

THE TRITERPENES OF *CHONDRILLA JUNCEA**

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By repeated crystallization of the saponified latex of *Chondrilla juncea*, Soler and Cambronero (1954; see also Cambronero 1953) isolated a substance which they named chundristerol, and regarded as a sterol because of its colour reactions. It had an empirical formula $C_{24}H_{40}O$ and contained one unreducible double bond with a secondary hydroxyl in such a position that oxidation gave a conjugated ketone in poor yield. Two formulae were considered, one being a 6- and the other a 16-hydroxy- $\Delta^{8(14)}$ -steroid. Each is remarkable through the absence of a 3-hydroxy group and the presence of a 5-carbon atom side chain at the 17-position. The molecular rotation differences between chundristerol and its derivatives are inconsistent with any of the known steroid or triterpenoid systems.

We were able to make an examination of *C. juncea* through the kindness of Dr. C. C. J. Culvenor, who provided a light petroleum extract of the methanol-soluble portion of the dried plant, and later with the dried plant itself. Repeated crystallization from ethanol of the light petroleum extract gave a small yield of crystals of constant melting point, called substance C and characterized as shown in Table 1. The melting points of this compound and its derivatives were variable with conditions, but in open tubes were approximately in agreement with those reported for chundristerol. The rotations, however, and the analyses when done on anhydrous samples, differ widely from those recorded for chundristerol.

When the methanol extract of the whole dried plant was saponified, a small yield of another compound called substance A was isolated through its insolubility in ether. The ether-soluble material was acetylated, and by repeated chromatography the acetate of a new compound, substance B, was isolated, as well as the acetate of substance C. Substances B and C were separable as the acetates only with difficulty and with poor recovery. They had no selective absorption in the ultraviolet, were unsaturated to tetranitromethane, and analysed as isomeric monohydroxytriterpenes. From Table 1 it seems likely that one of them is ψ -taraxasterol. *C. juncea* is a member of the family Compositae in which this triterpene commonly occurs.

Substance A appeared to be a heavily oxygenated steroid triol with a composition approximating to $C_{28}H_{48}O_5$. It gave a positive Lieberman-Burchard reaction, was unsaturated to tetranitromethane, and formed triesters. The infrared absorption spectrum of the alcohol showed no carbonyl bands, while the

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acetate showed no hydroxyl or sapogenin absorption (Wall *et al.* 1952). Hence substance A has only acetyltable hydroxyls and no carbonyl or carboxyl groups. The nature of the two non-hydroxylic oxygens is not known.

TABLE 1
PHYSICAL CONSTANTS OF SUBSTANCES ISOLATED FROM CHONDRILLA JUNCEA

Compound	Melting Point (°C)	$[\alpha]_D$	Reference
Chundristerol	215–216	+82	} Cambronero (1953)
Acetate	234–236	+85	
Benzoate	270–271	+56	
Substance A	308–309	—	} Experimental
Triacetate	169–170	–17	
Tribenzoate	199–200	+14	
Substance B			
Acetate	250–252	+95	} Experimental
Benzoate	260–262	+55	
Substance C	{ 222–224 212–218*	+49	Experimental
Acetate	{ 245–247 228–234*	+52	Experimental
Benzoate	{ 292–294 271–278*	+73	Experimental
ψ -Taraxasterol	220–221	+50	} Simonsen and Ross (1957)
Acetate	246–247	+53	
Benzoate	288–289	+68	

* Open tube.

Experimental

(a) *General*.—Melting points are corrected and taken in evacuated sealed tubes unless otherwise stated. Rotations were measured at 1–2% concentration in chloroform solution at $20 \pm 2^\circ \text{C}$ in a 1 dm tube. Ultraviolet absorption spectra were taken in ethanol solution, and infrared spectra in Nujol mull or CS_2 solution.

(b) *Isolation and Characterization of Substances A, B, and C*.—Air-dried *C. juncea* (11 lb) was extracted with hot methanol to give soluble material (70 g) which was saponified with ethanolic KOH. Extraction with ether gave substance A as an insoluble white powder (1.5 g), m.p. $308\text{--}309^\circ \text{C}$ ($285\text{--}288^\circ \text{C}$ open tube). For analysis this was dried by dissolving in toluene, concentrating and cooling (Found: C, 72.1; H, 10.3%. Calc. for $\text{C}_{28}\text{H}_{48}\text{O}_5$: C, 72.4; H, 10.4%). Acetylation with acetic anhydride–pyridine at 100°C gave substance A triacetate, crystallizing from chloroform–methanol, m.p. $169\text{--}170^\circ \text{C}$, $[\alpha]_D -17^\circ$ (Found: C, 69.4, 69.2; H, 9.3, 9.2%. Calc. for $\text{C}_{28}\text{H}_{54}\text{O}_8$: C, 69.1; H, 9.2%). Benzoylation with benzoyl chloride–pyridine gave substance A tribenzoate, crystallizing from chloroform–methanol, m.p. $199\text{--}200^\circ \text{C}$, $[\alpha]_D +14^\circ$, λ_{max} , 230 m μ (ϵ 44,000 (Found: C, 75.9; H, 7.8%. Calc. for $\text{C}_{39}\text{H}_{60}\text{O}_8$: C, 75.7; H, 7.8%).

The ether-soluble extract was acetylated (acetic anhydride-pyridine at 100 °C), and one half was chromatographed over alumina. Elution with light petroleum gave six fractions, Nos. 2, 3, and 4 of which were combined (10 g) and rechromatographed (20 fractions). Some of the material (2 g) eluted by light petroleum was sublimed and recrystallized to constant m.p. from chloroform-methanol to give substance B acetate, m.p. 250–252 °C, $[\alpha]_D^{25} +95^\circ$ (Found: C, 82.2; H, 11.3%. Calc. for $C_{32}H_{52}O_2$: C, 82.0; H, 11.2%). A portion (50 mg) of the acetate was hydrolysed by refluxing methanolic KOH (5 ml; 40%), and benzoylated (benzoyl chloride-pyridine at 100 °C) to give substance B benzoate, m.p. 260–262 °C, $[\alpha]_D^{25} +55^\circ$ (Found: C, 83.8; H, 10.3%. Calc. for $C_{37}H_{54}O_2$: C, 83.7; H, 10.2%).

Fraction 10 (1.1 g) of the original chromatogram was sublimed and recrystallized from chloroform-methanol to give substance C acetate, m.p. 245–247 °C, $[\alpha]_D^{25} +52^\circ$ (Found: C, 82.3; H, 11.1%. Calc. for $C_{32}H_{52}O_2$: C, 82.0; H, 11.2%). Hydrolysis (refluxing methanolic KOH) and recrystallization from ethanol gave substance C, m.p. 222–224 °C, $[\alpha]_D^{25} +49^\circ$, having identical m.p. and mixed m.p. with that isolated by direct crystallization of the total extract (Found (after crystallizing from chloroform-light petroleum): C, 84.7; H, 11.8%. Calc. for $C_{30}H_{50}O$: C, 84.4; H, 11.8%). Benzoylation with benzoyl chloride-pyridine (100 °C) gave substance C benzoate, m.p. 292–294 °C, $[\alpha]_D^{25} +73^\circ$ (Found: C, 83.8; H, 10.2%. Calc. for $C_{37}H_{54}O_2$: C, 83.7; H, 10.2%).

In open tubes substance C and its derivatives showed wide melting ranges considerably below the sharp melting points observed in evacuated sealed tubes. Both are shown in Table 1.

References

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