di-O-methyl-L-rhamnopyranose, (T_{rel} = 0.94); 2,3,4-tri-O-methyl-D-xylopyranose (T_{rel} = 0.46; 0.39); and 3,4-di-O-methyl-L-arabitol (T_{rel} = 2.68).

Periodate Oxidation of Medicoside J (I). A solution of 50 mg of glycoside (I) in 5 ml of 5% $NaIO_4$ was left at roomtemperature for 4 h. Then chloroform was added and the precipitate that deposited was separated off and was analyzed with the aid of GLC as described in [3]. No sugars were detected.

SUMMARY

The roots of Medicago sativa L. (family Fabaceae) have yielded a new triterpene glycoside – medicoside J – for which the structure of medicagenic acid 3-O-β-D-glucopyranoside 28-O-[O-β-D-xylopyranosyl-(1 → 4)-O-α-L-rhamnopyranosyl-(1 → 2)-β-L-arabinopyranoside) has been established.

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TRITERPENE GLYCOSIDES OF Astragalus AND THEIR GENINS.

XXI. CIRCULAR DICHROISM OF CYCLOARTANE KETONES

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The CD spectra of a number of natural and synthetic cycloartane ketones have been studied. The influence of 6α-hydroxy group on the Cotton effect due to a 3-keto function has been found. The Cotton effect has been determined for 6-oxo- and 11-oxocycloartanes.

In the present paper we consider some features of the circular dichroism (CD) spectra of cycloartane ketones.

In the CD spectra of oxocycloartanes a Cotton effect is observed in the 280-320 nm region which is due to the $n \rightarrow \pi^*$ transition in the carbonyl function. It is known that 3-oxocycloartanes unsubstituted in ring B are characterized by a negative Cotton effect. For example, in the case of cycloartenone (cycloart-24-en-3-one) an effect is observed at 315 nm ($\Delta\varepsilon$ = −0.99) [1], and in the case of the 3-oxo derivative (II) one at 296 nm ($\Delta\varepsilon$ = −1.39) (Table 1 and Fig. 1a). At the same time, as follows from the CD spectra of the 6α-hydroxy-3-oxocycloartanes (III-VI and VIII), the effect due to the 3-oxo function acquires a complex form: on the long-wave side (315-322 nm) a negative minimum appears, and in the region of shorter waves (280-290 nm) a positive maximum. This change in the nature of the CD curve is obviously caused by the presence of the 6α-hydroxy group [2]. Actually, one of the factors responsible for the negative sign of the effect for 4,4-dimethyl-3-oxo-5α-steroids is the interaction of the 4α-CH_3 group with the 6α-H atom [3]. There is no doubt that the replacement of the 6α-hydrogen atom by a hydroxy group will lead to a distortion

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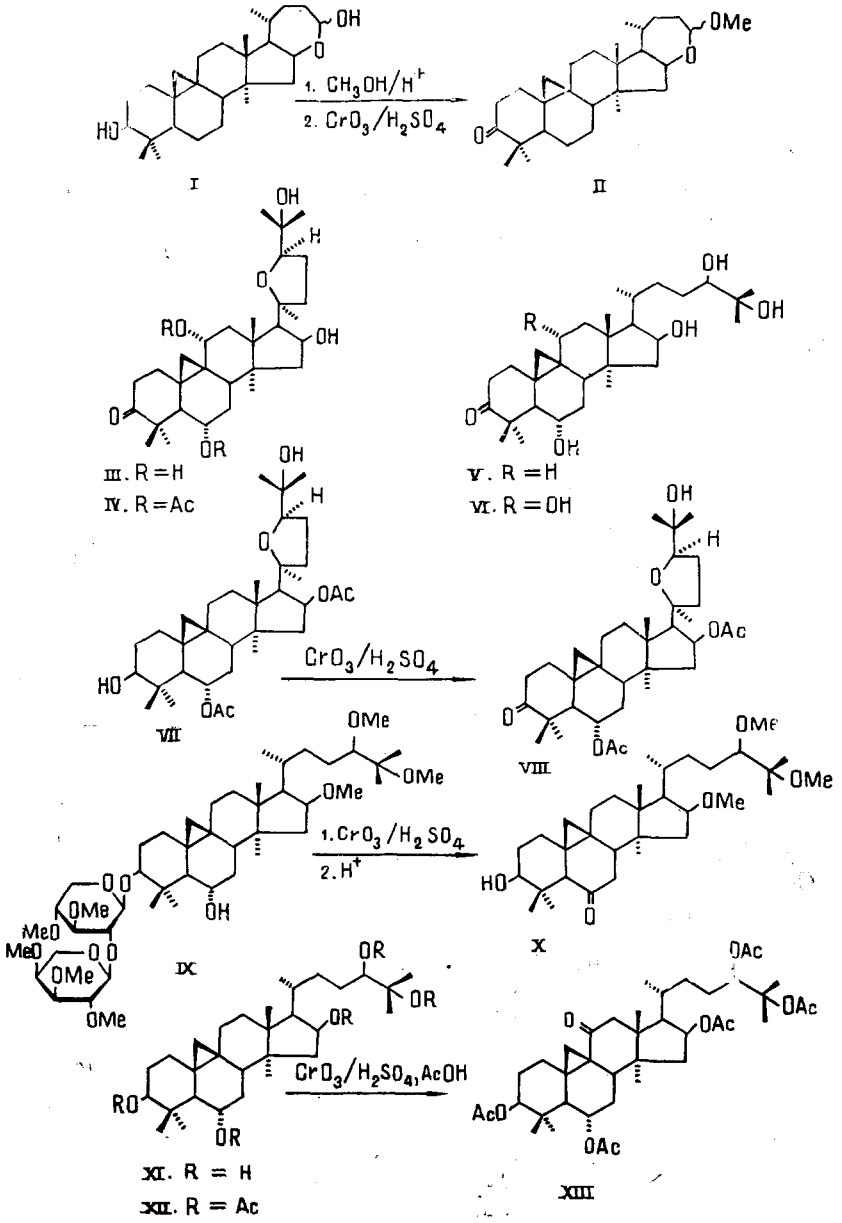
of the original conformation and, as a consequence, to a change in the shape of the CD curve. Another confirmation of the influence of a 6α-OH group on the conformational features of rings A and B may be the fact that when the hydroxyl under consideration is acetylated there is a mutual approach of the absolute values of the extrema in the CD curve (compounds (IV) and (VIII)).

6-Oxocycloartane (X) and 11-oxocycloartane (XIII) exhibit positive Cotton effects on the CD curve at 310 and 297 nm, respectively (Fig. 1, b).

The methylation of the semiacetal (I) [4] with methanol containing 0.5% of sulfuric acid followed by Jones oxidation [5] led to the 3-oxo-25-norcycloartane (II) (M^+ 428). The presence of the absorption band of a keto function in the IR spectrum of the latter and also a three-proton singlet observed in the PMR spectrum at 3.36 ppm showing the presence of methoxy group determined compound (II) as 24-methoxy-16β,24ξ-epoxy-25-norcycloartanone.



The 3-oxo derivative (VIII) was obtained by the Jones oxidation [5] of the diacetate (VII) [2]. Substance (VIII) had a molecular weight, M^+, of 572. In the mass spectrum of this compound the maximum peak was that of an ion with m/z 143, showing that the side chain had not changed. The PMR spectrum of the oxo derivative (VIII) lacked the H-3 signal, and at 3.64 ppm the resonance lines of H-24 were traced. Consequently, substance (VIII) had the structure of 6α,16β-diacetoxy-25-hydroxy-20S,24R-epoxycycloartan-3-one.

TABLE 1. Extrema on the Circular Dichroism Curves of Some Cycloartane Ketones [$\Delta\varepsilon(\lambda)$]

Compound	Cotton effect of the oxo group		
	C=O at C-3		C=O at C-6 & C-11
II	−1,39 (296 nm)	—	—
III	+1,44 (287 nm)	−0,1 (320 nm)	—
IV	+0,30 (280 nm)	0,28 (315 nm)	—
V	+1,60 (287 nm)	−0,04 (322 nm)	—
VI	+1,03 (290 nm)	−0,04 (318 nm)	—
VIII	+0,35 (283 nm)	−0,22 (315 nm)	—
X	—	—	+0,54 (310 nm)
XIII	—	—	+0,32 (297 nm)

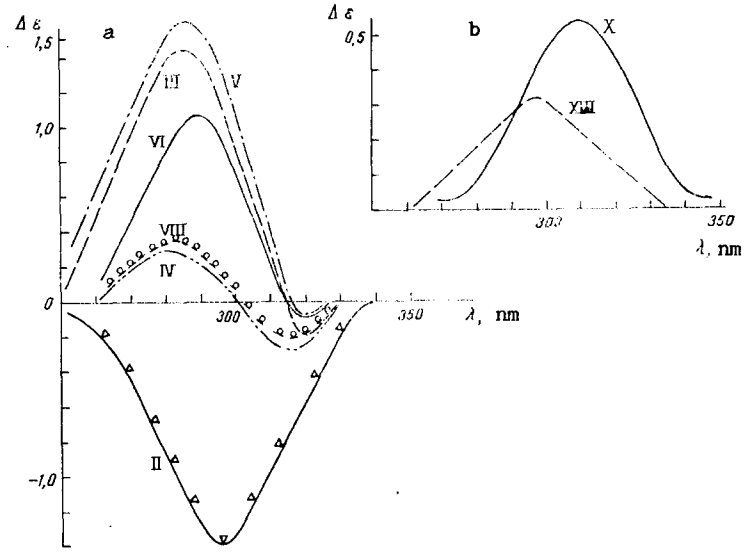


Fig. 1. CD curves of compounds (II-VI, VIII, IX, and XIII).

To elucidate the nature of the CD curve of the 6-oxocycloartanes, compound (X) was obtained. The Jones oxidation [5] of the octa-O-methyl derivative of askendoside C (IX), described previously [6], followed by acid hydrolysis led to the formation of compound (X) with M^+ 532, the IR spectrum of which contained an absorption band at 1705 cm^{-1}. As was to be expected, the PMR spectrum of compound (X) lacked the H-6 signal. The facts given determine substance (X) as 3β-hydroxy-16β,24,25-trimethoxy-24R-cycloartan-6-one.

The acetylation of cycloasgenin C (XI) gave the pentaacetate (XII) [7]. In order to introduce an oxo group into position 11, the pentaacetate (XII) was oxidized with the Jones reagent [5] in glacial acetic acid at room temperature. The oxidation product (XIII) (M^+ 716) had an absorption band in its IR spectrum at 1680 cm^{-1} which is characteristic for a conjugated ketone. The PMR spectrum of the substance under consideration, containing two doublets of a AB system at 2.37 and 2.52 ppm with ^2J = 17 Hz (2 H-12) showed that the oxo function was located at C-11.

EXPERIMENTAL

General Remarks. The following solvent systems were used: benzene—ethyl acetate (2:1) and 2) benzene—ethyl (3:1).

PMR spectra were recorded on Varian XL-200, Bruker WP-200, and JNM-4H-100-100 MHz instruments in deuterochloroform (δ, ppm; 0 − HMDS).

Circular dichroism curves were measured on a Jasco J-20 spectropolarimeter.

24-Methoxy-16β,24ξ-epoxy-25-norcycloartan-3-one (II) from (I). Norcycloartane (I) (17 mg, for its preparation see [4]) was dissolved in 4 ml of methanol containing 0.5% of sulfuric acid, and the solution was heated at 40°C for 8 h and was left at room temprature

for 12 h. Then it was poured into water and extracted with chloroform. The residue after the evaporation of the chloroform was dissolved in 5 ml of acetone, 0.05 ml of the Jones reagent [5] was added, and the mixture was stirred at 0°C for 10 min. Then 1 ml of methanol was added and the mixture was diluted with water and treated with chloroform. The solvent was distilled off and the residue was recrystallized from ethanol, giving 9.3 mg of ketone (II), $C_{28}H_{44}O_3$, mp 195-197°C, $[\alpha]_D^{21}$ + 80 ± 2° (c 0.3; chloroform–methanol (1:1)). ν_{max}^{KBr}, cm^{-1}: 3040 (CH_2 of a cyclopropane ring), 1710 (C=O at C-3). CD (c 0.1; methanol) $\Delta\varepsilon$ = −1.39 (296 nm). Mass spectrum, m/z (%): M^+ 428 (75.0), 413 (19.4), 396 (61.1), 381 (27.7), 311 (47.2), 290 (100), 219 (25.0), 177 (55.6). PMR ($CDCl_3$): 0.57 and 0.87 (1 H each, 2 H-19, d, ^2J = 4 Hz); 0.89 (3 H, s, CH_3); 0.93 (3 H, d, ^3J = 6.5 Hz, CH_3-21); 1.03, 1.09, 1.15 (3 H each, s, 3 × CH_3); 3.36 (3 H, s, OCH_3); 4.12 (2 H, m, H-16 and H-24).

6α,16β-Diacetoxy-25-hydroxy-20S,24R-epoxycycloartan-3-one (VIII) from (VII). A solution of 300 mg of cyclosiversigenin (VI); for preparation see [2]) in 50 ml of acetone at 0°C was treated with 1 ml of the Jones reagent [5] and the mixture was stirred for 10 min. After this, it was poured into 200 ml of water containing 1 g of sodium sulfite. The reaction products were extracted with chloroform. The residue after the appropriate working up of the chloroform extract and evaporation of the solvent was chromatographed on a column with elution by system 1. In this way, 60 mg of the noncrystalline substance (VIII) was isolated, $C_{34}H_{52}O_7$, $[\alpha]_D^{24}$ + 129.7 ± 2° (c 0.37; methanol), ν_{max}^{KBr}, cm^{-1}: 3570-3450 (OH), 1745-1700, 1255 (C=O at C3 and ester groups). CD (c 0.1; methanol): $\Delta\varepsilon$ = −0.22 (315 nm); $\Delta\varepsilon$ = +0.48 (283 nm). Mass spectrum, m/z (%): M^+ 572 (0.2), 557 (7.1), 554 (2.8), 513 (16.1), 437 (13.1), 393 (50.0). 201 (25,0), 143 (100). PMR ($CDCl_3$): 0.45 and 0.70 (each 1H, 2H-19, d, ^2J = 4 Hz), 0.95 (3H, s, CH_3), 1.04 (3H, s, CH_3), 1.09 (3H, s, CH_3), 1.10 (3H, s, CH_3), 1.15 (3H, s, CH_3), 1.26 (6H, s, 2 × CH_3), 1.96 (6H, s, 2 × CH_3COO), 3.64 (H-24, t), 4.61 (H-6, m), 5.33 (H-16, m).

3β-Hydroxy-16β,24,25-trimethoxy-24R-cycloartan-6-one (X) from (IX). A solution of 616 mg of the octamethyl ether of askendoside C (IX; for preparation, see [6]) in 40 ml of acetone at −8°C was treated with 0.6 ml of the Jones reagent [5], and the mixture was stirred at the same temperature for 1 h. Then it was stirred at room temperature for another 15 min. The excess of oxidant was decomposed by the addition of 5 ml of methanol. After dilution with 200 ml of water, the reaction products were extracted with chloroform. The residue after the appropriate working up and evaporation of the chloroform extract was dissolved in 55 ml of 0.5% methanolic sulfuric acid and the solution was heated at 60°C for 8 h. Then it was evaporated to a volume of 20 ml and was diluted with 150 ml of water, and the remaining methanol was evaporated off. The precipitate that deposited was separated off and chromatographed on a column with elution by system 2. This gave 180 mg of substance (X), $C_{33}H_{56}O_6$, mp 154-155°C (from ethyl acetate), $[\alpha]_D^{27}$ + 74.3 ± 2° (c 0.7; methanol) ν_{max}^{KBr}, cm^{-1}: 3500-3450 (OH), 3060 (CH_2 of a cyclopropane ring), 1705 (C=O at C-6). CD (c 0.1; methanol): $\Delta\varepsilon$ = +0.54 (310 nm). Mass spectrum, m/z (%): M^+ 532 (18.2), 517 (2.6), 514 (2.6), 500 (9.1), 489 (6.5), 485 (10.4), 427 (15.6), 395 (10.4), 327 (7.8), 256 (14.3), 213 (18.2), 149 (100). PMR ($CDCl_3$): 0.16 and 0.66 (each 1H, 2H-19, d, ^2J = 4 Hz), 0.80 (3H, s, CH_3), 0.84 (3H, d, ^3J = 6 Hz, CH_3-21), 0.92 (3H, d, CH_3), 1.22 (3H, s, CH_3), 2.84 (H-24, t), 3.14 (3H, s, OCH_3), 3.16 (3H, s, OCH_3), 3.20 (H-3, m), 3.40 (3H, s, OCH_3), 3.76 (H-16, m).

3β,6α,16β,24,25-Pentaacetoxy-24R-cycloartan-11-one (XIII) from (XI). Cycloasgenin C (XI; 1.008 g) was acetylated with 10 ml of acetic anhydride in 20 ml of pyridine at 100°C for 50 h. The reaction products after the usual working up were chromatographed on a column with elution by system 2. This gave 1.210 g of the pentaacetate (XII), $C_{40}H_{62}O_{10}$, mp 200-202°C (from ethanol), $[\alpha]_D^{25}$+ 120 ± 2° (c 0.1; methanol) [7].

The Jones reagent [5] (4 ml) was added to 1.1 g of the pentaacetate in 66 ml of glacial acetic acid, and the mixture was left at room temprature for 20 h. Then 4 ml of methanol was added, after which the reaction products were extracted with chloroform. The residue after the chloroform had been distilled off was chromatographed on a column with elution by system 2. Rechromatography in the same system of the products obtained yielded 626 mg (62%) of substance (XIII), $C_{40}H_{60}O_{11}$, mp 193-195°C (from ethanol), $[\alpha]_D^{22}$ + 147 ± 2° (c 0.72; methanol). ν_{max}^{KBr}, cm^{-1}: 3065 (CH_2 of a cyclopropane ring); 1740, 1250 (ester groups); 1680 (C=O at C-11). CD (c 0.12; methanol): $\Delta\varepsilon$ = +0.32 (297 nm). Mass spectrum, m/z (%): M^+ 716 (2.9), 656 (42.9)

614 (10.7), 596 (64.3), 554 (27.4), 536 (44.0), 494 (42.9), 476 (21.4), 434 (23.8), 427 (17.9), 367 (35.7), 307 (100), 259 (42.9), 215 (85.7), 199 (64.3). PMR ($CDCl_3$): 0.80 (3H, s, CH_3), 0.87 (3H, d, ^3J = 6 Hz, CH_3-21), 0.89 (3H, s, CH_3), 0.94 (3H, s, CH_3), 1.01 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1.41 (3H, s, CH_3), 1.89 (3H, s, CH_3COO), 1.95 (3H, s, CH_3COO), 1.99 (6H, s, 2 × CH_3COO), 2.01 (3H, s, CH_3COO), 2.37 and 2.52 (each 1H, d, ^2J = 17 Hz, 2H-12), 4.52 (1H, q, $^3J_1$ = 12 Hz, $^3J_2$ = 5 Hz, H-3), 4.77 (1H; td, $^3J_1$ = $^3J_2$ = 8 Hz, $^3J_2$ = 4 Hz, H-6), 4.98 (1H, q, $^3J_1$ = 11 Hz, $^3J_2$ = 3 Hz, H-24), 5.28 (1H, sx, $W_1/_2$ = kk,5 Hz, H-16).

SUMMARY

The Cotton effect has been determined for 6-oxo- and 11-oxocycloartanes. A 6α-hydroxy group imparts a complex form to the Cotton effect due to a 3-oxo function, separting it into two components: negative at 315-322 nm and positive at 280-290 nm.

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STRUCTURE OF CONVOSINE

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From the roots of the plant Convolvulus subhirsutum Regel et Schmalh. have been isolated seven known alkaloids and one new one, for which, on the basis of spectral characteristics, a comparative study with known alkaloids of the tropane series, and synthesis, the structure of (+)-N-isopropyl-3α-veratroyloxynortropane has been established.

The combined alkaloids have been isolated in an amount of 2.68% on the weight of the air-dry material from the roots of Convolvulus subhirsutum Regel et Schmalh. collected in the environs of Dzhilga, Chimkent province, KazSSR in the phase of the vigorous growth of the plant [4].

By separating the mixture of bases into phenolic and nonphenolic fractions and treatment of the nonphenolic fraction with citrate-phosphate buffer solution, and also by chromatography on a column of alumina, seven bases have been isolated: convolvine and convolamine [1], for the first time from this plant, and phyllalbine, convolidine [3], confoline, convoline [5], and subhirsine [6].

Continuing the separation of the mother liquors from the combined alkaloids by chromatography on a column of alumina, from ethereal eluates we isolated a minor base with mp 103-104°C which differed in its R_f values and spectral characteristics from the bases isolated previously, and we have called it convosine (I). The IR spectrum of convosine contains

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