CYCLIZATION AND REARRANGEMENT OF DITERPENOIDS.

VII. COMPOSITION OF THE HYDROCARBON FRACTION OF A MIXTURE OF THE PRODUCTS OF CYCLIZATION OF MANOOL AND SCLAREOL BY ORDINARY ACIDS

N. D. Ungur, A. N. Barba, and P. F. Vlad

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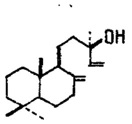
The hydrocarbon fractions of the products of the cyclization of manool and sclareol by a mixture of conc. sulfuric and formic or acetic acids have been investigated. It has been established that they contain, in addition to the $\Delta^{8}/^{9}$-pimaradiene, $\Delta^{8}(^{9})$-isopimaradiene, roasadiene, and 13-epirosadiene identified previously, the tetracyclic hydrocarbons (1R, 2S, 7S, 11S, 12R, 13R)-2, 6, 6, 11, 13-pentamethyltetracyclo $[10.2.1.0^{1.10}.0^{2.7}]$pentadeca-9-ene and (1S, 2R, 11S, 12R, 1R)-2, 7, 7, 11, 15-pentamethyltetracyclo$[10.2.1.0^{2.11}.0^{3.8}]$pentadeca(8)-ene.

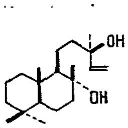
We have shown previously [1] that the fraction of oxygen-containing compounds produced by the cyclization of a number of labdane alcohols – manool (I), sclareol (II), and others – and their acetates by a mixture of conc. sulfuric and formic acids consists of the alcohols (III-VII) and their formates. We did not investigate the hydrocarbon fraction, since it was established [1] that the fraction of oxygen-containing substances produced by the cyclization of manool by a mixture of aqueous acetic and sulfuric acids under the conditions given in [2, 3] contained the same compounds (III)-(VII), and it was logical to assume that the hydrocarbon fractions of the cyclization products obtained under the conditions of [1] and of [2, 3] would have identical qualitative compositions, although they were not given in [2, 3].

Later, [4, 5] we found that the alcohols (V) and (VI) gave a mixture of the hydrocarbons (VIII) and (IX) under the action of common acids. It was therefore possible to assume that the latter are also present in the products of the cyclization of labanoids by common acids. To check this hypothesis, we have made a detailed study of the hydrocarbon fractions of the products of the cyclization of manool (I) by a mixture of aqueous sulfuric and acetic acids [2] and of sclareol (II) by a mixture of conc. sulfuric and formic acids [1]. The results of this investigation are given in the present paper.

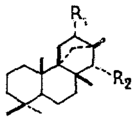
The mixture of hydrocarbons obtained on the interaction of manool (I) with a mixture of acetic and sulfuric acids [2] was separated by chromatography on a column of silica gel impregnated with silver nitrate into two fractions. The first fraction eluted from the column (∿28%) consisted of two components (1:5), which were separated on the individual state by rechromatography on the same adsorbent. By chromatographic and spectral (IR, PMR) comparison with authentic samples they were identified as the hydrocarbons (VIII) and (IX). The more polar fraction consisted of a mixture of four substances. They proved to be the known hydrocarbons (X-XIII) and were identified by a comparison with authentic samples using the GLC method. In this fraction, $\Delta^{8}(^{9})$-pimaradiene (X) and $\Delta^{8}(^{9})$-isopimaradiene (XI) predominated (∿85%, 1:1:3).



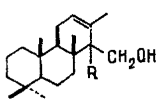
I

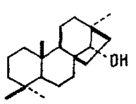


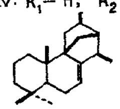
II



III. R_1= OH; R_2= H
IV. R_1= H; R_2= OH







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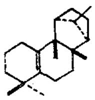
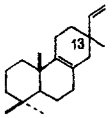
V. R=αH
VI. R=βH

VII

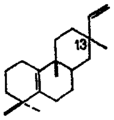
VIII



IX



X. 13αCH$_3$
XI. 13βCH$_2$



XII. 13αCH$_3$
XIII. 13βCH$_3$

An investigation of the hydrocarbon fraction of the product from the cyclization of sclareol (II) by a mixture of conc. sulfuric and formic acid [1] showed that it had the same qualitative composition as the hydrocarbon fraction obtained from manool that has been considered above. The amount of the tetracyclic hydrocarbons (VIII) and (IX) present in it was higher (38.5%) and their ratio was different (1:3). The more polar part of the hydrocarbon fraction had the same composition as the analogous fraction formed from manool on its reaction with a mixture of aqueous acetic and sulfuric acids.

Thus, it has been shown that the hydrocarbon fraction of the products of the cyclization of manool and sclareol by common acids under conditions given in the literature [1, 2] contain, together with the pimarane and rosane compounds identified previously, the tetracyclic hydrocarbons (1R, 2S, 7S, 11S, 12R, 13R)-2,6,6,11,13-pentamethyltetracyclo[10.2.1.$0^{1,10}$.$0^{2,7}$]pentadeca-9-ene (VIII) and (1S, 2R, 11S, 12R, 15R)-2,7,7,11,15-pentamethyltetracyclo[10.2.1.$0^{2,11}$.)^{3,2}]pentadeca-e(8)-ene (IX).

EXPERIMENTAL

Melting points were determined on a Böetius heated stage. Specific rotations were measured on a Polamat S instrument. IR spectra were taken in CCl_4 on a Specord 74 IR spectrophotometer.

Cyclization of Manool (I) by a Mixture of Aqueous Acetic and Sulfuric Acids. Manool (I) (1.80 g) was cyclized with a mixture of aqueous acetic and sulfuric acids as described in [2, 3], and the product (1.7 g) was saponified by boiling with 20 ml of 10% ethanolic KOH for 2 h. After the usual working up, 1.54 g of reaction product was obtained which was chromatographed on a column containing 25 g of neutral Al_2O_3 (activity grade III). Light petroleum ether eluted 867 mg of a hydrocarbon fraction, which was chromatographed on a column containing 23 g of SiO_2–$AgNO_3$ [6]. Petroleum ether eluted two fractions: 1) 230 mg, and 2) 580 mg. According to GLC (Chrom 5 chromatograph) FID, glass column 2.5 × 3.5 mm [sic], stationary phase 5% of SE-30 on Chromaton NAW-DMCS (0.16-0.20 mm), column temperature 180°C, evaporator temperature 250°C, carrier gas helium at the rate of 60 ml/ min, the latter consisted of a mixture of four substances. It was established by comparison with authentic samples that it included 13-epirosadiene (XII) (6.8%), rosadiene (XIII, 8.2%), $\Delta^{8(9)}$-pimaradiene (X, 37.4%), and $\Delta^{8}(^{9})$-isopimaradiene (XI, 47.6%). The first fraction was rechromatographed on a column containing 12 g of SiO_2–$AgNO_3$. Pentane eluted 106 mg of a liquid olefin (XI) $[\alpha]_D^{20}$ +2.9° (c 1.2; $CHCl_3$), which was identified by chromatographic and spectral (R, PMR) comparison with an authentic sample [4, 5], 87 mg of a mixture of the hydrocarbons (IX) and (X), and then 21 mg of the crystalline hydrocarbn (VIII), mp 92-93.5°C (from CH_3OH), which was identified by a chromatographic and spectral comparison with authentic samples.

Cyclization of Sclareol (II) with a Mixture of Conc. Sulfuric and Formic Acid. The hydrocarbon fraction (1.20 g) of the products of the cyclization of sclareol according to [1] was chromatographed on a column containing 30 g of SiO_2-$AgNO_3$. Petroleum ether eluted 380 mg of a mixture (1:3) of hydrocarbons (VIII) and (IX) (GLC results; conditions given above), and a mixture of petroleum ether and benzene (9:1) eluted 720 mg of a mixture of the hydrocarbons (X-XIII) in a ratio of ∿39:47:5:6. The retention times of the hydrocarbons (s) were: (IX), 740; (XIII), 819; (XII), 900; (VIII), 858; (XI) 939; (X) 1130.

SUMMARY

The hydrocarbon fractions of the products of the cyclization of manool and sclareol by a mixture of conc. sulfuric, acetic, of formic acids have been investigated in detail. It has been established that, in addition to the pimarane and rosane compounds identified previously, they include tetracyclic hydrocarbons – (1R, 2S, 7S, 11S, 12R, 13R)-2,6,6,11,13-pentamethyltetracyclo[10.2.1.$0^{1,10}$.$0^{2,7}$]pentadeca-9-ene and (1S, 2R, 11S, 12R, 15R)-2,7,7,11,15-pentamethylcyclo[10.2.1.$0^{2.11}$.$0^{3,8}$]pentadeca-3(8)-ene.

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TRITERPENE GLYCOSIDES OF Hedera taurica.

III. STRUCTURES OF HEDEROSIDES A_3, B, E_2 AND F FROM THE BERRIES OF CRIMEAN IVY

A. A. Loloiko, V. I. Grishkovets,
A. S. Shashkov, and V. Ya. Chirva

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Four triterpene glycosides – hederoside A_3, B, E_2, and F – have been isolated from the berries of *Hedera taurica* Carr. (Crimean ivy), family Araliaceae. On the basis of the results of acid hydrolysis and physiochemical methods of investigation the following structures have been suggested: A_3 – 3-O-(α-L-arabinopyranosyl)hederagenin; B – 3-O-(β-D-glucopyranosyl)hederagenin; E_2 – 3-O-[O-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranosyl]oleanolic acid; and F – 3-O-[O-β-D-glucopyranosyl-(1 → 2)-β-D-glucopuranosyl]hederagenin. Hederoside E_2 is a new glycoside of oleanolic aid.

Continuing investigations of the saponins of the berries of the Crimean species *Hedera taurica* Carr. [1, 2], we have analyzed the glycoside composition of the berries. TLC analysis showed the presence of six low-polarity components, which have been called, in order of increasing polarity, hederosides A, B, C, D, E, and F, in distinction to the taurosides from the leaves.

Preparative separation of the hederosides was effected by column chromatography on silica gel. The predominating components obtained – A, B, E, and F – were acetylated. TLC analysis showed that components A and E, unlike components B and F, were not individual compounds but consisted of mixtures of glycosides denoted in order of increasing polarity as hederosides A_1-A_3 and E_1 and E_2. The individual glycoside A_1-A_3, B, E_1, E_2, and F were isolated by the column chromatography of their acetates on silica gel. After deacetylation, the predominating hederosides A_3, B, E_2, and F were esterified with diazomethane and rechromatographed for additional purification.

The structures of the glycosides isolated were established with the use of the results of acid hydrolysis and their PMR and ^{13}C NMR spectra. The assignments of the signals in the PMR spectra were made with the aid of the procedure of ^1H_i–$\{^1H_j\}$ selective homonuclear double resonance, and in the ^{13}C NMR spectra by the use of the method of $^{13}C_i$–$\{^1H_j\}$ selective heteronuclear double resonance, by the observation of nuclear Overhauser effects (NOEs), by recording the J-modulated ^{13}C NMR spectra, and with the use of literature information on the chemical shifts of the C atoms of oleanolic acid, hederagenin, and unsubstituted methyl glycosides of sugars.

As a result of the acid hydrolysis of hederoside A_3, arabinose and hederagenin were detected, which permitted the assumption of the identity of hederoside A_3 and tauroside B [2].

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