Journal of Natural Products
Vol. 52, No. 5, pp. 1136-1138, Sep-Oct 1989

ISOLATION OF LANOSTA-9(11),24-DIEN-3β-YL ACETATE FROM *LEUZEA CARTHAMOIDES*

S.A. KHALID,*

Department of Pharmacognosy, Faculty of Pharmacy, University of Khartoum, P.O. Box 1996, Khartoum, Sudan

E. VARGA, K. SZENDREI,

Department of Pharmacognosy, University Medical School, P.O. Box 121, H-6701 Szeged, Hungary

and HELMUT DUDDECK

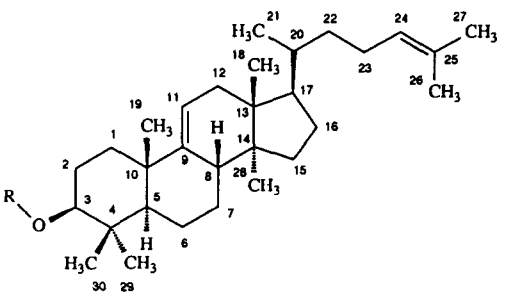
Ruhr-Universität Bochum, Fakultät für Chemie, Postfach 102148, D-4630 Bochum 1, West Germany

ABSTRACT.—Lanosta-9(11),24-dien-3β-yl acetate was isolated from *Leuzea carthamoides*. The structural assignments were mainly based on spectral evidence (^{1}H and ^{13}C nmr, nOe difference, and homonuclear and heteronuclear COSY). We recommend the trivial name parkeyl acetate. The isolation of this compound from *L. carthamoides* represents the first report regarding its occurrence among higher plants.

Leuzea carthamoides DC. [syn.: *Rhaponticum carthamoides* (Willd.) Iljin] (Compositae) has been used extensively in traditional and official medicine in Siberia as a natural stimulant and roborant (1). A wide range of compounds have been reported including flavanoids (2,3), thiophene (4,5), saponins (6–8), ecdysteroids (9–11) and an ill-defined triterpenoid (12). In this communication we wish to report the isolation of lanosta-9(11),24-dien-3β-yl acetate (parkeyl acetate) [**1**]. It is the first isolation of this compound from higher plants, although the synthesis of parkeyl acetate [**1**] has been described at least twice (13,14). With the exception of one report (15) concerning the isolation of the corresponding alcohol, parkeol [**2**], from shea-nut fat, there does not appear to be any information available about the isolation of such a triterpenoid from higher plants.

Compound **1** was analyzed for $C_{32}H_{52}O_2$ ([M]$^+$ 468). The band in the ir spectrum at 1740 cm^{-1} coupled with the hydrolysis of **1** to the corresponding alcohol **2** indicated the presence of an acetate group. All physico-chemical and spectral data of the triterpenoid alcohol **2** are in close agreement with those published (14) (see Experimental).

The structural assignment is based on a comparison of the ^{13}C-nmr data of parkeyl methyl ether (16). Further confirmation was obtained from nOe difference spectra. Irradiation of the olefinic proton induced intensity enhancements of the signals of H-1α, H-1β, and one of the H-12. Thus it is clear that the double bond is between H-9 and H-11. The position of the second double bond (C-



1 R=Ac
2 R=H

24/C-25) was proven by HH COSY cross peaks indicating allylic couplings between H-24 and H-26 as well as H-24 and H-27. Hydrolysis of parkeyl acetate afforded the corresponding alcohol parkeol.

Grimshaw *et al.* (12) have described the isolation of two poorly characterized triterpenoids from the same botanical source which they regarded as new triterpenoids (carthamenol and carthamenyl acetate). Our ^{1}H-nmr and the physico-chemical data are in close agreement with the fragmentary information published by these authors (12). Therefore, it is reasonable to suggest that their carthamenyl acetate is identical with parkeyl acetate. Based on the above evidence we recommend the use of parkeol and parkeyl acetate instead of carthamenol and carthamenyl acetate, respectively, to name the aforementioned compounds.

EXPERIMENTAL

The plant material originated from a large-scale cultivation at the University of Horticulture, Budapest, Hungary. A voucher specimen is deposited at the Department of Pharmacognosy, University Medical School, Szeged, Hungary. Two-year-old roots were collected in September. The dried pulverized root (3.2 kg) was extracted at room temperature with MeOH (50 liters). The solution was evaporated under reduced pressure. The filtered solution (300 g) was extracted with C_6H_6 (10 × 500 ml). The C_6H_6 extract was evaporated under reduced pressure to give an oil-like residue (58 g). The oil residue was chromatographed over a silica column (Kieselgel 40) and eluted with a petroleum ether/EtOAc gradient. Fractions were monitored by tlc (Kieselgel 60 F_{254}, Merck). Fractions eluted with petroleum ether-EtOAc (94:6) were evaporated, and the residue was crystallized from Me_2CO to give 1.75 g of parkeyl acetate as colorless plates. The mp of 160–162° is in good agreement with reported values: 159.5–160° (13) and 161–162° (14); ir (KBr) 2970, 1740 (C=O), 1377, 1240 cm^{-1}. The mass spectrum was in satisfactory agreement with literature data (14). The ^{13}C-nmr spectrum was assigned using literature data of parkeol methyl ether (16), and the ^{1}H signal assignment is based on a ^{1}H,^{13}C hetero-correlated 2D nmr experiment. In two cases (C-12 vs. C-22 and C-26 vs. C-27) the assignment given in the literature (16) had to be reversed.

All nmr spectra were recorded in $CDCl_3$ solution using a Bruker AM-400 spectrometer at 400.1 MHz (^{1}H) or 100.6 MHz (^{13}C). Solvent peaks were taken as internal reference; for ^{1}H, $CHCl_3$, δ = 7.24 and for ^{13}C, central peak of $CDCl_3$, δ = 77.0. For the multipulse experiments (nOe difference, DEPT, HH COSY and HC-COSY), standard Bruker software was employed.

^{13}C chemical shifts (δ, in $CDCl_3$, relative to the solvent peak with δ = 77.0): 170.9 (acetate C=O), 148.1 (C-9), 130.9 (C-25), 125.2 (C-24), 115.2 (C-11), 80.9 (C-3), 52.6 (C-5), 50.9 (C-17), 47.0 (C-14), 44.3 (C-13), 41.7 (C-8), 39.2 (C-10), 38.0 (C-4), 37.1 (C-22), 36.4 (C-12), 35.9 (C-20), 35.8 (C-1), 33.9 (C-15), 28.2 (C-29), 28.0 (C-7 and C-16), 25.7 (C-27), 24.9 (C-23), 24.2 (C-2), 22.3 (C-19), 21.3 (acetate Me), 21.2 (C-6), 18.5 (C-28), 18.3 (C-21), 17.6 (C-26), 16.8 (C-30), and 14.4 (C-18).

^{1}H chemical shifts (δ, in $CDCl_3$, relative to $CHCl_3$ with δ = 7.24): 5.21 (H-11), 5.08 (H-24), 4.46 (H-3), 2.14 (H-8), 2.03 (acetate), 2.05–2.00 (2 H-23), 1.9–1.85 (2 H-22), 1.76 (H-2α), 1.75 (H-16), 1.68 (H-27), 1.67 (H-2β), 1.65 (H-6α), 1.64 (H-7β and H-16), 1.62 (H-17), 1.59 (H-26), 1.56 (H-1α), 1.54 (H-6β), 1.43 (H-1β), 1.40 (H-12), 1.38 (H-20), 1.35–1.3 (2 H-15), 1.28 (H-7α), 1.06 (H-19), 1.04 (H-12), 0.96 (H-5α, dd, J = 11.8 and 2.5 Hz), 0.89 (H-21), 0.88 (H-30), 0.85 (H-29), 0.73 (H-28) and 0.63 (H-18). The stereochemical assignments of most of the diastereotopic protons within methylene groups of the tetracyclic framework are based on nOe difference experiments (irradiations on H-3, H-11, H-18, H-28, and H-29). Those of the remaining ones and within the side chain could not be achieved by our homo- and heteronuclear COSY experiments.

HYDROLYSIS OF COMPOUND **1**.—Compound **1** (30 mg) was refluxed in EtOH (5 ml) containing 5% KOH, the solution was diluted with H_2O, and the corresponding alcohol, parkeol [**2**], was extracted with CH_2Cl_2. Compound **2** was crystallized from MeOH as needles: mp 150–152°; ir (KBr) 3300 (OH), 2950, 1400, 1290 cm^{-1}. Analyzed for $C_{30}H_{50}O$ $[M]^+$ 426; the fragmentation pattern in the mass spectrum was consistent with published data (14). The ^{1}H-nmr spectrum of **2** was very similar to that of **1** except for peaks at δ = 3.20 (H-3), 0.97/0.80 (H-29/H-30), and the missing Ac signal.

ACKNOWLEDGMENTS

S.A.K. extends his sincere thanks to Alexander-von-Humboldt Stiftung for the award of a fellowship and the University of Khartoum for a sabbatical leave.

LITERATURE CITED

1. A.D. Turova, "Lekarstvennyje rastenija,"

Izdat. Medicina, Moscow, 1967, pp. 66–68.
2. V.G. Bukharov and S.P. Shcherbak, *Khim. Prir. Soedin.*, 280 (1967).
3. V.V. Vereskovskiy, *Khim. Prir. Soedin.*, 417 (1980).
4. A.A. Savina, Yu.E. Sklyar, D.A. Fesenko, and V.G. Klyaznika, *Khim. Prir. Soedin.*, 124 (1980).
5. E. Varga, K. Szendrei, and J. Reisch, *Herba Hung.*, **22**, 37 (1983).
6. A.S. Saratikov, E.A. Krasnov, G.D. Shadrina, M.I. Zotova, M.F. Nekhoda, R.A. Aksenova, and L.P. Alekseeva, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Biol. Nauk*, 88 (1970); *Chem. Abstr.*, **74**: 146286 (1971).
7. V.V. Vereskovskiy and J.M. Chekalinskaya, *Khim. Prir. Soedin.*, 578 (1977).
8. V.V. Vereskovskiy and J.M. Chekalinskaya, *Khim. Prir. Soedin.*, 525 (1978).
9. E.A. Krasnov, A.S. Saratikov, and G.D. Yakunina, *Khim. Prir. Soedin.*, 550 (1976).
10. A.U. Mamatchanov, M.R. Shamsutinov, and T.T. Shakirov, *Khim. Prir. Soedin.*, 528 (1980).
11. J.-P. Girault, R. Lafont, E. Varga, Zs. Hajdu, I. Herke, and K. Szendrei, *Phytochemistry*, **27**, 737 (1988).
12. J. Grimshaw, M. Jaruzelski, E. Lamer-Zarawska, and H. Rzadkowska-Bodalska, *Pol. J. Chem.*, **55**, 2355 (1981).
13. W. Lawrie, F.S. Spring and H.S. Watson, *Chem. Ind.*, 1458 (1956).
14. J.A. Croft, E. Ritchie, and W.C. Taylor, *Aust. J. Chem.*, **28**, 2019 (1975).
15. K.H. Bauer and H. Moll, *Fette Seifen*, **46**, 530 (1939).
16. J.W. Blunt and M.H.G. Munro, *Org. Magn. Reson.*, **13**, 26 (1980).

Received 9 September 1988