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A LIGNANE DERIVATIVE FROM *Lucilia nivea*

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Abstract.- The aerial parts of *Lucilia nivea* gave in addition to known compounds a new lignane derivative. Furthermore obliquin was present which together with some derivatives also was isolated from species of the closely related genus *Belloa*.

From the large tribe Inuleae only a few genera are distributed in Central and South America. Merxmüller et al.¹ have placed some of these in the *Lucilia* group (*Lucilia*, *Belloa*, *Facelis* and some small genera), subtribe Gnaphaliinae. As nothing is known on the chemistry of these species we have studied a *Lucilia* and three *Belloa* species out of the 18 accepted species which are distributed in high-elevation habitats throughout the Andes from Venezuela to Chile and Argentina.

The extract of the aerial parts *B. plicatifolia* Sagast. et Dillon gave the obliquin derivatives 1² and 2² as well as a mixture of phenols (3 - 5) which were separated as their acetates. The structures followed from the ¹H NMR spectra. Those of 1 and 2 showed the typical signals of trisubstituted coumarins and those of the dioxin ring with an isopropenyl residue typical for obliquin derivatives.^{2,6}

The aerial parts of *B. piptolepis* (Wedd.) Cabr. gave 1 - 3 and those of *B. turneri* Sagast. et Dillon in addition to 3 also the coumarin 7 which may be the precursor of 3.

The aerial parts of *Lucilia nivea* (Phil). Cabr. gave the triterpenes lupeol, betulenic acid and oleanolic acid,

3,6,7,8-tetramethoxy-5-hydroxyflavone, 4-methyl-2,5-dihydroxy-6-methoxy acetophenone and the lignane derivative 8. The ¹HNMR spectrum of the latter indicated the presence of an angelate of a dimer of a phenylpropane derivative. The molecular formula (C₂₇H₃₄O₇) agrees with a tetramethoxy derivative of an angelate of a substituted tetrahydrofuran. Spin decoupling showed that the latter was substituted at C-2, C-3 and C-4. The slightly broadened doublet at δ 4.84 obviously was due to H-7'. It was acoupled with a quintet at 2.60 which was further coupled with signals at δ 4.41, 4.27 and 2.74. As the latter was further coupled with the signals at δ 4.08 and 3.78 and that at δ 2.60 with the double doublets at δ 2.89 and 2.56 the whole sequence was established. The observed chemical shifts required the proposed substitution. Thus compound 8 is related to acuminatin², the corresponding desacyl derivative with different aromatic oxygen functions. Of course the ¹H NMR data are in part very similar.

The cocurrence of obliquin and its derivatives in *Lucilia* and *Belloa* species agrees with the placement of the *Lucilia* group in the subtribe Gnaphaliinae close to the *Helichrysum* group¹. These compounds have been reported from *Helichrysum*^{2,3}, *Helipterum*³, *Pleostachys*³, *Anaxeton*⁴, *Cassinia*⁴, *Stoebe*⁵ and *Phaenocona*⁶, all placed in the

subtribe Gnaphaliinae. The occurrence of the lignane **8** further supports this relationship as a closely related derivative has been isolated from a *Helichrysum* species².

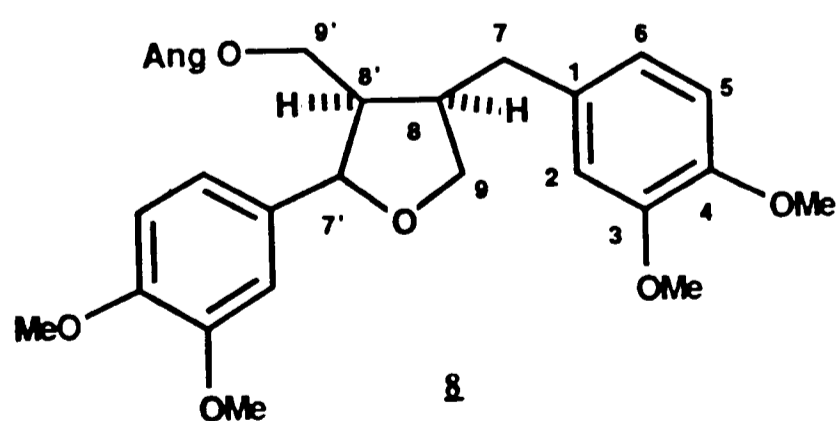
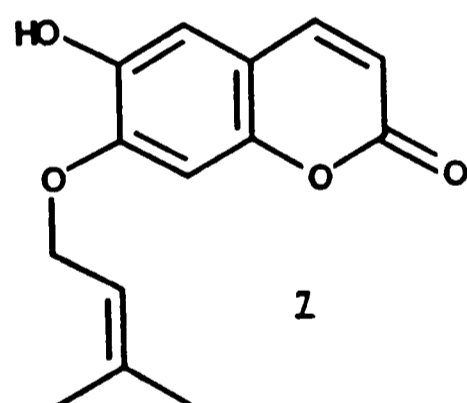
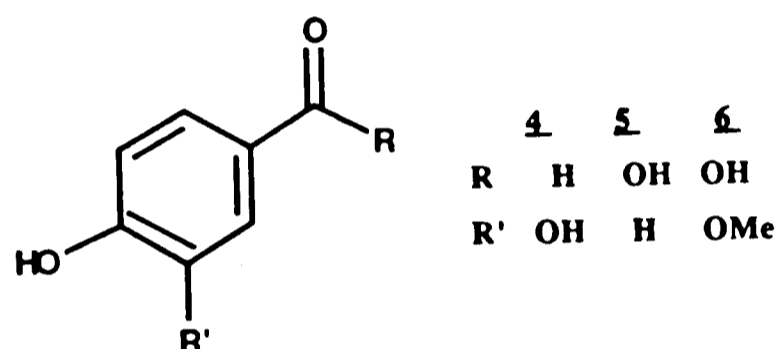
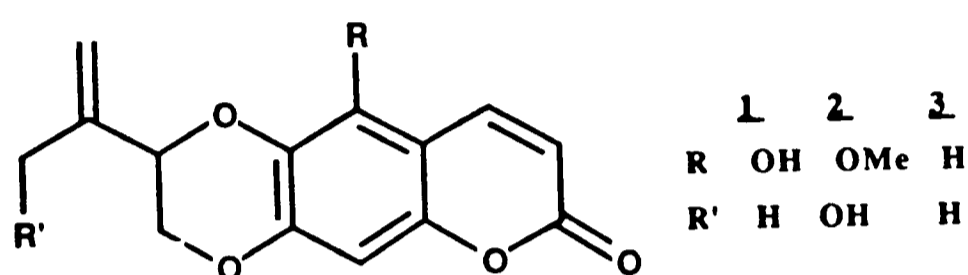
EXPERIMENTAL

The air dried plant material was extracted with MeOH-Et₂O-petrol, 1:1:1, and the extracts were worked-up and separated as reported previously⁷.

The extract of *Belloa plicatifolia* (380 g, collected in October 1987 in the Dept. Cajamarca, Peru, Cumbemayo, 3.500 m, voucher Sagastegui 13019) gave a polar fraction which afforded by HPLC (RP 8, flow rate, 3 mL/min, ca 100 bar, MeOH-H₂O, 4:1) 40 mg **1** (Rt 5.0 min), 15 mg **2** (Rt 4.5 min) and a mixture of **4** - **6** which after acetylation (Ac₂O, 1 h, 70°) gave by TLC (Et₂O-petrol, 1:1) 8 mg **4Ac**, 8 mg **5Ac** and 10 mg **6Ac**.

The extract of 85 g aerial parts of *B. piptolepis* (collected in November 1986 in the Dept. Moquegua, 77 km NE of Moquegua, 4050 m, Peru, voucher Dillon 4812) gave 6 mg **1**, 4 mg **2** and 5 mg **3** while that of *B. turneri* (110 g, voucher Sagast. 13085, collected in Dept. Cajamarca, Pozo Kuan, 3910 m, Peru) gave 8 mg **3** and 6 mg **7**.

The extract of the aerial parts of *Lucilia nivea* (670 g, collected in February 1989 in the Region del Bio-Bio, Chile, voucher Niemeyer 8939) gave by CC, TLC of HPLC(s.a.) 35 mg lupeol, 10 mg betulinic acid, 25 mg oleanolic acid, 20 mg 3,6,7,8-tetramethoxy-5-hydroxyflavone, 5 mg 4-methyl-2,5-dihydroxy-6-methoxyacetophenone and 5 mg **8** (HPLC), MeOH-H₂O, 7:3, Rt 7.2 min); colourless gum. IR ν^{max}, cm⁻¹: 1725 (C=CCO₂R); MS m/z (rel. int.): 470.230 [M]⁺ (73) (calc. for C₂₇H₃₄O₇: 470.230), 370 [M-AngOH]⁺ (65), 355 (89), 339 (17), 83 (100); ¹H NMR (CDCl₃, 400 MHz): 6.68 d, 6.71 dd, 6.80 d, 6.86 m (aromatic protons), 2.00 dq, 1.87 dq, 6.10 qq (OAng), 2.89 and 2.56 (dd, H-7), 2.74 (m, H-8), 4.04 and 4.78 (dd, H=9), 4.84 (d, H-7'), 2.60 (ddt, H-8'), 4.41 and 4.27 (dd, H-9'), 3.88, 3.87, 3.86, 3.85 (s, OMe); J [Hz]: 71,72 = 13; 71,8 = 5; 72,8 = 10; 8,91 = 6.5; 8,92 = 7, 91,92 = 8.5; 7'8' = 8',91' = 8',92' = 8', 8 = 7.



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