The ^{13}C NMR spectra were obtained on a Bruker WP-200 SY/50.3 MHz instrument with DMSO-d_6 as solvent.

SUMMARY

The ^{13}C NMR spectra of the coumarins obtuginin, capensin, and fraxetin-7-O-β-D-glucopyranoside have been studied. Some peculiar features of the spectra have been noted. A complete assignment of the signals in the ^{13}C NMR spectra of the coumarins studied has been made and their structures have been confirmed.

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STRUCTURE OF THE NEW MONOTERPENOID LIGANOLIDE

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The structure of the new ester liganolide $C_{27}H_{38}O_8$, isolated from the roots of <u>Ligularia thomsonii</u> has been established by x-ray structural analysis. Ligano-lide is a monoterpenoid including a six-membered ring with substituents at C(2), C(3), and C(4), and an epoxy group at C(1) and C(6).

A new ester — liganolide, $C_{27}H_{38}O_8$ (M^+ 490), mp 95-96°C (from hexane) — has been isolated by the petroleum ether extraction of the roots of <u>Ligularia thomsonii</u> (Clarke) Pojark, collected in the Chimgan area (Tashkent oblast). Its IR spectrum had absorption bands (ν_{max}^{KBr}) at 1743, 1720, 1710, 1235, and 1260 cm^{-1}, corresponding to —OCOCH$_3$ and OCO—C=C groups, and at 1645 cm^{-1} corresponding to a C=C group. The ^{13}C NMR spectrum (CDCl$_3$) had the following signals (ppm): 8 CH$_3$ — 2 × 15.03, 18.34, 18.93, 19.62, 19.81, 20.01, 24.01; 3 CH$_2$ — 25.28, 33.00, 114.54; 8 CH — 37.67, 58.86, 60.04, 67.87, 71.57, 73.92, 2 × 137.80; 6 C — 2 × 55.85, 57.31, 126.94, 127.13, 145.79; 2 C=O — 165.91, 169.22.

Thus, from these facts, which correspond to $C_{27}H_{38}O_4$ in the composition of liganolide, it is impossible to deduce the function of the other four oxygen atoms; moreover it is impossible to decide the main question — to determine the mutual positions of the functional groups found and the spatial structure.

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*Deceased.

TABLE 1.   Coefficients of the Equations X + By + Cz = D of the Main Planes of the Fragments of the (I) Molecule and the Deviation of the Atoms (σ) from the Planes

Plane	Atom	σ, Å	A	B	C	D
Six-membered ring	C (1)	0,01	−11,00	−1,27	0,69	6,90
	C (2)	0,00				
	C (5)	0,00				
	C (6)	0,01				
	C (3)	−0,43				
	C (4)	0,37				
1	C (19)	−0 01	9,35	2,98	0,30	−7,91
	C (20)	0,02				
	C (21)	−0,01				
	C (22)	−0,01				
	C (23)	0,00				
2	O (5)	−0,03	10,30	1,75	0,27	−7,40
	O (6)	0,00				
	C (10)	0,02				
	C (19)	0,00				
	C (20)	0,02				
3	C (11)	0,01	−8,65	14,92	7,10	−1,10
	C (13)	0,00				
	C (14)	−0,01				
	C (15)	0,02				
	C (16)	−0,02				
4	O (2)	−0,01	−8,21	10,74	4,86	−6,22
	C (11)	0 04				
	C (12)	−0,02				
	C (13)	−0,01				
5	C (4)	0,00	7,56	15,79	9,65	−1,35
	C (8)	−0,01				
	C (9)	0,00				
	C (10)	0,00				
6	C (3)	−0,03	10,82	3,47	4,30	6,81
	O (3)	0 04				
	O (4)	0,00				
	C (17)	−0,02				
	C (18)	0,00				

TABLE 2.   Interatomic Distances

Distance	r	Distance	r	Distance	r
C (1) — C (2)	1,49	C (6) — O (1)	1,45	C (17) — C (18)	1,45
C (1) — C (6)	1,51	C (8) — C (9)	1,33	C (19) — O (5)	1,31
C (1) — C (7)	1,51	C (8) — C (10)	1,54	C (19) — O (6)	1,24
C (1) — O (1)	1,45	C (10) — O (5)	1,48	C (19) — C (20)	1,49
C (2) — C (3)	1,53	C (10) — O (7)	1,56	C (20) — C (21)	1,49
C (2) — O (2)	1,44	C (11) — C (12)	1,16	C (20) — C (22)	1,37
O (2) — C (11)	1,37	C (11) — C (13)	1,56	C (22) — C (23)	1,47
C (3) — C (4)	1,54	C (13) — C (14)	1,56	C (24) — O (7)	1,49
C (3) — O (3)	1,43	C (13) — C (15)	1,30	C (24) — O (8)	1,44
C (4) — C (5)	1,52	C (15) — C (16)	1,45	C (24) — C (25)	1,46
C (4) — C (8)	1,49	C (17) — O (3)	1,39	C (25) — O (8)	1,43
C (5) — C (6)	1,51	C (17) — O (4)	1,20	C (25) — C (26)	1,54
				C (25) — C (27)	1,49

In order to determine the structure of liganolide (I) unambiguously, we have made an x-ray structural investigation of it the results of which have enabled structure (I) to be established and all the stereochemical aspects of this structure to be considered.
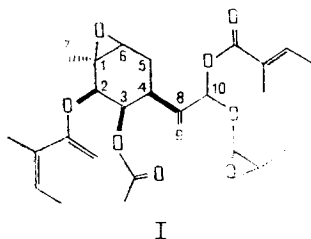

I

TABLE 3. Valence Angles (ω, degrees)

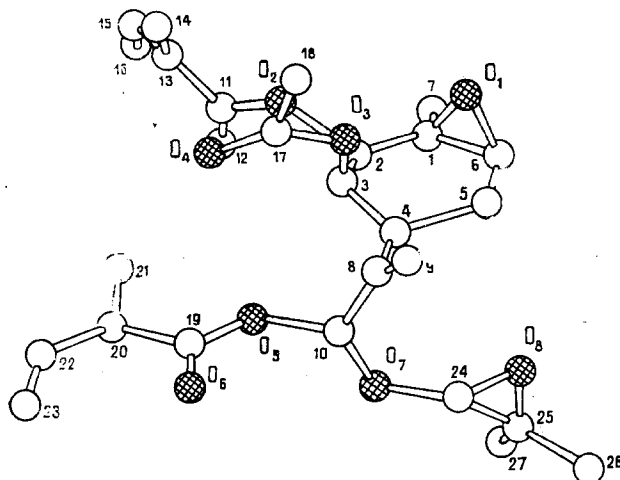| Angle	ω	Angle	ω	Angle	ω
C(1)—O(1)—C(6)	62,6	C(3)—C(4)—C(8)	109,2	O(3)—C(17)—O(4)	121,2
C(2)—O(2)—C(11)	116,9	C(8)—C(4)—C(5)	113,1	O(3)—C(17)—C(18)	110,4
C(3)—O(3)—C(17)	116,6	C(4)—C(5)—C(6)	113,4	O(4)—C(17)—C(18)	128,3
C(21)—O(5)—C(19)	116,2	C(5)—C(6)—C(1)	123,3	O(5)—C(19)—O(6)	123,4
C(10)—O(7)—C(24)	111,1	O(1)—C(6)—C(1)	58,7	O(5)—C(19)—C(20)	109,2
C(24)—O(8)—C(24)	61,2	O(1)—C(6)—C(5)	116,1	O(6)—C(19)—C(20)	127,4
C(2)—C(1)—C(6)	115,6	C(10)—C(8)—C(4)	117,3	C(19)—C(20)—C(21)	119,5
C(2)—C(1)—C(7)	118,7	C(10)—C(8)—C(9)	114,0	C(19)—C(20)—C(22)	119,9
C(6)—C(1)—C(7)	118.7	C(4)—C(8)—C(9)	128,7	C(22)—C(20)—C(21)	120,6
O(1)—C(1)—C(6)	58,8	O(5)—C(10)—O(7)	106,1	C(20)—C(22)—C(23)	127,4
O(1)—C(1)—C(2)	114 8	O(5)—C(10)—C(8)	107,5	O(8)—C(24)—O(7)	115,9
O(1)—C(1)—C(7)	116,1	O(7)—C(10)—C(8)	114,1	O(8)—C(24)—C(25)	59,3
C(3)—C(2)—C(1)	117,8	O(2)—C(11)—C(12)	124,4	O(7)—C(24)—C(25)	122,9
O(2)—C(2)—C(1)	108,6	O(2)—C(11)—C(13)	106,9	O(8)—C(25)—C(24)	59,5
O(2)—C(2)—C(3)	108,1	C(13)—C(11)—C(12)	128,3	O(8)—C(25)—C(27)	112,6
C(2)—C(3)—C(4)	108,8	C(11)—C(13)—C(15)	115,9	O(8)—C(25)—C(26)	116,1
O(3)—C(3)—C(4)	1'8,2	C(11)—C(13)—C(14)	116,0	C(24)—C(25)—C(27)	120,7
O(3)—C(3)—C(2)	109,3	C(15)—C(13)—C(14)	127,9	C(24)—C(25)—C(26)	121,7
C(3)—C(4)—C(5)	112,4	C(13)—C(15)—C(16)	132,7	C(27)—C(25)—C(26)	113,8

Fig. 1. Spatial structure of the liganolide molecule.

The spatial structure of (I) is shown in Fig. 1 as a projection on the (010) plane. Liganolide is a monoterpenoid and includes a six-membered saturated ring with various substituents in the C(2), C(3), and C(4) positions and an epoxy group in the C(1) and C(6) positions. The conformation of the ring and the spatial arrangement of the functional groups can be judged from Table 1, which gives the coefficients of the equations of the main planes and the deviations of the atoms from them. The six-membered ring has a half-chair conformation: the C(1), C(2), and C(6) atoms are present in one plane and the C(3) and C(4) atoms depart from it in opposite directions by 0.43 and 0.37 Å, respectively. The relative orientations of the functional groups in the ring are as follows: the Me group at C(1) is α-oriented and the substituents at the C(2), C(3), and C(4) asymmetric centers and also the epoxy group in the C(1)-C(6) position are β-oriented. The angles between planes 1 and 2 and between planes 3 and 4 are 0.9 and 0.8°, respectively, which favors the conjugation of

the π-electron systems in the substituents $CH_2=C-C=CH-CH_3$ and $CH_3-CH=C-C-O-$.
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\;\; |\quad\;\; |\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad -O\quad CH_3\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad O$

The double bonds in these groups have the cis arrangement relative to the ordinary C—C bond.

The $>CH-\overset{\overset{\displaystyle CH_2}{\|}}{C}-CH<$ and CH_3COO- groups are coplanar with accuracies of 0.04 and 0.01

TABLE 4. Coordinates of the Atoms (×10⁴) in the Structure of (I)

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
O (1)	2430 (10)	—0964 (5)	6478 (4)	C (11)	0816 (12)	—0815 (8)	4350 (5)
O (2)	1733 (8)	—0870 (5)	4877 (4)	C (12)	0003 (12)	0283 (6)	4339 (6)
O (3)	4088 (8)	—0346 (6)	5381 (4)	C (13)	1009 (12)	—1657 (7)	3848 (6)
O (4)	4550 (11)	—0250 (8)	4198 (5)	C (14)	2409 (14)	—2016 (10)	3776 (8)
O (5)	3770 (8)	2220 (5)	4601 (3)	C (15)	—0023 (16)	1094 (9)	3564 (7)
O (6)	5069 (10)	3241 (7)	4075 (4)	C (16)	—1364 (13)	—1774 (8)	3645 (9)
O (7)	3434 (13)	3185 (8)	5644 (5)	C (17)	4801 (13)	—0567 (8)	4776 (7)
O (8)	3406 (13)	2927 (6)	6963 (4)	C (18)	5760 (14)	—1240 (8)	4953 (7)
C (1)	1438 (10)	—0462 (6)	6102 (5)	C (19)	4232 (11)	2646 (8)	4038 (5)
C (2)	1805 (11)	—0125 (7)	5374 (5)	C (20)	3602 (11)	2293 (8)	3380 (6)
C (3)	3112 (11)	0325 (7)	5289 (5)	C (21)	2702 (8)	1513 (6)	3437 (4)
C (4)	3272 (11)	1048 (7)	5879 (5)	C (22)	3830 (10)	2701 (7)	2729 (5)
C (5)	3215 (10)	0643 (6)	6620 (6)	C (23)	4717 (12)	3454 (7)	2575 (5)
C (6)	2156 (11)	—0045 (6)	6723 (4)	C (24)	3888 (10)	3457 (6)	6373 (5)
C (7)	0085 (12)	—0784 (8)	6223 (7)	C (25)	3050 (10)	3867 (6)	6910 (4)
C (8)	4463 (13)	1574 (9)	5743 (6)	C (26)	3587 (12)	4427 (8)	7503 (6)
C (9)	5645 (10)	1389 (7)	5954 (7)	C (27)	1636 (10)	4059 (9)	6754 (7)
C (10)	4342 (11)	2460 (7)	5302 (5)				

Å, respectively. The lengths of the bonds and the values of the valence angles are given in Tables 2 and 3. The lengths of the ordinary $C_{sp^3}-C_{sp^3}$ bonds vary in the interval of 1.49-1.56 Å, i.e., within the limits of the experimental error of 0.02 Å they agree with the standard values [1]. No anomalous deviations are observed in the values of the valence angles (the starting deviations of their determination are not greater than 1°).

EXPERIMENTAL

IR spectra were taken on a UR-20 spectrophotometer (KBr); ^{13}C NMR spectra on a Varian CFT-20 spectrometer at a frequency of 200 MHz in $CDCl_3$, internal standard — TMS and mass spectra on a MKh 1310 instrument.

Isolation of Liganolide. The air-dried ground roots of Thomson golden ray (2 kg were extracted by the steeping method at room temperature four times for 12 h each time. The extracts were combined and concentrated. Crystals of liganolide, $C_{27}H_{38}O_8$, deposited in the concentrated extract. Single crystals of liganolide for x-ray structural analysis were grown from hexane solution. The space group and the parameters of the elementary cell were determined by the photometric method. The parameters were refined on a Sintex $P2_1$ diffractometer (Institute of Biorganic Chemistry of the UzSSR Academy of Sciences, with the participation of B. T. Ibragimov), using Cu K_α radiation: $a = 10.488$, $b = 14.884$, $c = 18.612$ Å; space group $P2_12_12_1$, $z = 4$, $d_{calc} = 1.126$ g/cm³. A three-dimensional set of intensities was obtained on the diffractometer mentioned, and 1546 reflections exceeding 2σ were used in the calculations. The structure was refined by the direct method using the Rentgen-75 program [2] in the automatic regime. The number of triple products obtained was 5250, the reference groups consisting of 10 reflections. An E-series was constructed from the best variant of the signs, and the nonhydrogen atoms were found in this (R factor 0.278). The structure was refined by the method of least squares (MLS), initially in the isotropic and then in the anisotropic approximation to R = 0.105. In order to find the coordinates of the hydrogen atoms, in the last stage of the MLS density difference syntheses were calculated. Only 21 hydrogen atoms out of the 38 were localized. The coordinates of the basis atoms from the last stage of the MLS (R = 0.089) are given in Table 4.

SUMMARY

The spatial structure of the monoterpenoid liganolide has been established on the basis of IR, mass, and ^{13}C NMR spectra and x-ray structural analysis.

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