# TETRACYCLIC DITERPENOIDS WITH A NEW CARBON SKELETON FORMING PRODUCTS OF THE CYCLIZATION OF LABDANE DITERPENOIDS

P. F. Vlad, N. D. Ungur,
and M. N. Koltsa

UDC 547.596/599

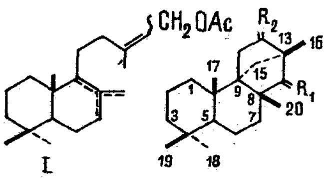
From the product of the cyclization of a mixture of isomeric ent-copalols (1) [1] with a mixture of formic and concentrated acids, we have isolated an oxygen-containing fraction (yield 47%) consisting of a mixture of five alcohols and their formates. Three of the alcohols proved to be known: isoagath-12-en-15-ols epimeric at $C_{14}$ [2] and 14α-hibanol [3]. For the other two alcohols, with the composition $C_{20}H_{34}O$, structures (2) and (3) were shown, these being based on a new carbon skeleton [4].

Alcohol (2), mp 160.5-161.5°C (from ethanol), $[\alpha]_D^{20}$ +13.9°.* IR spectrum ($cm^{-1}$): 1050, 3500 (weak band), 3636 (OH), 1367, 1384 (gem-dimethyl group). NMR spectrum: singlets of 3 H each at 0.83, 0.88, 0.94, 1.00, and 1.05 ppm (5 methyls on quaternary atoms), octet at 2.18 ppm (1 H, $J_1$ = 14 Hz, $J_2$ = 7.2 Hz, $J_3$ = 3.6 Hz), broadened doublet at 3.46 ppm (1 H, J = 6.8 Hz (CHOH)); $M^+$ 290. Chromium trioxide in pyridine oxidized it to a ketone (4), mp 102-103°C, $[\alpha]_D^{21}$ +15.3°. IR spectrum, $cm^{-1}$: 1742 (cyclopentanone), 1416 ($CH_2CO$ group). 2,4-Dinitrophenylhydrazone, mp 212-213°C. When its thioketal (mp 139-140.5°C) was desulfurized with Raney nickel, a hydrocarbon (5) was obtained with mp 72-73°C (from $CH_3OH$), $[\alpha]_D^{20}$ +16.8°. NMR spectrum: singlets of 3 H each at 0.79, 0.83, 0.90, 0.96, and 1.06 ppm.

Alcohol (3), mp 133-134.5°C (from petroleum ether), $[\alpha]_D^{20}$ +4.4°. IR spectrum, $cm^{-1}$: 1058, 3530 (band), 3645 (OH), 1370, 1388 (gem-dimethyl group). NMR spectrum, ppm: singlets of 3 H each at 0.83, 9.87, 0.95, 1.03, and 1.06 (five $CH_3$ groups on quaternary carbon atoms), 3.21 (singlet, 1 H, >CHOH). Its oxidation gave a ketone (6) with mp 105-105.5°C: $[\alpha]_D^{20}$ −110°. IR spectrum: 1738 $cm^{-1}$ (cyclopentanone). Ketone (6) did not give derivatives under the usual conditions. Under severe conditions it was reduced by the Wolff-Kizhner [Kishner] method with the formation of the alcohol (3) and the hydrocarbon (5). According to $^{13}C$ NMR, the molecules of compounds (2-6) each have four quaternary and one teritary carbon atoms.

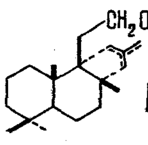
On successive oxidation with p-methoxycarbonylperbenzoic acid, reduction with lithium tetrahydroaluminate, acetylation with acetic anhydride in pyridine, and dehydration with phosphorus oxychloride in pyridine, ketone (4) was converted into a mixture of esters (7). The ester with the semicyclic double bond was cleaved with osmic acid and sodium p-iodate to form a keto ester (8), mp 162-163°C, IR spectrum: 1745 $cm^{-1}$ (cyclopentanone and acetate groups).

The combination of the facts given demonstrates the carbon skeleton shown in formulas (2) and (3) for the alcohols isolated. A negative Cotton effect in the CD spectrum of the keto ester (7) shows the cis linkage of its rings B and C [5] and simultaneously establishes the stereochemistry of cyclic system at $C_8$, $C_9$, and $C_{13}$ that is shown in formulas (2-6).

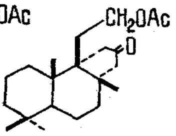


I

|  | $R_1$ | $R_2$ |
|---|---|---|
| 2. | $H_2$ | OH(H) |
| 3. | OH(H) | $H_2$ |
| 4. | $H_2$ | O |
| 5. | $H_2$ | $H_2$ |
| 6. | O | $H_2$ |



7



8

---

*The specific rotation was measured in $CHCl_3$. The IR spectra were recorded in $CCl_4$ and the NMR spectra in $CDCl_3$ with TMS as internal standard, the chemical shifts being given in the δ scale.

Institute of Chemistry, Academy of Sciences of the Moldavian SSR, Kishinev. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 581-582, July-August, 1979. Original article submitted March 30, 1979.

0009-3130/79/1504-0509$07.50

It has been found that alcohols (2) and (3) are also formed in the cyclization of other labdane compounds, not only under the conditions described in this paper but also under different conditions.

## LITERATURE CITED

1. P. F. Vlad and G. V. Lazur'evskii, Izv. Akad. Nauk MoldSSR, No. 12, 69 (1961).
2. G. Cimino, D. de Rosa, S. de Stefano, and L. Minale, Tetrahedron, 30, 645 (1974).
3. O. E. Edwards and R. S. Rosich, Can. J. Chem., 46, 1113 (1968).
4. P. F. Vlad, M. N. Koltsa, and N. D. Ungur, Abstracts of the Fifth Indo-Soviet Symposium on the Chemistry of Natural Compounds [in Russian], Evevan (1978), p. 18.
5. D. N. Kirk and W. Klyne, J. Chem. Soc., Perkin Trans. 1, 762 (1976).

---

# TRITERPENE COMPOUNDS OF *Campanula patula*

L. S. Teslov

UDC 547.913

In an investigation of a chloroform extract of the epigeal part of *Campanula patula* L. (rambling bellflower) on Silufol plates we detected the presence of triterpenoids. A concentrated chloroform extract was treated with a 5% solution of KOH, the alkaline extract was acidified, and the precipitate that deposited was repeatedly washed with ethanol. Then it was chromatographed on a column of silica gel L 40/100 μ (Czechoslovakia): ursolic acid was isolated, and it was purified by a method described in the literature [1]. After repeated recrystallization from petroleum ether and ethanol, crystals were obtained with mp 268-270°C, $[\alpha]_D^{20}$ $\pm 47.4°$ (c 0.44; chloroform). The ursolic acid isolated had the same $R_f$ values as an authenatic sample.

The alkali-treated chloroform extract was also chromatographed in columns of silica gel with elution by petroleum ether–chloroform. In this way, three crystalline substances (A, B, and C) were isolated. They all gave a positive Lieberman-Burchard reaction and were revealed on Silufol with solutions of antimony tetrachloride and sulfuric acid.

Substance A, composition $C_{32}H_{52}O_2$, had mp 238-241°C (ethanol), $[\alpha]_D^{20}$ +67° (c 0.56; chloroform); mol. wt. 468 (mass spectrometry). IR spectrum: 1740 and 1250 $cm^{-1}$ (C=O of an ester grouping). In the PMR spectrum, a narrow signal at 1.98 ppm is due to an acetyl group. Analysis of IR, PMR, and mass spectra and a comparison of them with those given in the literature [2, 3] enabled substance A to be characterized as β-amyrin acetate [4].

## LITERATURE CITED

1. Y. T. B. Wu and L. M. Park, J. Am. Pharm. Assoc., 42, 602 (1953).
2. J. Karliner and C. Djerassi, J. Org. Chem., 31, 1945 (1966).
3. M. Shamma, R. E. Glick, and R. O. Mumma, J. Org. Chem., 27, 4512 (1962).
4. C. R. Mitra and G. Misra, Phytochemistry, 4, 345 (1965).

---

Leningrad Institute of Pharmaceutical Chemistry. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 582-583, July-August, 1979. Original article submitted March 21, 1979.

0009-3130/79/1504-0510$07.50