Extraction and Purification

Freshly harvested roots, stored in a freezer for 2 months, were extracted with a mixture of Et_2O and light petroleum (b.p. 40–60°) (1/2, v/v). After evaporation of the bulk of the solvent, the oily concentrate was chromatographed on a column of silica gel with petroleum with increasing quantities of Et_2O. Further purifications were carried out on thick TLC; Merck silica gel HF_{254} with 40% Et_2O in petroleum (v/v) as eluent. Recrystallization was from a mixture of Et_2O and pentane; m.p. 75–76·5°.

Spectral Data

UV. λ_{max} (pentane) 333, 328, 318, 266, 257, 228 nm. (ϵ 6800, 8000, 8900, 12,500, 14,000, 11,000).

IR ($CHCl_3$). OH at 3340 and 1335 cm^{-1}, vinyl 886 cm^{-1}, aromatic ring 1585 and 1439 cm^{-1}.

NMR (TMS internal standard). 1,2,4, trisubstituted aromatic ring 3·39 τ (doublet $J = 1$ c/s, 1H), 3·28 τ (double doublet $J = 1$ and 8 c/s, 1H), 2·71 τ (doublet $J = 1$ c/s, 1H); methylgroup 7 6 τ (singlet, 3H); vinyl group 4·67 τ (doublet $J = 2$ c/s, 1H), 4·49 τ (doublet $J = 2$ c/s, 1H); OH group 6·48 τ (doublet $J = 10$ c/s, 1H), H atom 3·88 τ (double multiplet, $J = 10$ c/s). Mass spectrum: M^+ 162,0684 (calculated 162,0680).

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TRITERPENIC ALCOHOLS FROM THE SHOOTS OF *HELIANTHUS ANNUUS*

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IT HAS been shown previously that great quantities of triterpenic pentacyclic alcohols of different types accumulate in the flowers and the seeds of *Calendula officinalis*. In other organs of this plant only small quantities of β-amyrin and erythrodiol, biosynthetic precursors of oleanolic acid, are present.[1] In *Helianthus annuus*, however, considerable quantities of triterpenic monols and diols were found, not only in the flowers and the seeds, but also in the shoots and the roots.[2] On silver nitrate–silica chromatograms these compounds had chromatographic properties identical with monols such as lupeol, taraxasterol, ψ-taraxasterol and the amyrins, and with the diols calenduladiol, faradiol, brein and erythrodiol. The chromatographic analysis of the selenium dioxide oxidation products of the amyrins revealed the presence of two compounds, one unoxidized (most probably α-amyrin) and the second one oxidized with R_f values the same as the oxidation product of β-amyrin.

The direct identification of the triterpenic alcohols present in the shoots of *Helianthus annuus* was performed by co-crystallization of the labelled compounds, isolated from this plant with unlabelled known triterpenic alcohols isolated from the flowers of *Calendula officinalis*.

3-week-old shoots of sunflower plant without cotyledons and roots, of total weight 2 g, were administered with 400 μC $^{14}CO_2$ during 2 hr at illumination 40,000 lx. The shoots were then transferred to a vessel with tap water and illuminated with light of intensity

[1] Z. KASRZYK and Z. WOJCIECHOWSKI, *Phytochem.* **8**, 1921 (1969)
[2] K. STRUBY and Z. KASPRZYK, *Acta Soc. Botan. Pol.* in press

3000 lx during 6 hr. The harvested plants were homogenized in methanol and then the residue extracted with boiling methanol. The filtrate was hydrolysed in 10% KOH for 1 hr. The hydrolysate was diluted with an equal volume of water, the methanol removed by distillation and the aqueous residue extracted with ethyl ether. This extract contained triterpenic monols and diols. Further separation and purification of these compounds was conducted by chromatography on plates with SiO_2, Al_2O_3 and SiO_2–$AgNO_3$ according to the method described previously.[1] Purified radioactive monols and diacetates of diols were mixed with corresponding non-radioactive compounds obtained from *Calendula officinalis* flowers in amounts 25–50 mg according to the method previously described.[3] Individual mixtures were crystallized three times from ethanol. After each crystallization the melting point was determined and the specific activity measured by means of thin-window GM counter of efficiency about 10%.

The results obtained, presented in Table 1, indicate that the monols isolated from the shoots of *Helianthus annuus* are identical with lupeol, taraxasterol, ψ-taraxasterol, and α-amyrin, and the diols with calenduladiol, faradiol, brein and erythrodiol.

TABLE 1

Compound	Number of crystallizations	Specific radioactivity counts/min/mg	Melting points,(°)
Lupeol	—	805	209–212
	1	810	210–214
	2	821	212–216
	3	818	212–218
Taraxasterol	—	515	208–219
	1	529	—
	2	506	213–224
	3	511	215–224
ψ-Taraxasterol	—	347	197–210
	1	301	199–213
	2	427	207–218
	3	420	212–220
α-Amyrin	1	1130	179–189
	2	1099	180–190
	3	1099	184–192
Calenduladiol-diAc	—	333	179–190
	1	298	180–192
	2	300	182–192
	3	323	184–193
Faradiol-diAc	—	374	128–155
	1	392	130–160
	2	389	—
	3	353	135–162
Brein-diAc	—	133	192–200
	1	104	192–201
	2	104	194–201
	3	102	195–202
Erythrodiol-diAc	—	406	—
	1	448	182–190
	2	445	—
	3	440	187–198

[3] Z. KASPRZYK and JAN PYREK, *Phytochem.* 7, 1631 (1968).