EtOAc affording capillin,[5] 1-phenyl-2,4-hexa-diyne-1-ol,[5] vanillin, and scoparone.[1] There is no previous record of the isolation of the first three compounds from *A. scoparia.* All compounds were identified by direct comparison with authentic materials, by m.m.p., co-chromatography (TLC) and IR and NMR analysis.

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GERMACRANOLIDES FROM *CENTAUREA SERIDIS**

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Key Word Index—*Centaurea seridis*; Compositae; sesquiterpene lactones; germacranolides; artemisiifolin; C_{15}-acetylartemisiifolin; salonitolide; coumarins; scopoletin.

In connection with our investigations on *Centaurea* (Compositae, tribe Cynareae) we report here the isolation and structure determination of three germacranolides from *Centaurea seridis* L., a species widely distributed on the Mediterranean Spanish coast.[1]

Column chromatography of the alcoholic extract of the aerial parts yielded three bitter tasting compounds. The least polar one, C_{15}–acetylartemisiifolin (Ib), of empirical formula $C_{17}H_{22}O_5$, M^+ 306, shows IR bands indicative of OH, double bond, acetate and α-methylene-γ-lactone. The last group was characterised by means of the pyrazoline derivative II and by NMR: the spectrum of Ib exhibits a doublet at 3·60 (1H, J 3 Hz) and a very deformed signal at 3·78 τ (1H). The mass peaks at $M^+ - 42$ and $M^+ - 60$, together with the C_{17} formula and IR and NMR data indicate that Ib is a C_{15} lactone monoacetate. In addition to the above mentioned signals the NMR spectrum shows a 3-protons singlet at 8·30 τ assigned to a vinylic Me group. On the whole, the spectrum is poorly resolved; this is a feature characteristic of germacranolides lactonized at C_8 which in solution at room temperature exist in several conformations.[2] Saponification of Ib gave artemisiifolin (Ia), whose physical and spectral data agree with those given by Porter *et al.*[2] Ia was also isolated from the plant. It proved to be identical in all respects with the compound prepared from cnicin.[2] Hydrogenation of Ib with $NaBH_4$ yielded salonitolide (IV),[3] identical with the third germacranolide isolated from the plant. IV was also obtained by hydrogenating Ia over Pd–C, thus confirming Mabry's opinion on the identity of dihydroartemisiifolin and salonitolide.[2]

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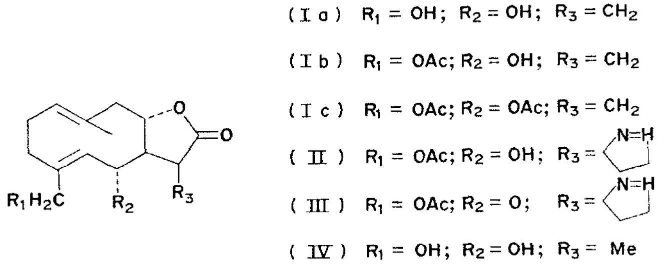
* Part XIX in the series "Constituents of Compositae". For Part XVIII see GONZÁLEZ, A. G., BERMEJO, J., BRETÓN, J. L. and FAJARDO, M. (1973) *Anal. Quim.* **69**, 667.

[1] WILLKOMM, M. and SANGE, J. (1870) *Prodomus Florae Hispanicae*, Vol. II, p. 141, Schweizerbart, Stuttgart (reprinted 1972 by Strauss & Cramer, Stuttgart).

[2] PORTER, T. H., MABRY, T. J., YOSHIOKA, H. and FISCHER, N. H. (1970) *Phytochemistry* **9**, 199.

[3] SUCHY, M., HÉROUT, V. and ŠORM, F. (1965) *Coll. Czech. Chem. Commun.* **30**, 2863.

The location of the acetyl group in Ib was determined by the following spectroscopic and chemical methods. The NMR signal for the H_{13a} (i.e. the proton trans to the γ-lactone carbonyl) in Ib appears distorted and paramagnetically shifted (3·78 τ). In the acetate Ic this signal is restored to normal position and shape (3·68 and 4·13, *d*, *J* 3 Hz).[4] This result suggests an interaction between the H_{13a} and a near perturbing hydroxyl, similar to that observed for C_6-lactones containing a C_8-αOH group.[5] Oxidation of II with Jones reagent gave the neutral compound III, $C_{18}H_{22}O_5N_2$, which in the IR shows strong bands at 1780 and 1740 cm^{-1} but no OH function. Its NMR spectrum does not present the typical singlet of an aldehyde proton at C_{15}, hence the primary OH group at this C atom in Ib must be acetylated. The UV spectrum of III is anomalous (λ_{max} 323 nm, ϵ 320), probably due to transannular interaction of the germacrane double bonds and lack of coplanarity of the α,β-unsaturated chromophore.



(I a) R_1 = OH; R_2 = OH; R_3 = CH_2
(I b) R_1 = OAc; R_2 = OH; R_3 = CH_2
(I c) R_1 = OAc; R_2 = OAc; R_3 = CH_2
(II) R_1 = OAc; R_2 = OH; R_3 =
(III) R_1 = OAc; R_2 = O; R_3 =
(IV) R_1 = OH; R_2 = OH; R_3 = Me

The coumarin scopoletin was also isolated from this plant.

EXPERIMENTAL

M.ps determined on a Kofler block, are uncorrected. Unless otherwise indicated, compounds were recrystallized from light petrol.–EtOAc and optical rotations measured in $CHCl_3$. NMR spectra were recorded in $CDCl_3$ with TMS as internal standard at 60 MHz if not otherwise stated. Column and dry column chromatography were performed on silica gel 0·2–0·5 and 0·063–0·2 mm, respectively. Acetates were prepared with Ac_2O in pyridine at room temp. overnight.

Extraction. The air-dried, ground aerial part of the plant (11·6 kg), collected in June on Saler Beach (Valencia, Spain), were extracted with EtOH in a Soxhlet. The concentrated extract was dissolved in EtOH (1 l.), treated with a soln of $Pb(OAc)_2$ (25 g) in H_2O (2 l.) and left at room temp. for 24 hr. After filtering and distilling off the EtOH the aq. phase was extracted with $CHCl_3$. Evaporation of the solvent gave a residue (100 g) which was chromatographed on silica gel (800 g) eluting with C_6H_6–EtOAc 9:1, 7:3 and 1:1.

Scopoletin, m.p. 206–209°, obtained by dry column chromatography of the first fractions eluted with C_6H_6–EtOAc (9:1) and identified by comparison with an authentic sample (m.m.p., IR, UV, NMR spectra superimposable).

C_{15}-*Acetylartemisiifolin* Ib, eluted with C_6H_6–EtOAc (9:1). Needles, m.p. 102–104° $[\alpha]_D$ 48° (*c* 0·10) (Found: C, 66·98; H, 7·34. $C_{14}H_{22}O_5$ requires: C, 66·65; H, 7·24%). ν_{max}^{Nujol} 3460 (OH), 1760 (γ-lactone, OAc), 3120, 1670, 1650 (double bonds), 1260 cm^{-1} (OAc). NMR [100 MHz, $(CD_3)_2CO$]: τ 3·60 (1H, *d*, *J* 3 Hz) and 3·78 (1H, broad) [conjugated =CH_2], 3·8–4·8 (4H, broad), 5·04 (2H, broad, vinylic H), 8·30 (3H, broad *s*, Me–C_{10}). MS: *m/e* 306 (M^+, 4%), 264 (3%), 246 (12%). By acetylation gives *artemisiifolin diacetate* Ic (physical, IR, NMR data identical with those reported).[2]

Pyrazoline derivative II. A soln of Ib (615 mg) in $CHCl_3$ (35 ml) was left with excess CH_2N_2 in Et_2O at room temp. overnight. After evaporating the solvent *in vacuo* the residue was chromatographed on a dry column. C_6H_6–EtOAc (4:1) eluted II, prisms, m.p. 101–103° (light petrol.–C_6H_6), $[\alpha]_D$ 94° (*c* 0·10) (Found C, 62·14; H, 6·91; N, 8·06. $C_{18}H_{24}O_5N_2$ requires: C, 62·05; H, 6·94; N, 8·04). $\nu_{max}^{CHCl_3}$ 3550 (OH), 1780 (γ-lactone), 1725 (OAc), 1665 cm^{-1} (double bonds). NMR: τ 4·80–6·70 (complex signal), 7·97 (3H, *s* OAc), 8·60 (3H, broad *s*, Me–C_{10}).

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[4] The *exo*-methylene group in $\Delta^{11(13)}$-6α-acetoxy-germacran-8,12-olide appears at this same position. TADA, H. and TAKEDA, K. (1971) *Chem. Commun.* 1391.

[5] YOSHIOKA, H., MABRY, T. J., IRWIN, M. A., GEISSMAN, T. A. and SAMEK, Z. (1971) *Tetrahedron* **27**, 3317.

Oxidation of II. A soln of II (100 mg) in Me_2CO (5 ml) at 0° was treated with Jones reagent till the orange colour persisted, left at room temp. for 15 min, poured into H_2O (400 ml) and extracted with EtOAc. Dry column chromatography (C_6H_6–EtOAc, 4:1) of the residue gave III, fine needles, m.p. 151–153°, $[\alpha]_D$ −221° (*c* 0·10) (Found: C, 59·61; H, 6·44; N, 7·17. $C_{18}H_{22}O_5N_2$ requires: C, 59·33; H, 6·64; N, 7·69%). λ_{max}^{EtOH} 323 nm (ϵ 320). ν $1780_{max}^{CHCl_3}$ (γ-lactone), 1740 cm^{-1} (CO). NMR: τ 7·86 (3H, *s*, OAc), 8·15 (3H, broad *s*, Me–C_{10}).

Artemisiifolin. Ia, eluted with C_6H_6–EtOAc (7:3). Prisms, m.p. 128–130°, $[\alpha]_D$ 53°. Yields the *diacetate* Ic, identical with the product obtained from Ib (TLC, IR, NMR spectra superimposable). Ia was also obtained from cnicin by the procedure described,[2] and by saponification of Ib; both reaction products proved to be identical with the natural sample (m.m.p., TLC, IR, NMR spectra superimposable).

Salonitolide IV, eluted with C_6H_6–EtOAc (1:1). Neeldes, m.p. 183–184°, $[\alpha]_D$ 116°. It was shown to be identical with authentic material (m.m.p., TLC, IR, NMR spectra superimposable). IV was also obtained by hydrogenating Ia and by $NaBH_4$ treatment of Ib in EtOH as usual.

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KAURANOID DITERPENES IN *ESPLETIA* SPECIES

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Plants. E. humbertii; E. littlei; E. timotensis. Previous work. None.

Present work. Dried leaves and bark of *Espletia littlei* were ground and extracted with light petrol. The acidic fractions from these extracts were obtained by treatment with 5% Na_2CO_3, the components separated by chromatography on SiO_2 columns, and identified by comparison with authentic specimens. (—)-Kaur-9(11)-16-dien-19-oic acid,[1] $C_{20}H_{28}O_2$ (M^+ 300), m.p. 155–158°, $[\alpha]_{578}$ 33 (EtOH), IR, NMR and m.m.p. was isolated from all three species. In addition to this 15-α-hydroxy-kaur-16-en-19-oic acid,[2] $C_{20}H_{30}O_3$ (M^+ 318), m.p. 220–223°, IR, NMR and m.m.p. was obtained from *E. timotensis;* (—)-16-α-hydroxy-kaurane, $C_{20}H_{34}O$ (M^+ 290), m.p. 211–215°, $[\alpha]_{578}$ —38($CHCl_3$), IR, NMR and 15-α-acetoxy-kaur-16-en-19oic acid,[1] $C_{22}H_{32}O_4$ (M^+ 360), m.p. 172–173°, $[\alpha]_{578}$—81° ($CHCl_3$), IR, NMR and m.m.p. were isolated from *E. humbertii.*

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