and to establish their formulas and structures, we determined their melting points, molecular weights (cryoscopic method) [3], and elementary compositions [4] and recorded their UV and IR spectra (on SP-800 and URION spectrophotometers, respectively).

From the fraction isolated with ethanol, secondary separation on a column filled with alumina yielded a substance $C_9H_6O_3$ with mol. wt. 165.8 and mp 219-222°C. The IR spectrum of the substance had adsorption bands of a hydroxy group (3550, 3400 cm^{-1}) and of an unsaturated ketone (1690 cm^{-1}). On the basis of literature information, the absorption band at 1780 cm^{-1} can be assigned to the carbonyl of a lactone ring [5]. The spectra were recorded at 35°C in KBr tablets: 0.0035 g of substance to 0.3 g of KBr.

A comparative analysis of IR and UV spectra and physicochemical indices enables the substance isolated to be identified as umbelliferone [5]. Compound (II), $C_{10}H_8O_3$, isolated from the same fraction and recrystallized from ethyl acetate, had mp 193-195°C and mol. wt. 178.2. Its IR spectrum was characterized by the following absorption maxima: 1740 cm^{-1} (absorption band of a —C—O group in an ester), 1687 cm^{-1} (absorption band of an unsaturated ketone), and 1775 cm^{-1}, which can be assigned to the absorption band of the carbonyl of a lactone ring.

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A comparison of the IR spectra and physicochemical constants of substances (II) with literature information [5, 6] permitted the substance to be identified as the methyl ether of umbelliferone.

The UV spectra of the other substances were similar to those of (I) and (II), which permitted them also to be assigned to the lactone group.

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ESTERS OF *Cuscuta lehmanniana*

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On studying in the flowering phase the epigeal part of *Cuscuta lehmanniana* Bge (Lehmann's dodder) growing on elms (Ulmus) in the region of Tashkent, we detected substances giving a positive reaction with diazotized sulfanilamide which were not, however, coumarins. For their isolation, the dried and comminuted raw material was extracted with methanol. The extract was concentrated, washed with petroleum ether, and evaporated to dryness. The dry residue obtained was chromatographed on a column filled with KSK silica gel. The column was washed with petroleum ether and mixtures of it with ethyl acetate with gradually increasing concentrations of the latter, 1-liter fractions being collected. Fractions 4-8 yielded a crystalline substance (I) with the composition $C_{10}H_{10}O_3$, mp 139°C, M^+ 178, R_f 0.62 (chromatography on Silufol; petroleum ether—ethyl acetate (3:1) system; spots revealed with the diazo reagent). On the basis of spectral characteristics (UV, IR, NMR, and mass spectra) and also of the saponification products, (I) was identified as the known methyl p-coumarate [1]. Fractions 10-12 yielded substance (II) with the composition $C_{25}H_{40}O_4$, mp 94-97°C (from petroleum ether), M^+ 404, R_f 0.59, which we have called cuscutin.

UV spectrum: λ_{max} 235, 248, 305, 335 nm (log ε 4.06, 4.08, 4.12, 4.26); in the presence of alkali it gave a bathochromic shift by Δ55 nm, showing the presence of a free phenolic hydroxyl.

The IR spectrum had bands at (ν_{max}, cm^{-1}) 3490 and 3350 (hydroxy groups), 1690 (carbonyl of an ester of an unsaturated acid), 1640, 1605, 1585 (aromatic nucleus).

The NMR spectrum of cuscutin showed signals from the protons of a 1,3,5-trisubstituted benzene ring: singlets at 7.20, 6.95, and 6.84 ppm (1H each), and also of two olefinic protons from a trans-hydroxycinnamic acid residue — doublets at 7.55 and 6.22 ppm, J = 15.5 Hz (1H each); a triplet at 4.17 ppm (2H) corresponds to the hemiacyl protons of the alcoholic moiety. In the strong field there are the signals of methylene protons at 1.21 ppm (29H) and a triplet at 0.84 ppm (3H — primary methyl group). On saponification with alkali, cus-

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